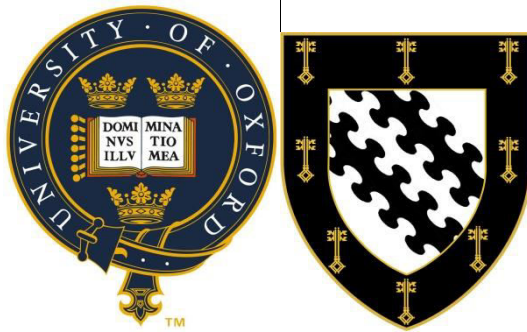


High Resolution Paleo-monsoon Records from Peninsular Indian Speleothems

by

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Department of Earth Sciences and Exeter College, Oxford



Thesis submitted to the University of Oxford for the degree of
Doctor of Philosophy in Earth Sciences

Submitted in Hilary term, 2017

Supervised by Prof. Gideon Henderson and Prof. Rosalind Rickaby

I was just speculating about a hypothesis. I know I don't know nothing.

-Miller's Crossing

Declaration

I declare that this thesis is entirely my own work and has not been submitted to any other university for any degree, diploma or other qualifications.

Abstract

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The Indian Summer Monsoon is a major component of the global climatic system. Stalagmites have a proven ability to provide information of such monsoon systems. In this thesis, examination of cave records and field work provides a framework of the spatial and temporal distribution of stalagmites in peninsular India. Stable oxygen isotope records from stalagmites are supported by trace element records. An aragonite stalagmite from the west coast of India suggests that changes in growth surface can effect precipitation through time available for dissolved inorganic carbon removal. Calculation of empirical partition coefficients from the aragonite stalagmite indicates that U/Ca, Sr/Ca and P/Ca ratios may be paleo-aridity indicators through the process of Prior Aragonite Precipitation. There may also be source and/or temperature control on the partitioning of Sr/Ca into the aragonite stalagmite. These are the first trace element measurements for stalagmites from peninsular India and some of the few available from aragonite stalagmites. The $\delta^{18}\text{O}$ composition of a calcite stalagmite from central India that grew from 3130 to 2100 years BP is consistent with the hypothesis that $\delta^{18}\text{O}$ is controlled by air parcel trajectory and amount of rainout between source and cave site. P/Ca and U/Ca records from this stalagmite provide information on past rainfall conditions. Correlation analysis of $\delta^{18}\text{O}$, P/Ca and U/Ca indicates that rainfall amount was not the dominant control on $\delta^{18}\text{O}$ composition at this cave site. Examination of a stalagmite that has diagenetically altered from aragonite to calcite shows that the $\delta^{18}\text{O}$ system is extremely susceptible to diagenesis. Sr/Ca and U/Ca of the primary aragonite are retained in secondary calcite. Higher Mg/Ca ratios in secondary calcite compared to primary aragonite indicates that diagenetic fluid adds material to the primary carbonate. The variation in U-Th ages are caused by differential addition and losses of U and Th isotopes.

Extended Abstract

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Peninsular India experiences the first landfall of the monsoon before winds travel further east. The Indian Summer Monsoon provides 80% of South and Southeast Asia's annual precipitation which is vital to sustaining the region's agriculture and supports nearly a quarter of the world's population. Monsoon variability causes frequent floods and droughts. The monsoon is also a major global climatic system; it affects and is affected by changes taking place in other parts of the global climatic system. Despite this, our understanding of the monsoon and past variation in the monsoon remains poor due to short instrumental records and a paucity of paleoclimate records.

This thesis focuses on the reconstruction of past monsoon from peninsular India using speleothems. Speleothems are powerful archives of past climate as they can be precisely dated using absolute radiometric techniques and provide multiple proxies of past climate. The high resolution continental $\delta^{18}\text{O}$ records from speleothems can be directly compared with $\delta^{18}\text{O}$ records from ice cores and ocean cores allowing investigation of spatially variable changes as climate fronts move across regions. This enables direct comparison of climate in distant regions. In addition, the availability of multiple proxies from speleothems allows us to decouple larger circulation changes from local changes in rainfall and temperature.

Chapter 1 introduces the Indian Summer Monsoon system and speleothems as proxy sources to study the monsoon. It outlines the goals and structure of the thesis. Chapter 2 discusses published speleothem-based climate data from India and investigates the spatial

and temporal distribution of speleothems from peninsular India. Chapter 3 provides details of methods used in this thesis.

Chapter 4 discusses equilibrium precipitation conditions for oxygen isotopes in an aragonite stalagmite from Akalagavi cave. Aragonite speleothems are typically fast growing with high concentrations of uranium that allow precise age measurement. However, there is an ongoing debate about whether the stable isotopes of carbon and oxygen precipitate under equilibrium conditions in this fast growing aragonite and hence a question about their fidelity as paleoclimate recorders. This chapter begins by reporting measurements of cave site temperature, humidity, rain water, drip water and modern carbonate. Along with previously published $\delta^{18}\text{O}$ record of this sample, they are discussed and interpreted in the context of published equations and models of equilibrium precipitation. There appears to be equilibrium precipitation in modern carbonate growth and specific subsamples from the sample stalagmite. 'Ponding' of drip water on the growth surface results in precipitation that has departed most from oxygen isotopic equilibrium. Changes in the growth surface of the stalagmite, so that the angle relative to horizontal changes, may also alter fractionation processes by changing the time available for carbonate removal. This implies that the time available for CO_2 degassing and Dissolved Inorganic Carbon depletion is not only controlled by the drip rate but may also be controlled by angle of growth surface. This control is more effective at high temperatures where reactions are faster.

Chapter 5 presents the first documented study of trace element measurements from peninsular India and one of the few studies on aragonite speleothems. Measurements have been made on the same sample studied in Chapter 4 from Akalagavi cave. Bedrock, well water, spring water and drip water measurements are used to understand the sources of trace elements found in this stalagmite. Based on drip water and seasonal resolution stalagmite subsample measurements, this study gives empirical partition coefficients for Sr/Ca , U/Ca , Mg/Ca , P/Ca , Na/Ca , Rb/Ca , K/Ca and Mn/Ca and provides evidence for the use

of Prior Aragonite Precipitation as a proxy for paleo-aridity. It indicates a marine source for Na/Ca, S/Ca and a marine and lithological source for Mg/Ca. It also shows a method for seasonal demarcation of layers based on concentration of detrital material (Mn/Ca). There is significant correlation between U/Ca and $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ giving a potential way to isolate kinetic control on $\delta^{18}\text{O}$ from a larger climatic/environmental control.

Chapter 6 continues examination of the stalagmite from Akalagavi cave. Trace element and stable isotope measurements from white layers that are likely to have precipitated during the monsoon rainfall period (i.e. months of June, July, August and September) are compared to instrumental temperature and rainfall records (1900 to 2000 AD). Correlation analysis indicates that no single process dominantly controls multiple trace element distribution. There is significant correlation between P/Ca and $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ giving a potential way to isolate kinetic control on $\delta^{18}\text{O}$ from a larger climatic/environmental control. Growth rate (measured through lamina width) is not a significant control on the trace element distribution in this sample; instead SST and land temperature appears to be a dominant influence, particularly on Sr/Ca measurements.

Chapter 7 looks at a calcite stalagmite collected from Kotumsar cave located in central India. U-Th dating indicates that the sample grew between 3400 and 2100 years BP. Texturally disturbed growth restricts the interpretation of proxy record from this stalagmite to the growth period between 3130 and 2100 years BP. The $\delta^{18}\text{O}$ record from this stalagmite extends the existing 1200 year record (from 1200 years BP to the modern) by 1000 years. There is consistent offset in $\delta^{18}\text{O}$ records between this region and stalagmites collected from Oman and Eastern China. This supports modelling results that suggest an air parcel trajectory control through amount of rainout between source and cave site. Examination of climate control on trace element relationships indicates that high P/Ca and U/Ca in the stalagmite are periods of high infiltration resulting in increased transport of P and U in the form of colloids and organic complexes. There is little correlation between P/Ca- $\delta^{18}\text{O}$ and

U/Ca- $\delta^{18}\text{O}$ indicating that rainfall amount is not the dominant control on $\delta^{18}\text{O}$ at this cave site.

Lastly, Chapter 8 investigates the effect of diagenesis on the geochemistry of a stalagmite. The stalagmite sample was collected from Valmiki cave located in south India. U-Th dating suggests that the primary aragonite precipitated approximately 21 ky BP and subsequently underwent diagenesis. Parts of the sample are altered from primary aragonite to secondary calcite. The change in mineralogy exerts significant control on the stable isotope and trace element composition of the sample. The hierarchy of mineralogical control is $\delta^{18}\text{O} > \text{Na/Ca} > \text{Sr/Ca} > \text{Mg/Ca} > \text{U/Ca}$. $\delta^{18}\text{O}$, a major element of CaCO_3 is the most susceptible to alteration. $\delta^{18}\text{O}$ of the secondary calcite may have precipitated in equilibrium with the water causing diagenesis. There is addition of Mg/Ca from the water causing diagenesis to the secondary calcite. Mg/Ca ratios can be used to differentiate between primary calcite, primary aragonite and secondary calcite although this may also indicate that the Mg/Ca concentration of the water mediating diagenesis is different from that precipitating as primary calcite. Sr and U of primary aragonite are retained in the secondary calcite structure. Th is lost during diagenesis from aragonite to calcite. Calcite ages are not necessarily older to aragonite. The variation in ages is caused by differential addition/losses of U and Th in primary aragonite and secondary calcite.

The research undertaken as a part of this thesis demonstrates the potential of using stalagmites from peninsular India to reconstruct past climate from this region. It provides a framework of the spatial and temporal distribution of stalagmites from this region that can be used for further work. It investigates the potential of using aragonite stalagmites to reconstruct past climate. Examination of trace element measurements suggests the likely controls on their distribution in stalagmites from this region. The thesis shows the benefit of using cave measurements of drip water and temperature, published equilibrium relationships for the carbonate-water system and trace element ratios to constrain the

interpretation of oxygen isotopes that are traditionally used as proxies from stalagmites. The records have ramifications for the climatic interpretation of proxies from stalagmites, particularly aragonite stalagmites, and for further stalagmite-based paleoclimate reconstructions from peninsular India.

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List of Abbreviations, Definitions and Datasets

General

a	annum (years)
y	years
ky	kilo years, 10^3 years
ka	kilo annum 10^3 years
BP	Before Present
AD	Anno Domini
ppb	parts per billion
ppm	parts per million
μm	micrometre, 10^{-6} m
mm	millimetre, 10^{-3} m
cm	centimetre, 10^{-2} m
m	meter
km	kilometre, 10^3 m
μg	microgram, 10^{-6} g
mg	milligram, 10^{-3} g
g	gram
ml	millilitre, 10^{-3} litre
μl	microliter, 10^{-6} litre
PRL	Physical Research Laboratory, collaborating institute located in Ahmadabad, India
MRC	Mhadei Research Centre, help with field and monitoring work
asl	above sea level also called above mean sea level or amsl
C3	Type of carbon fixation in plants
dpm	drops per minute

Geochemical data

$$\delta^{18}\text{O} = (((^{18}\text{O}/^{16}\text{O})_{\text{sample}} / (^{18}\text{O}/^{16}\text{O})_{\text{standard}}) - 1) * 1000\text{‰}$$

$$\delta^{13}\text{C} = (((^{13}\text{C}/^{12}\text{C})_{\text{sample}} / (^{13}\text{C}/^{12}\text{C})_{\text{standard}}) - 1) * 1000\text{‰}$$

$$\delta\text{D} = (((^2\text{H}/^1\text{H})_{\text{sample}} / (^2\text{H}/^1\text{H})_{\text{standard}}) - 1) * 1000\text{‰}, \text{ where D = Deuterium} = ^2\text{H}$$

vPDB $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ of sample measured with respect to Vienna Pee Dee Belemnite standard for carbonate measurements

vSMOW $\delta^{18}\text{O}$ and δD measured with respect to Vienna Standard Mean Ocean Water standard for water measurements

α = the fractionation factor

For fractionation between calcite and water, $\alpha = (^{18}\text{O}/^{16}\text{O})_{\text{calcite}} / (^{18}\text{O}/^{16}\text{O})_{\text{water}}$

For fractionation between aragonite and water, $\alpha = (^{18}\text{O}/^{16}\text{O})_{\text{aragonite}} / (^{18}\text{O}/^{16}\text{O})_{\text{water}}$

pCO₂ Partial pressure of carbon dioxide gas

k_{Tr} Partition coefficient of respective trace element also called Distribution coefficient or D_{Tr}

¹⁴C Radiocarbon

N Normality

M Molar concentration or Molarity

Mmol/mol mill mole per mole

U-Th uranium-thorium

cps counts per second

DIC Dissolved Inorganic Carbon

Climate regimes and components

AMO Atlantic Multi-decadal Oscillation

AMOC Atlantic Meridional Overturning Circulation

IPWP Indo-Pacific Warm Pool

ITCZ Inter-tropical Convergence Zone

NHSI Northern Hemisphere Summer Insolation

ISM	Indian Summer Monsoon
EAM	East Asian Monsoon
SST	Sea Surface Temperature
MIS	Marine Isotope Stage
EDC	EPICA Dome C ice core
EPICA	European Project for Ice Coring in Antarctica
WAIS	West Antarctic Ice Sheet
NGRIP	North Greenland Ice Core Project
H1	Heinrich event 1
LIA	Little Ice Age
CIS	Chinese Inter-stadials
GIS	Greenland Inter-stadials
MWP	Medieval Warming Period
IPCC	Inter-governmental Panel on Climate Change
PAGES	Past Global Changes
RCP	Representative Concentration Pathways

Datasets

GHCN	Global Historical Climate Network
CRUTEM4	Climate Research Unit Temperature
CRU TS 3.23	Climate Research Unit Time Series Version 3.23
HadISST	Hadley centre sea Ice and Sea Surface Temperature
KNMI	Koninklijk Nederlands Meteorologisch Instituut
GNIP	Global network of Isotopes in Precipitation
WISER	Water isotope System for Data Analysis, Visualization and Electronic Retrieval

**References for databases have been given in the Bibliography*

Chapter 1

Introduction

1.1 Overview

The South Asian monsoon provides 80% of the region's annual precipitation which is vital to sustaining the region's agriculture and provides water, nutrition and livelihood for nearly a quarter of the world's population (figure 1.1). Monsoon variability contributes to frequent floods and droughts in the region. The monsoon is also a major global climatic system; it affects and is affected by changes taking place in other parts of the global climatic system. Speleothems (such as stalagmites) provide high resolution, multi-proxy records combined with tight age control to reconstruct monsoon variability in continental regions.

This chapter summarises the monsoon system; the past and current state of knowledge. It provides an overview of speleothems as archives to study the monsoon and introduces the study area. It concludes with research goals and structure of this thesis.

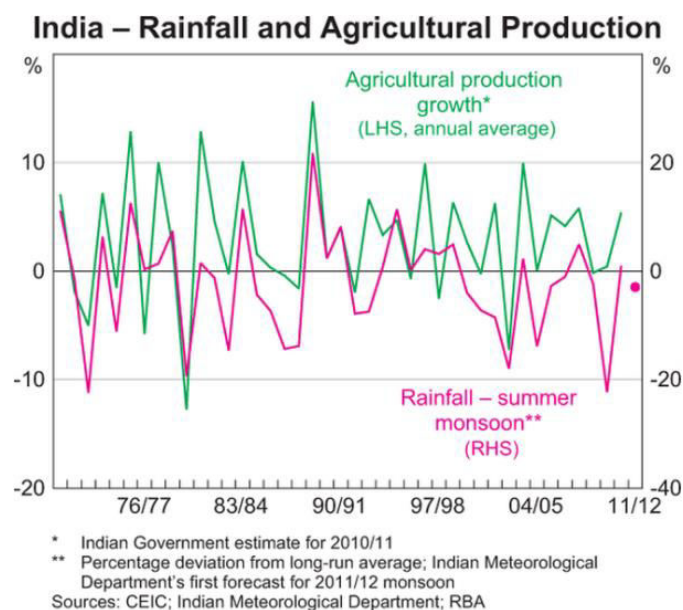


Figure 1.1: The graph shows data on agricultural production growth in India (green line - left axis) and the Indian summer monsoon rainfall deviation from average (pink line - right axis). Time in Years AD is given on the X-axis. There is remarkable correlation between agricultural production and rainfall amount. Given that the monsoon is a global climatic phenomenon, it also shows the control of global climatic variation on regional agricultural production and economic growth in monsoon regions. Data sources have been indicated below the figure.

1.2 The global monsoon system

Kutzbach, 1987 and *Webster et al, 1998* provide historical context to the development of this field. Early studies considered the monsoon to be a local physical phenomenon and attempts to understand its structure and variability were based on local effects. As observations from multiple locations became available to researchers, they found indications that the monsoon was intertwined with larger global scale processes. Sir Gilbert Walker showed that the global atmosphere possesses coherent patterns of low frequency variability (*Walker, 1923; Walker, 1924; Walker, 1928; Walker and Bliss, 1932*) and placed the monsoon within a context of global atmospheric circulation. This was later corroborated by *Troup, 1965* and *Berlag, 1966* and many others. The variability is associated with differential heating of hemispheres due to Earth's orbital parameters and differential heating of land versus ocean which in turn is unevenly distributed between hemispheres.

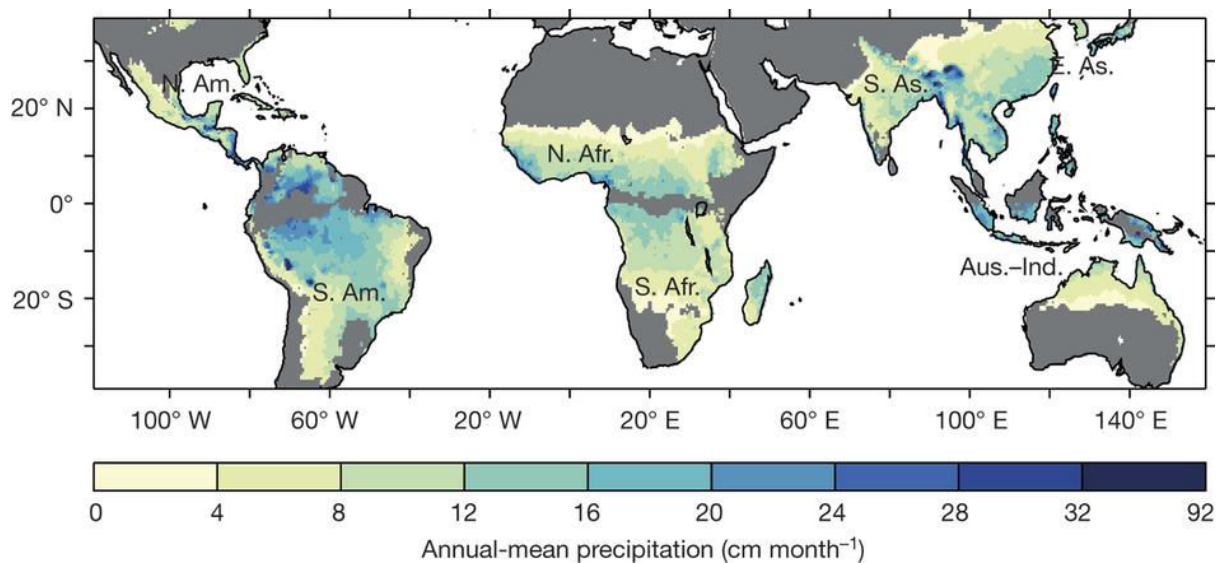


Figure 1.2: The approximate global monsoon precipitation domain is here defined where the local summer-minus-winter precipitation rate exceeds 6 cm/month and the local summer precipitation exceeds 50% of the annual total. During any individual year, it is possible for the monsoon to affect a broader area than shown here. Summer denotes June through August for northern hemisphere and December through February for the southern hemisphere. Colours denote annual mean precipitation. Monthly global gridded, high-resolution (0.5°) precipitation data from 1901–2010 from the University of Delaware were used. The regional monsoons are North American (N.Am.), North African (N.Afr.), South Asian (S. As.), East Asian (E. Asian), South American (S. Am.), South African (S. Afr.) and Australian (Aus.-Ind.). Figure and description sourced from *Mohtadi et al, 2016* and is based on the work by *Wang and Ding, 2007*.

The monsoon is now defined as a global scale atmospheric overturning circulation which determines the primary precipitation characteristics over the Asian-Australian, American and African continents and can be viewed as an integrated global monsoon system (*Trenberth et al, 2000*) (figure 1.2).

Of the various patterns of low frequency variability, the Southern Oscillation (set within the context of the East-West Walker Circulation) is one aspect of global scale atmospheric circulation patterns thought to be of particular significance to the monsoon. The Southern Oscillation is a pattern of zonal circulation in the tropics. The easterly trade winds transport cold upwelling water off the coast of Peru toward the west (figure 1.3). This water, now at the surface, is soon warmed by the Sun. The process drives further upwelling to the east while the west is characterised by warm, wet, low pressure weather as collected moisture is released. This is called the neutral state. Every 3-5 years on average, there is absence of cold upwelling waters and is referred to as El Niño condition, while La Niña with a similar periodicity, is characterised by warm water travelling farther west than the neutral state (*Bjerkens, 1969*). Whichever part of the ocean is the warmest is where increased convection associated with the rising branch of the Walker circulation so that La Niña is associated with more convection and more rainfall in India. This link between the atmospheric Southern Oscillation to the El Niño phenomenon that occurs in the ocean ties the tropical atmospheric circulation to the ocean circulation, which has a longer 'memory' in comparison to the atmosphere. The ocean transports a significant amount of heat, especially in the tropics, but the ocean has a larger heat capacity and takes a longer time to propagate disturbances in temperature which gives it a longer 'memory'. This understanding is expected to aid the predictability of the joint system (*Bjerkens, 1969*).

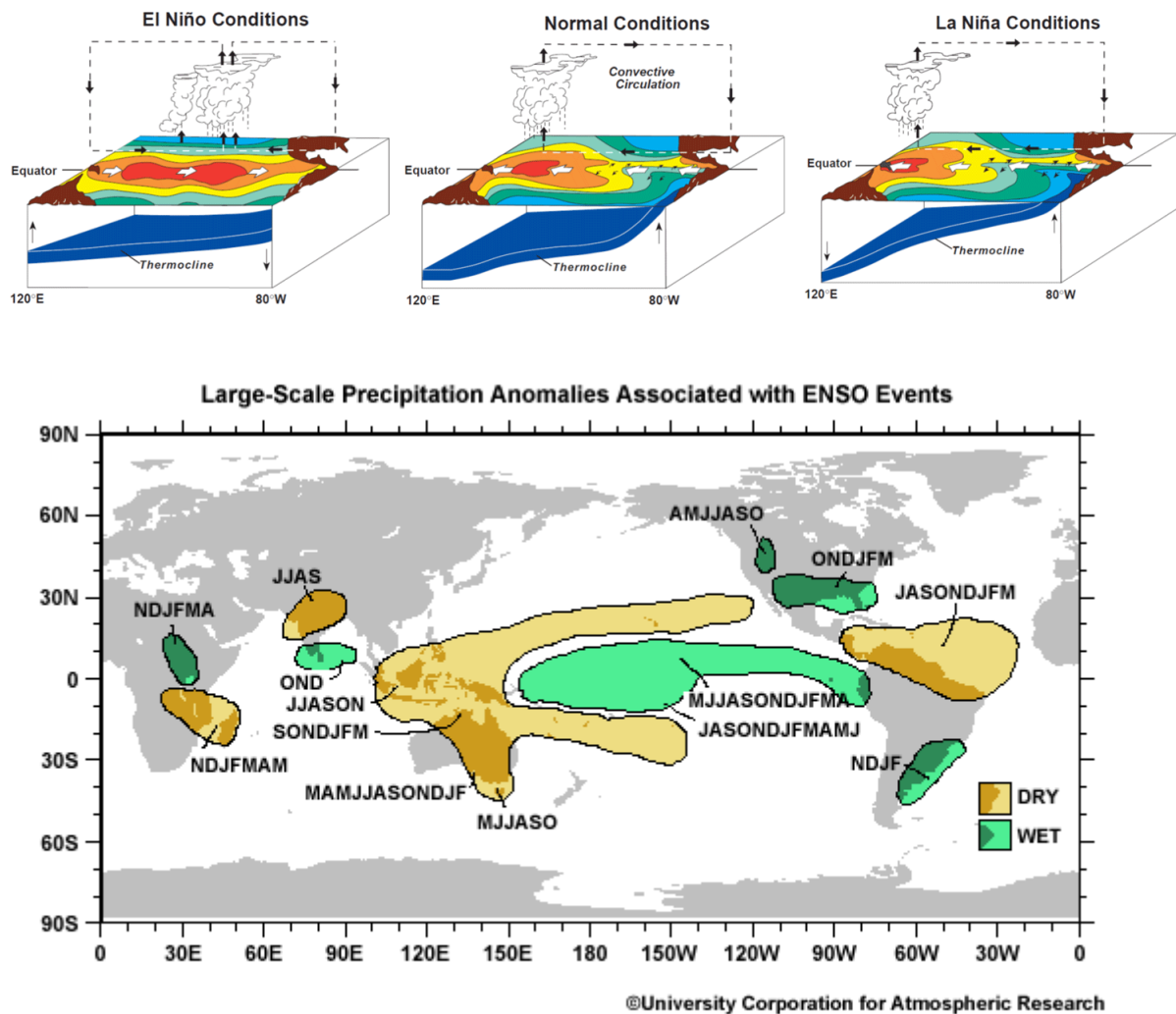


Figure 1.3: The figure on top shows a model of surface temperatures, winds, areas of rising air, and the thermocline (an abrupt temperature gradient in a body of water shown by the blue surface) in the tropical Pacific during El Niño, normal and La Niña conditions. *Figure and description taken from National Oceanic and Atmospheric Administration (NOAA).* The figure below is the geographic and seasonal distribution of large scale precipitation anomalies associated with El Niño. Labels on the figure indicate months of the year with altered precipitation typical for the respective geographic regions. *Figure and description from University Corporation for Atmospheric Research (UCAR).*

While the Southern Oscillation addresses the zonal component of the monsoon, movement of the Inter-Tropical Convergence Zone (ITCZ) addresses the meridional component or the Hadley cell of the monsoon in equatorial regions such as Asia. The Hadley cell is formed by air warmed by the sun and rising at the equator, flowing toward the North and South poles, cooling and returning to the surface of the Earth in sub-tropics, and flowing back to the equator along the surface of the Earth (figure 1.4). These surface winds are the Trade winds.

The Northeast and Southeast Trade winds form a front at the Equator called the ITCZ. The ITCZ can be considered to be the climatological equator. During northern hemisphere winter, the ITCZ is deflected to the south of the equator due to high pressure winds from the north and dry northeast trade winds blow from the Asian landmass onto the ocean. During northern hemisphere summer, the ITCZ shifts to the north of the equator, the southeast trade winds turn southwest due to Coriolis forces, and carry water from the oceans and rain down across the Asian landmass.

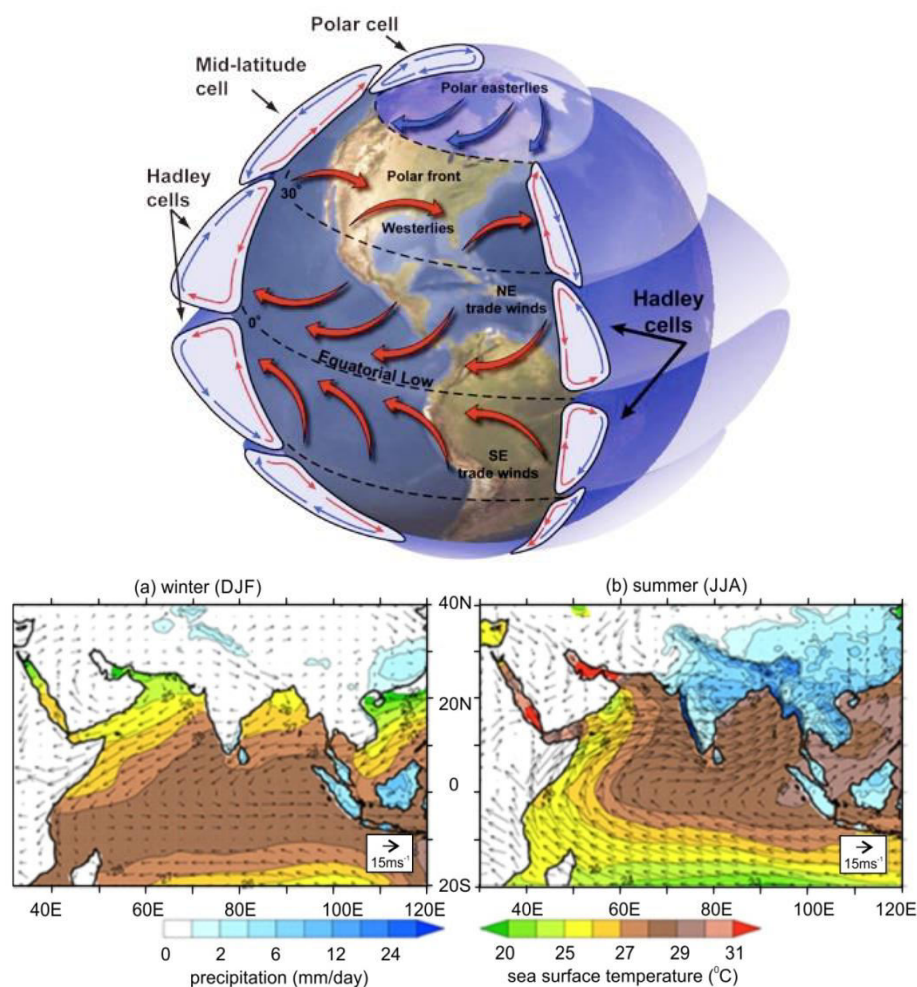


Figure 1.4: The image on top is of global winds and shows the Hadley cell component and associated Northeast (NE) and Southeast (SE) Trade winds (*NASA*). The arrows in the figures below show prevailing wind direction over the Asian region during winter (a) and summer (b) respectively. Precipitation amounts in mm/day are indicated by a blue colour scale over continental regions while SST's are indicated by a coloured scale over the ocean. The south-westerly winds during the summer carry moisture from the Indian Ocean, raining down over the Asian continental region (*Royal Meteorological Society*).

The driving mechanisms of the global monsoon circulation can thus be summarised as follows (*Webster et al, 1998*):

- i) The differential heating of land and ocean and the resulting atmospheric pressure gradient force between differentially heated regions.
- ii) The impact of planet rotation, relative to the orographic form of the continental surface and differential heating, which determines the character of monsoon flow in the atmosphere and ocean.
- iii) Moisture processes that determine the strength, vigour and location of major monsoon precipitation by storing, redistributing and selectively releasing, in the vicinity of the summer hemisphere continents, the solar energy arriving over most of the tropics and subtropics.

These processes are intertwined making individual processes difficult to consider independently. Despite significant advances made in the field, the extent and intensity of monsoon are still often under-simulated (model evaluation based on simulation of mean climate, of historical climate change, of variability on multiple time-scales and of regional modes of variability) by climate models (*Flato et al, 2013*) and there is low confidence in future projections of the amount of rainfall for several monsoon domains (*Christensen, 2013*) (figure 1.5). Poor simulations of monsoon dynamics mostly arise from the complexity of this land-ocean-atmosphere system that in turn interacts with other tropical and extra-tropical systems. It is expected that the effect of temperature change due to global warming will be more rapid over continents than the ocean so that continental scale land-sea thermal contrast will become larger in summer than in winter. This should result in a stronger summer monsoon and weaker winter monsoon (*IPCC, Fourth Assessment Report, Working Group 1: The Physical Science Basis, 2007*). But models indicate that the intensities (velocity potential fields at 200 hpa) of global scale atmospheric circulations of tropical Hadley, Walker and monsoon circulation will weaken in the future (*Tanaka et al, 2005*) possibly

through a reduction in the meridional thermal gradient for the Asian region (*Ueda et al, 2006*). Despite the weakening of the circulation, however, higher temperatures will result in atmospheric moisture build up due to increasing capacity of the atmosphere to hold moisture with increasing temperatures and hence more precipitation for the Indian monsoon region (*Douville et al, 2000; IPCC, 2001; Ashrit et al, 2003; Meehl and Arblaster, 2003; May, 2004; Ashrit et al, 2005*).

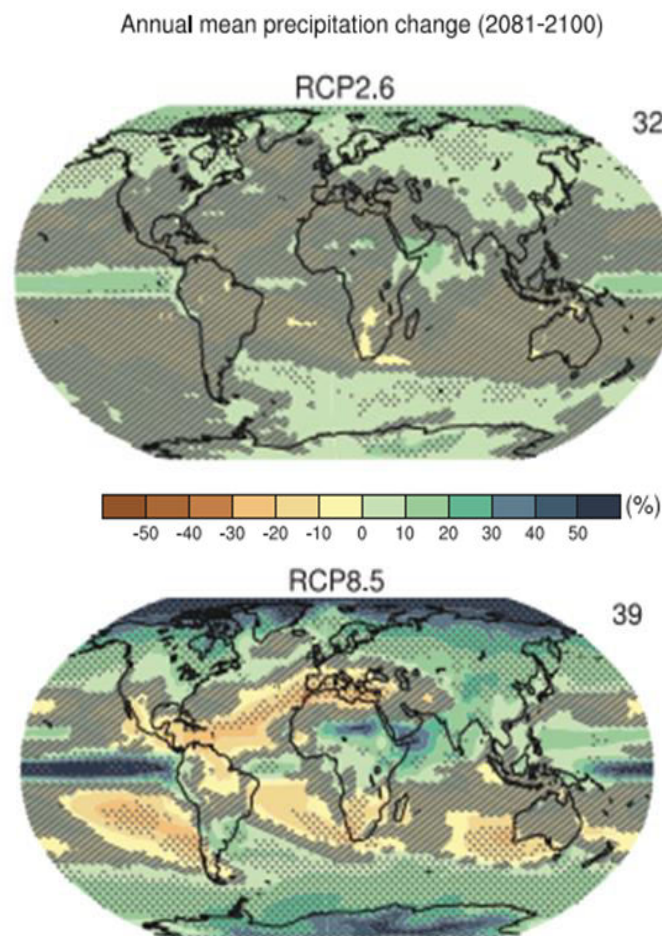


Figure 1.5: Maps of multi-model results for scenarios RCP2.6 and RCP8.5 in 2081-2100 of average percent change in mean precipitation. Changes are shown relative to 1986-2005. The number of CMIP5 models to calculate the multi-model mean is indicated in the upper right corner of each panel. Hatching indicates regions where multi-model mean signal is less than 1 standard deviation of internal variability. Stippling indicates regions where the multi-model mean signal is greater than 2 standard deviations of internal variability and where 90% of models agree on the sign of change. The figure and description are from *IPCC AR5*. RCP: Representative Concentration Pathway. CMIP5: Coupled Model Inter-comparison Project Phase 5. Further details of RCP's CMIP5 and the modelling of this figure can be found in *IPCC AR 5, Working Group 1, The Physical Science Basis, 2013*.

Long term records from proxy archives allow understanding of orbital and millennial processes driving the monsoon. Past climate conditions enable isolation of dominant processes such as changes in northern hemisphere glaciation or the Atlantic Meridional Overturning Circulation (AMOC). Long term records allow investigation of monsoon behaviour in conditions different from those seen in the modern instrumental records but which nevertheless may be seen in the future.

1.3 Past variations in the Asian monsoon

Since the monsoon is controlled by differential heating, it is sensitive to Earth's orbital variations.

Precession (periodicity of 19 kilo years or ky and 23 ky) affects the seasonal cycle of incoming solar radiation and its hemispheric distribution. Amount of rainfall and amplitude of annual rainfall cycle are enhanced in the northern hemisphere and reduced in the southern hemisphere during a precession minimum and vice versa during a precession maximum. During a precession minimum, northern hemisphere summer is characterised by higher insolation and a stronger land-sea thermal gradient, which increases the intensity of wind circulation and increases the moisture holding capacity of the atmosphere (*Kutzbach, 1981; Merlis et al, 2013*). A number of proxy records from the Arabian Sea show variation with a precessional periodicity (for example, *Schultz et al, 1998; Altabet et al, 1995*) and records with a similar periodicity have been found in oxygen isotope records from speleothems (for example, *Wang et al; 2001, Kathayat et al, 2016*) (figures 1.6 and 1.7). The anti-phase, inter-hemispheric response of proxies and hence monsoon systems in the two hemispheres has been explored in *Cheng et al, 2012*.

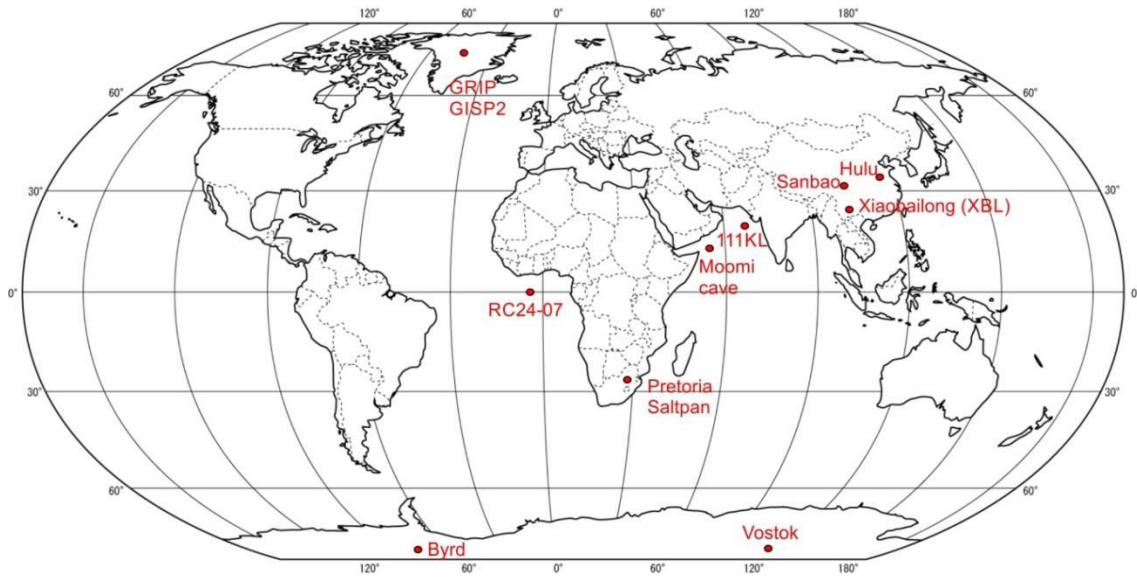


Figure 1.6: The location of records shown in figures 1.7 and 1.8 have been plotted on a world map.

Unlike precession, changes in obliquity (periodicity of 41 ky) affects the seasonality of incoming solar radiation equally in both hemispheres, but there is stronger variation of insolation at higher latitudes. Despite this, obliquity is thought to have an effect on the monsoon either indirectly through high latitude forcing associated with ice sheet and sea ice formation (*deMenocal, 1995*) or directly by changing the inter-hemispheric insolation gradient and the meridional insolation gradient in the summer hemisphere (*Mantsis et al, 2014; Bosmans et al, 2015*).

The timing and response of different monsoon systems to precession and obliquity forcing and the degree to which they respond are still debated (*Mohtadi et al, 2016*).

The Atlantic sea water $\delta^{18}\text{O}$ variance is dominated by a 100 ky cyclicity (given for 0 to 780 ka) (*Lisiecki and Raymo, 2005*), the water exchange between the Mediterranean Sea and the Atlantic Ocean in turn modulates the $\delta^{18}\text{O}$ of water sources that feed speleothems in this region, generating a 100 ky variation in Soreq and Peqiin (both caves located in Israel) speleothem records (*Bar-Matthews et al, 2003*). But this is not seen in the Asian monsoon records which are dominated by variations in precession and obliquity.

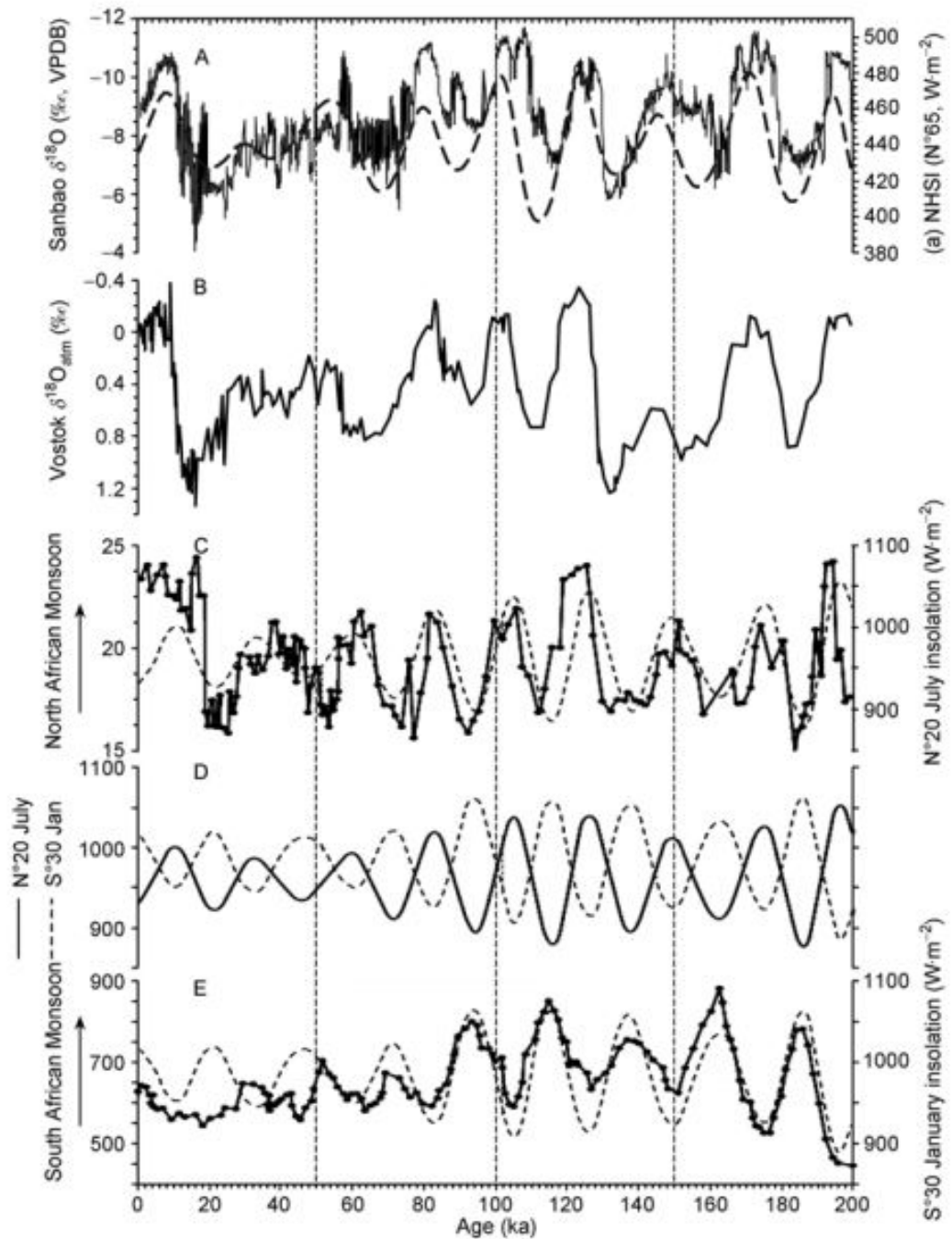


Figure 1.7: Precession periods of the monsoon in the northern and southern hemispheres over the last 200 ky. (A) Stalagmite $\delta^{18}\text{O}$ from Sanbao and Hulu caves, South China (solid line). Dashed line shows summer insolation at 65°N . (B) $\delta^{18}\text{O}_{\text{air}}$ from Vostok ice-core. (C) North African monsoon index based on diatom counting at Core RC24-07, tropical East Atlantic (solid line). Dashed line shows July insolation at 20°N . (D) Summer insolation at low latitudes in the northern (solid line, July at 20°N) and southern (dashed line, January at 30°S) hemispheres. (E) Precipitation-based South African monsoon variations estimated from sediment properties in the Pretoria saltpan, South Africa (solid line). Dashed line indicates January insolation at 30°S . A and B modified from Wang *et al*, 2008. C, D and E modified from Partridge *et al*, 1997. The figure and description are from Wang, 2009. Locations of records are shown in figure 1.6.

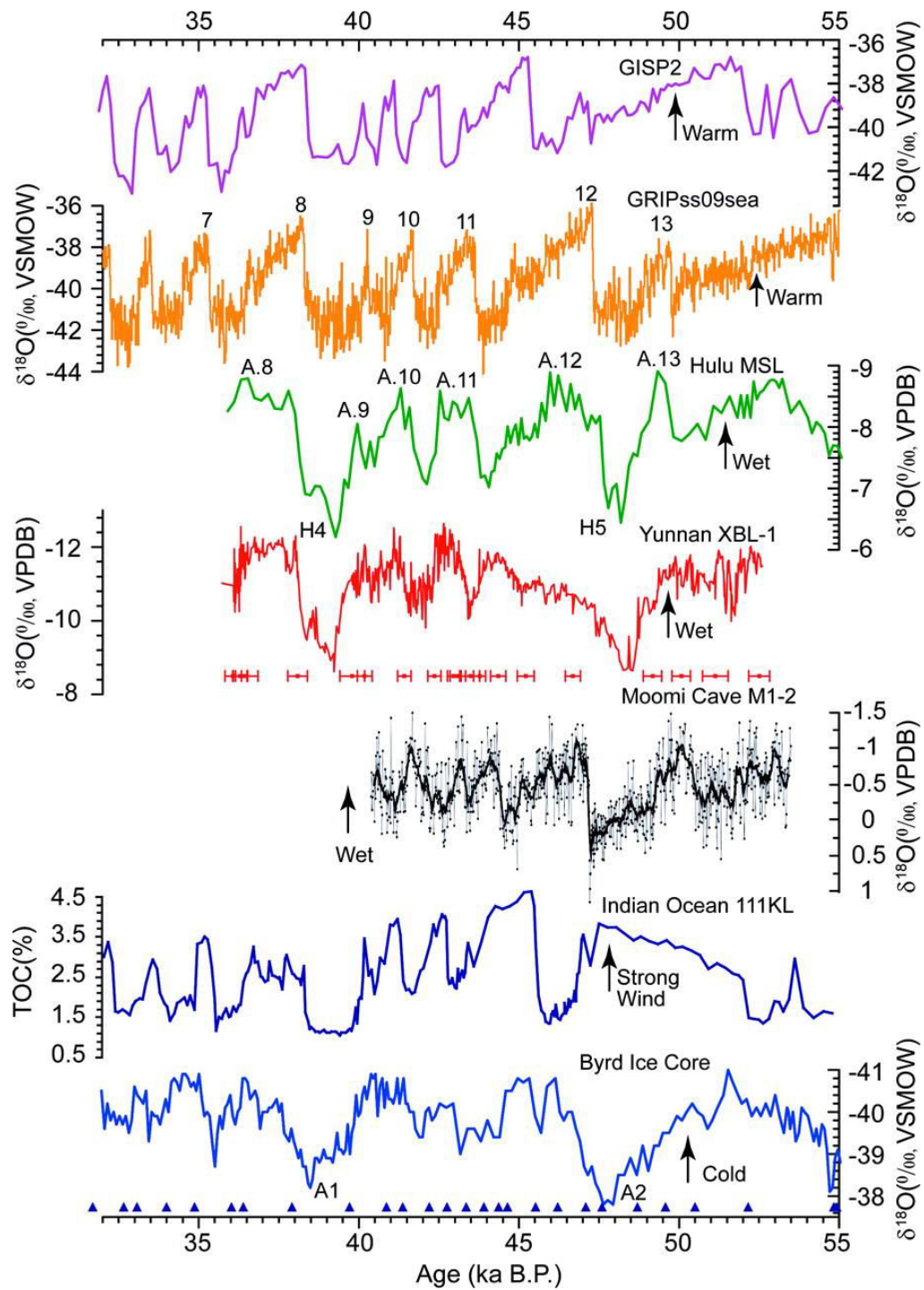


Figure 1.8: Millennial scale events in the Asian monsoon. Comparison of $\delta^{18}\text{O}$ records of XBL-1 (red) (Cai *et al*, 2006), Hulu (green, MSL, Wang *et al*, 2001), Moomi (black, Burns *et al*, 2003), Greenland Ice Core Project (GRIP) (ss09sea) (dark yellow, Johnsen *et al*, 2001) Greenland Ice Sheet project (GISP2) (pink, Grootes and Stuvier, 1997) Byrd (blue, Blunier and Brook, 2001; 28 tie points are indicated with triangles at bottom) and Total Organic Carbon (TOC) record (dark blue, Schulz *et al*, 1998) of Indian Ocean core 111KL. Errors indicate ^{230}Th ages and 2σ errors. Numbers 8 - 13 and A.8 - A.13 indicate Greenland Interstadials (GIS) and Chinese Interstadials (CIS), respectively. $\delta^{18}\text{O}$ scales are reversed for XBL-1, Hulu and Byrd ice core (increasing down) as compared to Greenland ice cores (increasing up). The figure and description are from Cai *et al*, 2006. Locations of records are shown in figure 1.6.

Millennial scale events (such as the well-known Heinrich and Dansgaard-Oeschger events) were first identified in the Greenland ice cores and are formally called Greenland Inter-Stadials (GIS) (*Dansgaard et al, 1993; Meese et al, 1997; North Greenland Ice Core Project members, 2004*). The Sanbao cave $\delta^{18}\text{O}$ record of the past 224 ky, which tracks the Hulu and Dongge cave records in China for all overlapping time intervals, is dominated by the 23 ky long precessional cycle but is also punctuated by millennial scale events similar to GIS (*Wang et al, 2008*) (figures 1.6 and 1.8). Such millennial scale events of peaks in $\delta^{18}\text{O}$ observed in the Asian speleothems are now called Chinese Inter-Stadials (*Wang et al, 2001; Kelly et al, 2006*) and Indian Inter-Stadials (*Kathayat et al, 2016*) respectively depending on the monsoon region and point to the relationship between the monsoon and climate of other regions. Forcing mechanisms for these millennial scale events have been explained by changing rates of North Atlantic Deep Water (NADW) formation, resulting in changing heat transport to the North Atlantic (*Broecker, 1994*). It is thought that the changing ice volume associated with orbital changes may have significant influences on millennial scale events (*Wang et al, 2008*). Depending on the relative timing of the millennial scale and the orbital scale variations, the superposition may result in the appearance of a monsoon lead or lag relative to insolation (*Wang et al, 2008*).

1.4 Modern Indian climate

The most distinctive physical features of India are the high Himalayan mountain ranges to the north and the triangular region to the south bounded by the Arabian Sea to the west, Bay of Bengal to the east and the Indian Ocean to the south (figure 1.9). This triangular region is called peninsular India. Both coasts have mountain ranges running along them. The Western Ghats running along the Arabian Sea coast are ~1500 m in elevation and form an orographic boundary to the moisture carried from the Arabian Sea. The areas to the west of the Ghats receive much higher rainfall than those to the east. The Eastern Ghats are less continuous with lower elevations than the mountains to the west. The Vindhyan and Satpura mountain

ranges and the Chota Nagpur Plateau to the North show similar elevations and form a loose northern boundary to peninsular India.



Figure 1.9: Physical map of India. The triangular region between the Arabian Sea and the Bay of Bengal is referred to as peninsular India. *Source: www.worldmaps.net.*

The Himalayas bar the influx of cold winds from icy Tibetan plateau and northerly central Asia keeping the bulk of the Indian subcontinent warmer than other locations at similar latitudes (*Posey, 1994*). Simultaneously, the low atmospheric pressure system at Thar Desert located to the northwest of India which reaches temperatures of 45°C in peak summer, plays a role in attracting moisture laden southwest monsoon winds that, between June and October, provide majority of India's rainfall.

The Indian Meteorological Department designates four climatological seasons (figure 1.10):

- (i) Winter extends from December till March with temperatures in peninsular India ranging from 15 to 25°C.
- (ii) Summer or Pre-monsoon season lasting from April to June. These are the hottest months of the year with temperatures increasing to the ranges of 32-40°C.

- (iii) Monsoon or rainy season lasts from July to September and is dominated by the southwest monsoon during which most of peninsular India receives nearly ~80% of the total annual rainfall. The remaining 20% is from pre-monsoon rain through atmospheric disturbances such as thunderstorm development in the Bay of Bengal and post-monsoon rain from Northeast trade winds (see iv).
- (iv) Post-monsoon or autumn lasts for the two months of October and November. There is little rain in peninsular India at this time with the exception of Tamil Nadu state. This state located to the southeast corner of India receives most of its rain during this time. The moisture is carried by northeast winds carrying moisture from the Bay of Bengal.

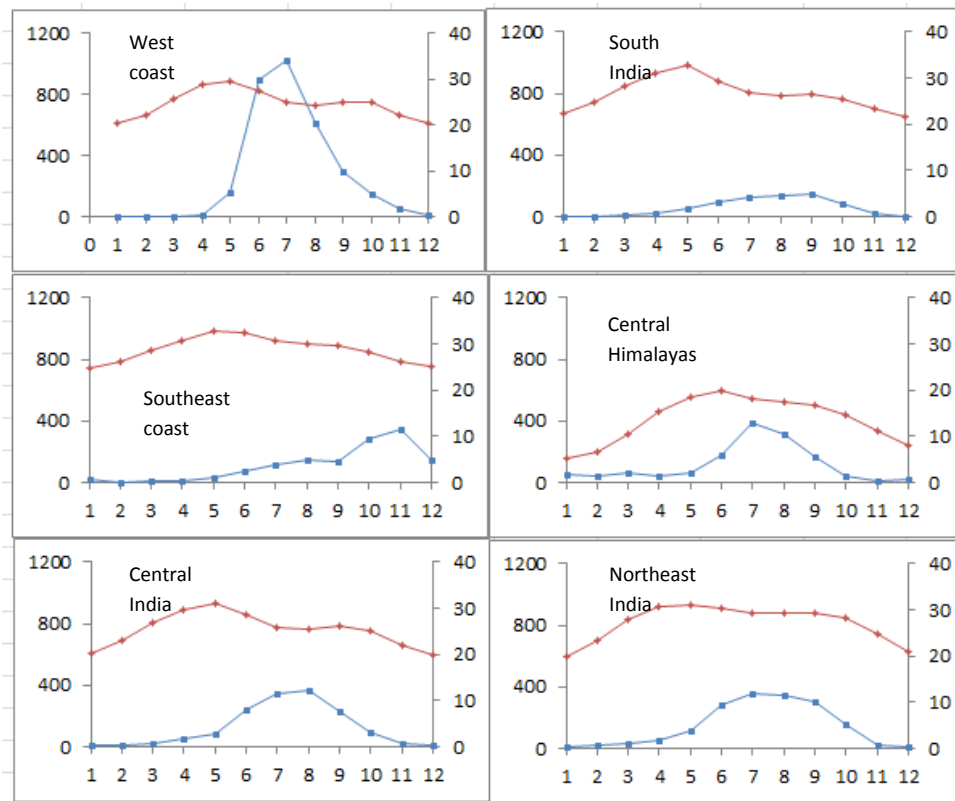


Figure 1.10: Monthly rainfall and temperature patterns in different regions of India. Rainfall is in mm on the left axis and shown by the blue line. Temperature is in °C on the right axis and shown by the maroon line. The regions have been written to the top left of each figure. Data is from Global Historical Climate Network (GHCN) hosted by Koninklijk Nederlands Meteorologisch Instituut (KNMI) Climate Explorer and is the monthly averages of data from 1951-2016 AD.

During the monsoon period, convective rainfall dominates peninsular India's weather. A high summer temperature difference between central Asia and the Indian ocean accompanied by the northward shift of the ITCZ result in the Southeast trade winds turning westerly due to Coriolis forces as they cross the equator. These winds carry copious amounts of water from the Indian Ocean, which falls as precipitation over peninsular India. This southwest monsoon can be thought of as two branches, the Bay of Bengal branch and the Arabian Sea branch. The latter has a much stronger impact on peninsular India. The Arabian Sea branch blows eastward towards the Himalayas. The Bay of Bengal branch initially tracks the eastern coast and then swerves northwest at the Himalayan orographic barrier and proceeds over the Indo Gangetic plain. During winter, when the winds change direction and begin blowing from the Northeast, the Tamil Nadu region on the South-eastern coast of India receives some rainfall from Bay of Bengal moisture. This seasonal reversal of meridional temperature and pressure gradients and associated wind circulations which constitute the summer and winter monsoons is the most outstanding feature of the Indian meteorology (*Kumar et al, 1995*).

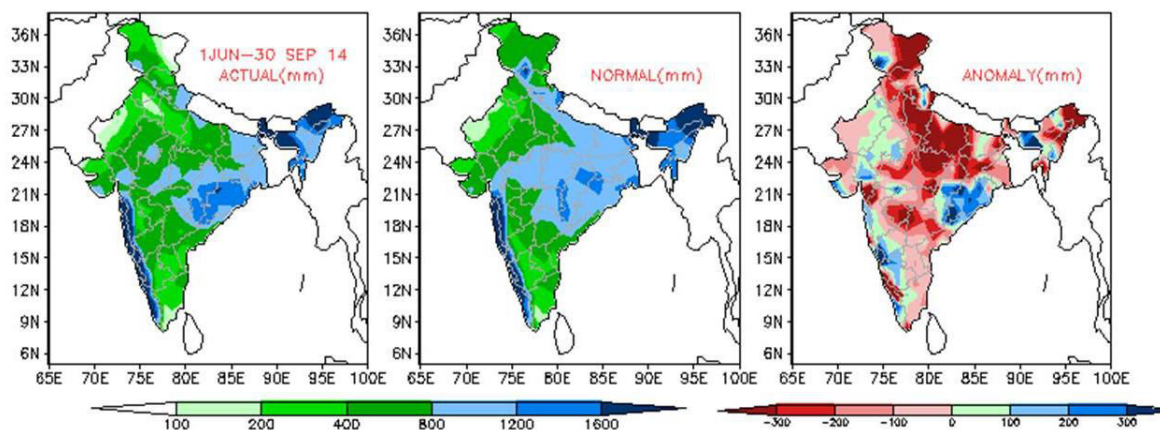


Figure 1.11: Inter-annual variability in rainfall. Total monsoon rainfall for the monsoon period (June-September, 2014 AD), a particularly low rainfall year, with left hand plot showing the total measured rainfall, middle plot showing the normal conditions and right hand plot showing the difference. Figure from the Indian Meteorological Department.

The spatial distribution of mean annual rainfall over peninsular India shows that the west coast receives very high rainfall of over 2000 mm while the rain shadow regions of central southern peninsula receive less than 500 mm (figure 1.11). The inter-annual variability is high over low rainfall regions and low over high rainfall regions (*Parthasarathy, 1984*). For example, rainfall variation in 2014 AD, a particularly low rainfall year, has been shown in figure 1.11.

Two external factors known to cause inter-annual variability in the Indian Summer Monsoon (ISM) during the modern instrumental period include ENSO and the Himalayan/Eurasian snow cover. El Niño is associated with reduction in rainfall while La Niña is associated with enhanced rainfall over peninsular India. However, in recent times observations have shown that the ENSO-ISM relationship has been weakening (*Kripalani and Kulkarni, 1997; Kumar et al, 1999; Ashok et al, 2001*). The factors causing weakening and the current dominant drivers of inter-annual variability are still debated. Satellite snow cover estimates indicate a negative relationship between snow cover (snow mass) and the monsoon. Excessive snow during preceding winter is unfavourable for the subsequent monsoon season (*Blanford, 1884; Hahn and Shukla, 1976; Khandekar, 1991; Kripalani et al, 1996; Bamzai and Shukla, 1999*). This relationship is also weakening in recent times (*Kripalani et al, 2003*).

While the year-to-year variability in the ISM arises from Indo-Pacific SST's (Sea Surface Temperature) such as the ENSO phenomenon and snow cover anomalies, a substantial component of variability also stems from intra-seasonal oscillations in monsoon precipitation termed as active-break periods which exhibit a hierarchy of quasi periods (8-7 days, 10-20 days, 30-60 days) (*Webster et al, 1998; Goswami and Mohan, 2001*). The active-break periods produce a distinct spatial structure in the form of an east-west precipitation dipole. During an 'active' period there is positive anomaly in the amount of precipitation over western and central India and a negative anomaly in the amount of precipitation over

northeast and southeast India. During a 'break' period, the 'signs' are reversed (*Guhathakurta and Rajeevan, 2008; Rajeevan et al, 2010*). This spatial pattern is diminished in years of weak active-break periods and vice versa.

The long term trends in instrumental rainfall and temperature records for peninsular India have been given in figures 1.12 and 1.13. Analysis of ISM rainfall (for the period 1871-2001 AD) generated by area-weighting rainfall amounts of 306 well distributed rain gauges across the country obtained from the Indian Meteorological Department show that there are year-to-year random fluctuations. But on the seasonal to century scale, the most prominent variations on the inter-annual scale are monsoon seasons with above and below normal rainfall respectively (*Kripalani et al, 2003*). Different reasons have been suggested such as decadal variability of the Pacific Ocean (*Webster et al, 1998*), events in the northern hemisphere mid-latitudes (*Kripalani et al, 1997; Kripalani and Kulkarni, 1999*) and solar irradiance (*Kulkarni et al, 2001*).

No trend is observed in the extreme events of floods and droughts across time (dataset of 1871-2001 divided into two equal halves and compared, dataset of 1871-2001 divided into global warming period of 1910-1945 and 1976-2001 i.e. 62 years compared with the remaining years) (*Kripalani et al, 2003*). However, long term trends in the frequency of cyclonic disturbances over Bay of Bengal and Arabian Sea using 100 years of data (1890-1999) show a decreasing trend (*Singh, 2001*).

There is weakening of monsoon general circulation based on model experiments of several large scale indices that describe Asian summer monsoon (*Stephenson et al, 2001*).

On analysing global warming forcing (global warming period: 1910 to 1945 and 1976 to 2001 i.e. 62 years), it appears that there is no clear evidence to suggest that mean monsoon rainfall, frequency and intensity of extreme events or decadal variability are affected by global warming (*Kripalani et al, 2003*).

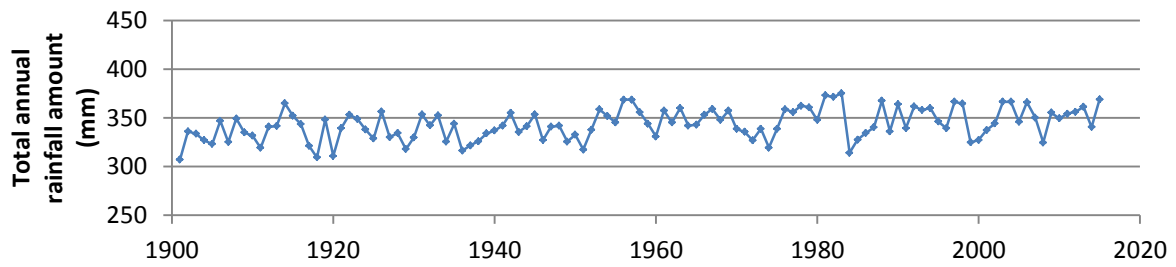


Figure 1.12: Total annual rainfall in peninsular India (in mm) across time (in years AD). Data from CRU TS3.24 is hosted by KNMI Explorer. Rainfall has been averaged over $5^{\circ} \times 5^{\circ}$ grid boxes.

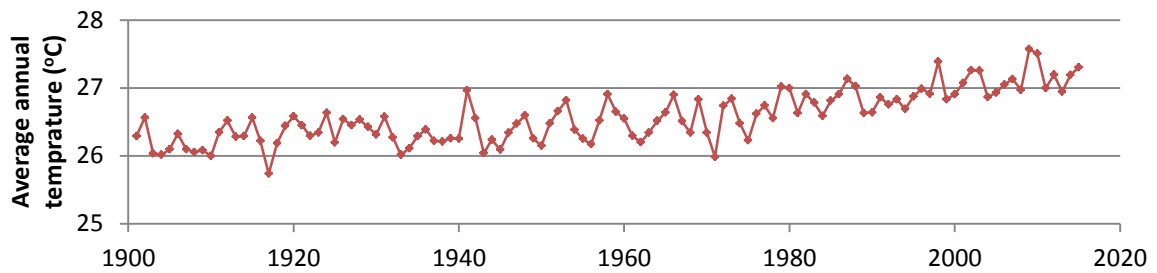


Figure 1.13: Average annual temperature in peninsular India (in °C) across time (in years AD). Data from CRU TS3.24 is hosted by KNMI Explorer.

1.5 Paleoclimate reconstruction for India

Paleoclimate records from proxy sources such as glaciers and lake records have been described below. Figure 1.14 gives the location of the records. The main ice core records for the Indian region have been obtained from the Tibetan plateau by *Thompson et al (1989, 1997, 2000)*. They find that the $\delta^{18}\text{O}$ record covering the last 110 ky BP (Before Present i.e. before 1950 AD) closely tracks the GISP2 CH_4 (Greenland Ice Sheet project-methane record) record indicating that global CH_4 and tropical hydrological cycles are linked (figure 1.15). The record indicates that the Late Glacial Stage (13-10 ky BP) in the Tibetan plateau is characterised by colder, wetter and dustier conditions than seen in the Holocene. The $\delta^{18}\text{O}$ record of the last 60 years is comparable only with the values going as far back as 6-8 ky BP suggesting similarly warm temperatures to those seen during the Holocene maximum (9-5 ky BP) which was also a period of increased monsoon intensity.

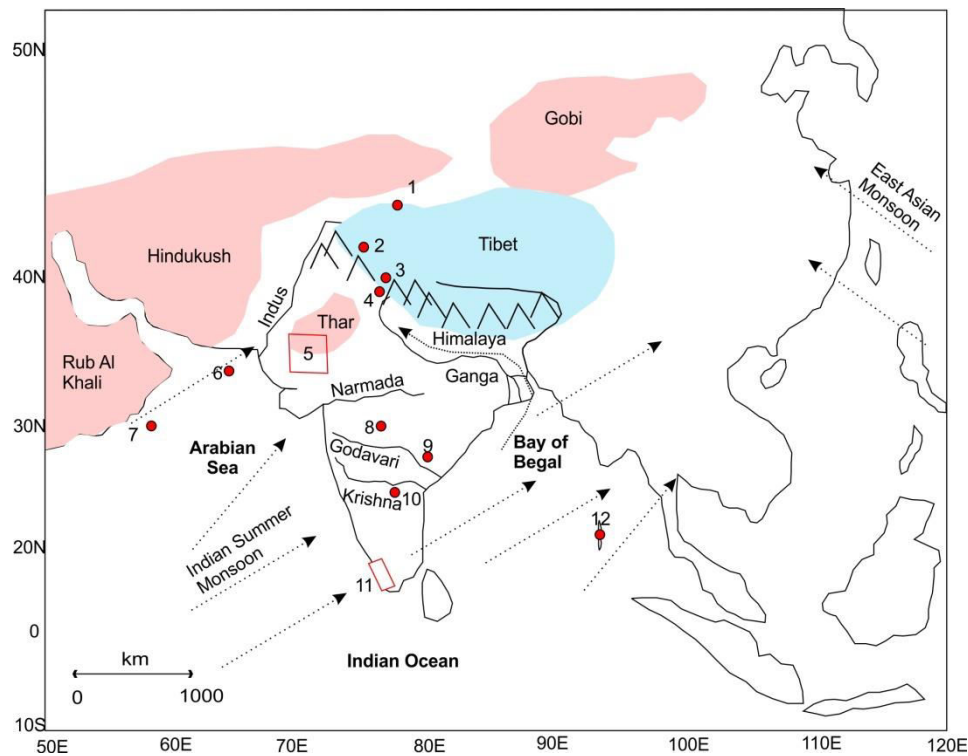


Figure 1.14: Location of important proxy archives used for paleoclimate reconstruction of India on a physical map of the Asian region. Deserts are in pink, the Tibetan plateau is shown in blue. The Himalayan mountain chain, main Indian rivers and monsoon wind directions have been shown. 1. Guliya ice core record (Thompson *et al*, 1997) 2. Nanga Parbat glaciers and glacial deposits (Phillips *et al*, 2000) 3. Peat deposit pollen record (Phadtare and Pant, 2006) 4. Bittoo (Kathayat *et al*, 2016), Timta (Sinha *et al*, 2005), Panigarh (Liang *et al*, 2015), Chulerasim (Kotlia *et al*, 2016), Dharamjali (Sanwal *et al*, 2013) cave speleothem records 5. Lake and dune records (Prasad and Enzel, 2006) 6 and 7. Arabian Sea sediment core records (Sirocko *et al*, 1993; Overpeck *et al*, 1996) 8. Lonar lake record (Prasad *et al*, 2014) 9. Dandak cave speleothem record (Sinha *et al*, 2007) 10. Valmiki cave speleothem record (Lone *et al*, 2014) 11. Kerala tree ring record (Borgaonkar *et al*, 2010) 12. Baratang cave speleothem record (Laskar *et al*, 2013)

Glaciers and glacial deposits show that during the last 100 ky BP, MIS 4 (Marine Isotope Stage 4: MIS's are alternating warm and cool periods of the Earth's paleoclimate deduced from the oxygen isotope record of deep sea core samples reflecting temperatures derived from them, also called Oxygen Isotope Stages or OIS's) (~80-65 ky BP) witnessed a larger extension of glaciers than MIS 2 (~25-15 ky BP) which is thought to be the coolest period in the last 100 ky BP. This is thought to be due to increased precipitation during MIS 4 (Phillips *et al*, 2000).

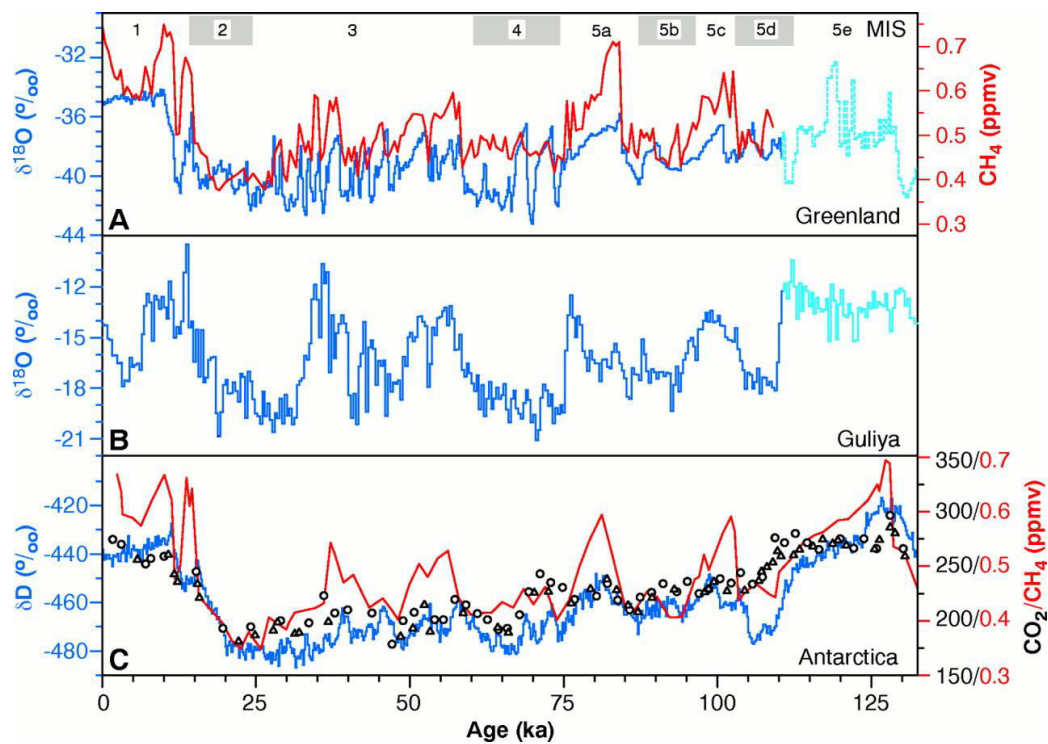


Figure 1.15: (A) The GISP $\delta^{18}\text{O}$ (blue) and CH_4 (red) record are shown with time for the past 132 ka (*Brook et al, 1996*). The record is compromised by ice deformation below 110 ka as shown by the light blue dotted line. (B) The Guliya (Tibetan plateau: *Thompson et al, 1997*) $\delta^{18}\text{O}$ record over the past 110 ka. (C) Vostok δD (blue), CH_4 (red) and CO_2 (black) which display temporal continuity below MIS 5d. The figure and description are from *Thompson, 1997*.

The recently published Bittoo cave speleothem record by *Kathayat et al, 2016* from Central Himalayas is the longest $\delta^{18}\text{O}$ record from India so far. They find that there is coherence between the speleothem-based $\delta^{18}\text{O}$ records obtained from Central Himalayan and East Asian monsoon domain, suggesting that both these systems exhibit a coupled response to changes in precession induced northern hemisphere summer insolation. There is little time lag between the two records. They also identify millennial scale events, called Indian interstadials in the record. The Bolling-Allerod inter-stadial has been previously detected in the Timta cave speleothem $\delta^{18}\text{O}$ record by *Sinha et al, 2005*. Based on the departure to more negative $\delta^{18}\text{O}$ values caused by a larger degree of rainout during the inter-stadial, they suggest that ISM was enhanced during the inter-stadial in this region. The speleothem $\delta^{18}\text{O}$ and mineralogical variation records of the last few millennia from the same region show evidence of Little Ice Age (LIA), a period of cold temperatures in the northern hemisphere

between 1300 to 1870 AD and the Medieval Warm Period (MWP), a period of warm temperatures in the North Atlantic between 950 to 1250 AD. Drier conditions during MWP and post-LIA is evidenced by precipitation of aragonite instead of calcite layers in the speleothem (Panigarh cave; *Liang et al, 2015*) while the LIA period shows calcite deposition (Panigarh cave; *Liang et al, 2015*) and lighter $\delta^{18}\text{O}$ values, which are interpreted as an increase in precipitation (Chulerasim cave: *Kotlia et al, 2016* and Dharamjali cave: *Sanwal et al, 2013*). However, the southern Indian caves show the opposite trend for LIA and MWP with MWP showing lighter $\delta^{18}\text{O}$ values interpreted as a time of higher precipitation (Dandak cave: *Sinha et al, 2007*; Baratang cave: *Laskar et al, 2013*). A second significant record from this region shows that peninsular Indian $\delta^{18}\text{O}$ values also change synchronously with speleothems from Southern China i.e. the East Asian monsoon domain during the last deglaciation ~ 14.8 ky BP (Valmiki cave: *Lone et al, 2014*).

Departure to more negative $\delta^{18}\text{O}$ values of foraminifera and increase in percentage abundances of *Globigerina bulliodes* coupled with other proxies from Arabian Sea cores suggest increased upwelling and intensity of the monsoon during early to mid-Holocene and weaker monsoon during the Last Glacial Maximum (24 ky BP) (*Sirocko et al, 1993*; *Overpeck et al, 1996*). This is supported by river sediment discharge records from the Arabian Sea and the Bay of Bengal (*Kale, 2007*).

There are a few studies that are based on lake and dune records. *Prasad and Enzel, 2006* find that lake levels were higher from ~ 7.2 -6 ky BP and the onset of aridity, especially in the northwest of India, could have begun by ~ 5.3 ky BP. They compare these terrestrial records to marine records and find that episodes of strongest and weakest monsoon were not always associated with wettest and driest episodes respectively in northwest Indian lakes. *Prasad et al, 2014* published a high resolution multiproxy reconstruction of Holocene paleoclimate from a sediment core from Lonar lake located in Central India. They find that there were two prolonged droughts between 4.3-3.9 and 2-0.6 ky BP. They demonstrate that

the regional warming of the Indo-Pacific Warm Pool (IPWP: an oceanic area enclosing the 28.5°C isotherm in the western Pacific) plays an important role in causing prolonged droughts in this region through changes in meridional overturning circulation and position of anomalous warm cell. This record also suggests that the long term influence of conditions like ENSO on the ISM began at only ~2 ky BP and is coincident with warming of the IPWP.

Centennial scale climate records (pollen, diatoms, phytoliths, organic matter and magnetic susceptibility) from Central Himalayan region show a weakening of monsoon from 3.2 to 2 ky BP (*Phadtare and Pant, 2006*).

A pre-monsoon temperature reconstruction from tree rings in the western Himalaya, each record extending for 500 years or more, show brief cooling periods of ~40 years that are supported by glacier extension records (*Yadav et al, 2004*). A dendroclimatic reconstruction from north-eastern Himalaya going back to 1507 AD shows decadal variation in temperature but no significant change in temperature over the last five centuries (*Bhattacharyya and Choudhary, 2003*). The oldest tree ring based reconstruction for this area is a 523 year (1481-2003 AD) tree ring width chronology of Teak (*Tectona grandis*) from Kerala state located to the southwest tip of India by *Borgaonkar et al, 2010*. They find a higher frequency of occurrence of low tree growth in years of deficient ISM rainfall associated with El Niño years. There are several other reconstructions based on tree ring width and $\delta^{18}\text{O}$ of tree ring cellulose from peninsular India (for example, *Shah et al, 2007*; *Ram et al, 2011*; *Sinha et al, 2011*; *Managave et al, 2011*), but these records are usually restricted to the instrumental period.

To summarise, the Indian paleoclimate records indicate that,

- i) Global methane and tropical hydrological cycles are linked.
- ii) Temperatures similar to today were accompanied with an increase in monsoon intensity on the Tibetan plateau in the past.

- iii) Extension of glaciers in the central Himalayan region is associated with temperatures (which control the amount of melting) and amount of precipitation (controlling amount of snow build-up).
- iv) Central Himalayan and East Asian monsoon domains exhibit coupled response to changes in precession with little time lag between the two records.
- v) Events taking place in the North Atlantic region have affected the ISM in the past but monsoon response is different in the Himalayan and the peninsular Indian regions. There may not be spatially uniform changes in the long term precipitation amount in India in response to various drivers.
- vi) Monsoon intensity (wind velocity) to do with circulation changes is a different component of the monsoon from change in the amount of precipitation.
- vii) The link between ENSO-ISM may not have been constant even in the recent past (i.e. even beyond the last 2000 years).

1.6 Speleothems and speleothem proxies

The investigation of proxies for the monsoon and other climate phenomena quickly made it apparent that instrumental records of ~100 years do not capture the full extent of climate variability. Periodicities in proxy records also showed that driving mechanisms and changes occur at much longer timescales than can be investigated with instrumental records.

Several proxy archives have been investigated to understand long-term monsoon variation (section 1.5). But a major limitation to understanding the monsoon has been the lack of long term, high resolution and widespread records from tropical continental regions. Each proxy source has its benefits and limitations and needs to be carefully selected based on the question trying to be answered. For example, drilling into high altitude and high latitude ice sheets has revolutionized our understanding of climate particularly at time scales of millennia and shorter. These records have taught us about the variability of climate, how rapidly climate can change and have provided unique records of past atmospheric

composition. Ice cores are often considered to be the 'gold standard' of climate proxies. They provide high resolution records through lamina counting, direct records of the atmosphere at the time of their formation and several proxies to understand various aspects of the climate. But ice cores have their limitations. Lamina counting is precise for the last ~30,000 years but beyond that ice compaction effects make the stratigraphy increasingly imprecise. Ice cores are also restricted to high latitude and high altitude regions. These are also regions without major human populations and thus, less immediately relevant for regional climate reconstructions. They do not capture variability in major climate systems such as the monsoon.

Speleothems offer several advantages over other paleoclimate archives:

- i) Speleothems are scattered over most continental areas and are physically and chemically robust and are relatively protected from erosion.
- ii) They provide exceptional chronology for at least the last 400,000 years through absolute radiometric dating, offering a huge potential for establishing lead-lag relationships in the climate system. This is a significant advantage over other dating methods that require reservoir corrections or 'tuning' (*Henderson, 2006*). Speleothem carbonate also has lower detrital thorium content than surface carbonates (for example, lacustrine carbonate and tufa) making their ages more precise.
- iii) They provide long, continuous records representing timescales from months to millions of years, which is matched by ice cores, but other archives tend to have strengths either in their high resolution (for example, tree rings) or long duration (for example, marine sediments). Most importantly, this capacity of generating high resolution time series has enabled evaluation of the climatic and environmental information of speleothem-proxies with instrumental records (for example, *Frisia et al, 2003; Treble et al, 2005; Matthey et al, 2010*).

- iv) Speleothems contain a host of proxies ranging from chemical (stable isotopes, trace elements, fluid inclusions and organic content), to physical changes in the stalagmite (mineralogy, crystal fabric, growth morphology and lamina thickness). Multiple proxies increase confidence in the climate and environmental interpretation.
- v) The global network of speleothems, allows investigation of spatially variable changes such as how climate fronts move across continental regions through time and enable direct comparison of climate in distant regions (*Wang et al, 2004*).

Some of the best stalagmite records have been found in the Asian monsoon regions. As described above, they show abrupt changes in monsoon strength on millennial time scales, with a pattern similar to those seen in ice core and sediment records from the North Atlantic region (*Wang et al, 2001; Fleitmann et al, 2003*). Widespread speleothem records from tropical regions across Asia, Africa and the Americas are thus increasingly being used to understand the global monsoon.

1.6.1 Speleothem formation

Moore, 1952 recognized a need to specify an unambiguous term for mineral deposits that grew within caves and proposed 'speleothem' (in Greek, *spelaion* means cave and *thema* means deposit). Stalagmites, stalactites and other secondary carbonate deposits that have precipitated from groundwater dripping into a cave or flowing through the cave are together called speleothems. The process of their formation is shown in figure 1.16. Meteoric water percolating into the soil equilibrates with soil CO₂ produced by root respiration and decomposition of organic matter. The dissolved CO₂(aqueous) forms a weak carbonic acid, H₂CO₃, with water. The carbonic acid primarily dissolves carbonate phases such as limestone and dolomite of the surrounding rock (along with other material in its path). When this water reaches the cave, the concentration of CO₂ in the water is usually higher than in the cave air and CO₂ is expelled till equilibrium is reached with the cave

atmosphere. The degassing of carbon dioxide from the drip water triggers the reverse reaction resulting in precipitation of carbonate within the cave.

To use speleothems to reconstruct past variation in climate and environmental conditions they must show a clear signal of past conditions and we must be able to determine their age and growth period.

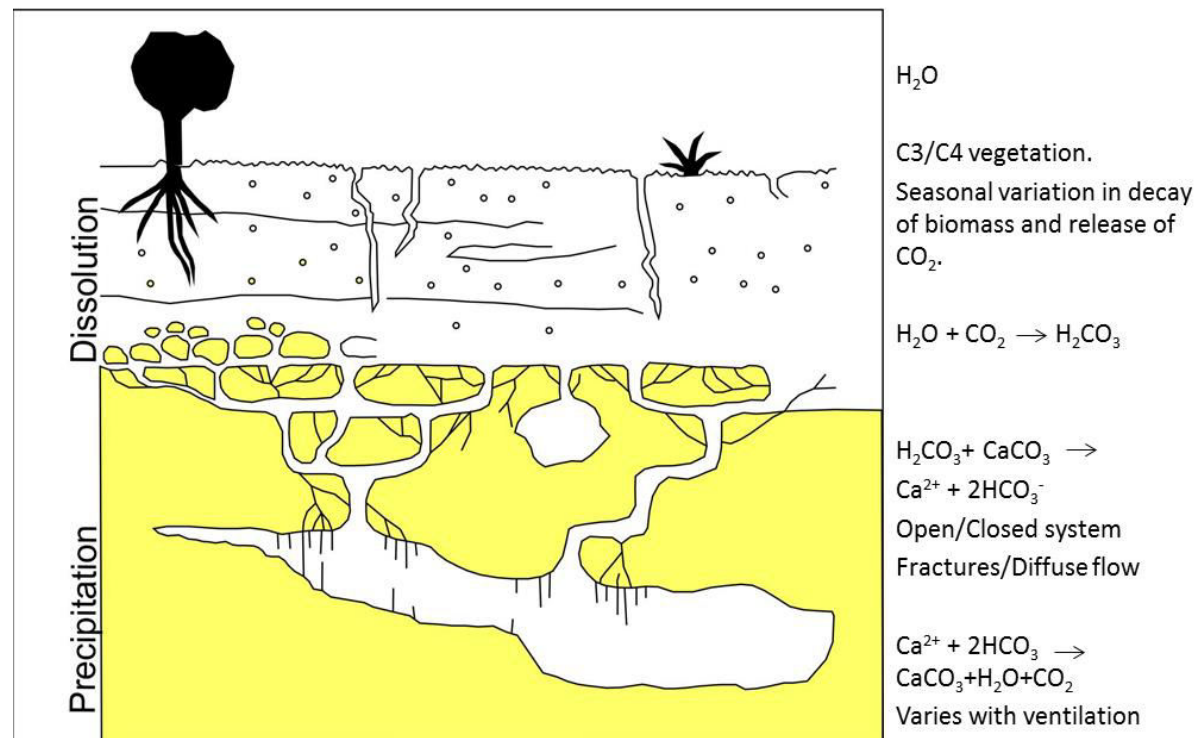


Figure 1.16: Schematic overview of speleothem formation. Reactions taking place at each stage along with dominant controlling factors have been given to the right. Stalactites (ceiling) and stalagmites (floor) have been shown. The figure is modified from *Fairchild et al, 2006*.

1.6.2 Speleothem proxies

a) Oxygen Isotopes

Oxygen isotopes in water are fractionated by physical processes such as evaporation and precipitation. A measurement of oxygen isotopic composition (expressed as $\delta^{18}\text{O}$) along any point on the growth axis of the speleothem is related to the oxygen isotopic composition of the meteoric water that infiltrated into the cave at that time.

The relationship between $\delta^{18}\text{O}$ of the speleothem and drip water under near-equilibrium conditions depends on the $\delta^{18}\text{O}$ composition of drip water and the temperature at which precipitation related fractionation occurs i.e. the cave temperature (*Hendy, 1971; McDermott, 2004 and references therein*). Barring cave ventilation effects, the temperature of a cave is constant through the year and reflects the mean annual surface air temperature (*Hendy and Wilson, 1968*).

Drip water $\delta^{18}\text{O}$ is anticipated to approximate the $\delta^{18}\text{O}$ of regional rainwater (*McDermott, 2004 and references therein; Fairchild et al, 2006 and references therein*) which in turn reflects the moisture source, extent of rain out between moisture source and study (*Craig, 1961*) and the 'amount effect' related to monsoon convection in tropical regions (*Dansgaard, 1954*). This not only gives information of regional rainfall but also of global circulation patterns and external drivers such as changes in northern hemisphere ice volume.

Thanks to pioneering early work done by *Epstein and Mayeda (1953)*, *Dansgaard (1964)*, *Rozanski et al (1982 and 1993)* and *Gat (1996)*, the fundamentals of isotopes in global precipitation are well established. Similarly, extensive cave monitoring in diverse climatic regimes, geochemical modelling and cave analogue laboratory experiments, have increased our understanding of paleoclimate reconstruction using $\delta^{18}\text{O}$ from speleothems (for example, *Hendy, 1971; Mickler et al, 2006; Matthey et al, 2010; Dreybrodt and Scholz, 2011; Day and Henderson, 2011*).

However, increasing number of speleothem studies from diverse geographic locations show that the interpretation of $\delta^{18}\text{O}$ in terms of climate and environmental factors is complex and requires site specific investigation (*Lachniet, 2009*). Long term measurements of seasonal $\delta^{18}\text{O}$ of precipitation are lacking in regions like peninsular India making it difficult to establish even the modern relationship between $\delta^{18}\text{O}$ and rainfall. $\delta^{18}\text{O}$ of drip water can

further be modulated by high intensity precipitation events (*Lawrence and Gedzelman, 1996*), local evaporation conditions (*Cuthbert et al, 2014*) and fracture versus diffuse flow within the epikarst (*Hartland et al, 2012*), requiring a site specific monitoring programme that runs for at least one complete annual climate cycle. Measured fractionation of oxygen in speleothem carbonate is typically greater than that expected by laboratory-based studies for similar temperatures (*Coplen, 2007; Tremaine et al, 2011*) so that the $\delta^{18}\text{O}$ of speleothems cannot be used for quantitative reconstruction of temperature or precipitation. The factors governing precipitation of speleothems under isotopic equilibrium conditions for oxygen are still debated and there is ongoing research to quantify departure from equilibrium (*Mickler et al, 2006; Dreybrodt and Scholz, 2011; Day and Henderson, 2011*). Speleothems are generally composed of calcite, the stable polymorph of calcium carbonate. But speleothems can also be composed of aragonite which may or may not undergo diagenesis at some time after initial precipitation. For this reason, aragonite speleothems are not frequently studied and there are few published studies on $\delta^{18}\text{O}$ variation in aragonite speleothems. On the other hand, recent studies have shown that aragonite speleothems often show high growth rates and their high uranium concentrations allow for very precise dating making them an attractive source for high resolution climate records (see *Lachniet et al, 2012* and *Lachniet, 2015*).

b) Carbon Isotopes

Where $\delta^{18}\text{O}$ relates to hydrological circulation patterns, $\delta^{13}\text{C}$ typically reflects local changes taking place in the cave environment. $\delta^{13}\text{C}$ is controlled by a number of processes and often requires focused long-term cave monitoring before the $\delta^{13}\text{C}$ record of the stalagmite can be interpreted. Perhaps for this reason, few studies provide interpretation of $\delta^{13}\text{C}$ records although these are routinely measured along with $\delta^{18}\text{O}$. Processes influencing speleothem $\delta^{13}\text{C}$ include:

- (i) Decomposition of organic matter and respiration of plant roots and microbes control concentrations of ^{12}C enriched CO_2 dissolved in percolation water. These are in turn controlled by temperature and precipitation (*McDermott, 2004*).
- (ii) The photosynthetic pathway of vegetation fractionates the carbon isotopes to different extents. It may reflect seasonal changes in dominant vegetation or reflect longer term changes in vegetation due to a change in precipitation patterns (*O'Leary, 1988; Farquhar et al, 1989; Bar-Matthews et al, 1997; Kohn, 2010*).
- (iii) Open versus closed soil dynamics. An open system allows for continuous exchange between percolating water and an infinite reservoir of soil CO_2 . Under these conditions, the $\delta^{13}\text{C}$ reflects the isotopic composition of the soil with no detectable imprint from the host rock. Under closed system conditions, the water is isolated from soil CO_2 reservoir, and since CO_2 is consumed in the carbonation reaction, there is exchange with the host rock and the $\delta^{13}\text{C}$ composition of percolating water reflects the isotopic composition of the host rock as well (*Salomons and Mook, 1986; Hendy, 1971*).
- (iv) Periods of low infiltration and/or high cave ventilation result in increased calcite precipitation upstream of the stalagmite (for example, on the stalactite) preferentially removing ^{12}C from drip water via degassing. This is referred to as Prior Calcite Precipitation (PCP) (*Atkinson, 1977; Baker et al, 1997*) or Prior Aragonite Precipitation (PAP) (*Jamieson et al, 2016*).
- (v) The extent of CO_2 degassing during speleothem precipitation where ^{12}C is preferentially lost in the degassed $\text{CO}_2(\text{gas})$. Such degassing shows specific patterns in measurements along the growth axis and along a single lamina and are useful for understanding extent of departure from equilibrium conditions during speleothem precipitation and hence the interpretation of the $\delta^{18}\text{O}$ record. The extent of degassing is controlled by a number of factors such as drip rate, cave air pCO_2 and

the saturation state of drip waters (*Hendy, 1971; Dreybrodt and Scholz, 2011; Day and Henderson, 2011*).

c) Trace elements

Trace elements in speleothems include a number of elements that may replace calcium in the calcite or aragonite structure (for example, Mg, Sr, Ba) or those carried as colloids (for example, Th) or those forming complexes with organic matter (for example, U and P).

Paleoclimatic reconstructions from speleothems have traditionally focused on carbon and oxygen isotopes. The addition of trace elements to the geochemical toolbox allowing for multiple proxies to understand the climatic and environmental conditions at a particular cave location, are a recent but promising new addition. The idea of using multiple proxies from a single source is not a new one. For example, trace elements in ice cores are a direct measure of fluxes from bulk precipitation and have been widely used to interpret air mass origins and component mass fluxes (*Wolff et al, 2006*). And fixed ion ratios in sea water have permitted a number of trace element applications in calcareous marine organisms (for example, *Henderson, 2002*). But unlike polar and marine environments, speleothems grow in complex cave environments where the transport and precipitation of trace elements can vary within a single cave chamber and on seasonal timescales (*Fairchild and Treble, 2009*). However, an increasing number of studies of trace element incorporation into speleothems in various climatic settings supported by drip water monitoring, cave analogue experiments and advances in instrumentation and analytical techniques are enabling the identification of key processes that control concentration of trace elements.

The interpretation of trace elements that replace Ca is based on their compatibility with the crystal (calcite or aragonite) lattice which determines their partition coefficient (*Fairchild and Baker, 2012*). For example, Mg, Ba and Sr are all incompatible in calcite in comparison to calcium so that increasing precipitation of calcite leads to an increase in the ratio of these

trace element ratios to Ca in the fluid phase. This may happen when there are locally drying conditions in the epikarst allowing calcite to precipitate before drip waters have reached the cave i.e. PCP thus forming a promising proxy for locally drying conditions (for example, *Fairchild et al, 2000; Johnson et al, 2006*). However, a common challenge is deciphering changes induced by carbonate precipitation from changes in the flux of these elements from the surrounding environment, and from variations in partition coefficients resulting from changes in factors such as temperature, growth rate and competing ions (*Fairchild and Treble, 2009; Hartland et al, 2012; Baldini et al, 2012*). Covariance between multiple trace element ratios and stable isotopes may indicate a dominant common controlling process, such as PCP, which increases confidence in the paleoclimatic interpretation.

1.6.3 Speleothem age and growth period

The age control on speleothems is one of the main reasons that they form excellent proxy sources. They are dateable by uranium-series radiometric methods which yield absolute chronologies at unprecedented precision for the last ~500 ka (*Edwards et al, 1987; Luo, 1997*). Speleothems form from groundwater and are located within caves, both of which are largely conducive to the formation of ‘clean’ samples i.e. samples with low detrital thorium content than surface carbonates like tufas.

For young speleothem samples i.e. samples that haven’t had sufficient time for ^{234}U to decay to ^{230}Th in concentrations large enough to be distinguished from the detrital Th contribution, (described further in section 3.3.10), radiocarbon dating supported by C14 bomb-spike measurements can be used instead (for example, *Yadava et al, 2004, McCabe-Glynn et al, 2013*). Unlike uranium-series dating, radiocarbon dating requires an additional reservoir correction.

Speleothems, especially those growing in regions with strong annual climatic cycles such as the monsoon, also often show distinct annual laminae. In these cases, lamina (also referred

to as layer or band) counting can give the growth period of the speleothem. This can be tied to radiocarbon or uranium-series ages to give a tighter age control on the speleothem. Laminae also allow for the demarcation of distinct annual marker horizons within the speleothem (for example, *Johnson et al, 2006*). In modern young speleothems, laminae allow for direct comparison with instrumental records thus refining proxy interpretation.

There is increasing refinement in U-Pb dating of speleothems and dating capabilities using this method have been extended to the Pliocene (2.88 to 5.33 million years or My BP) (*Woodhead et al, 2006; Pickering et al, 2010*). Ongoing further refinement of uranium-series dating is in instrumentation (ability to measure lower concentrations, simultaneous measurement of U and Th isotopes) and analytical methods (Laser Ablation Inductively Coupled Plasma Mass Spectrometry or LAICPMS and subsamples with lower laboratory blanks). Both advances will also allow for smaller sample sizes thus increasing the resolution at which uranium-series dates can be obtained.

1.6.4 A note on aragonite speleothems

Stalagmites in caves dominantly precipitate as calcite or aragonite. Higher Mg/Ca favours aragonite by inhibiting calcite growth, as confirmed by numerous laboratory experiments (for example, *Burton and Walter, 1987; De Choudens-Sanchez et al, 2009*). Aragonite speleothems are normally limited to caves developed in dolomitic bedrock which is an obvious source of Mg (for example, see tables 1.1 and 1.2). A second mechanism for increase in Mg/Ca of drip waters is through the process of prior carbonate precipitation (for example, during dry periods) resulting in limited aragonite precipitation in a stalagmite that is dominantly composed of primary calcite (for example, *McMillan et al, 2005; Wassenburg et al, 2012*).

The use of aragonite stalagmites as paleoclimate proxies has become increasingly common because of their often exceptional uranium-series dating precision and fast growth rates,

which allow near-annual climate resolution. However, aragonite is known to be susceptible to open-system behaviour and may recrystallize to calcite under typical cave conditions. Such diagenesis may result in the movement of uranium or thorium or both (*Ortega et al, 2005; Hopley et al, 2009; Lachniet et al, 2012*). Further, the fidelity of the oxygen isotopic variations preserved in aragonite stalagmites is not yet as firmly established as for calcite stalagmites (*Lachniet, 2015*). Trace elements have also been applied to aragonite speleothems but less commonly than to calcite stalagmites. A key limitation is the non-thermodynamic nature of partition coefficients (term explained later in text) during calcium carbonate precipitation in most natural contexts (*Morse and Bender, 1990*). Element partitioning is made particularly complicated by the orthorhombic structure of aragonite which leads to a variety of forms whose crystal faces can have different trace element affinities (*Finch et al, 2003; Fairchild and Treble, 2009*).

Figures 1.17 and 1.18 and tables 1.1 and 1.2 show the distribution of aragonite speleothems around the world. The listed studies are a result of a Google Scholar search for the key words 'aragonite' and 'speleothem'. To the best of our knowledge, the list encompasses majority of the studies published on aragonite speleothems. The figures indicate that aragonite stalagmites are found in peninsular India. Since aragonite stalagmites are less frequently studied than calcite stalagmites but are found in peninsular India, this section briefly explores their global distribution and forms i.e. stalagmites composed entirely of primary aragonite, stalagmites with distinct layers of primary aragonite and primary calcite, stalagmites composed of diagenetic calcite or some combination of these forms.

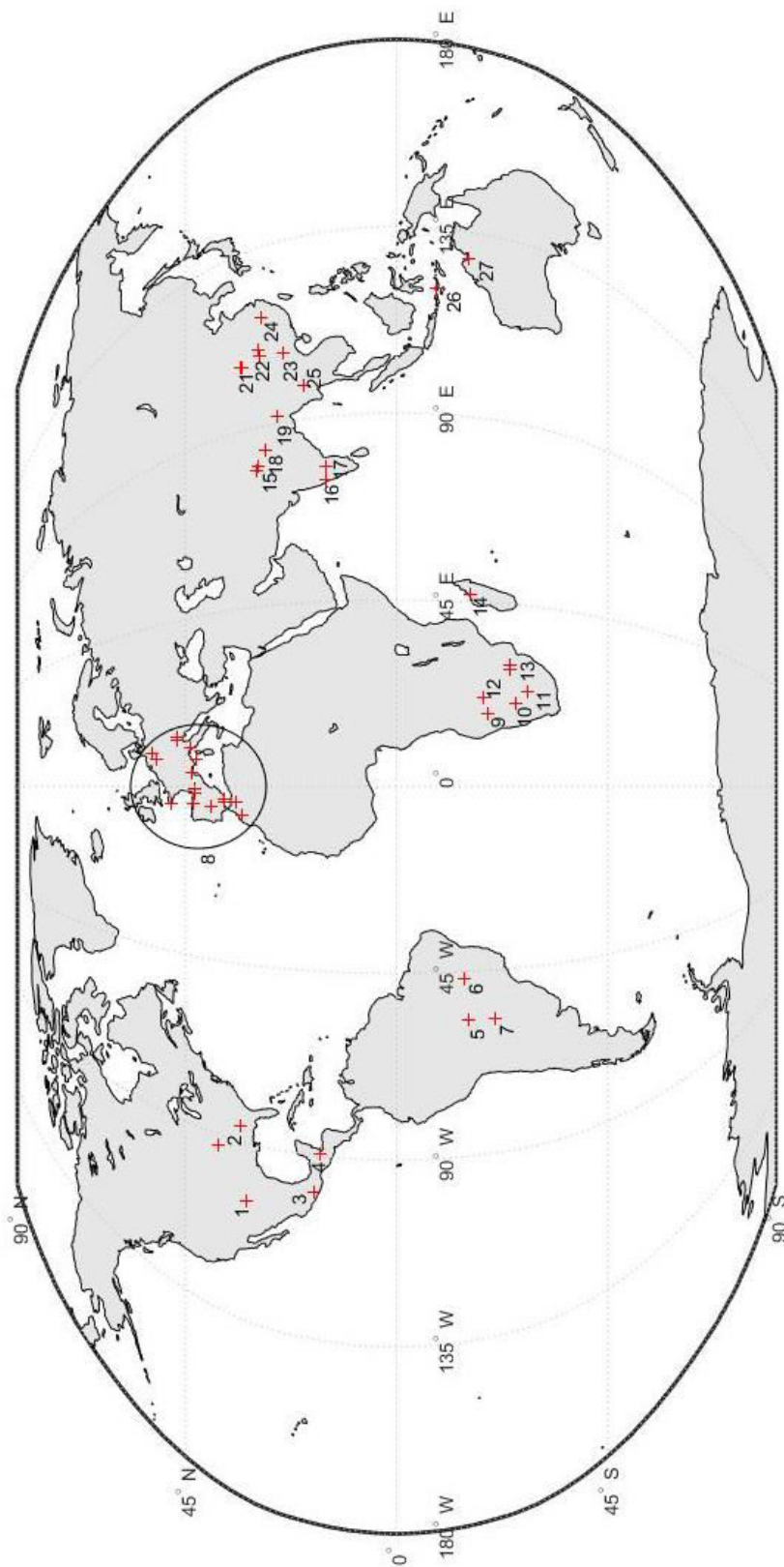


Figure 1.17: Global distribution of aragonite speleothems. Information of individual locations has been given in table 1.1.

Code	Cave	Country	Entity	Lithology	Aragonite/Calcite form	Reference
1	Hidden	USA	89029, 89037	Not given	Primary aragonite and primary calcite	Polyak and Asmerom, 2001
2	DeSoto; Onandaga	USA	Multiple actively growing stalagmite tips; DSSG-4; Single stalagmite, not named; ON-3	Dolomite; Dolomite and limestone	Primary aragonite stalagmites; Primary calcite and primary aragonite	Lambert and Aharon, 2010; Aharon et al, 2012; Denniston et al, 1999; Denniston et al, 2000
3	Juxtlahuaca	Mexico	JX-1; JX-6	Dolomite	Primary aragonite, primary calcite and secondary calcite	Lachniet et al, 2012; Lachniet, 2015
4	Yok Balum	Belize	YOK-G, YOK-I	Limestone, dolomitised limestone	Primary aragonite	Jamieson et al, 2016; Lechleitner et al, 2016
5	Curupira	Brazil	CUR4	Not given	Primary aragonite	Novello et al, 2016
6	Sao Bernardo	Brazil	SBE3	High Mg limestones, dolostones	60-90% aragonite. No evidence of diagenesis.	Moquet et al, 2016
7	Joao Arruda	Brazil	ST-JA3	Dolostones, limestones	Primary aragonite	Bertaux et al, 2002
8	See figure 1.18 and table 1.2					
9	Dante	Namibia	DP1	Dolomite	Primary aragonite and primary calcite	Sletten et al, 2013
10	Sudwala	South Africa	SC1	Dolomite	Primary aragonite, primary calcite and secondary calcite	Green et al, 2015
11	Wonderwerk	South Africa	W-1	Dolomite	Primary calcite and primary aragonite	Brook et al, 2010
12	Drotsky/Gowihaba	Botswana	D18; BD51	Dolomitic marbles	Primary aragonite and primary calcite	Brook et al, 1992; Railsback et al, 1999
13	Cold Air; Wolkberg	South Africa	T5; T7; T8; W5	Dolomite	Primary aragonite and primary calcite	Repinski et al, 1999; Lee-Thorp et al, 2001; Finch et al, 2001; Finch et al, 2003; Finch et al, 2004; Holzkamper et al, 2009
14	Anjohibe	Madagascar	MA1; MA2	Dolostones, limestones	MA1-Primary aragonite; MA2-Primary calcite and primary aragonite	Brook et al, 1999
15	Chulerasim; Dharamjali; Panigarh	India	Single stalagmite, not named; DH-2; PG-1	Limestone; Dolomite and limestone; Limestone	Primary aragonite; Primary aragonite with some calcite in alternate layers; Primary aragonite and primary calcite	Kotlia et al, 2017; Duan et al, 2013; Sanwal et al, 2013; Liang et al, 2015
16	Akalagavi	India	Single stalagmite, not named	Limestone, dolomite	Primary aragonite	Yadava et al, 2004
17	Valmiki	India	VSPM4	Dolomite	Primary aragonite	Lone et al, 2014
18	Sidhi Baba	Nepal	SB-18; SB-19	Dolomite	Primary aragonite and primary calcite	Denniston et al, 2000
19	Mawmluh	India	MAW-0201	Not given	Primary aragonite	Myers et al, 2015
21	Dayu; Xianglong	China	DY-1; XL21	Dolomite; Not given	Primary aragonite; Primary aragonite and primary calcite	Tan et al, 2009; Tan et al, 2013
22	Furong; Lianhua	China	FR0510-1; FR5; A1; LH2; LHD1	Limestone, dolomite; Limestone, dolomite	Primary aragonite; primary aragonite	H-C Li et al, 2011; T-Y Li et al, 2011; Cosford et al, 2008; Zhang et al, 2013; Yin et al, 2014
23	Xianren	China	YXR5	Not given	Primary aragonite	Shen et al, 2013
24	Shennong	China	SN3; SN15	Limestone and dolostone	Primary aragonite and secondary calcite	Zhang et al, 2014
25	Namjang	Thailand	NJ-1	Limestone and dolomite	Primary aragonite	Cai et al, 2010
26	Liang Luar	Indonesia	LR06-C5	Limestone	Primary calcite and primary aragonite	Ayliffe et al, 2013
27	KN-51	Australia	2 calcite and 17 aragonite stalagmites	Limestone	Primary aragonite, primary calcite and secondary calcite	Denniston et al, 2013

Table 1.1: Global distribution of aragonite speleothems. Locations of caves have been shown in Figure 1.17.

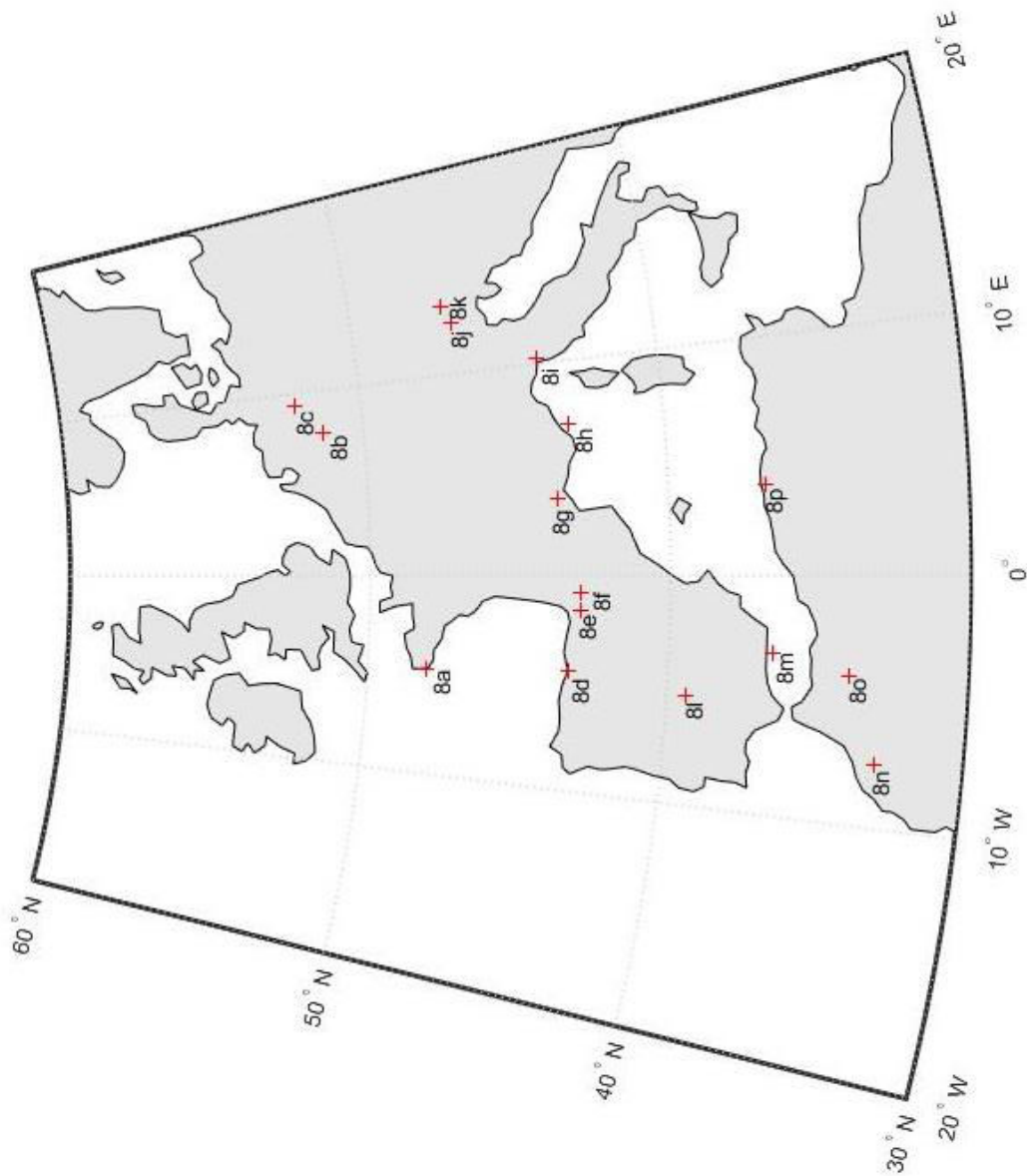


Figure 1.18: Distribution of aragonite speleothems between 30°N to 60°N and 20°W to 20°E. Information of individual locations has been given in table 1.2.

Code	Cave	Country	Entity	Lithology	Aragonite/Calcite form	Reference
8a	Pont-de-Ratz	France	22 stalagmites, stalactites and flowstones	Dolomite and limestone	Primary aragonite, primary calcite and secondary calcite	<i>Perin et al, 2014</i>
8b	Huttenblaserschachthöhle	Germany	HSBH-1	Limestone	Primary aragonite and primary calcite	<i>Yang et al, 2015</i>
8c	Reisenberghöhle	Germany	RBH 34	Limestone	Diagenetically altered speleothem	<i>Scholz et al, 2014</i>
8d	El Soplaio	Spain	Multiple samples; Flowstones; 4 aragonite stalagmites	Dolostones, limestone, dolomite	Primary calcite, primary aragonite and calcite cement	<i>Rossi et al, 2016; Gazquez et al, 2014; Rossi et al, 2010</i>
8e	Basajuan Etxea/Ayerdi III	Spain	Multiple stalagmites	Dolostones and magnesites interbedded with sandstones and shales, chalcopryrite in dolostones.	Primary aragonite, primary calcite and secondary calcite	<i>Martin-Garcia et al, 2014</i>
8f	Pierre Saint Martin	France	6 inactive stalactites	Limestone	Primary aragonite, primary calcite and secondary calcite	<i>Ortega et al, 2005</i>
8g	Grotte de Clamouse	France	CL26; CL27; Multiple samples	Dolomites and limestones	Primary calcite, primary aragonite and secondary calcite	<i>Frisia et al, 2002; Mcmillan et al, 2005</i>
8h	Serra do Courel	Spain	ESP03	Not given	Primary aragonite and primary calcite	<i>Railsback et al, 2011</i>
8i	Antro del Corchia	Italy	CC26	Dolomites, marbles, dolomitic marbles, schists	Diagenetically altered speleothem	<i>Bajo et al, 2016</i>
8j	Obstanser Eishöhle	Austria	Five active stalactites	Dolomite with pyrite	Primary aragonite	<i>Spotl et al, 2016</i>
8k	Kozak	Austria	Multiple stalagmites and flowstones	Dolomite	Primary aragonite	<i>Spotl et al, 2016</i>
8l	Castañar	Spain	Multiple speleothem samples	Not given	Primary aragonite, primary calcite and dissolution	<i>Alonso-Zarza et al, 2011</i>
8m	Las Alpujarras; Nerja	Spain	Flowstone, no name; Single stalagmite, no name	Not given; Dolomite marbles	Primary aragonite; Primary aragonite	<i>Gotte and Richter, 2009; deCisneros and Caballero, 2011</i>
8n	Grotte Prison de Chien/Dog's Prison	Morocco	HK1; HK3	Calcite and subordinate dolomite	Primary aragonite, primary calcite, no evidence for diagenesis	<i>Wassenburg et al, 2012</i>
8o	Grotte de Piste	Morocco	GP2; GP5	Dolomite with limestone intervals	Primary aragonite, primary calcite and secondary calcite	<i>Wassenburg et al, 2012; Wassenburg et al, 2013</i>

Table 1.2: Distribution of aragonite speleothems between 30°N to 60°N and 20°W to 20°E. Locations of caves have been shown in Figure 1.18.

Figure 1.17 shows that aragonite speleothems have been found between latitudes 45°S to ~45°N and across all continents apart from Antarctica. The pattern of occurrence of aragonite in the different cave systems varies. Some studies are based on speleothems that are composed entirely of primary aragonite (*Repinski et al, 1998; Repinski et al, 1999; Brook et al, 1999; Finch et al, 2001; Thorp et al, 2001; Bertaux et al, 2002; Finch et al, 2003; Yadava et al, 2004; Cosford et al, 2008; Tan et al, 2009; Gotte and Richter, 2009; Lambert and Aharon, 2010; Rossi et al, 2010; Cai et al, 2010; Cisneros and Caballero, 2011; H-C Li et al, 2011; T-Y Li et al, 2011; Aharon et al, 2012; Zhang et al, 2013; Shen et al, 2013; Yin et al, 2014; Lone et al, 2014; Myers et al, 2015; Novello et al, 2016; Spotl et al, 2016; Jamieson et al, 2016; Lechleitner et al, 2016; Kotlia et al, 2017*). Where the cause for aragonite (versus calcite precipitation) has been discussed in studies, presence of high-Mg rocks resulting in high Mg/Ca ratios of drip waters is given as an explanation for preferential aragonite precipitation. For example, in Furong cave located in China, high Mg/Ca ratios in drip waters of 1-6 mol/mol measured over a 3 year monitoring period are used to explain the presence of aragonite speleothems (*T-Y Li et al, 2011*). In Obstanzer Eishöhle cave located in Austria, pyrite bearing host rock allows for acidic solutions driving drip water Mg/Ca ratios and resulting in aragonite speleothem precipitation (*Spotl et al, 2016*). Whereas in Yok Balum cave, prior carbonate precipitation resulting in elevated Mg/Ca ratios in drip waters explains the formation of primary aragonite speleothems (*Lechleitner et al, 2016*).

Other studies are based on speleothems that have stratigraphic layers of primary aragonite and primary calcite with no evidence for diagenesis or formation of secondary calcite (*Brook et al, 1992; Brook et al, 1999; Railsback et al, 1999; McDermott et al, 1999; Denniston et al, 1999; Denniston et al, 2000a; Denniston et al, 2000b; Polyak and Asmerom, 2001; Finch et al, 2004; McMillan et al, 2005; Holzkamper et al, 2009; Brook et al, 2010; Railsback et al, 2011; Wassenburg et al, 2012; Tan et al, 2013; Sletten et al, 2013; Sanwal et al, 2013; Ayliffe et al, 2013; Yang et al, 2015; Rossi and Lozano, 2016*). Rossi and Lozano,

2016, in their detailed study on calcite-aragonite transitions in the same stalagmite find that apart from possible substrate effects, drip water Mg/Ca is the only obvious control on calcite-aragonite transitions. In the studied stalagmites and pools, calcite- and aragonite-precipitating drip waters are separated by an initial (i.e. at stalactite tips) Mg/Ca threshold at ≈ 1.1 mol/mol. Within the analysed ranges of pH (8.2–8.6), CO_3^{2-} concentration (1–6 mg/L), supersaturation ($\text{SI}_{\text{aragonite}}$: 0.08–1.08; $\text{SI}_{\text{calcite}}$: 0.23–1.24), drip rate (0.2–81 drops/min) and dissolved Zn (6–90 $\mu\text{g/L}$), they observe no unequivocal influence of these parameters on CaCO_3 mineralogy. Elevated Mg/Ca ratios in drip waters due to moisture deficit driving prior carbonate precipitation verified by covariation of Mg/Ca and S/Ca ratios is an established cause of speleothems that precipitate as both aragonite and calcite in different stratigraphic layers (*McMillan et al, 2005; Wassenburg et al, 2012*).

Remaining studies are based on speleothems that show signs that primary aragonite has been post-depositionally transformed to secondary calcite (*Frisia et al, 2002; Ortega et al, 2005; Hopley et al, 2009; Lachniet et al, 2012; Wassenburg et al, 2013; Denniston et al, 2013; Perrin et al, 2014; Martin-Garcia et al, 2014; Scholz et al, 2014; Zhang et al, 2014; Lachniet et al, 2015; Bajo et al, 2016*). *Lachniet et al, 2012* and *Lachniet, 2015* suggest that aragonite precipitation is caused by high Mg/Ca ratios caused by dolomitic bedrock dissolution whereas diagenetic episodes are caused by flushing events during high rainfall periods reducing water-rock interaction time and reduced Mg/Ca ratios in drip waters. *Scholz et al, 2014* suggest multiple possibilities such as mixing corrosion by two parcels of water mixing or fast flow of water or change from open-to-closed system conditions of host rock dissolution.

1.7 Overview of thesis

Past climate of peninsular India is currently poorly understood due to the paucity of paleoclimate records. A greater understanding of past climate from peninsular India and the

dominant drivers and mechanisms is important to understand variability of the monsoon and assess the processes driving monsoon change. Towards this larger goal, the current project aims to answer the following:

- i) What is the temporal and spatial distribution of speleothems in peninsular India?
Are there physical limitations i.e. absence of speleothems covering a particular time period, or speleothems with open systems or high detrital thorium concentrations?
- ii) Can the interpretation of $\delta^{18}\text{O}$ of these speleothems be constrained using cave monitoring studies and trace element measurements?
- iii) Investigating stable isotope, trace element and uranium-thorium systems of aragonite stalagmites.
- iv) When was the rainfall higher in peninsular India?
- v) What were the chief controls on precipitation in the Indian peninsular region?
- vi) What was the relationship of the ISM with the global monsoon?

Chapter 2

Indian Speleothem Records and Peninsular Indian Caves

2.1 Overview

Conducting paleoclimate work on speleothems from peninsular India requires the presence of suitable caves where speleothems can be recovered for analysis. This chapter briefly discusses the published speleothem-based paleoclimate data from Indian caves. It outlines existing evidence for suitable caves, based on scientific literature, as well as tourism websites and other online sources. It provides details of the caves visited as part of the research presented in this thesis. And further, it lists samples collected and explores the feasibility of setting up cave monitoring programmes based on the cave survey.

2.2 Speleothem-based paleoclimate records from Indian caves

Figure 2.1 and table 2.1 (table extends across two pages) indicate the location and give a list of published speleothem records from India. These records are described in detail below the table.

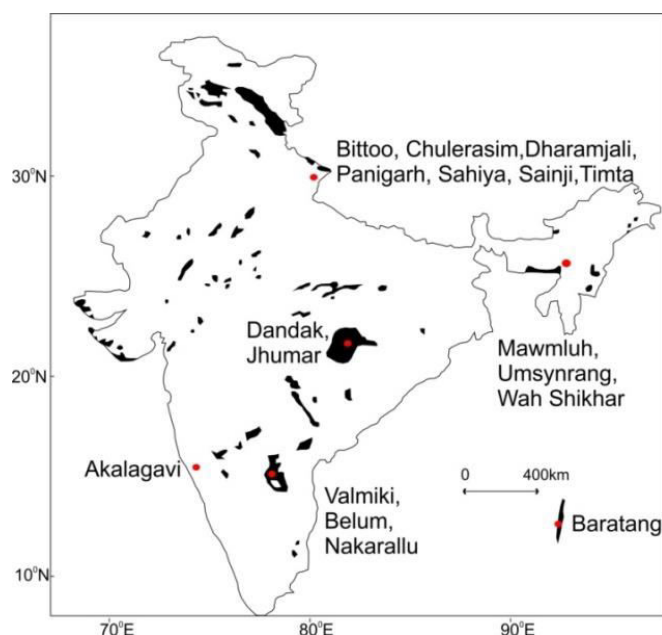


Figure 2.1: Cave locations plotted on a carbonate map of India. The black patches on the map indicate carbonate formations. Red dots indicate locations of caves with published speleothem records.

No.	Cave Name	Location: State	Latitude	Longitude	Elevation (m asl)	Start Year (y BP)	End Year (y BP)	Dating method	Number of Dates	Mineralogy	Proxy measured	Equilibrium test
1	Akalagavi	Karnataka	14° 59'	74° 31'	521	284 +/- 7	-47 +/- 7	Radiocarbon dating, layer-counting, C-14 bomb spike	1	Aragonite	$\delta^{18}\text{O}$, $\delta^{13}\text{C}$	Hendy test
2	Baratang	Andaman and Nicobar Islands	12° 05'	92° 45'	20	2050	-57	U-Th dating, radiocarbon dating, C-14 bomb spike	17	-	$\delta^{18}\text{O}$	Hendy test
3	Belum	Andhra Pradesh	15° 06'	78° 06'	288	108000 +/- 8000	99000 +/- 2000	U-Th dating	11	-	$\delta^{18}\text{O}$	-
4	Bittoo	Uttarakhand	30° 47'	77° 46'	3000	283817 +/- 3000	874 +/- 400	U-Th dating	167	Calcite	$\delta^{18}\text{O}$	Replication
5	Chulerasim	Uttarakhand	29° 53'	79° 21'	3000	328 +/- 60	0 +/- 60	U-Th dating	7	Aragonite	$\delta^{18}\text{O}$, $\delta^{13}\text{C}$	-
6	Dandak	Chattisgarh	19° 00'	82° 00'	400	1350 +/- 50	0 +/- 50 years	U-Th dating	13	Calcite	$\delta^{18}\text{O}$	Along growth layer
7	Dharamjali	Uttarakhand	29° 31'	80° 12'	2200	1780 +/- 500	60 +/- 190	U-Th dating	5	Aragonite	$\delta^{18}\text{O}$, $\delta^{13}\text{C}$, growth rate	-
8	Jhumar	Chattisgarh	18° 52'	81° 52'	600	875 +/- 250	-58 +/- 250	U-Th dating	4	Calcite	$\delta^{18}\text{O}$	Replication
9	Mawmluh	Meghalaya	25° 15'	91° 42'	1160	12395 +/- 400	3653 +/- 30	U-Th dating	11	Calcite	$\delta^{18}\text{O}$	-
10	Mawmluh	Meghalaya	25° 15'	91° 42'	1160	-13 +/- 2	-63 +/- 2	U-Th dating	-	-	$\delta^{18}\text{O}$	-
11	Nakarallu	Andhra Pradesh	-	-	-	3300	1700	U-Th dating	-	-	$\delta^{18}\text{O}$	-
12	Panigarh	Uttarakhand	29° 33'	80° 07'	1520	694 +/- 20	-55 +/- 34	U-Th dating	5	Calcite and aragonite	$\delta^{18}\text{O}$, $\delta^{13}\text{C}$, %aragonite, reflectance, luminescence	-
13	Sahiya	Uttarakhand	30° 36'	77° 52'	1190	2091 +/- 30	-56 +/- 30	U-Th dating	28	-	$\delta^{18}\text{O}$	-
14	Sainji	Uttarakhand	30° 16'	79° 18'	1478	4000 +/- 400	200 +/- 130	U-Th dating	10	Aragonite and calcite	$\delta^{18}\text{O}$, $\delta^{13}\text{C}$	-
15	Timta	Uttarakhand	29° 50'	82° 02'	1900	15215 +/- 200	11664 +/- 400	U-Th dating	22	-	$\delta^{18}\text{O}$	-
16	Umsynrang	Meghalaya	25° 50'	91° 59'	825	11000	-57	U-Th dating	36	-	$\delta^{18}\text{O}$, $\delta^{13}\text{C}$	-
17	Valmiki	Andhra Pradesh	15° 09'	77° 49'	420	15700 +/- 90	14700 +/- 50	U-Th dating	9	Aragonite	$\delta^{18}\text{O}$	-
18	Wah Shikhar	Meghalaya	25° 15'	91° 52'	1290	551 +/- 300	-57 +/- 230	U-Th dating	4	-	$\delta^{18}\text{O}$	-

No.	Cave Name	Modern climate interpretation	Past climate interpretation	Conference abstract/Paper	Author	doi	Data	Notes
1	Akalagavi	Amount effect	Rainfall amount	Paper	Yadava et al, 2004	10.1191/0959683604hi728rp	-	-
2	Baratang	Amount effect	Rainfall amount	Paper	Laskar et al, 2013	10.1002/ggge.20203	-	Large U-Th errors. Radiocarbon dating preferred for ages. Error not clear.
3	Belum	Amount effect	Rainfall amount	Paper	Narayana et al, 2014	10.1016/j.quaint.2014.12.014	-	-
4	Bittoo	-	Intensification/s tronger rainfall	Paper	Khatyat et al, 2016	10.1038/srep24374	-	-
5	Chulerasim	Amount effect, vegetation cover change	Rainfall amount	Paper	Kotlia et al, 2016	10.1016/j.quaint.2016.04.007	-	-
6	Dandak	Amount effect	Rainfall amount	Paper	Sinha et al, 2007	10.1029/2007GL030431	https://www.ncdc.noaa.gov/paleo/study/8639	-
7	Dharamjali	Amount effect	Rainfall amount	Paper	Sanwal et al, 2013	10.1016/j.quaint.2013.03.029	-	-
8	Jhumar	Amount effect	Rainfall amount	Paper	Sinha et al, 2011	10.1029/2011GL047713	https://www.ncdc.noaa.gov/paleo/study/11937	-
9	Mawmluh	Amount effect	Rainfall amount	Paper	Berkelhammer et al, 2012	10.1029/2012GM001207	https://www.ncdc.noaa.gov/paleo/study/12912	-
10	Mawmluh	Nino SST, Indian Ocean Dipole	Nino SST, Indian Ocean Dipole	Conference abstract	Oster et al, 2014	-	-	American Geophysical Union
11	Nakarallu	Amount effect	Rainfall amount	Conference abstract	Sinha et al, 2016	-	-	European Geosciences Union
12	Panigarh	Amount effect	Rainfall amount	Paper	Liang et al, 2015	0.1016/j.quascirev.2015.07.011	-	-
13	Sahiya	Amount effect	Rainfall amount	Paper	Sinha et al, 2015	10.1038/ncomms7309	Supplementary material	-
14	Sainji	Amount effect	Rainfall amount	Paper	Kotlia et al, 2015	10.1016/j.quaint.2014.10.066	-	-
15	Timta	Amount of rainout from source to cave	Amount of rainout from source to cave	Paper	Sinha et al, 2005	10.1130/G21498.1	https://www.ncdc.noaa.gov/paleo/study/11712	-
16	Umsynrang	ITCZ movement	Rainfall amount	Conference abstract	Breitenbach et al, 2007	-	-	American Geophysical Union
17	Valmiki	Amount effect	Rainfall amount	Paper	Lone et al, 2014	10.1016/j.palaeo.2013.12.010	-	-
18	Wah Shikhar	Amount effect	Rainfall amount	Paper	Sinha et al, 2011	10.1029/2011GL047713	https://www.ncdc.noaa.gov/paleo/study/11937	-

Table 2.1: A summary list of published Indian speleothem records. The age errors given are approximates.

2.2.1 Orbital-scale variation in the Indian Summer Monsoon (ISM)

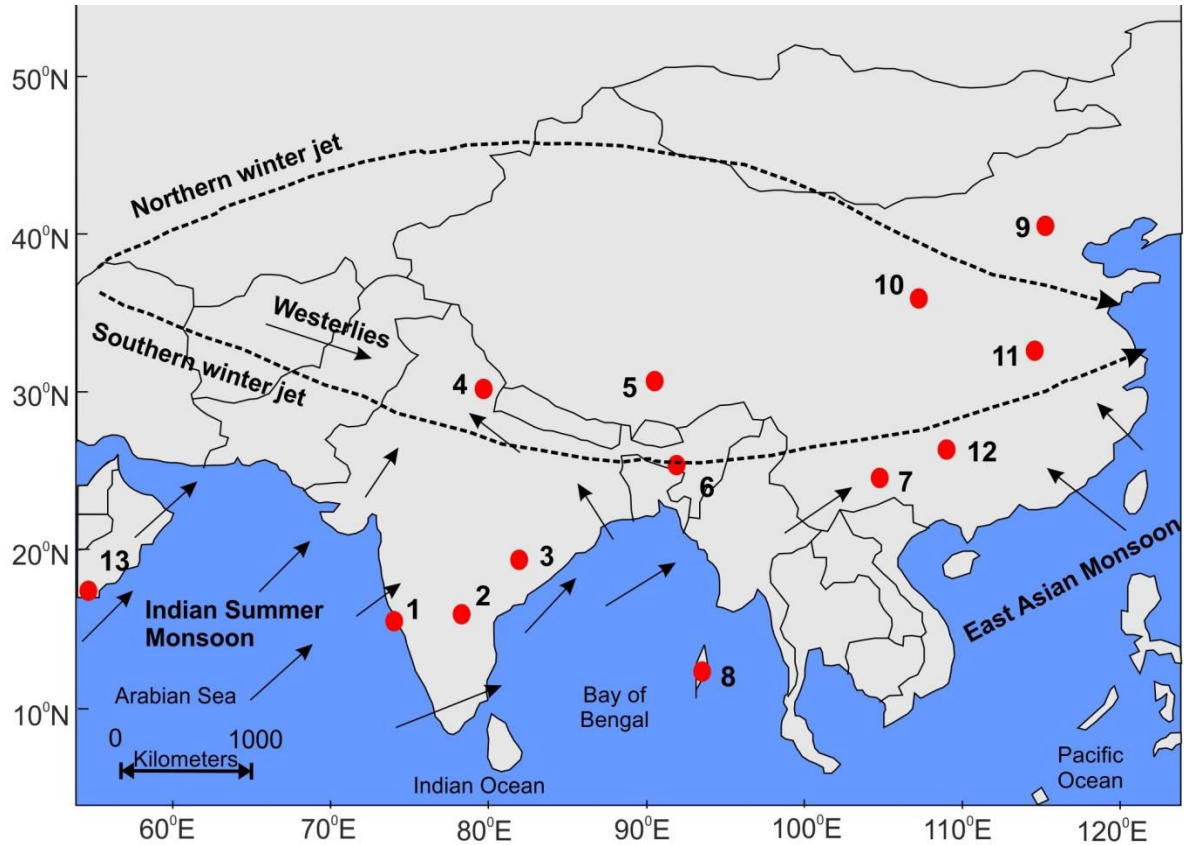


Figure 2.2: Map showing the locations of caves and moisture transport directions mentioned in the text. (1) Akalagavi (2) Belum, Valmiki (3) Dandak, Jhumar (4) Bitto, Timta, Dharamjali, Sainji, Panigarh, Chulerasim, Sahiya (5) Tianmen (6) Wah Shikhar, Mawmluh (7) Xiabailong (8) Baratang (9) Shihua (10) Dayu and Wanxiang (11) Buddha and Heshang (12) Dongge (13) Kahf Defore, Oman

There is ongoing debate whether precession induced changes to the monsoon are a result of land-sea temperature contrast which responds sensitively to insolation changes as suggested by East Asian speleothem $\delta^{18}\text{O}$ records (*Wang et al, 2008; Cheng et al, 2009; Cheng et al, 2012*) or a change acting in conjunction with global ice volume and equatorial latent heat transport from the southern Indian ocean (*Clemens and Prell, 1991; Clemens and Prell, 2003*) which could explain the phase lag seen in ocean records. The North Indian Bitto cave $\delta^{18}\text{O}$ record (*Kathayat et al, 2016*) varies in phase with July Northern

Hemisphere Summer Insolation (NHSI) without significant temporal lags, supporting the view that the tropical, sub-tropical monsoon variability is driven by precession induced changes in NHSI (figure 2.3). The Bittoo cave $\delta^{18}\text{O}$ record shows abrupt excursions to extremely low $\delta^{18}\text{O}$ values at rising limbs of NHSI followed by hiatuses thought to be caused by under-saturation of calcium in the drip water as a result of strong rainfall, resulting in a cessation of growth. Speleothem growth during glacial times is continuous and extensive with heavy $\delta^{18}\text{O}$. These observations agree well with model simulations which show that variability of $\delta^{18}\text{O}$ of precipitation in South and East Asia are inversely correlated with Indian Summer Monsoon (ISM) intensity on orbital timescales (*Battisti et al, 2014; Liu et al, 2014; Caley et al, 2014*).

Kathayat et al, 2016 also suggest that variations in speleothem $\delta^{18}\text{O}$ records from the Indian Summer Monsoon (ISM) and East Asian Monsoon (EAM) subsystems are broadly in phase on orbital and millennial timescales. This is significant since analyses show that $\delta^{18}\text{O}$ variability in the Bittoo cave area results from large scale upstream changes in monsoon circulation and moisture transport history (*Sinha et al, 2015*) but is not complicated by changes in moisture source, whereas the East Asian $\delta^{18}\text{O}$ records are complicated by mixed moisture sources (figure 2.2). Further, comparison of the North Indian record with both Antarctic ice core and southern Indian ocean Sea Surface Temperature (SST records) over the last glacial period suggest that southern hemisphere climate processes do not play a dominant role in regulating ISM variability on orbital time scales (figure 2.3).

Conversely a short speleothem $\delta^{18}\text{O}$ record from Belum cave in the peninsular Indian region (*Allu et al, 2015*) covering a span of 9 ky from 108 to 99 ky BP indicates that the deglaciation moving from colder stadial Marine Isotope Stage (MIS) 5d to warmer inter-stadial MIS 5c shows a divergent trend between ISM and the EAM. The $\delta^{18}\text{O}$ record has been interpreted in terms of the amount of rainfall and suggests that there is a step like reduction in rainfall moving from the stadial to the inter-stadial. The record is promising since it

showcases the presence of speleothems from peninsular India covering glacial-interglacial timescales and is of a high resolution (~ 85 years) for a time period for which not many high resolution records are available. Unfortunately, the record itself covers a very short time span and coincides with the hiatus period of the Bittoo cave record making interpretation difficult.

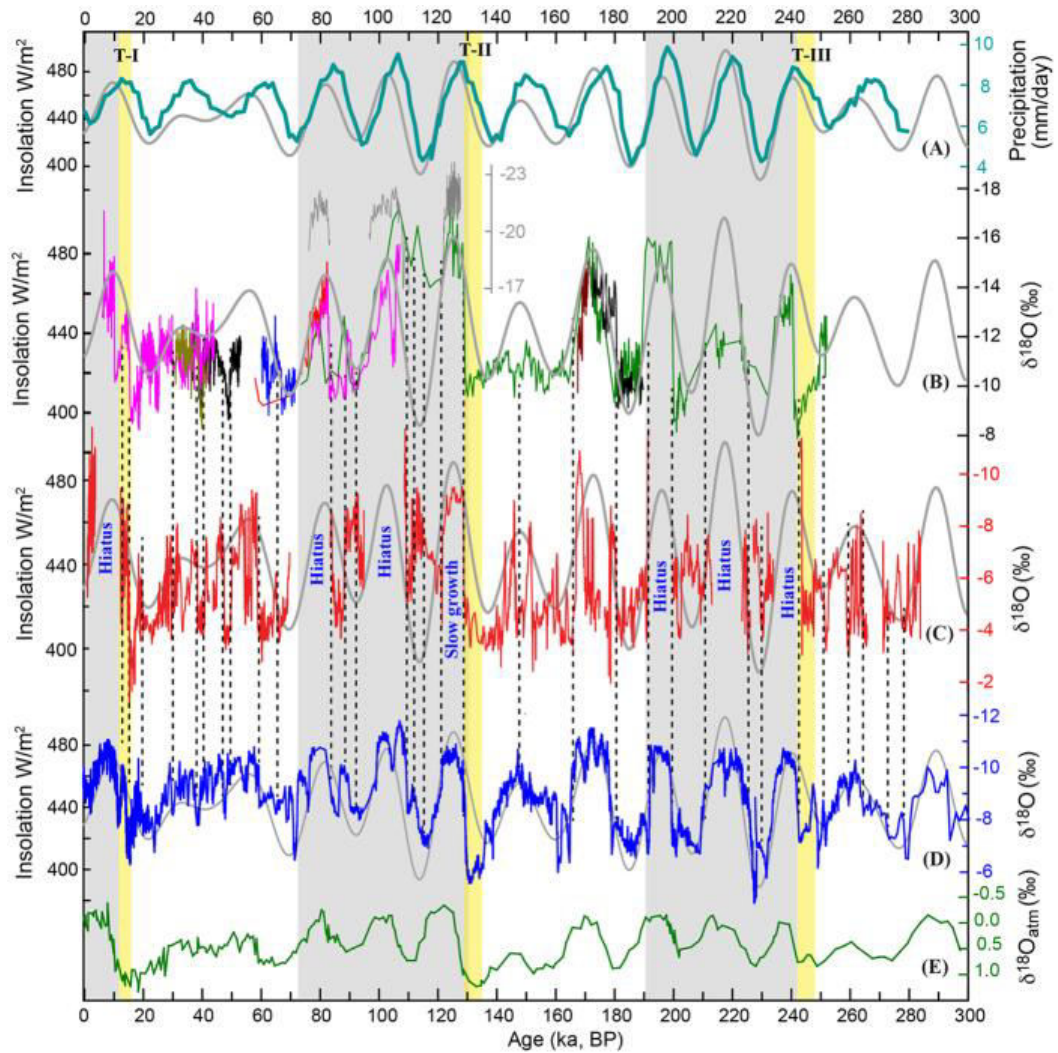


Figure 2.3: Comparison of ISM and EAM records over the past 280 ky. (A) Simulated average summer (June-August) precipitation rate in the ISM region using a fully coupled global ocean-atmosphere model (FOAM) (Kutzbach *et al*, 2008). (B) Xiabailong and Tianmen (grey) records, China (Cai *et al*, 2010; Cai *et al*, 2015) in the transition area between ISM and EAM domains. (C) The ISM record from Bittoo cave (Kathayat *et al*, 2016). (D) The composite EAM record (Cheng *et al*, 2012). (E) The atmospheric $\delta^{18}\text{O}$ record from Antarctic ice core EDC (Landais *et al*, 2010) is plotted for comparison. The grey curves represent July 21 insolation at 65°N (Berger, 1978). Vertical dashed lines depict correlations of abrupt ISM and EAM shifts. Yellow bars indicate glacial terminations I to III. Grey shading depict interglacial time periods. The figure and description are from Kathayat *et al*, 2016.

2.2.2 Millennial-scale variation in the Indian Summer Monsoon (ISM)

The north Indian Bittoo cave speleothem record (*Kathayat et al, 2016*) shows that millennial scale events, namely the Indian stadials/inter-stadials, correlate with their counterparts in Greenland (*Wolff et al, 2010*) and Chinese speleothem records (*Cheng et al, 2006; Wang et al, 2008*). The record supports model simulations showing that $\delta^{18}\text{O}$ variability in this region is inversely correlated with ISM intensity on millennial timescales (*Pausata et al, 2011*). The magnitude of positive excursions ($\sim 5\text{‰}$ for Heinrich, Dansgaard-Oeschger and Younger Dryas) is more than twice as large as those observed in Chinese $\delta^{18}\text{O}$ records. In addition, both the Indian and Chinese speleothem $\delta^{18}\text{O}$ records show a distinct peak at 18 ky BP which is neither seen in Greenland nor Antarctic ice cores (figure 2.4).

Indian stadials (inter-stadials) are associated with increases (decreases) in Antarctic temperatures and decreases (increases) in dust loadings, thus manifesting a typical bipolar see-saw pattern (*Stocker and Johnson, 2003*). Antarctic temperature change is typically small and gradual on millennial scales and needs a physical mechanism or amplifier to explain how it drives Asian monsoon variability. *Kathayat et al, 2016* suggest that the similarity between Antarctic and Asian monsoon $\delta^{18}\text{O}$ records is most likely a manifestation of their response to the same forcing such as change in SST's triggered by changes in the Atlantic Meridional Overturning Circulation (AMOC) (*WAIS divide project members, 2015*).

A high resolution (~ 20 year) speleothem $\delta^{18}\text{O}$ record from Timta cave by *Sinha et al, 2005*, also located in north India, similarly shows departure to more negative $\delta^{18}\text{O}$ values during the Bolling-Allerod inter-stadial (15.2 to 11.7 ky BP) compared to glacial and Younger Dryas times.

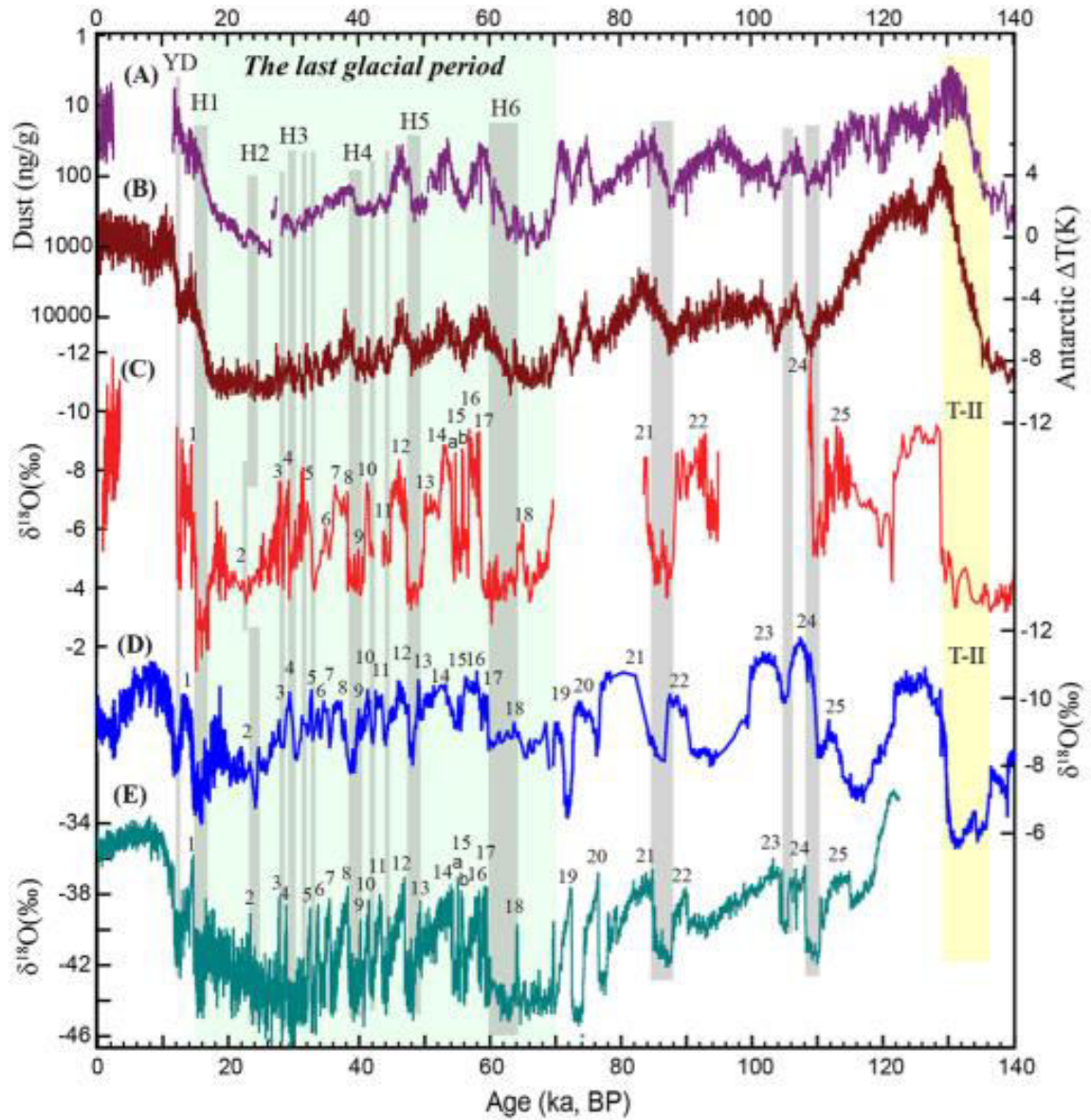


Figure 2.4: Millennial scale records for the Asian monsoon. (A) Dust record from Antarctic ice core EDC (*Lambert et al, 2008*). (B) Temperature record from Antarctic ice core EDC (*Jouzel et al, 2007*). (C) Bittoo cave $\delta^{18}\text{O}$ record (*Kathayat et al, 2016*). (D) EAM $\delta^{18}\text{O}$ record (*Cheng et al, 2012*). (E) Greenland NGRIP $\delta^{18}\text{O}$ record (*Wolff et al, 2010*). Vertical grey bars indicate weak ISM events and their correlations to weak EAM events, cold events in Greenland and higher temperatures and less dust loading in Antarctica. The yellow bar shows glacial termination II. Numbers depict Indian (C), Chinese (D) and Greenland (E) inter-stadials respectively. These millennial scale variations are synchronous within age uncertainties. Light green shading is the last glacial period. The figure and description are from *Kathayat et al, 2016*.

The Valmiki cave $\delta^{18}\text{O}$ record (*Lone et al, 2014*) from peninsular India covers a time span of 1000 years from 15.7 to 14.7 ky BP and overlaps partially with the Timta cave record. The

high resolution record (~ 5 years) reveals intervals of strong monsoon activity during the later phases of Heinrich event H1 and shows synchronous multi-decadal variability between ISM and EAM (Dykoski *et al*, 2005; Yang *et al*, 2010) even for peninsular India. The record demonstrates that strong monsoon events during late H1 preceded the inception of Termination Ia (~ 14.7 ky BP). A lag of 100 years between Termination Ia in Valmiki and NGRIP (NGRIP, 2006) may indicate change in tropical atmospheric patterns in response to northern hemisphere changes or simply an age error between the records.

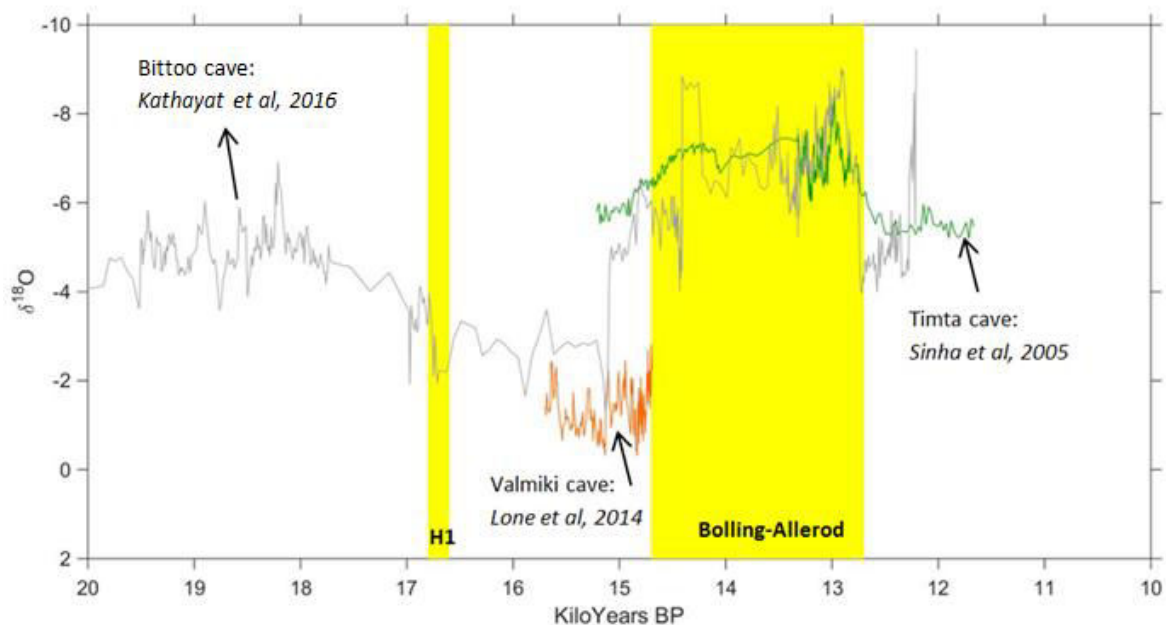


Figure 2.5: Millennial scale events in Indian speleothem records. The north Indian Bittoo cave record (grey), north Indian Timta cave record (green) and peninsular Indian Valmiki cave record (orange) have been shown. The yellow vertical bars mark Heinrich event H1 and the Bolling- Allerod interstadials. The Valmiki cave speleothem is composed of aragonite and $\delta^{18}O$ values have not been corrected to calcite values. Valmiki cave data are from GetData graph digitizer.

2.2.3 Holocene variation in Indian Summer Monsoon (ISM)

The Indian Holocene speleothem $\delta^{18}O$ records mainly address the response of the monsoon to the Little Ice Age (LIA) (1300 to 1850 AD). The LIA is characterised by regionally specific temperature departure from an overall global cooling trend over the last millennium (PAGES 2k consortium, 2013). Temperature reconstructions across the globe indicate a cooling

trend beginning between 1200-1500 AD with cooling in North America and the Southern Hemisphere lagging that in the Arctic, Europe and Asia (*PAGES 2k consortium, 2013; Ogilvie and Jonsson, 2001; Massé et al, 2008; Kobashi et al, 2011; Larsen et al, 2011; Cunningham et al, 2013*). Recent analysis of the global energy budget during the last milleium indicates that LIA cooling is dominantly driven by volcanic forcing with minor land use, greenhouse gas and insolation forcings (*Atwood et al, 2016*).

North Indian speleothem $\delta^{18}\text{O}$ records indicate an increase in rainfall during the LIA (Dharamjali cave-*Sanwal et al, 2013*; Sainji cave-*Kotlia et al, 2014*; Panigarh cave-*Liang et al, 2015*; Chulerasim cave-*Kotlia et al, 2016*) while peninsular Indian speleothems (Dandak cave-*Sinha et al, 2007*; Jhumar cave-*Sinha et al, 2011*) and a speleothem record from the Andaman islands in the Bay of Bengal (Baratang cave-*Laskar et al, 2013*) indicate a decrease in rainfall during the LIA. This pattern of wetter LIA to the north (Shihua cave: *Ku and Li, 1998*; Dayu cave: *Tan et al, 2009*; Buddha cave: *Paulsen et al, 2003*; Wanxiang cave: *Zhang et al, 2008*) and drier to the south (Dongge cave: *Wang et al, 2005*; Dongge and Heshang caves: *Hu et al, 2008*) is broadly seen in Chinese speleothem records as well. The records also vary in terms of a dry early LIA or a generally dry LIA with a wet episodes. However, a wetter LIA is indicated by a speleothem $\delta^{18}\text{O}$ record (Akalagavi cave-*Yadava et al, 2004*) and tree ring records (*Borgaonkar et al, 2010*) from the west coast of India (figure 2.6).

The interpretation of North Indian $\delta^{18}\text{O}$ records show some complications associated with mixed mineralogy/aragonite speleothems, but careful petrography measurements (*Liang et al, 2015; Kotlia et al, 2016*) coupled with a similar pattern seen in Chinese speleothems give confidence in the interpretation of a wet LIA in North India. The central Indian $\delta^{18}\text{O}$ records, namely from Dandak and Jhumar caves, are from calcite stalagmites, are of high resolution and are well replicated. The Akalagavi cave speleothem is composed of aragonite. Both the Akalagavi and Baratang records have been dated with a combination of radiocarbon and ^{14}C

bomb-spike methods, all other speleothem records mentioned above have been dated using uranium-thorium dating methods (table 2.1).

Different reasons have been suggested for the decrease in rainfall during the LIA in peninsular India by *Sinha et al, 2007* such as a solar influence (*Kodera, 2004; Newton et al, 2006; Shindell et al, 2006; Emile-Geay et al, 2007*) and influence of changing North Atlantic SST's (*Goswami et al, 2006*). The interpretation for North Indian speleothem $\delta^{18}\text{O}$ variation is more complex. ~80% of the rainfall in the Central Himalayas is brought by the ISM while ~20% is winter precipitation carried by the Westerlies. One idea is that during an otherwise weak ISM period, stronger Westerlies may have resulted in increased precipitation during the LIA (*Kotlia et al, 2012; Sanwal et al, 2013; Kotlia et al, 2015; Kotlia et al, 2016*). The varying influence of the ISM and Westerlies are caused by shifts in the mean position of the ITCZ (*Mehta et al, 2012*). While *Liang et al, 2015* suggest that contrasting records are a result of increased 'breaks' in ISM (see section 1.4) during the LIA. At the same time it is also possible that a weaker ISM and cooler ocean and continental temperatures may have pushed more depressions along the path of the southern winter jet, which brings more winter precipitation to the central Himalayan region (figure 2.2). These winter depressions are thought to be steered by the upper Westerley jet (*Barry and Chorley, 2009*).

In a separate record from Sahiya cave (~2 ky BP to present, figure 2.6) in the central Himalayas, from a study looking at the influence of human induced aerosol emissions versus natural variability of the ISM, *Sinha et al, 2015* find that periods of strong (weak) monsoon circulation are characterised by enhanced (reduced) flux of isotopically depleted Bay of Bengal moisture and reduced (enhanced) flux of isotopically enriched Arabian sea moisture. This inference rests in part on the observation that non-monsoon precipitation is an insignificant source of surface water infiltrating into the cave. Based on this interpretation of the $\delta^{18}\text{O}$ record, they infer that the magnitude of ISM multidecadal oscillations are comparable to model estimates of anthropogenic forced trends of mean monsoon rainfall in

the 21st century under various RCP scenarios (*Menon et al, 2013*). Results from the *Sinha et al, 2015* study also suggest that anthropogenic-forced changes in monsoon rainfall will remain difficult to detect in speleothem $\delta^{18}\text{O}$ records, against a backdrop of large natural variability.

Sinha et al, 2011 explore the idea of active-break periods (see section 1.4 for more information on active-break periods) by looking at two spatially separated speleothem $\delta^{18}\text{O}$ records, Jhumar cave from peninsular India and Wah Shikhar cave from northeast India. They find that the two records are anti-correlated on centennial timescales (1399 to 2008 AD, $n=390$, $r=-0.34$). They also exhibit opposing behaviour between periods with a persistently 'active dominated' (1700 to 2007 AD) and a 'break dominated' regime (1400 to 1700 AD) (figure 2.6). The switch between these regimes occurs abruptly (within decades) at a time when a proxy record of upwelling intensity from the Arabian sea suggest an abrupt increase in monsoon winds (*Anderson et al, 2002*). The switch is thought to be related to a changing tropical Pacific hydrology regime and the resulting SST gradient (*Conroy et al, 2010*). This suggests that internally generated intraseasonal variability can vary on centennial timescales, implying a leading role of internal dynamics in governing ISM response to external changing boundary conditions.

The Medieval Warm Period (MWP) (750 to 1450 AD) has an inconsistent $\delta^{18}\text{O}$ pattern and does not typify a major warming in North Indian records (*Sanwal et al, 2013; Kotlia et al, 2015*). *Liang et al, 2015*, find that the MWP is characterised by the precipitation of calcite (thought to precipitate preferentially compared to aragonite during wetter conditions in the speleothem) in their central Himalayan speleothem. They suggest that this is due to warmer North Atlantic and Eurasian landmass temperatures resulting in an increased pressure gradient and hence a stronger ISM. At the same time, this causes the Westerlies to be displaced to the North causing reduced winter precipitation. The Dandak cave record from peninsular India (*Sinha et al, 2007*) shows a relatively strong ISM during the MWP. The

Baratang cave record from Andaman islands in the Bay of Bengal (*Laskar et al, 2013*) shows that the MWP had the strongest monsoon in the last 4 ky. Conversely this record shows a strong reduction in monsoon during 2100 to 1800 years BP coinciding with the Roman Warm Period.

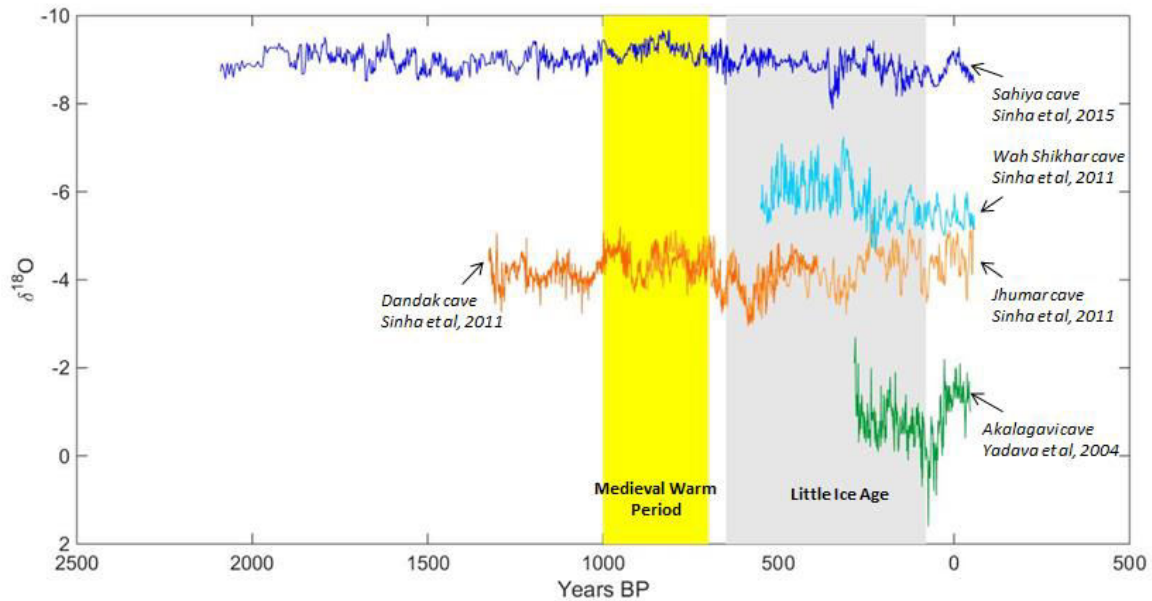


Figure 2.6: Indian speleothem $\delta^{18}\text{O}$ records for the last 2 ky (records with data available on NOAA's speleothem database or a supplementary material have been plotted, Akalagavi data was shared by the authors through personal communication). The response of speleothem $\delta^{18}\text{O}$ from central India to MWP and LIA (orange: Dandak cave). The switch from 'break' dominated to 'active' dominated regimes at 1700 AD (250 years BP) has been shown by the East Indian record (light blue: Wah Shikhar cave) and central Indian record (light orange: Jhumar cave). The Sahiya cave record (dark blue) from central Himalayas shows that the variability in $\delta^{18}\text{O}$ over the last 6 decades is within the range seen in the last two millennia. The Akalagavi cave record (green) shows significant variability and has been interpreted to reflect variability in the amount of precipitation.

Berkelhammer et al, 2013 have published a record from Mawmluh cave in northeast India that spans most of the Holocene (12500 to 3600 years BP). The record shows a significant departure at ~4 ky BP which has been interpreted as a period of drought. A similar event has been detected by records spanning across the Mediterranean, Middle East, North Africa, North America and China (*Weiss, 2012*). Although conversely the Oman (*Fleitmann et al, 2003*) and Dongge (*Wang et al, 2005*) ISM records do not show this anomaly. The cause of the 4 (or 4.2) ky event is still speculative (figure 2.7).

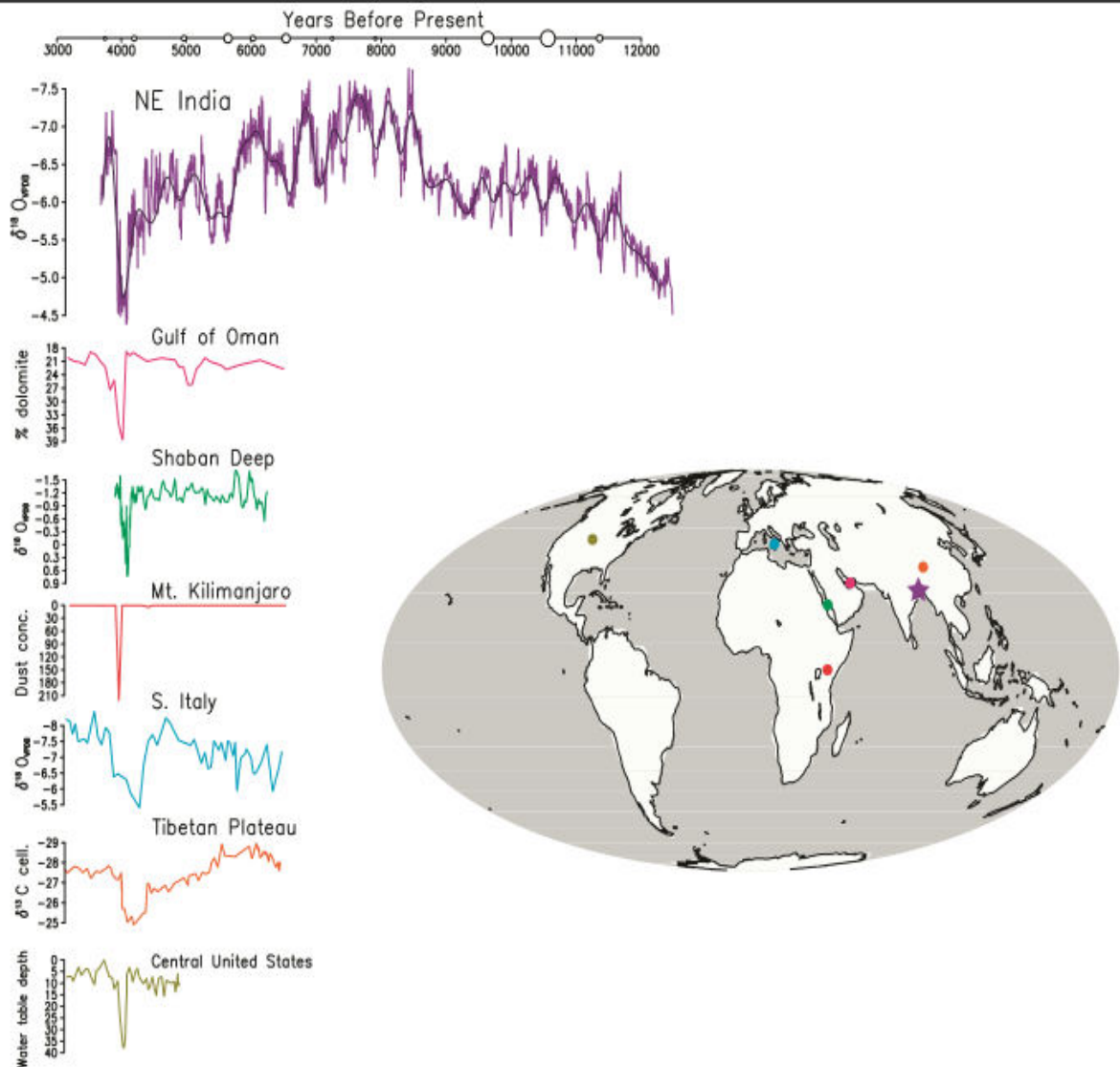


Figure 2.7: The KM-A (Mawmluh) isotope record from northeast India is shown both as raw data (purple) and smoothed using a Lanazos filter (black). Dots on the x-axis are used to delineate locations where U-Th dates were used to generate the age model. The size of the dot is proportional to the uncertainty. The location of the records is marked on the map as a star. A stack of additional records whose locations are represented with colour coding on the map are shown for comparison. Gulf of Oman dolomite record (*Cullen et al, 2000*), the Shabhan Deep foraminifera record (*Arz et al, 2006*), Mount Kilimanjaro dust record (*Thompson et al, 2002*), southern Italy speleothem record (*Drysdale et al, 2006*), Tibetan plateau $\delta^{13}C$ sedimentary cellulose (*Hong et al, 2013*) and lake level record from central United States (*Booth et al, 2005*). The figure and description are from *Berkelhammer et al, 2013*.

2.3 Context to the current thesis project

Section 2.2 describes the existing speleothem-based paleoclimate records from India and the important climate findings from them. They also highlight some challenges. For example,

- (i) Apart from the Bittoo cave record, the remaining records typically cover only brief snap shots of time.
- (ii) Chulerasim, Valmiki and Akalagavi cave records have been derived from speleothems composed of aragonite. Equilibrium precipitation of $\delta^{18}\text{O}$ and trace element studies in aragonite speleothems have been explored but are not well established.
- (iii) Belum cave record shows great promise in obtaining records around the time period of 100 ky BP from the proximal regions of the ISM but indicates challenges with U-Th dating.
- (iv) The interpretation of $\delta^{18}\text{O}$ in the context of the monsoon started out as quantification of local rainfall (*Yadava et al, 2004; Yadava and Ramesh, 2005*), but this has changed over time (for example, *Lachniet, 2009; Dayem et al, 2010*). An increase in the number of speleothem $\delta^{18}\text{O}$ records, comparison with instrumental records as well as modelling studies have widened the scope of interpretation of $\delta^{18}\text{O}$.
- (v) There are a number of speleothem studies that have emerged from the north Indian i.e. the central Himalayan region but in contrast, very few records are available from peninsular India.

Peninsular India marks the first landfall of the ISM before it proceeds to the East into the Asian landmass i.e. it is the proximal end of the monsoon. It is not complicated by mixed moisture sources and thus forms an important target area to understand the ISM including the drivers and responses of the monsoon to climate events occurring at orbital and

millennial timescales, in response to volcanic events or in response to changes taking place in other parts of the climate system such as the North Atlantic and Pacific oceans. Previous paleoclimate work undertaken on peninsular Indian speleothems has shown that they provide high resolution replicate records (for example, records from Dandak and Jhumar caves figure 2.6) and cover snapshots of time going back for the last 110 ky at least. On the other hand, the interpretation of $\delta^{18}\text{O}$ records, the interpretation of records from aragonite stalagmites (which are thought to be less stable than calcite) and the reason for such short records is not well understood.

The aim of the field work undertaken as a part of this DPhil project was to identify caves that contain speleothems suitable for paleoclimate work. In addition, monitoring work was undertaken to enable a multi-proxy approach to constraining the interpretation of the $\delta^{18}\text{O}$ record using cave drip water $\delta^{18}\text{O}$ composition, cave temperature and humidity measurements and trace element measurements. Trace elements also provide independent paleoclimate and environmental information.

2.4 Evidence for caves in peninsular India

Not all caves in karst regions are decorated (i.e. contain speleothems) and not all decorated caves are suitable for paleoclimate work. Perhaps the most important precondition to select a speleothem that is likely to yield suitable paleoclimate records is a cave that is reasonably closed to the outside environment, such that the temperature and humidity conditions in the cave are relatively constant over the year. This is an important prerequisite for enabling conditions as near to equilibrium precipitation of oxygen isotopes as possible.

The map in figure 2.1 shows the location of major caves in the respective karst regions on a carbonate map of India while the map in figure 2.8 shows the location of peninsular Indian caves with respect to topography and GNIP (Global Network of Isotopes in Precipitation) sites. Each region has been addressed separately below.

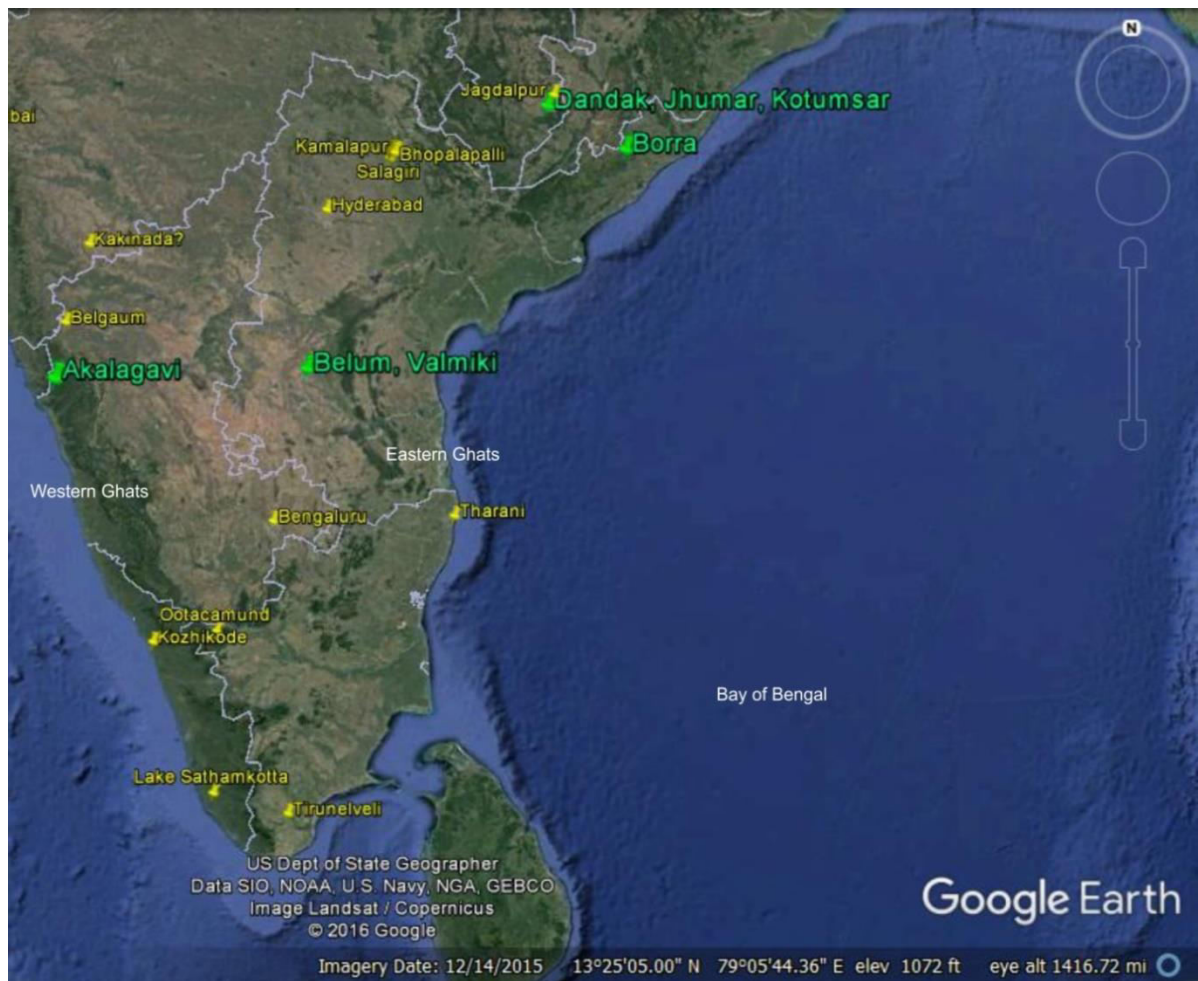


Figure 2.8: Location of main caves in respective karst regions (green) and GNIP locations (yellow) have been shown on a satellite map of peninsular India.

- i) Akalagavi cave: A sample from Akalagavi cave had been collected in 1997 by the collaborating group from Physical Research Laboratory (PRL), India. Based on paleoclimate records from this sample (*Yadava et al, 2004*), fieldwork was undertaken to survey this and other caves from the same karst region. Evidence for other caves in the same region comes from conversations with collaborators at PRL who have previously conducted fieldwork in the area, with biodiversity researchers working in the area, with locals working in a pilgrimage temple located at Ulavi village close to Akalagavi cave, and from travel blogs. The aim was to map relevant caves, collect drip waters for stable isotope and trace element geochemistry,

measure drip rates, temperature and humidity, deploy temperature loggers and identify potential for retrieving more samples.

- ii) Belum, Valmiki and Bila Surgam caves: There were two published speleothem climate records from this region, one each from Valmiki cave (*Lone et al, 2014*) and Belum cave (*Allu et al, 2014*). There are a number of other caves from this region that have been mentioned in karst publications (for example, *Dar et al, 2011*) and archaeological publications (for example, *Petraglia et al, 2009*). Of the many caves in the region, we targeted visits to known decorated caves based on the above mentioned publications to look for potential promising samples and to characterise relevant cave sites.
- iii) Borra: Borra is a well-known decorated tourist cave close to the East coast. A prior visit to the cave and photographs on tourism websites indicate that it is a large open airy cave with little potential for stable speleothem climate records. But reports from collaborators at PRL of passages below the main chamber not open to tourists warranted a visit.
- iv) Kotumsar: Kotumsar cave is possibly located in the most promising region in peninsular India for speleothem based paleoclimate records since stalagmites from Dandak and Jhumar caves from the same region have given high resolution, replicate records of $\delta^{18}\text{O}$ (Dandak cave: *Sinha et al, 2007; Berkelhammer et al, 2010*; Jhumar cave: *Sinha et al, 2011*). Kotumsar cave has not been targeted previously for paleoclimate records but there are a number of biospeleological publications based on the cave (for example, *Reddy, 2006; Biswas, 2010; Rajput and Biswas, 2012*) which suggest that the cave is decorated and has conditions suitable for paleoclimate studies. Unfortunately, the delicate political situation in the area did not allow fieldwork to be undertaken at that time. We were however able to work on a sample that had previously been collected from this cave by our collaborators at

the Physical Research Laboratory (PRL), India. The cave site has been characterised with the help of previously published material.

Although there are more carbonate zones in peninsular India, no further record of decorated caves were found in papers on karst regions, speleothems, speleology or archaeology. Tourism websites and blogs were also searched but do not mention any more caves. It is worth exploring the region further but within the remit of this thesis, a field work of three weeks was planned in January, 2015 with our collaborators at PRL (Physical Research Laboratory, Ahmadabad, India) and the most promising caves mentioned above were visited.

2.5 Field work and site characterization

2.5.1 Akalagavi and other caves in the same karst region

Akalagavi cave, located on the west coast of India, marks the first landfall of onshore winds during the summer monsoon, before they move across the country to cause rain across peninsular India. The $\delta^{18}\text{O}$ signature of rain water and thus speleothems will therefore be free from mixed source and continentality effects. It lies upstream of several other caves located further to the east and thus is a promising location to try quantitative reconstruction of the monsoon from spatially separated cave records. This involves differencing coeval $\delta^{18}\text{O}$ values from two caves, such that secondary controls on $\delta^{18}\text{O}$ (for example, moisture source, moisture transport, non-local rainfall, temperature) are circumvented and the resulting $\Delta\delta^{18}\text{O}$ signal is controlled directly by the amount of rain falling between the two sites (*Hu et al, 2008*). A previously published paleoclimate record from this cave (*Yadava et al, 2004*) covers the modern instrumental period with a high growth rate and annual laminae allowing unprecedented precision in interpreting paleoclimate records, ideal for such a quantitative reconstruction. The annual resolution would also allow for calibration of the stable isotope and trace element records with instrumental records.

a) Characterization of the cave area

The caves are located 3 km from Ulavi village in Karnataka state, India. The region is 30 km away from the Arabian Sea and is a part of the Western Ghat mountain chain that runs parallel to the coast. Hills in the region reach altitudes of ~600 m. The geology of this area consists of basement granites, overlain by the Proterozoic Kaladgi basin with Deccan basalts and laterites in patches (*Ramakrishnan and Vaidyanathan, 2008*). The caves are located in limestone/dolomite formations of the Kaladgi basin, and overlain by soils varying from a deep red to greyish in colour. Ulavi village is in the Radhanagri-Mhadei-Anshi-Dandeli forest corridor and they are protected sanctuaries. The corridor shows thick mixed deciduous C3 vegetation. The area immediately above the caves is forested with no agriculture.

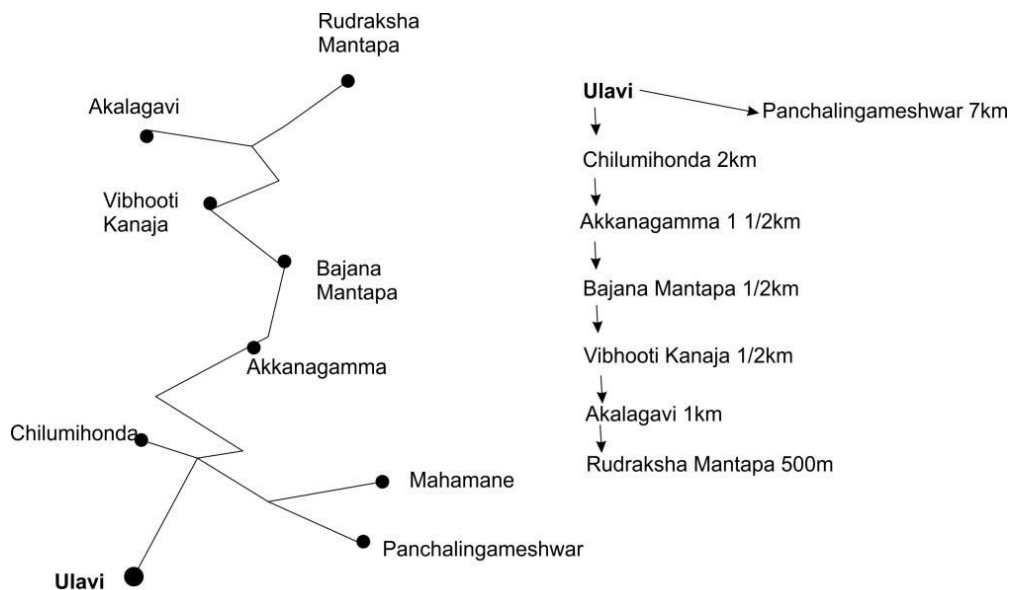


Figure 2.9: A rough sketch map of all the caves found in the area around Akalagavi cave. Approximate progressive distances have been given to the right. The figure is not to scale or direction and simply gives an idea of the number of caves in the region and their distances relative to each other.

Local guides suggested a few caves that may show decoration and drips, visits were restricted to these caves; namely, Akalagavi, Vibhooti Kanaja, Akkanagamma/Bajana Mantapa and Panchalingameshwar (figure 2.9 and table 2.2).

Akalagavi cave has two small openings to the outside but apart from this, the cave is reasonably closed suggesting that the cave may have high humidity and constant temperatures around the year. The cave has multiple drip locations and stalactites although only one other stalagmite was found. It seemed to be the most promising cave for paleoclimate work from this region so the remainder of the field visit was restricted to the exploration and measurements of this cave.

No.	Cave Name	Decorated?	Open/ Closed cave	Active drips	Suitable/ Unsuitable for paleoclimate records	Comments
1	Akalagavi	Yes: stalagmites, stalactites and flowstones	Closed	Yes	Suitable	Few stalagmites, many 1-2 cm long stalactites
2	Vibhoothi Kanaja	Yes: flowstones	Open	No	Unsuitable	
3	Akkanagamma/ Bajana Mantapa	No	Open	No	Unsuitable	There is some confusion as to which cave was visited.
4	Panchalingam- eshwar	Yes: single stalagmite	Open	Yes	Unsuitable	Deity stalagmite, dissolution at the tip of the stalagmite indicating that the drip is unsaturated for Ca at certain times.

Table 2.2: Characteristics of caves in the Akalagavi karst region.



Figure 2.10: Images of caves from Akalagavi cave region. (A) '5-headed deity' stalagmite from Panchalingameshwar cave (B) Decoration from Vibhoothi Kanaja cave.

b) Akalagavi cave ($14^{\circ} 59' \text{ N}$, $74^{\circ} 31' \text{ E}$, 521 m asl)

The cave is located 10 m up a steep cliff-side with a further 30 m of overhang above it, the top of which is difficult to access. Access to the cave is with the help of a fixed sturdy metal ladder (figure 2.12). Beyond the ladder there is a crawling passage for 10 m from a ledge to the first chamber of the cave. Water is pooled at the bottom, where it is removed through gravity flow by a pipe. Further details of the cave can be seen in the cave map (figure 2.11).

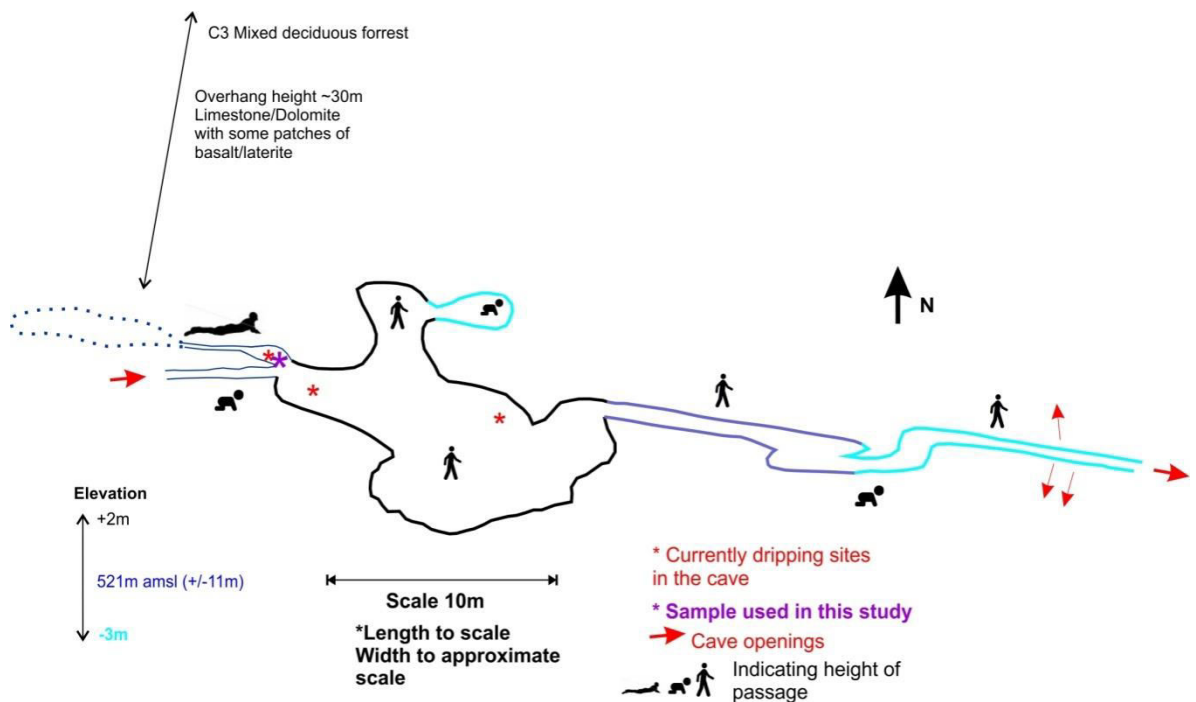


Figure 2.11: Akalagavi cave map. Cave size parameters were measured with a DistoX instrument, which allows distances to be measured using a laser pointer, combined with a compass/clinometer. The map was produced using the software Survox and modified using CorelDRAW. The dashed line indicates a chamber that was seen but which could not be entered because of the very narrow passage that led to it. The floor sounds hollow as if there is a passage below, but no opening to such a passage was found.

At the end of the crawling passage there is a chimney like cavity which contained the stalagmite sample that had been previously removed by PRL (initial results have been published in *Yadava et al, 2004*). The chimney like cavity contains numerous dripping sites with one large stalactite and several 1-2 cm long stalactites (figure 2.13). There is pooling of

drip water on a ledge in this cavity. There are two extremely narrow crawling passages at the end of the chimney like cavity; no decoration was seen to the extent that the passage could be crawled. To the right, moving away from the chimney like cavity are two cave chambers. Both chambers show extensive dripping sites in specific zones with numerous 1-2 cm long stalactites. One more stalagmite was seen in a chamber but it has multiple heads and is the only stalagmite remaining in the cave, and to the best of our knowledge, on the west coast of India, so it was not removed. One chamber leads to a dead end while the second leads to a 25 m long passage way which ends in a narrow scar like opening. Access to the cave from this side is limited since the scar is up a steep cliff. The passageway shows flowstones and rim stones. They were inactive at the time of the visits in January, 2015 and a subsequent monitoring visit in March, 2016. Based on the field work we decided to continue work on the stalagmite previously removed by PRL. There was modern carbonate growth at the site from where the sample had been previously removed.

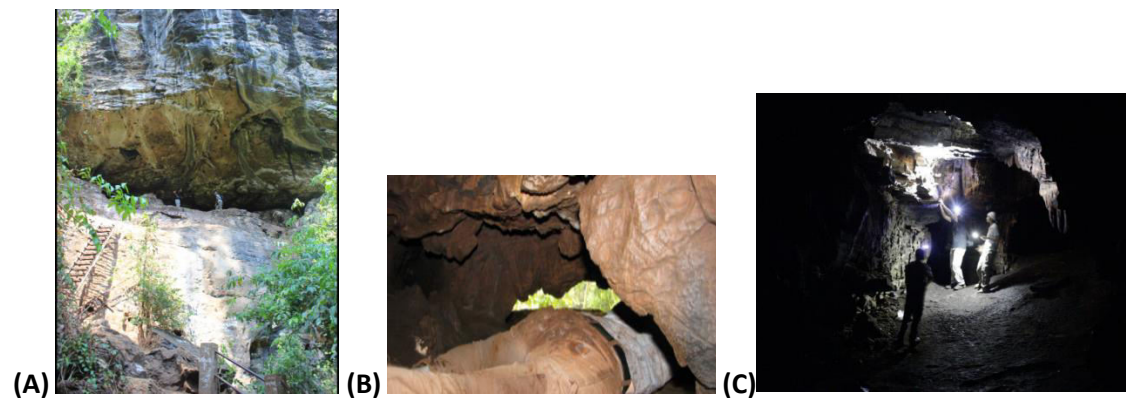
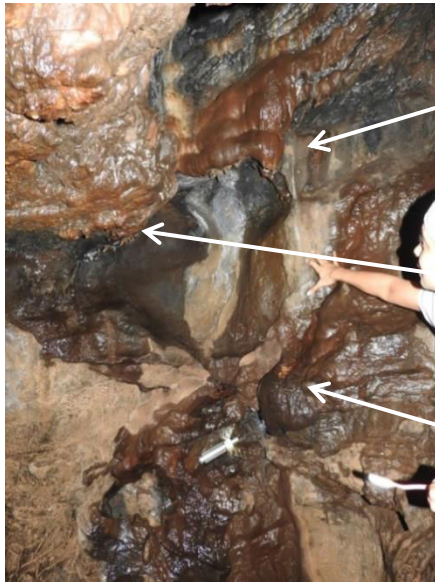


Figure 2.12: Akalagavi cave site. (A) Entrance to Akalagavi cave is up a steep cliff accessed by a permanently installed ladder. (B) Entrance to the cave itself is through a narrow crawling passage that extends for 10 m. (C) The main chamber of the cave.



Larger stalactite over which drip water flows before dripping on the sample.

Smaller stalactites, more typically found in the cave. Drip water flows *through* these stalactites.

Scar of sample stalagmite.

Figure 2.13: Akalagavi stalagmite sample location, drip water feeding it and stalactites typically found in the cave.

c) Logistics

Access to the caves from Ulavi village is controlled by the Forest Department. The gate to enter the forest is open between 9 am and 6 pm but requests can be made of the forest guard on duty. A four-wheel drive is recommended for the dirt track leading from Ulavi to Akalagavi, or the distance can be walked instead (~4 km). Jeeps and cave guides can easily be hired from Ulavi village centre on the same day or with a day's notice. There are steps for 1 km from the end of the dirt track to the cave.

Ulavi is a small village around a temple that attracts a number of visitors from nearby cities. The village can get very crowded on special festival days and weekends. Stay and food can be organized at Ulavi.

2.5.2 Belum, Valmiki, Bila Surgam and other caves in the same karst region

The rainfall amount in this region is 700 mm per year and is half that of Akalagavi and Kotumsar cave regions. This region likely feels the stress of low rainfall before regions closer to the coast and this amplified signal should be reflected by speleothems. Previous

paleoclimate records (Valmiki cave: *Lone et al, 2014*; Belum cave: *Allu et al, 2015*) from stalagmites in this region suggest that the stalagmites are much older and can be targeted for specific climatic events such as glacial-interglacial cycles and Heinrich events.

A comprehensive review of the caves of this region has been given in *Dar et al, 2011*. The karst region is well developed and may have a number of decorated caves. However, given the limited time available for fieldwork within the remit of this thesis, it was not possible to visit all the caves. Valmiki, Belum and Bila Surgam were chosen for further exploration. Valmiki and Belum caves have published paleoclimate records establishing that speleothems from these caves are suitable for paleoclimate work. Bila Surgam has been extensively studied by archaeologists who find evidence of human habitation before and after the Toba eruption of (74 ky) (*Petraglia et al, 2009*). Publications indicated that the cave system is well explored and is familiar to the local guides and hence was selected for this field work.

a) Characterization of the cave area

Valmiki, Belum and the other caves in this region are located in Kurnool district of Andhra Pradesh state. The caves have developed in the karst region of the half-moon shaped Proterozoic Cuddapah Sedimentary basin that lies above the Dharwad craton and covers 44,500 sq km (*Narayanaswami 1966; Qureshy et al. 1968; King 1872; Crawford and Compston, 1973; Kailasam 1976; Dutt, 1981; Murthy 1981; Kaila and Tewari, 1985; Kale 1991 {Referenced as Vivek S.}; Ramam and Murty, 1997; Kasipathi et al. 2008; Raju, 2009*).

A full review of the karst region has been given in *Dar et al, 2011* and only information relevant to this field work has been summarised here. The region shows open scrub vegetation and agricultural land. Valmiki cave is located in dolomitic hills (figure 2.14). The hills have moderate dips of 5-18°. Valmiki cave is 317 m in length and 77 m in depth and is the deepest known cave in south India (*Gebauer, 1985*). It shows the presence of infiltration

water during the monsoon (from observations on the soil of the deepest part, it seems that a stream is meandering through the clay/silt deposits and possibly some water filling occurs after intense recharge). The cave ends near the bottom of the valley which constitutes the local base level. They find that irrigation wells in the region show variable discharge typical of highly heterogeneous aquifers.

Belum cave is 3225 m in length and 29 m in depth. It lies in a limestone formation (*Gebauer 1983, 1985*) (figure 2.14). The limestone is extremely fine grained and compact. It dips at an angle of 0 to 10° towards the northeast. The limestone is surrounded in various parts by quartzites and shales. The cave shows a dendritic pattern and is thought to be phreatic in origin. Streams emerging from swallow holes in the quartzite infiltrate within a short distance of emerging onto the limestone. Springs in the area show sharp reactions in response to rainfall events. In Belum cave, a temporary stream can be followed in phreatic conduits for several 100 m but it dries up quickly after. Bila Surgam cave is also located within the same limestone formation (figure 2.14).

b) Belum cave (15° 06' N, 78° 06' E, 288 m asl)

Belum cave channel was created by the flow of Chitrakut river (figure 2.15). 3500 m of the cave was surveyed in 1984 of which 2500 m was opened for tourists in 2002 AD and is now gated and protected. Some of the cave rock has been cut and modified to enable this. Prior to 2002 AD, locals used to take speleothems from the cave for religious purposes as well as to make white powder for decoration.

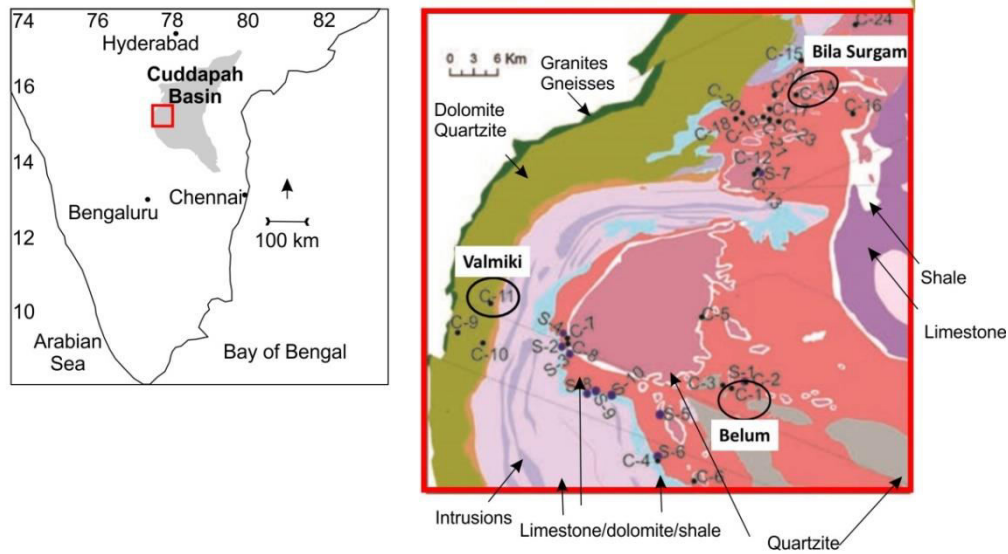


Figure 2.14: Location of caves have been shown on a geological map of the Cuddupah sedimentary basin (modified from *GSI, 1997*). Faultlines and lithology have been indicated. Their stratigraphic relationship can be seen in the original figure by *Dar et al, 2011*. S stands for spring locations and C for cave locations. Cave names have been given in table 2.3. The caves visited as a part of this field trip have been highlighted in black. Valmiki cave is also called Kuruva Bali Guha. The figure is from *Dar et al, 2011*.

	ID	Cave name	Longitude	Latitude	Length [m]	Depth [m]	Geology	Reference
Sector Kolimigundla	C1	Belum Guhalu	78°06'41.4"	15°06'7.6"	3225	-29	Narji lim.	Gebauer 1983, 1985
	C2	Belum Karst Spring	78°07'30.0"	15°06'47.2"	65		Narji lim.	Gebauer 1983
	C3	Chirutipuli Guha	78°06'06.7"	15°06'19.5"	92	-9	Narji lim.	Gebauer 1983, 1985
	C4	Bugga Guhalu	78°01'30.3"	15°00'34.8"	>10		Narji lim.	
	C5	Nela Bilam	78°04'27.12"	15°10'59.04"	>100	-14	Narji lim.	Gebauer 1985
	C6	Bandarlappalle Guha	78°04'12.2"	14°59'37.3"	117	-18	Narji lim.	
Sector Dhone	C7	Munagamanu Gavi	77°55'9"	15°09'11.2"	864	-16	Narji lim.	Gebauer 1985, 1997
	C8	Udagamanu Gavi	77°54'57.9"	15°09'0"	100		Narji lim.	Gebauer 1997
	C9	Panchalingaswami Guha	77°47'10.0"	15°09'35.0"	58	-10	Vempalle dol.	Gebauer 1985
	C10	Langu Gavi	77°49'43.0"	15°11'39.0"	65		Narji lim.	Gebauer 1997
	C11	Kuruva Bali Guha	77°49'04.8"	15°09'00.2"	318	-77	Vempalle dol.	Gebauer 1985
	C12	Yaganti caves	78°8'23.7"	15°21'3.1"	139		Narji lim.	Gebauer 1983
Sector Yaganti	C13	Yerra Zari Gabbi	77°08'11.5"	15°20'49.9"	684	-48	Narji lim.	Gebauer 1983
	C14	Bila Sorgam	78°11'7.1"	15°26'13.1"	700	-40	Narji lim.	Gebauer 1983
	C15	Sanyasula Gavi	78°10'50"	15°28'40"	234	-18	Narji lim.	Gebauer 1983, 1985
	C16	Kottala Guhalu	78°15'	15°25'	65	5	Narji lim.	Gebauer 1983
	C17	Nemmalasilla Gavi	78°09'02"	15°25'15"	35		Narji lim.	Gebauer 1997
	C18	Muchchatleswara Gavi	78°06'43"	15°24'35"	50		Narji lim.	Gebauer 1997
Sector Betamcherla	C19	Boya Dari Gavi	78°08'45"	15°24'40"	40		Narji lim.	Gebauer 1997
	C20	Chintamanu Gavi	78°07'12"	15°24'55"	100		Narji lim.	Gebauer 1997
	C21	Errabadda Caves	78°09'06"	15°24'35"	60		Narji lim.	Gebauer 1997
	C22	Road cave	78°09'34.7"	15°26'06.7"	20		Narji lim.	
	C23	Jan Galu Gavi	78°09'50"	15°24'25"	40	-17	Narji lim.	Gebauer 1997
	C24	Krishnammakona 5	78°15'	15°31'	140		Narji lim.	Gebauer 1997
Other area	C25	Chillavaripalle cave	77°50'06.4"	14°36'43.7"	86	-7	Vempalle dol.	Shibasaki 1985

Table 2.3: List of natural caves developed in two of the three karstified formations of the Cuddupah basin (compilation of original data and data published in *Gebauer 1985, 1997* and *Gebauer and Abele, 1983*). Kuruva Bali Guha is another name for Valmiki cave. The table is from *Dar et al, 2011*.

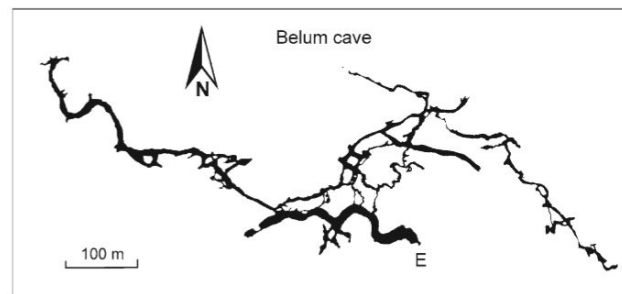


Figure 2.15: Belum cave pattern (figure from *Dar et al, 2011*).

Only one of the cave chambers, called Banyan tree, was visited during the field work. Despite artificial air circulation, humidity in this part of the cave is nearly 100%. The hygrometer probe forms a film of moisture and is unable to record humidity levels clearly. There is moisture on cave wall surfaces. There is an artificial pond and fountain 300 m away from the Banyan tree chamber inside the cave. According to the cave guides, approximately 500 people per day visit Belum cave but only a 100 people per day venture towards Banyan tree since it is a narrow passage with high temperature and humidity levels. There are few bats in the cave. Two stalagmite samples were collected from this part of the cave, a sample that was fallen to the side (Banyan Tree 1) and a sample that was removed from the path (Banyan Tree 2) (figures 2.16 and 2.17).

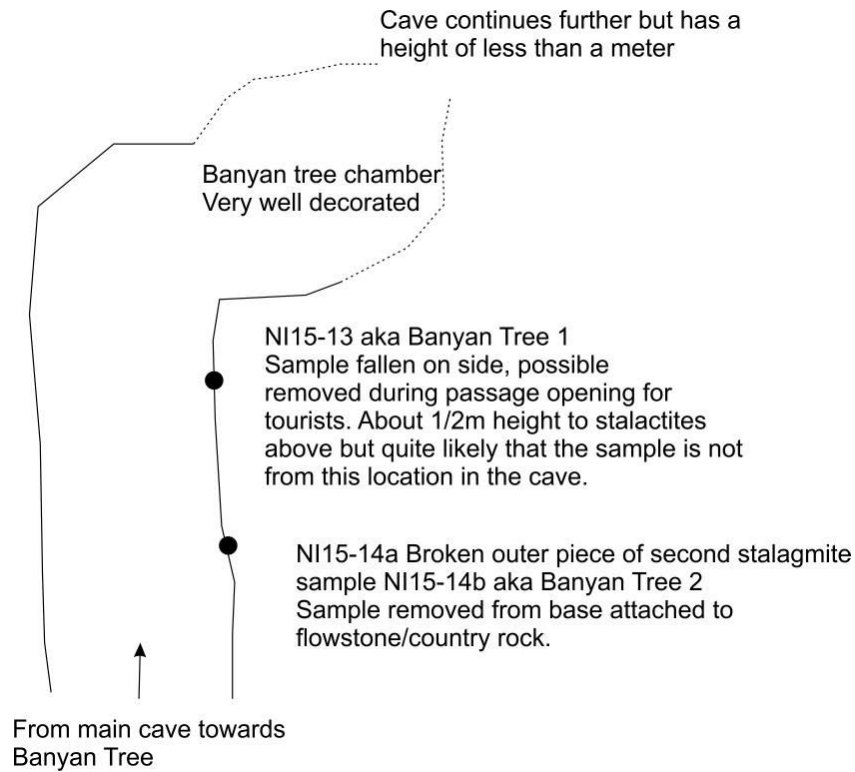


Figure 2.16: Rough sketch map showing location of stalagmite samples collected from Belum cave.

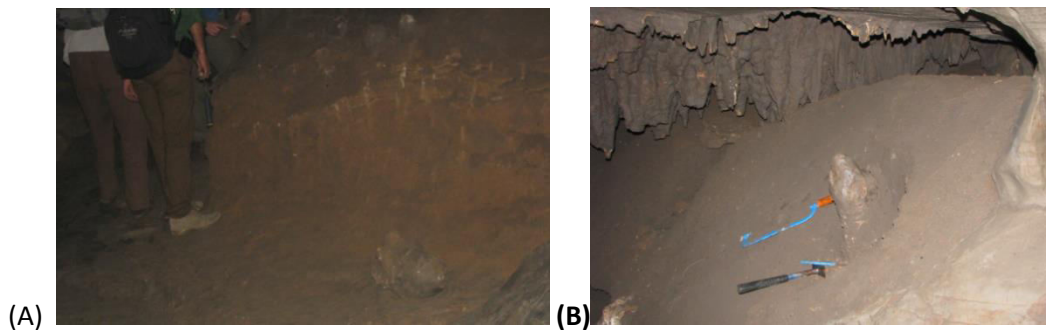


Figure 2.17: Images of Belum cave. (A) Fallen sample referred to as NI15-13 or Banyan Tree 1 and (B) Sample removed from the cave called NI15-14a or Banyan Tree 2.

The cave has been monitored for 3 years and results have been published in *Yadava et al, 2016*. They find that the temperature at the entrance of the cave is 27°C with a relative humidity of 45%. In the inner chambers of the cave, the temperature rises to 30.5°C with relative humidity of 87%. Both parameters have been measured with hand-held devices. There are still some current dripping zones in the cave, especially during peak monsoon

rainfall season i.e. dripping during particularly heavy rainfall events but not during the entire monsoon period.

The cave guides that undertook monitoring have observed that the temperature is $\sim 30^{\circ}\text{C}$ without electricity but rises to 33°C once the cave lights have been switched on for long periods of time. The relative humidity is 100% without artificial air circulation and 80% with it.

c) Valmiki cave or Kuruva Bali Guha ($15^{\circ} 09' \text{ N}$, $77^{\circ} 49' \text{ E}$, 420 m asl)

The entrance to the cave is located ~ 25 m up a red shaly carbonate hill with gently dipping beds. The beds are jointed with siliceous veins. The entrance is a few meters across (figure 2.19) but opens up wider once inside. There was local knowledge of a second cave passage, but due to time constraints, we followed the passage that lead to the known decorated part of the cave (figure 2.18) and the sample stalagmite was removed from a ledge at the end of this passage.

The temprature in the cave is 32.8°C measured on a handheld thermometer. Two HOBO temprature data loggers were deployed in the cave but have not been collected yet. Humidity in the cave is nearly 100%. The hygrometer sensor had a film of moisture on it so the exact humidity could not be measured. Based on the size of the entrance and the depth at which the sample stalagmite is located, it is unlikely to be quickly affected by changes in outside temperature and humidity conditions except during cave flooding (figure 2.19).

Drip waters for stable isotope and trace element analysis were collected from one of the drip waters feeding the deity stalagmites. The sample itself did not show any drip in January, 2015. Modern growth was also collected from the top of one of the 'deity' stalagmites free from any obvious human influences.

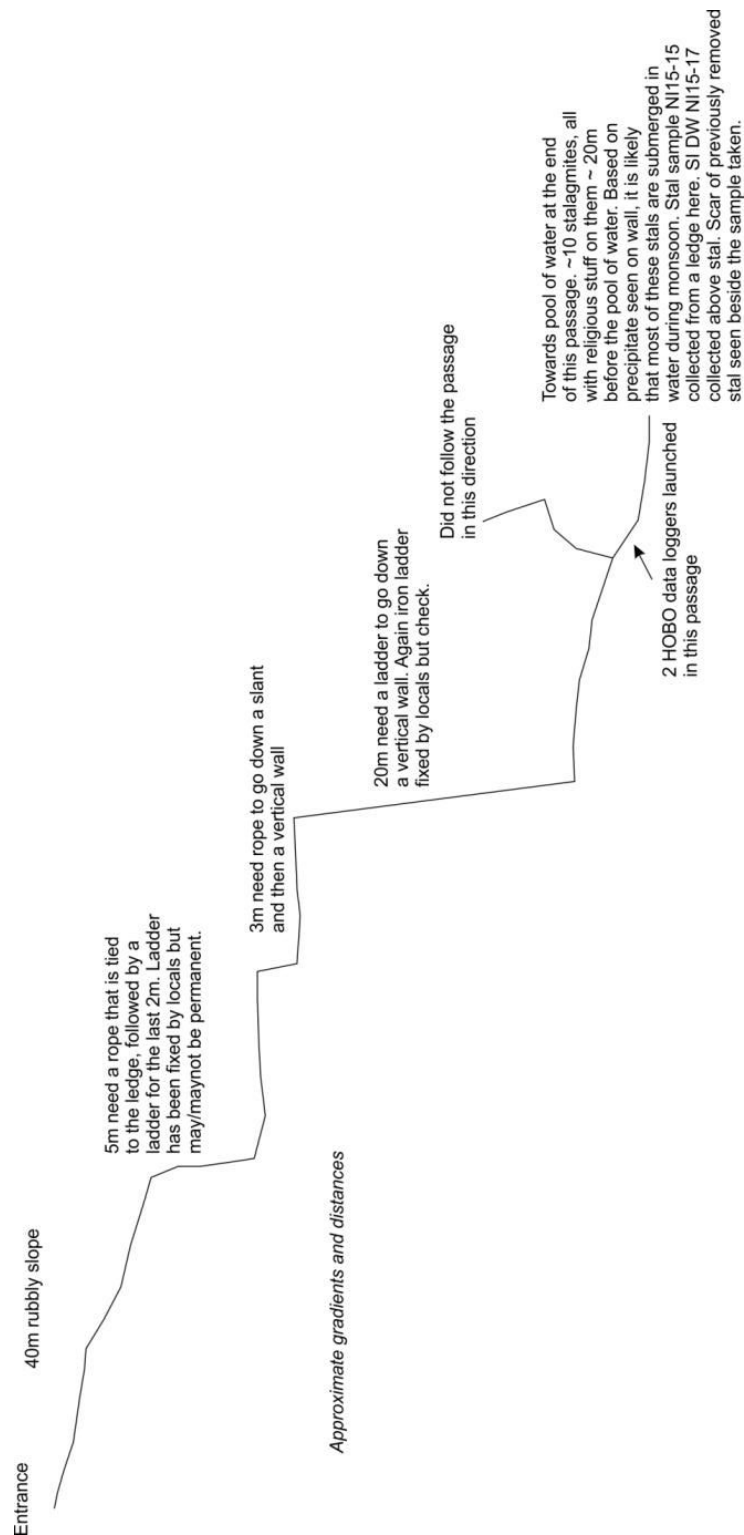


Figure 2.18: Sketch map of Valmiki cave with distances, inclinations, sampling and monitoring locations marked.

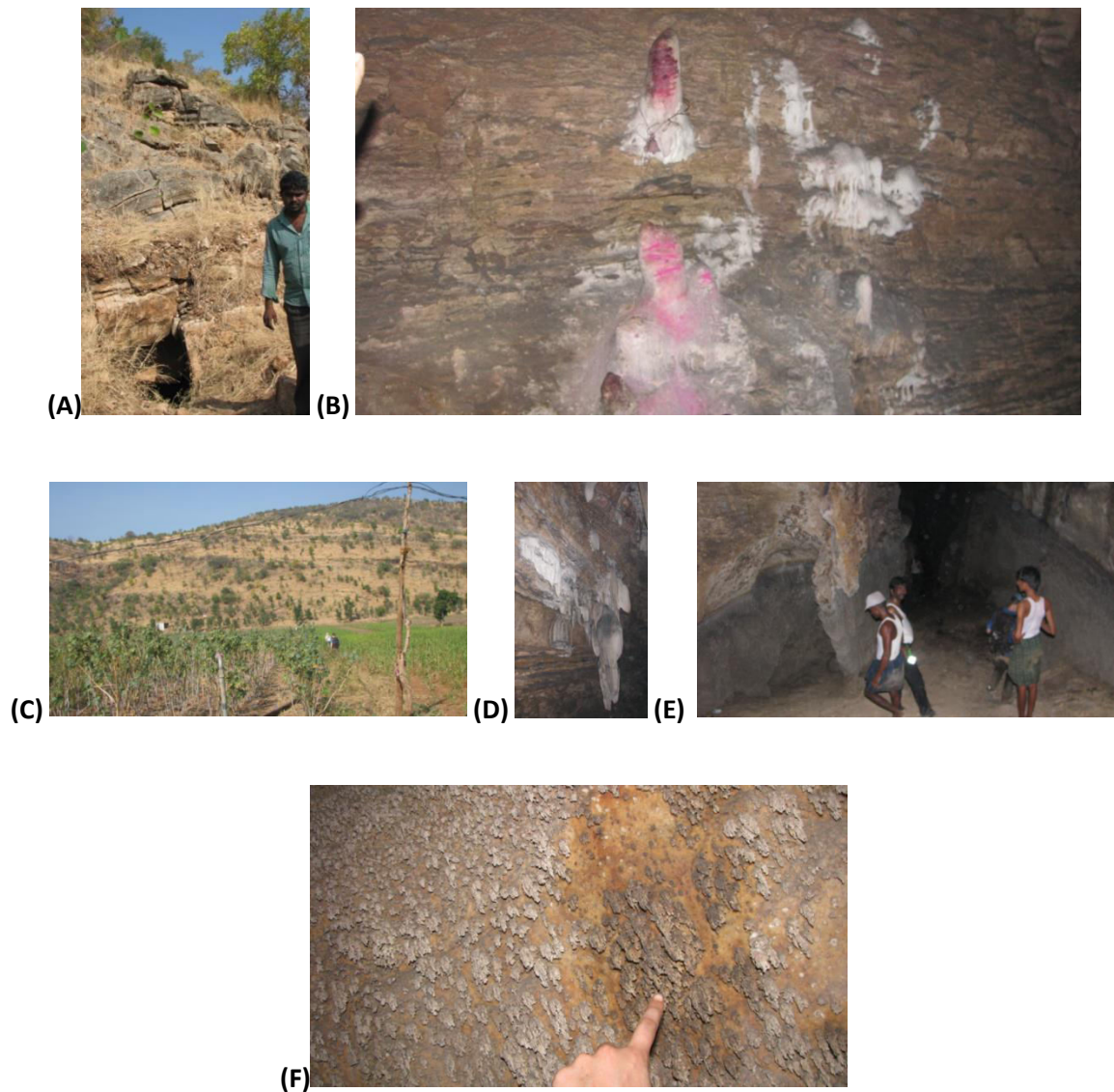


Figure 2.19: Images of Valmiki cave site. (A) Cave entrance. (B) 'Deity' stalagmites. The stalagmites are ~20 cm in height. (C) The cave entrance is 20 m above the little white hut seen to the left of the photo. Open scrub vegetation on the hill with some indication of the gently dipping beds. (D) Curtain carbonate decoration and stalactites are prominently seen in the cave but only 10 stalagmites were seen, all located in the area from which this sample was collected. (E and F) The dark grey colour on the wall marks the cave flood line. The texture in close up has been shown in (F) and is called cave popcorn. This is thought to be irregular growth rather than reworking although if the water is still acidic when it enters the cave, partial redissolution is possible. Towards the back of (E), the outline of a man in a white shirt can be made out. To the right of this man are multiple stalagmites which are family deities. Above them is a ledge from which this sample has been removed. The ledge is above the cave popcorn flood line.

d) Bila Surgam cave or Bettamcherla cave (15° 26' N, 78° 11' E, 360 m asl)

It is located off the Gutti-Kurnool road, close to Bettamcherla. The area has cement factories and limestone quarries. The limestone beds are white-grey in colour with silica bands and the overburden is reddish, slaty and weathered. Local guides estimate that the passages are ~ 2 km in length. They have heard that there is growth in the deeper parts of the cave though that part of the cave has been damaged by water flow. There is no major water flow in the monsoon inside the cave at present.

The cave is actually laid out as a series of caves located along the same cliff face (see *Haslam et al, 2010* for cave map and chamber names).

Cave 1: Charnel House is a chimney like deep chamber with 100's of bats. There were no visible signs of growth.

Cave 2: Purgatory cave is 10 m ahead of Charnel House on the same cliff. Significant stalactite growth can be seen but the roof of the cave has fallen in. About 500 m of the cave passage was explored but very minor calcite growth was observed. Field guides estimate that there is some growth at the lowest point of the cave, a km further, along with a pool of water. Due to constraints of time with the relatively low likelihood of finding any decoration based on the initial 500 m of passage way, the cave was not explored further.

Cave 3: This cave is referred to as Cathedral or Fairy cave. As the name suggests, it has a large open roof, there is decoration but again the roof has fallen in. No obvious stalagmite samples could be seen. The cave was not explored further.

Cave 4 and Cave 5: They are together called Chapter house and are located one above the other. Cave 4 is a big airy open cave with limited decoration. Cave 5 extends for just 10 m and there is no evidence of decoration.

e) Logistics

Belum cave is a tourist cave and sections of it are well lit up with artificial ventilation. There are guides who can navigate the passages of the cave. The other caves are located within a few hours distance of Belum cave and can be reached with cars. Belum cave guides can assist in finding these caves and further contacting locals familiar with the caves. Most caves are set up for occasional visitors and have basic ladders and ropes set up but it is highly recommended to navigate the caves with the help of locals. Gutti is a big township with hotels and restaurants located close to these cave sites.

2.5.3 Borra cave (18° 10' N, 83° 0' E, 705 m asl)

Borra cave is located in the Eastern Ghat mountain chain. It is an ideal location to track the eastern extremity of moisture being carried from the Arabian Sea as well as moisture being sourced from the Bay of Bengal. However the cave itself is an open airy chamber and is unlikely to be suitable for paleoclimate work. It has a large number of stalactites, flowstones and active drips but limited stalagmite formation. There is a passage under the cave that was surveyed. The passage has a few small actively dripping stalactites and a couple of stalagmites but this passage has a big opening and low humidity giving an initial impression that the cave maybe unsuited for paleoclimate work. The Gosthani River flows 10 m below the cave. The cliff in which the cave is located as well as the bed rock of the river is composed of limestone/marble. However the area shows dominant khondalite lithology with limited carbonate formation and it is unlikely that there are more caves in this area.

2.5.4 Kotumsar cave (18° 52' N, 81° 56' E, 560 m asl)

Kotumsar cave (from where a sample had been previously retrieved by PRL), could not be visited during the course of the DPhil study due to the current sensitive political situation in the area. Information for the cave area has been obtained from previous publications on the

area and relevant details have been summarised here. The cave area is a part of Indravati catchment of Bastar Craton (figure 2.20) and has been extensively studied. The carbon and oxygen isotopic data and trace element data for the carbonate bedrock in the region have been measured by *Maheshwari et al, 2005*. *Dutta et al, 1985* appraise the natural resources of the basin (like soil, water and building stone). Drainage, Digital Elevation Model (DEM's) and soil erosion maps of the basin have been given by *Vemu and Pinnamaneni, 2011*. The geological map shown in figure 2.20 is accompanied by a fence diagram (figure 2.21) constructed from data from multiple boreholes in the region by *Mukherjee et al, 2012*.

Speleothems from Kotumsar have not been previously studied, but Jhumar and Dandak caves from the same karst region (figure 2.8) have published high resolution, replicated paleoclimate records (figure 2.6). A number of papers have been published on the biospeleology and some radiocarbon work of Kotumsar cave (for example, *Pati and Agrawal, 2002; Reddy, 2006; Yadava et al, 2007; Biswas, 2010*) and is in fact the most biologically explored cave of India. They have described the physical features of the cave that have been summarised here. Kotumsar cave (figure 2.22) is formed in limestone on the banks of Kanger River which flows through Kanger Valley National Park. The cave is near Jagdalpur town, in Bastar district, Chattisgarh state. The cave was discovered in 1958 and is one of the largest in India. The cave entrance is a vertical fissure in the wall of a hill. It has a narrow twisted opening measuring ~15 m in length. The cave is honeycombed in its structure, consisting of several irregular chambers. The main tunnel of the cave is nearly 500 m long and has several lateral and downward passages. The roofs and walls of the different chambers are lined with colourful dripstone formations resulting from precipitation of calcite.

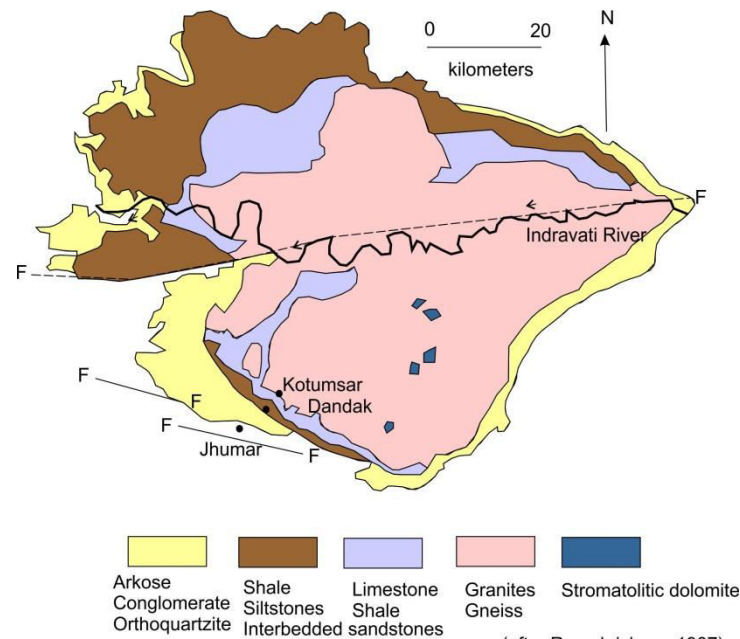
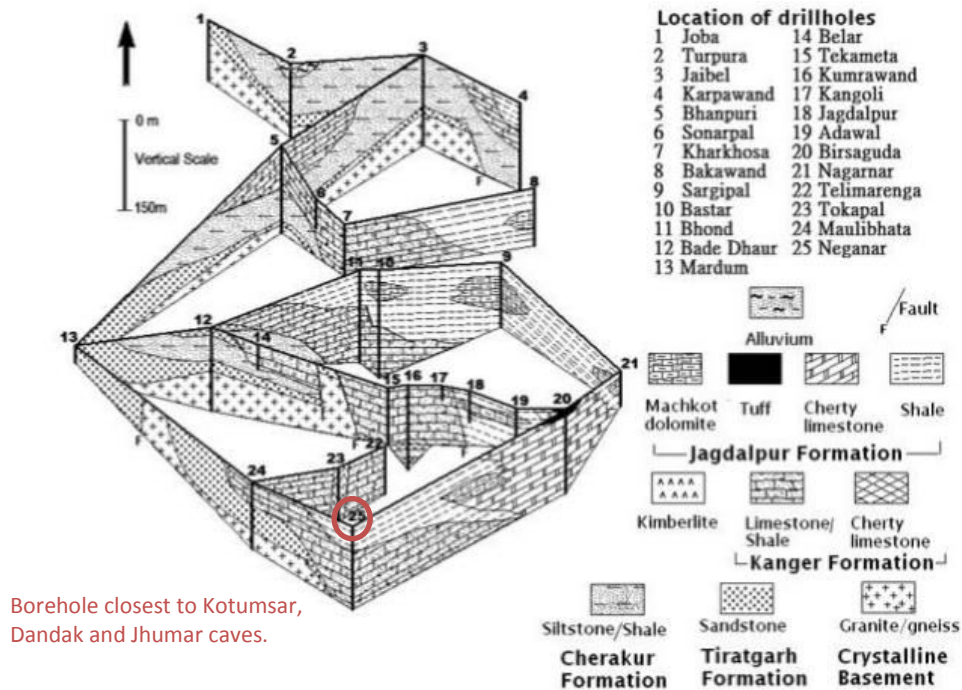


Figure 2.20: Geological map of Kotumsar cave area *Ramakrishnan, 1987; GSI, 2005*.



Borehole closest to Kotumsar, Dandak and Jhumar caves.

Figure 2.21: Fence diagram of Kotumsar cave area, constructed with lithological data from Central Ground Water Board (CGWB) boreholes and formations mapped by officers of the Geological Survey of India (GSI) (*Ramakrishnan, 1987; GSI, 2005*). The figure and description have been taken from *Mukherjee et al, 2012*. Kotumsar cave is situated near borehole 25.

The chambers of the cave are floored with either rocks or pebbles of various dimensions or by surface derived soil/clay deposits. The cave is subject to frequent flooding during the monsoon season and has religious significance where one part of the cave is frequented by tourists who burn incense and leave rubbish behind.

Some of the abiotic parameters measured during the 1980's and 1990's by *Biswas, 1992a, 1992b* and *Pati and Agrawal, 2002* show that the air and water temperatures remained relatively stable at an annual average of $28.25 \pm 1.23^{\circ}\text{C}$ and $26.33 \pm 0.9^{\circ}\text{C}$ respectively (range = $25\text{-}32.7^{\circ}\text{C}$ for air; $22.9^{\circ}\text{C}\text{-}29.3^{\circ}\text{C}$ for water).

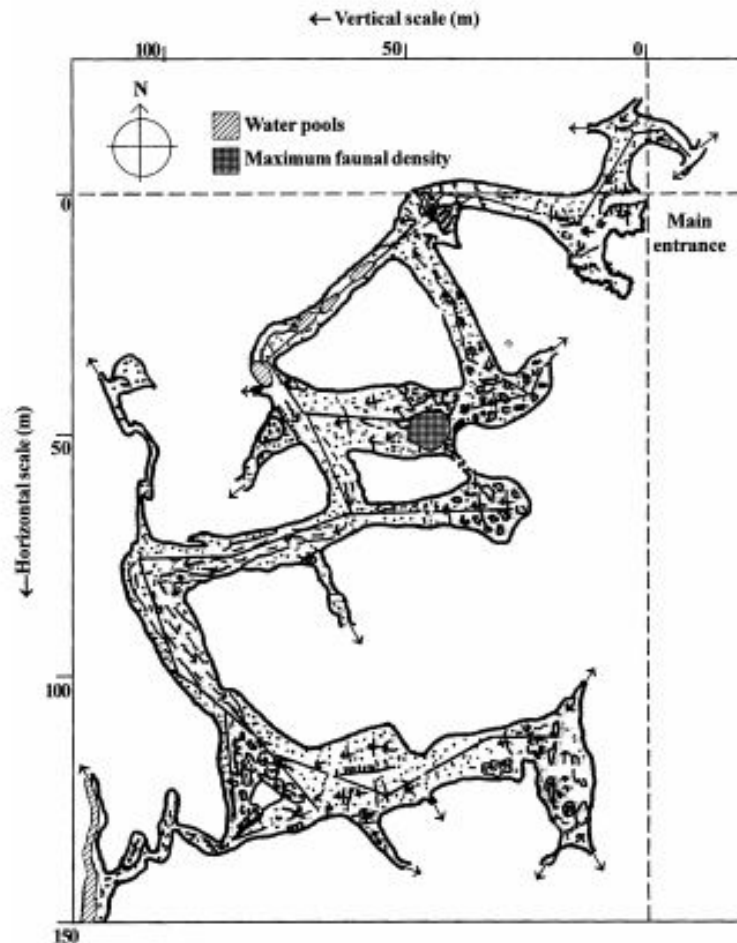


Figure 2.22: Plan of Kotumsar Cave indicating location of perennial water pools and area of maximum faunal density. The figure and description are taken from *Patti and Agrawal, 2002*.

2.6 Samples collected during field work

Samples collected during the three-week field work conducted in January, 2015 have been listed in tables below. The abbreviations are explained at the end of the tables.

Akalagavi cave

<i>Sample code</i>	<i>Sample collected</i>	<i>Location within cave</i>	<i>Source</i>
NI15-1	DW TE +SI	Main cave	Multiple stalactites
NI15-2	DW TE +SI	Entrance passage to main cave	Multiple stalactites 38 dpm
NI15-3	DW TE+SI	Chimney-like cavity drip	Single stalactite 122 dpm
NI15-4	DW TE+SI	Chimney-like cavity drip	Single stalactite 68 dpm
NI15-5	DW SI	Chimney-like cavity drip	Same drip as NI15-3 Collected by guide
NI15-6	DW SI	Chimney-like cavity drip	Same drip as NI15-4 Collected by guide
NI15-7 a,b,c	Modern growth	Chimney-like cavity	
NI15-8	DW TE +SI	Chimney-like cavity drip 10 cm from NI15-3 and 4	Single stalactite 10 dpm
NI15-9	DW TE+SI	Chimney-like cavity drip, close to NI15-3	Single stalactite 9dpm Collected by guide
NI15-10	Soil sample	Narrow passage beyond chimney-like cavity	
NI15-11	Rock sample	Hill of cave	
NI15-12	SW TE+SI	Spring close to cave	

Belum, Valmiki and Bila Surgam caves

NI15-13	Stalagmite sample	Banyan Tree passage of Belum cave	Fallen sample i.e. Banyan Tree 1
NI15-14 a,b	Stalagmite sample	Banyan Tree passage of Belum cave	Removed sample and its broken piece i.e. Banyan Tree 2
NI15-15	Stalagmite sample	Valmiki cave	Removed from ledge above current water line
NI15-16	Modern growth	Valmiki cave	Collected from ledge beside sample

			stalagmite
NI15-17	DW TE +SI	Valmiki cave	Collected from water dripping onto deity stal. below ledge from which sample was obtained
NI15-18	Piece of stalagmite	Valmiki cave	Small piece picked from floor of cave
NI15-19	Piece of stalactite	Bila Surgam cave	Broken off fallen stalactite from collapsed roof outside cave
NI15-20	Rock sample	Bila Surgam cave	

Borra Cave

NI15-21 a,b,c,d,e,f	DW TE+SI Modern growth	Borra cave near Shiva temple	Multiple stalactites Some samples collected in plastic sample bags and PP bottles then transferred to glass vials. Be wary!
NI15-22 a,b	DW SI Modern growth	Borra cave from path	Multiple stalactites Directly in glass vial 10ml in 15mins
NI15-23 a,b,c	DW SI+TE Modern growth	Borra cave Last chamber fast growing stal	Drip from roof Collected in PP transferred to glass vial after 6 hours 20dpm
NI15-24 a,b	DW SI Modern growth	Passage below main Borra cave	Multiple stalactites
NI15-25 a,b	DW SI Modern growth Pieces of stalagmite	Passage below main Borra cave	3 stalactites

Table 2.4: Sample collection made during the three-week field work conducted in January, 2015. The samples have been code named Nikita India 2015 i.e. NI15, followed by serial numbers. Drip water (DW) samples have been collected for trace element (TE) measurements in polypropylene (PP) bottles and for stable isotope (SI) measurements in glass bottles (see chapter 3 on Methodology for details of collection methods). Drip rate has been calculated as drops per minute (dpm) in most cases.

2.7 Potential for establishing monitoring programmes based on the cave survey

- i) Akalagavi: Akalagavi cave is in a protected forest area which severely limits footfall since access is with a ~4 km trek or locally hired jeeps but access to the cave site itself is not managed. Apart from carefully hidden data loggers, no automated devices can be deployed in the cave. Monitoring by nearly daily visits by locals can be arranged but access to the forest area is restricted in the monsoon by the Forest Department. The shallow passage access to the main cave area is also likely flooded during the monsoon, further restricting access.
- ii) Belum, Valmiki: Belum cave is extremely well suited for monitoring work. It is a well-protected and carefully managed tourist site. It has extensive cave passages that are not accessible to tourists where automated systems can be set up. Data loggers and glass plates can be deployed in Valmiki cave but no visible automated devices can be deployed. Given the difficulty in accessing the deep level of the cave, footfall is severely restricted but is nevertheless present. The same reason precludes daily monitoring by locals but weekly monitoring is certainly feasible. There are reports of other passages in the cave that can be explored in the future.
- iii) Borra: Borra cave is similar to Belum cave. Should it prove a promising cave site for paleoclimate work, careful automated and manual monitoring can be arranged for this cave.
- iv) Kotumsar: It is hoped that the current disturbed political situation will not persist in the future. Similar to Akalagavi cave, Kotumsar cave is a tourist site located with a protected forest area. But no further comments can be made regarding the feasibility of monitoring until the cave site is visited.

Chapter 3

Field and Laboratory Methods

3.1 Overview

To reconstruct the past climate of peninsular India with stalagmite records required collection of suitable samples from this region. Ideally, such samples would be from multiple sites, have grown over long and/or interesting periods of climate history, and be suitable for accurate U-Th age dating. To achieve this absolute requirement for samples, I established collaboration with Physical Research Laboratory (PRL), and conducted fieldwork in peninsular India to collect additional samples. The first portion of this chapter describes field work methods of site characterization, sample collection and monitoring. The caves that were visited and selected for further research work have been described in the previous chapter.

This chapter also describes laboratory methods used to produce the geochemical data revealed in the following result chapters. Methods include stalagmite sample preparation, subsampling procedures and the processing of subsamples for U-Th age determination, mineralogical, stable isotope and trace element analysis. Methods specific to particular samples are detailed within relevant result chapters. With the exception of sample cutting and the stable isotope analysis of one sample (from Kotumsar cave), all laboratory work and chemical techniques detailed in the thesis were undertaken at the University of Oxford.

3.2 Field methods

In the limited time available at each cave site, a quick survey was made of accessible chambers and passages of the caves. A few caves showed no decoration or showed

decoration that would not be suitable for obtaining paleoclimate records (for example, stalagmites in large open airy chamber or flowstones). A note was made of such conditions but no further survey was undertaken of such caves. Caves from which suitable stalagmite samples were retrieved or which showed potential for future work have been characterised more fully. Characterisation included accurate GPS co-ordinates, appraisal of local vegetation type and density, bedrock composition and structure, geological and geographical setting. Every effort was made to obtain cave dimensions through previous publications, mapping during this fieldwork or through drawings of rough sketch maps where full scale surveys were not possible. Samples of well water, spring water, drip water and rainwater were collected. A bedrock sample was collected to aid interpretation of stalagmite geochemistry. Temperature and humidity measurements were made and temperature loggers have been deployed in relevant caves. A photographic record was kept of each site.

3.2.1 Cave map

Cave size parameters were measured with a DistoX instrument, which allows distances to be measured using a laser pointer, combined with a compass/clinometer. The map was produced using the software Survex and modified using CorelDRAW.

3.2.2 Stalagmite sample collection

Cave deposits take thousands of years to form and are irreplaceable. Akalagavi cave is in a protected forest area. Belum and Borra caves are under the jurisdiction of the tourism board. Both preclude the removal of samples without prior permission and are hence protected. Stalagmites are considered to be deities by Hindus and are inherently protected by local people. Despite this, speleothems may be lost as objects of curiosity, for calcium carbonate powder to decorate courtyards and for scientific study. They may also be disturbed by incense and other symbols of religious significance placed on them by

worshippers. Keeping these factors in mind, every care was taken prior to removing samples from a cave.

Two stalagmite samples (one each from Belum cave and Valmiki cave) were carefully removed from their base using a rock chisel. One stalagmite sample (from Belum cave) had been removed a few years earlier in order to create a path for tourists. It was lying on the side of the path and was simply picked up from there. The samples were cushioned with newspaper and placed in gunny bags for protection during transportation. Two stalagmite samples (one each from Kotumsar cave and Akalagavi cave) had been previously removed by PRL and were shipped to the University of Oxford. Sample locations, where known, have been indicated on cave maps.

3.2.3 Modern carbonate growth collection

Chips of modern carbonate growth were removed using a rock chisel and stored in labelled sample bags. The top and base of the chips were clearly marked to keep track of the most recent to progressively older precipitation.

3.2.4 Water sample collection

Water samples for stable isotope analysis were collected in 8 ml glass vials. The glass vials had been previously rinsed with distilled water (15 M Ω), dried and stored in sample bags. Samples were collected by holding vials directly under the drip, sometimes with the help of a funnel. If the funnel was required, it was carefully wiped with Kimwipe and rinsed with the drip water to be collected before using it for actual collection. As far as possible, the vials were filled to the brim. Most vials have an extra plastic or aluminium seal on the inside of the plastic caps to prevent leakage and evaporation. The vials were further sealed and protected for transport with multiple layers of Parafilm. The sample code was written on

the glass bottle (this can rub off if the vial is wet on the outside), Parafilm and the sample bag into which they were placed. Parafilming was done within a few hours of collection.

Water samples for trace element geochemistry were collected in 15 ml polypropylene (PP) bottles. Bottle cleaning and sample collection procedures are the same as that described for the glass vials above.

Rain water samples were collected for 24 hour periods intermittently throughout the monsoon season of 2015 by Mhadei Research Centre (MRC), a field research station located 100 km away from Akalagavi cave. A plastic measuring cylinder was left in the open for a period of 24 hours. A record was kept of date, time and amount of water collected. The water was filled into 8 ml glass vials and sealed with Parafilm.

All vials were sealed and stored in a way that temperature, leakage and evaporation would not affect their isotopic composition.

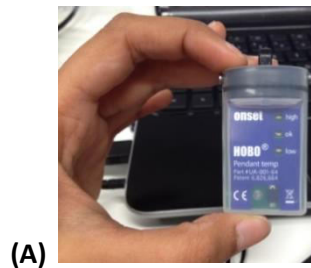
3.2.5 Bedrock sample collection

Bedrock samples were taken from the same cliff as the cave and stored in sample bags.

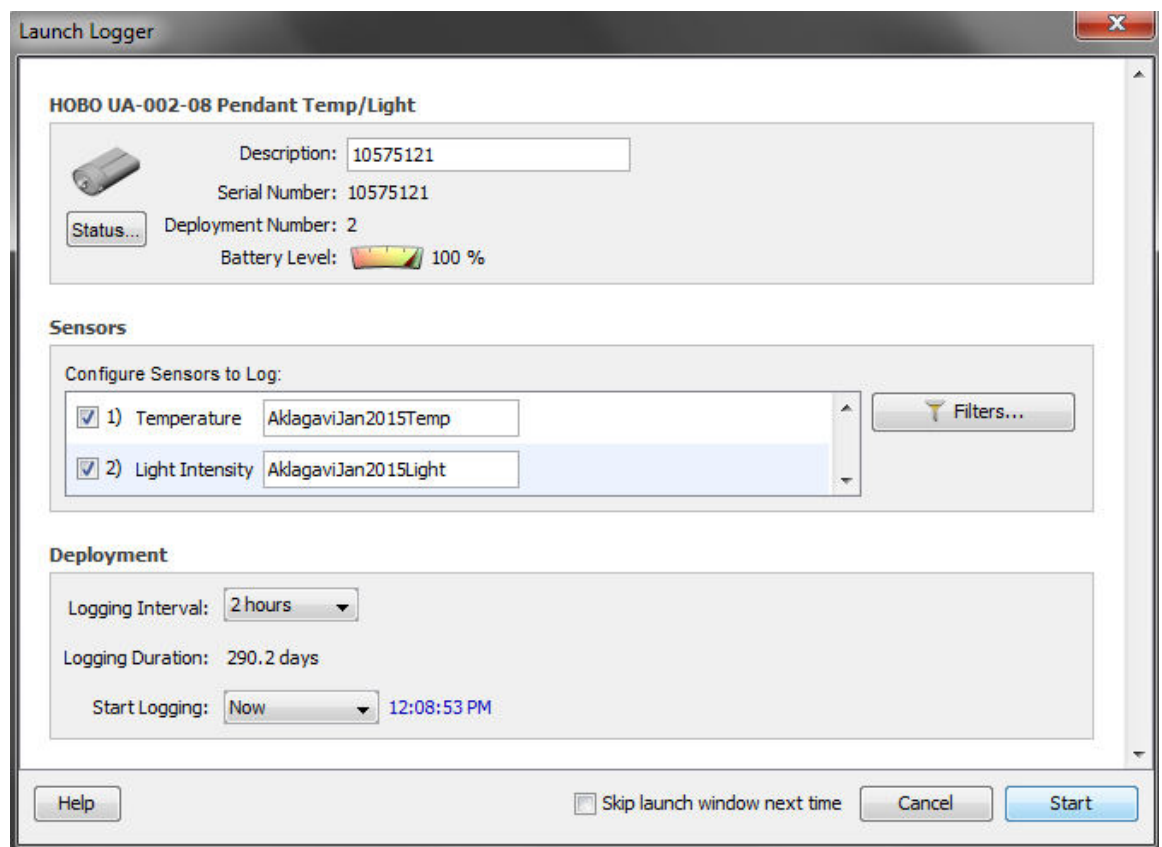
3.2.6 Cave monitoring

Due to budget and time constraints, only one extended field visit could be conducted during this project. This field visit indicated both the potential and the challenges of establishing field monitoring programmes at the cave sites. The caves are frequently visited by tourists and local villagers, making placement of any monitoring equipment challenging, so that only small temperature loggers which could be well hidden were deployed. HOBO temperature and light data loggers are cheap, small, robust and easy to deploy (figure 3.1). They have an accuracy of $\pm 0.53^{\circ}\text{C}$ and a battery life of 1 year for typical use. HOBO temperature data loggers come with the ability to measure exposure to light. This is potentially useful in a cave where the number of visitors may be estimated through the number of torch light

exposures. However, there was no feasible way to hide the data logger and allow it to measure exposure to light. Hence this feature was eventually not used. Three HOBO loggers were deployed in Akalagavi cave and two HOBO loggers were deployed in Valmiki cave. Data from successful deployments are described in the respective result chapters. No attempt at more complete monitoring of cave conditions (for example, CO₂ and humidity) could be conducted within the confines of this thesis work (see section 2.6).



(A)



(B)

Figure 3.1: (A) HOBO temperature and light data logger. (B) HOBO logger deployment details.

3.3 Laboratory methods

3.3.1 Stalagmite sample cutting

A Dramet E200 instrument (figure 3.2) fitted with a vertical blade and automatic stage movement control was used for cutting. The instrument is installed in PRL. All samples were cut lengthwise in PRL, prior to shipping one section to the University of Oxford. Surface polishing was not performed on any of these samples due to concerns that the process would introduce alien powder into the porous sample surface.

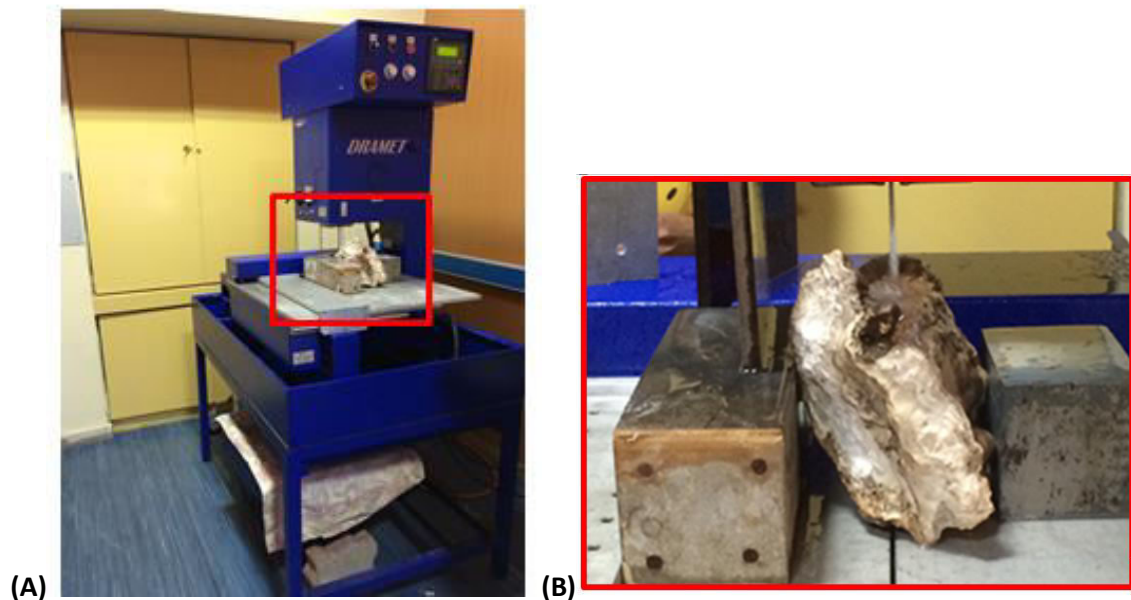


Figure 3.2: (A) Dramet E200 with automatic stage movement control. (B) Vertical blade cuts the sample lengthwise. There is cold water continuously running along the blade to reduce friction.

3.3.2 Laboratory conditions

All powder samples (as far as possible) are handled in the Preparatory laboratory at the University of Oxford and dissolved samples are handled in the metal-free clean laboratory or the respective instrument laboratories. Due to low concentration of trace elements (including U and Th isotopes measured for age determination) and in order to avoid

contamination of subsamples, most trace element chemistry was carried out under metal-free clean laboratory conditions. The metal-free clean laboratories are also specific to particular analysis, i.e. all stalagmite related chemistry is handled in a designated laboratory to prevent contamination with other samples (such as corals and sea water). The metal-free clean laboratory in the University of Oxford is over pressured with class 1000 HEPA-filtered (High Efficiency Particulate Air) air. Dilutions and column chemistry for U and Th isotopes were carried out in hoods, also over pressured with filtered air. Latex gloves, Tyvek suits and clean-laboratory-use-only shoes were worn to reduce contamination of the laboratory.

3.3.3 Cleaning and contamination reduction procedures

- i) All subsampling was carried out in the Preparation laboratory at the University of Oxford which is almost exclusively used for generation and preparation of small carbonate samples to prevent contamination.
- ii) The Preparation laboratory was cleaned the night before (to allow any dust to settle by the morning), and bench surfaces were wiped with tissue and water.
- iii) Care was taken that only a single sample was milled at one time in the laboratory to prevent any cross contamination. Samples were covered with aluminium foil when not being worked on.
- iv) The cut surface of samples were washed with de-ionized (15M Ω) water (DI water) prior to milling to remove any surface particulates, and dried overnight in a laminar flow hood at room temperature.
- v) Tungsten carbide drill bits were used for milling the sample. Stainless steel blades were used to transfer drilled subsample powder from the sample to the centrifuge tubes (see point viii). The drill bits and blades used for subsampling were cleaned with ethanol and Kimwipe prior to and between each successive measurement.
- vi) Compressed air is used to clean the sample between each measurement.

- vii) To prevent contamination from sample surface, the uppermost $\sim 20 \mu\text{m}$ of surface material has been removed from the target area by drill and compressed air flow prior to subsampling.
- viii) Subsamples were collected into 2 ml polypropylene centrifuge tubes (manufactured by Eppendorf) that have been similarly cleaned with compressed air. The tubes were stored in plastic racks under controlled standard laboratory conditions.

3.3.4. Subsampling strategy

The formula, $\text{mass} = \text{density} \times \text{volume}$, was used to calculate the volume and in turn the dimensions of the sample that would have to be milled in order to extract the required quantity of powder. In each case, sufficient subsample powder for U-Th, mineralogical, stable isotope and trace element measurements, as required, were milled at the same time and aliquots were taken from the bulk subsample stock powder for each separate analysis (table 3.1).

<i>Number</i>	<i>Analysis</i>	<i>Quantity of Powder (mg)</i>
1	XRD/FTIR measurements (for determination of mineralogy)	2
2	Stable isotope analysis	0.04
3	Trace element analysis	0.09
4	Uranium-thorium (U-Th) dating	50-300

Table 3.1: Quantity (mass) of subsample powder required for various analytical procedures.

Due to lateral evolution of solution in the thin film on the tip of a stalagmite, subsampling for stable isotope and trace element analyses was orientated along the dominant growth axis of the stalagmite, where the first calcium carbonate is thought to precipitate (*Hendy, 1971; Fairchild et al, 2006*) while subsamples for U-Th dating were taken off the growth axis.

Trench subsampling was preferred for stalagmite samples that were compact. Multiple discrete drill holes were preferred for stalagmite samples that showed annual laminae where the target was to subsample only the compact layers presumed to have precipitated during the monsoon season and at the same time to prevent contamination from the porous non-monsoon layers rich in detrital material (figure 3.3). After recommendations of *Fairchild et al, 2006*, the width of the high resolution sample trenches exceeds the subsampling interval. This allows recovery of sufficient subsample mass from a shallower trench while reducing potential layer mixing at depth where the growth layers may vary differently from what is seen on the surface. A wider trench also reduces bias from the curvature of the drill bit. Since the drill bit is circular, it may result in a bias caused by the layer-width of the sample and the subsampling interval. A 0.8 mm drill bit was used to make a trench of 2 mm in width, 1 mm in depth and a sampling resolution of 1 mm. It was observed that a drill bit with a smaller diameter was prone to breaking but this large diameter created both a 'dishing' effect and 'curvature' bias. To accommodate for this, the drill bit was used to mill at a resolution of 0.25 mm in 4 successive lines for the required resolution of 1 mm (figure 3.3).

Spatial referencing was enabled by making notches using the drill bit for every 10th subsample. Careful notes were made during the milling process on sample scans and in a laboratory notebook. Samples were rescanned following milling so that subsamples can be clearly linked to their position on the stalagmite (figure 3.3).

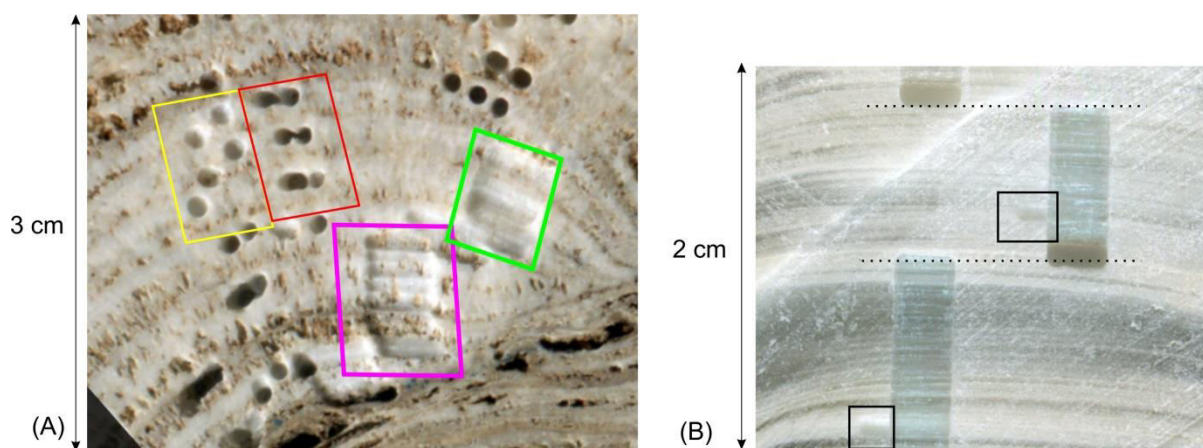


Figure 3.3: Various sampling strategies and a method for spatial referencing have been shown. (A) Yellow box: Discrete milling using a dentist's drill and a 0.8 mm drill bit of every white and brown layer. Red box: Discrete milling using a dentist's drill and a 0.8 mm drill bit of every white layer. This strategy was used for one sample from Akalagavi cave. Pink box: Trench milling using a 0.8 mm drill bit for subsamples of 0.8 mm resolution. It shows 'curvature' bias and 'dishing' effect. Green box: Trench milling using a 0.8 mm drill bit but moving it in increments of 0.25 mm to reduce 'curvature' and 'dishing' bias. The drill bit can be moved incrementally 4 times (i.e. 0.25 mm x 4) for 1 mm resolution subsamples. This strategy was used for one sample from Kotumsar cave. (B) Black boxes: Spatial referencing, where required, was done by marking a notch extending beyond the trench for every 10th subsample. Dotted lines: Change of trench axis to precisely follow growth axis direction was done carefully along a specific layer.

3.3.5 Instruments used for subsampling

Trench subsampling was performed on a New Wave micromill. It facilitates the milling of points, lines and curves with an accuracy of $\pm 10 \mu\text{m}$. The instrument allows individual sampling paths of the desired width, depth and orientation to be automatically replicated along the x-axis. A tungsten carbide drill bit with a diameter of 0.8 mm was used.

Multiple discrete drill holes and subsampling for U-Th dating was performed using a hand-held dentist's drill fitted with the same tungsten carbide drill bit with a diameter of 0.8 mm.

3.3.6 Mineralogical characterization of subsample powders using FTIR or XRD

In this thesis, FTIR-ATR (Fourier Transform Infra Red – Attenuated Total Reflectance) is used to make semi-quantitative measurements of calcite and aragonite proportions in a subsample. Vibrational characteristics are related to molecular structure and atomic

composition and consequently are capable of providing information on structural differences between polymorphs of the same mineral, in this case calcite and aragonite (CaCO_3). These vibrational characteristics are measured via infrared absorbance and the resulting raw data is processed into a spectrum using Fourier Transform. It provides a quick and easy way of determining the primary carbonate mineralogy of subsample stalagmite powders. It uses less than 2 mg of subsample powder and the subsample powder is simply mounted on a stage for analysis, no further processing is required so that the powder can be retrieved and reused for further/different analysis. The analysis of each subsample takes less than 10 minutes. The instrument is an Agilent Cary 640 Spectrometer fitted with a GladiATR Single Reflectance Diamond ATR accessory (Pike Technologies). The instrument and methodology has been described in *Loftus et al, 2015*. In this thesis, comparisons were made with the calcite-aragonite-vaterite peaks given by *Vagenas et al, 2003* and restricted to estimating whether mineralogy is dominantly calcite or aragonite. Calibration for precise percentages of aragonite and calcite would require calibration with well-known mixtures of aragonite and calcite from representative stalagmite samples, which was not conducted here.

X-Ray diffraction (XRD) is used to make precise quantitative measurements of the proportions of aragonite and calcite in a subsample. It is a technique which uses waves (in this case X-rays) with a known frequency, when the waves reach a sample, the sample acts like a diffraction grating, producing bright spots at certain angles. The atomic spacing can then be determined using Bragg's law which allows us to differentiate between polymorphs. XRD measurements were performed on PANalytical Empyrean Series 2 powder diffractometer configured with a PIXcel 1D Detector. The intensity at diffraction peaks 104 ($2\theta = 29.5^\circ$) and 221 ($2\theta = 46^\circ$) were considered to quantify calcite and aragonite respectively. The quantification of a subsample is carried out by comparison with standard samples with defined compositions (*Kralj et al, 1990; Kontoyannis and Vagenas, 2000*). The

subsample is mounted onto Si plates with acetone for analysis. It takes 10 minutes for the analysis of a single subsample.

In comparison with the FTIR-ATR method, the powder XRD method provides precise percentage quantification and was used for the determination of mineralogy after 2015, when the XRD instrument was fitted in the Department of Earth Sciences at the University of Oxford.

3.3.7 Carbonate stable isotope analysis

All carbonate subsamples (apart from subsamples of one sample from Kotumsar cave which were analysed at PRL, details are in chapter 7) were analysed on a Delta V Advantage isotope mass spectrometer fitted with a Kiel IV carbonate device at the University of Oxford. 30 - 40 μg of carbonate powder are weighed in an aluminium foil boat on a Sartorius microbalance accurate to 0.05 μg and transferred to glass vials that go directly into the instrument. Racks of 44 vials were measured in each analysis run lasting up to 24 hours. In the instrument, the powder aliquots are reacted with 105% dry phosphoric acid at 70°C to produce H_2O and CO_2 gas (*McCrea, 1950*). The eluted gas is passed through a series of cryogenic traps to remove H_2O and any non-condensable gas components. The relatively pure CO_2 gas is transferred to Delta V for $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ analysis. Measurements in the thesis have been reported in ‰ relative to the vPDB (Vienna Pee Dee Belemnite) standard.

Normalization and external errors are calculated from repeat measurements of NBS-18 and NBS-19. NBS-18 has a $\delta^{18}\text{O}$ value of -23.2‰ and a $\delta^{13}\text{C}$ value of -5.014‰ (*Friedman et al, 1982; Hut, 1987; Stichler, 1995; Coplen et al, 2006*), and NBS-19 has a $\delta^{18}\text{O}$ value of -2.20‰ and $\delta^{13}\text{C}$ value of +1.95‰ (*Friedman et al, 1982; Hut, 1987; Coplen et al, 2006*). We assume that the phosphoric acid-carbonate fractionation is the same for NBS 19 and our calcite samples (*Coplen, 1996*). The WILEY standard is used to measure internal reproducibility. It has a $\delta^{18}\text{O}$ value of -7.25‰ and $\delta^{13}\text{C}$ value of -0.39‰ (based on long term measurements at

the University of Oxford). At least 4 subsamples of each standard were measured during each run. Aliquots of standards were of similar weights as the subsamples being measured. The order in which subsamples were being measured was randomised to prevent incorrect interpretation of artefacts caused due to instrumental drift.

Following analysis, glass vial rims were wiped with a Kimwipe to remove instrumental grease. They were washed between runs by submersing in deionised water (15 Ω) with soap and ultra-sounding for 10 minutes ~3 times while changing water each time. Clean vials were dried in a heated cupboard and covered with aluminium foil. They were stored, still covered, in the laboratory.

3.3.8 Water stable isotope analysis

Water stable isotope analysis was carried out on Gas Bench II installed in the University of Oxford. 0.5 ml of water samples are pipetted into 10 ml screw top vials using disposable pipettes. For D/H analysis, a platinum catalyst is added. The vials are sealed with septa and all air is removed from the sample vials by an automated, autosampler-assisted flushing procedure which uses a mixture of H₂ or CO₂ in He. The H₂ or CO₂ in the flushing He stream is used as equilibration gas. After the required equilibration time (D: 40 minutes, ¹⁸O: 20 hours), the whole batch of subsamples is analysed (*Nelson, 2000*).

Iso-Analytical Limited standards IA-R054, IA-R055, IA-R063, IA-R064 and IA-R065 provide normalization (table 3.2). External error is calculated from repeat measurements of IA-R053. Oxford-distilled is used to measure internal reproducibility. All water isotopic data are reported relative to vSMOW (Vienna Standard Mean Ocean Water) standard.

Similar to carbonate subsamples, the order in which subsamples were being measured was randomised. The screw tops are disposed after measurement and the vials are washed with the same procedure mentioned above for carbonate analysis.

<i>Standard</i>	<i>D‰ vSMOW</i>	<i>¹⁸O‰vSMOW</i>	<i>Reference</i>
IA-RO53	-61.97 +/- 2.10	-10.18 +/- 0.20	<i>Iso-Analytical Limited, Report of Analysis, 2007</i>
IA-RO54	+4.93 +/- 0.85	+0.56 +/- 0.23	<i>Iso-Analytical Limited, Report of Analysis, 2007</i>
IA-RO55	+843.43 +/- 2.60	+108.63 +/- 0.33	<i>Iso-Analytical Limited, Report of Analysis, 2007</i>
IA-RO63	+11.26 +/- 1.34	-0.41 +/- 0.11	<i>Iso-Analytical Limited, Report of Analysis, 2014</i>
IA-RO64	-98.32 +/- 1.13	-12.34 +/- 0.13	<i>Iso-Analytical Limited, Report of Analysis, 2014</i>
IA-RO65	-269.07 +/- 1.31	-33.57 +/- 0.08	<i>Iso-Analytical Limited, Report of Analysis, 2014</i>
Oxford Distilled	-49.924 +/- 0.864	-53.767 +/- 0.885	Long term laboratory measurement

Table 3.2: ¹⁸O and D isotopic values of respective water standards as published in Iso-Analytical reports. The errors are 1 σ .

3.3.9 Trace element analysis

Trace element ratio measurements (i.e. trace element/Ca) follow the method published by *Rosenthal et al, 1999* using a Thermo-Finnigan Element 2 sector field ICPMS with an ESI (Elemental Scientific) nebulizer and an Aridus desolvation unit. 70-150 μ g of powder were weighed using aluminium foil boats as described for stable isotope analysis. The subsample powders were transferred to acid cleaned 2 ml polypropylene centrifuge tubes (manufactured by Eppendorf). Acid cleaning follows the protocol suggested by *Laxen and Harrison, 1981*. Centrifuge tubes are soaked for 24 hours in 10% HNO₃ and dried in a flow hood in a metal-free clean laboratory before being closed and sealed in sample bags. The tubes are not reused.

Subsamples are initially diluted to 2 ml by addition of 2% distilled HNO₃ to give ⁴⁰Ca concentrations of 10 to 20 ppm to prevent the instrument from clogging with dissolved solids, which increases instrumental drift. Dilution is done in the Element laboratory. These subsamples are measured to produce an intensity calibration line formed by measuring three ultrapure calcium standards; on the basis of these measurements all subsamples are diluted to 10 ppm ⁴⁰Ca in the metal-free clean laboratory for further analysis. Two racks of

40 subsamples are measured in a single run. It takes ~4 hours for the ^{40}Ca concentration check run of 80 subsamples and ~20 hours for the trace element concentration run of 80 subsamples.

Care is taken to use milli-Q (18 M Ω) water and diluted acids from the same source bottle for all measurements, standards and blanks. Subsample measurements are bracketed with five dilutions of a multi-element standard sourced from Merck or ICP Centipur single high-purity Standards' for which accuracy has been previously certified against NIST (National Institute of Standards and Technology) spectrometric standard solutions. The five-point calibration is run after every 20 subsamples to correct for instrumental drift. Separate quality check standards for Ca and trace elements are also run after every 20 subsamples. Accuracy and precision are measured against 'Repeat' standards that are run after every 10 subsamples. Blanks have been measured and corrected for. The same procedure is used for the measurement of water and bedrock samples as well except that dilutions were made to 5 ppm and 1 ppm ^{40}Ca respectively, to protect the detector from excess Mg that may be found in water and bedrock subsamples. The instrument scans each element 20 times with 10 millisecond integrations each time. The data was reduced using an in-house MATLAB code created and run by Robert Owen.

The trace elements typically measured in this thesis are Mg, Sr, Ba, Mn, Fe, Na, S, Y, U, P, Co, Cd, Th, Zn, Rb, Pb and K. They are measured and reported as ratios to Ca. Of these, Y, Cd, Ba, Pb, Th and U are run at low resolution ($m/\Delta m = 300$). K is run at high resolution ($m/\Delta m = 10000$). All other elements are run at medium resolution ($m/\Delta m = 4000$). The increase in resolution is necessary for certain elements to resolve interfering peaks. Of these trace element ratios, Co/Ca, Cd/Ca and Th/Ca were typically below detection limit for the peninsular Indian stalagmites measured in this thesis. In addition to these three trace element ratios; Ba/Ca, Mn/Ca, Fe/Ca, Y/Ca, U/Ca and Zn/Ca were below detection limit in the water samples measured in this thesis. Fe/Ca, Mn/Ca and Zn/Ca typically have low

precision percentages. Detection limits and precision percentages specific to each run have been given in data tables in respective chapters.

3.3.10 U-Th chronology

Age determination using U-Th method is based on the calculation after *Kaufman and Broecker, 1965*:

$$[^{230}\text{Th}/^{238}\text{U}]_{\text{total}} = 1 - e^{(-\lambda_{230}t)_{\text{secularequilibrium}}} + (\delta^{234}\text{U}(t) / 1000)_{\text{excess}}(\lambda_{230}/\lambda_{230} - \lambda_{234})(1 - e^{(\lambda_{234} - \lambda_{230})t})$$

Where,

$[^{230}\text{Th}/^{238}\text{U}]$ is the activity ratio

$$\delta^{234}\text{U} = 1000 * [(^{234}\text{U}/^{238}\text{U})_{\text{m}} / (^{234}\text{U}/^{238}\text{U})_{\text{eq}} - 1]$$

$(^{234}\text{U}/^{238}\text{U})_{\text{m}}$ is the measured mass ratio

$(^{234}\text{U}/^{238}\text{U})_{\text{eq}}$ is the mass ratio at secular equilibrium

For derivation, see *Richards and Dorale, 2003* and *Edwards et al, 2003*.

^{238}U , ^{234}U , ^{230}Th and ^{232}Th measurements are required for age determination. Measurements are made on the Multi Collector Inductively Coupled Plasma Mass Spectrometer (MCICPMS), however, the calcium carbonate matrix clogs the cones of the MCICPMS reducing sensitivity and also induces matrix effects that change the mass bias in the instrument (*Thomas, 2006; Mason and Henderson, 2010*). Column chemistry is performed to separate U and Th from the matrix and from each other. Detailed account of Oxford specific procedures can be found in the DPhil thesis of Thomas, 2006, with mass spectrometry details in *Mason and Henderson, 2010*. They have been briefly summarised below.

a) Reagents

18 M Ω water was used in all U-Th chemistry. It was deionised using a milli-Q element water polisher (called milli-Q water).

All acid reagents used in sample preparation were quartz distilled from reagent grade.

b) Cleaning procedures**Teflon beakers (manufactured by Savillex)**

All Teflon beakers were cleaned following a standard protocol before use. The procedures follow a dilute and dissolve protocol rather than scrubbing which may damage internal surfaces. The following cleaning procedure was followed:

- i. Wipe Teflon beakers with ethanol inside and out to completely remove any marker pen ink and organics.
- ii. Reflux each Teflon beaker in concentrated reagent grade HNO₃ (16M) overnight (or longer) at 120°C, let it cool, acid to waste.
- iii. Wash with deionised water (15 M Ω) in a big glass beaker, shake, water to waste. Repeat 3 times.
- iv. Teflon beakers and lids in a glass beaker, cover with 7.5M reagent grade HNO₃ on a hotplate overnight (or longer) at 120°C, let it cool, acid back to bottle once cool. Acid reused ~10 times before being changed.
- v. Wash Teflon beakers and lids with milli-Qwater in a big glass beaker, shake, water to waste. Repeat 3 times.
- vi. Reflux each Teflon beaker with distilled concentrated HCl (10M) overnight, at 120°C, let it cool, acid to waste.
- vii. Wash Teflon beakers with milli-Q water in a big glass beaker, shake, water to waste. Repeat 3 times.
- viii. Dry down on hotplate (45-60 minutes), lids not tight.

- ix. Close and store in ziplock bags.

Columns

The Biorad columns used for chemical separation of U and Th were rinsed thoroughly with milli-Q. They were then stored in 2M HNO₃ and 2M HCl alternately. The acid is changed at least 4 times, with columns soaking overnight in each acid before the acid is changed. Even after the cleaning process, columns are stored in one of the dilute acids.

Resin

Biorad AG1-X8 resin used for column chemistry is batch cleaned prior to use to remove 'fines'. Fines not only clog the column and cones of the MCICPMS but also 'collect' Th, reducing the yield of chemistry.

A small batch of resin as required for the immediate step of chemistry was further rinsed with ~1M HCl. The mildly acidic milli-Q was added to the resin and shaken vigorously and allowed to settle overnight before the water was removed and replaced with a fresh batch and the process was repeated at least 3 times. The resin was stored in a similarly mildly acidified milli-Q.

Pipette tips

Pipette tips were soaked overnight in 10% distilled HNO₃ and dried in the flow hood prior to use. During use, the pipette tip was again rinsed by pipetting milli-Q and then the solution (milli-Q or acid) that needs to be pipetted prior to actual use.

Centrifuge tubes

Subsamples are transferred to centrifuge tubes for measurement in the MCICPMS. Centrifuge tubes are soaked for 24 hours in 10% HNO₃ and dried in a flow hood in a metal-

free clean laboratory before being closed and sealed in sample bags (*Laxen and Harrison, 1981*).

c) Subsample mass

Precision in an MCICPMS used for the measurement of U and Th isotopes is strongly dependant on counting statistics, where the standard error of the measurement reflects the number of atoms measured, with greater number of atoms leading to higher precision (standard error is standard deviation divided by the square root of the number of measurements). An estimate of the subsample mass required is made keeping in mind that the aim is to get a 1‰ precision on the ^{230}Th measurement since it is the lowest concentration isotope being measured and therefore limiting to overall precision. An estimate of subsample mass is made using the following steps,

- i) An estimate of ^{238}U concentration of subsamples is obtained from trace element analysis on Thermo-Finnigan Element 2 using the method described in section 3.3.9. A direct estimate of ^{230}Th concentration is difficult to obtain using the protocol described in 3.3.9 due to its low concentration in subsamples.
- ii) The age of the sample is estimated from previous publications on samples from the same or nearby caves and is used in the basic age equation (which presumes secular equilibrium) to derive the number of ^{230}Th atoms expected in the subsample:

$$[^{230}\text{Th}/^{238}\text{U}] = (1 - e^{-\lambda^{230}t})$$

Where,

$[^{230}\text{Th}/^{238}\text{U}]$ is the activity ratio

t is time

Kaufman and Broecker, 1965

- iii) The MCICPMS at the University of Oxford used for measurement of U and Th isotopes gives a signal of 2.5 volts (V) for 25 ppb (parts per billion) dilution of

separated ^{238}U solution (separated from the calcium carbonate matrix using column chemistry). This is a conservative estimate of signal, the sensitivity of the instrument is usually double this. This sensitivity measurement is used to calculate the approximate number of counts per second (cps) of ^{230}Th that would be obtained from the instrument using the formula $1 \text{ volt} = 6.24\text{E}7 \text{ cps}$.

- iv) The target is to obtain a ^{230}Th signal of least 100 cps keeping in mind that the yield of column chemistry is not 100% but varies between 40 to 90% and the estimate of subsample mass needs to be adjusted for this. ~ 100 cps ensures a 1% precision on the ^{230}Th measurement and that the measurement of sample ^{230}Th will be at least 10 times the chemistry blank (blank ^{230}Th typically varies between 0 to 10 cps) to reduce uncertainty on the measurement. The blanks typically obtained are low but still form a significant uncertainty due to low concentration of ^{230}Th in samples.
- v) While this calculation gives the minimum amount of subsample powder that will be required to obtain a meaningful age, the maximum amount of subsample powder is limited by the column chemistry protocol used for separation of U and Th from the calcium carbonate matrix. The existing column chemistry protocol is designed to work with a maximum of 300 mg of carbonate powder.

d) Spike

When using an MCICPMS to measure more than one isotope, the uncertainty in the measurement of a ratio of two isotopes is far less than the intensity of each isotope since the mass spectrometer measures the various isotopes simultaneously. While the intensity of signal over a run could vary with plasma and filament condition, the variation would be similar for both isotopes, leading to more precise ratios than absolute intensity measurements. ^{238}U , ^{234}U , ^{230}Th and ^{232}Th are the relevant isotopes for U-Th dating. A mixed ^{236}U - ^{229}Th spike (isotopes of U and Th that are rarely found in nature) is added to facilitate precise U-Th dating through measurement of $^{238}\text{U}/^{236}\text{U}$, $^{234}\text{U}/^{235}\text{U}$ and $^{230}\text{Th}/^{229}\text{Th}$. The spike

is also used to calculate the yield of each column i.e. to calculate the amounts of U and Th lost during separation chemistry.

For ease in procedure and to reduce errors due to repeated weighing, a mixed U-Th spike is used rather than two mono-element spikes. However, a mixed spike should be such that sufficient amount of ^{229}Th can be added to each subsample so that it is not the smallest isotope being measured (keeping in mind counting statistics) while still maintaining the large dynamic range of measurements that need to be made. Further details of making a spike suitable for carbonate U-Th chronology measurements have been given in *Mason and Henderson, 2010*. The $^{229}\text{Th}/^{236}\text{U}$ spike used in the measurements in this thesis is referred to as the Oxford Carbonate Spike and its composition has been given in table 3.3.

e) Spike mass calculation

Uranium ratios of spike to sample are such that the uncertainties arising from abundance sensitivity are reduced. For thorium, ratios close to the standards used during instrumental measurements are preferred since they give confidence in the accuracy of measurements. This adjustment is particularly important because standard bracketing method is not used for Th measurements (*Mason and Henderson, 2010*).

Two rules were followed to calculate the mass of spike to be added to each subsample:

- i) $^{235}\text{U} < ^{236}\text{U} < ^{238}\text{U}$ (number of atoms)

This is the ratio present in natural carbonates so the idea is to keep to the same ratio with the spike as well. Since the spike is more than 99% ^{236}U which is not found naturally, the quantity of spike used should be between the ^{235}U and ^{238}U concentrations present in the subsample. The natural ratio of $^{238}\text{U}/^{235}\text{U}$ is 137.88 (*Bopp et al, 2009*) and is similar to that obtained for the U standard CRM-145 ($^{238}\text{U}/^{235}\text{U} = 137.849$) (*New Brunswick Laboratory –*

Certificate of Analysis, 2010) used for U analysis in the MCICPMS and is used as a reference for this calculation.

ii) $0.060926 < \text{atomic ratio } ^{230}\text{Th}/^{229}\text{Th} < 0.7716$

The first value is the $^{230}\text{Th}/^{229}\text{Th}$ of Mac1 standard and the second value is $^{230}\text{Th}/^{229}\text{Th}$ of THIS-2-250 standard used for measurements in the MCICPMS (*Mason and Henderson, 2010*)

The logic used to calculate Th is different from that used for U. ^{230}Th is so low in concentration that it cannot be measured on the Faraday Cups and has to be measured on the ion counters of the MCICPMS. Measurements on the ion counters require an additional 'gain' correction (see section 3.3.10 k). In order to make this correction, $^{230}\text{Th}/^{229}\text{Th}$ values of the subsample are kept close to that of the standards.

A software called DONKEY, developed at the University of Oxford by Andrew Mason, was utilised to optimise spike mass addition.

	^{229}Th	^{230}Th	^{232}Th	^{233}U	^{233}Pa	^{234}U	^{235}U	^{236}U	^{238}U	Th atomic weight	U atomic weight
Mass (amu)	229.031755	230.033127	232.038054	233.039628	233.0402	234.040946	235.043924	236.045562	238.050784		
Half-life	7900 _a	75690 _b	$1.40100 \times 10^{+10}$ _c	$1.59 \times 10^{+5}$ _d	7.657×10^{-2} _e	245250 _b	$7.0381 \times 10^{+8}$ _f	$2.34 \times 10^{+7}$ _d	$4.4683 \times 10^{+9}$ _f		
λ	8.77×10^{-5}	9.158×10^{-6}	4.94752×10^{-11}	4.359×10^{-6}	9.052	2.8263×10^{-6}	9.8485×10^{-10}	2.96×10^{-8}	1.5513×10^{-10}		
Oxford Carbonate Spike											
Atomic %	0.99598	0.00006	0.00396	0	0	3.865×10^{-11}	4.20573×10^{-5}	0.999727537	0.000230406	229.043725	236.045982
Conc. g/g	2.43494×10^{-10}							9.09591×10^{-8}			
2 σ %	2.4							0.8			

Table 3.3: The half-lives and decay constants (λ) of all isotopes of interest (^a Goldstein et al, 1989; ^b Cheng et al, 2000; ^c Holden et al, 1990; ^d Holden et al, 1989; ^e Usman and MacMohan, 2000; ^f Jaffey et al, 1971). The atomic abundance in natural materials and in the Oxford Carbonate Spike have been given. The spike concentrations and associated uncertainties as calibrated by Robinson, 2002.

f) Spike dilution and addition to subsamples

All weighing was performed on a 5-place analytical balance (0.00001 g) in the weighing room of the metal-free clean laboratory with a precision better than ± 0.0001 g. The weighing process is adapted from Thomas, 2006. An aluminium foil jacket reduces the erroneous measurements resulting from static caused by the Teflon spike bottle and Teflon beakers. To ensure a reliable mass, bottles and beakers are weighed at least three times until a reproducible number is obtained i.e. a number that is not showing a consistent rise or fall but that varies only in the last decimal point. These three measurements are then averaged. Since it is a mixed U-Th spike, the uncertainty in spike measurement is not important in the age calculation.

The stock spike is stored in a dropper bottle which is protected with Parafilm. This prevents evaporation and contamination. The mass of spike added is assessed by weighing the spike bottle, adding the spike to a cleaned Teflon beaker and weighing the spike bottle again. The difference in weight is considered to be the quantity of spike that has been added to the Teflon beaker.

The spike is then diluted gravimetrically in the Teflon beaker with 7.5M quartz distilled nitric acid to yield sufficient volume to facilitate spike addition to subsamples by pipette.

The subsample powders were transferred from centrifuge tubes to respective Teflon beakers in the balance room and weighed. The powders were then diluted with 300 μ l -2 ml of milli-Q water using a pipette (the amount of water depends on the mass of subsample powder) in a hood in the metal free clean laboratory. This limits the spike (in nitric acid) from effervescing when added to the subsample powders. Each subsample was spiked by

pipetting the dilute spike solution into the beaker and firmly replacing the beaker cap. The Teflon beaker containing the dilute spike is weighed between each addition.

g) Sample dissolution and equilibration

The spiked-subsample solutions were further diluted with milli-Q and small aliquots of 300 μl of 7.5M HNO_3 , until all powder was completely dissolved. Between each aliquot addition, the Teflon beaker was closed so that only the evolved gas could escape rather than scattering of any effervescence. After dissolution, any material along the sides was captured by rolling the solution around the closed saviilex.

Some samples that were 'dirty' required additional procedures for dissolution. In such cases, the following methods were progressively tried:

- i) Adding more milli-Q.
- ii) Drying down and dissolving in 3-4 ml of distilled concentrated nitric acid.
- iii) Drying down and dissolving in 3-4 ml of distilled concentrated hydrochloric acid.
- iv) Drying down and dissolving in aqua regia.
- v) Drying down and dissolving in distilled dilute hydrofluoric acid. If this step was employed, the sample was re-dissolved in an excess of hydrochloric acid to dissolve any fluoride compounds that may have formed.

Different substances apart from CaCO_3 may be present in the sample powders and may dissolve in different concentrations and different acids, for example silicates or organics. The processes employed are a balance between increasing chemical blanks (due to the addition of different acids) and dissolving all the subsample powders including U and Th that may be present as detrital material and inclusions. However, these further steps were required only for one sample (BLM, Appendix II).

Once dissolved, 2 ml of concentrated distilled nitric acid was added before refluxing the samples overnight to equilibrate the sample with the spike. Sample fractions were then dried down again to ensure the conversion of salts to nitric form.

h) Column chemistry

The protocol used for column chemistry is given in table 3.4 and is an updated version of *Thomas, 2006*. The separation method is based on 'stick-unstick' chemistry, where affinity of U and Th for resin is changed using different acids. CaCO_3 has a low affinity for the resin and is removed first.

U-Th-Ca separation					
Calibrated for 300 mg					
Date: _____	Title: _____			Initials: _____	
<u>Samples:</u>					
1.	2.	3.	4.	5.	6.
7	8	9	10	11	12
Samples heated in HNO ₃ overnight				[]	
Samples heated to incipient dryness				[]	
Samples converted to nitrate form				[]	
Samples dissolved in 4 ml 7.5N HNO ₃				[]	
Clean 2ml columns in 7N HNO ₃ and rinse with Milli-Q					
<u>Column protocol:</u>					
2 ml Biorad columns filled with 2 ml new resin slurry				[]	
(washed 1x8 anion-exchange resin 100-200 mesh)					
Washed with 10 ml H ₂ O, 10 ml 6M HCl, 10 ml H ₂ O				[] [] []	
Conditioned with 2x5 ml 7.5M HNO ₃				[] []	
Load samples directly from sample beaker				[]	
Wash columns with 2x2 ml 7.5M HNO ₃ , adding the first 2 ml				[] []	
to the sample beaker and adding it directly to the column					
Convert the column with 4x0.25 ml, 1x0.5 ml 6M HCl				[] [] [] [] [] []	
Elute Th cut with 2x1 ml, 2x2 ml 6M HCl				[] [] [] [] [] COLLECT Th	
Elute U cut with 2x1 ml, 2x4 ml H ₂ O				[] [] [] [] [] COLLECT U	
in original beakers					
Dry down each cut (without boiling)				Th [] U []	
Add 0.2 ml of conc HNO ₃ to each cut and dry down				Th [] U []	
Dissolve in 42 µl of 7.5N HNO ₃ to store for mass spec				Th [] U []	
(add 958 µl Milli-Q to make 1 ml 2% HNO ₃)					

Table 3.4: Method for column chemistry to separate U and Th from the CaCO₃ matrix

i) Blanks

<i>Number</i>	<i>Blank code</i>	<i>Batch date</i>	$^{232}\text{Th}/^{230}\text{Th}$	^{232}Th	^{230}Th	^{238}U	<i>Comments</i>
			<i>atomic</i>	<i>mass (gm)</i>	<i>mass (gm)</i>	<i>mass (gm)</i>	
1	N1_7	27/03/2013	639	4.10E-15	2.64E-12	1.72E-10	Clean calcite
2	N2Blank1	14/04/2015	1919	7.00E-16	1.35E-12	4.97E-11	Clean calcite
3	N2Blank2	14/04/2015	6888	5.52E-16	3.84E-12	2.31E-11	Clean calcite, resin washed twice in column
4	N2Blank3	15/04/2015	800	7.25E-16	5.85E-13	4.00E-11	Dirty calcite
5	N2Blank4	15/04/2015					Dirty calcite, blank lost during measurement on MCICPMS
6	N2Blank5	13/04/2015	-850	-3.68E-17	3.16E-14	3.22E-11	Clean aragonite
7	N3Blank1	19/10/2015	856	1.05E-15	9.03E-13	1.60E-09	Medium U conc aragonite
8	N3Blank2	14/10/2015	861	6.20E-16	5.38E-13	2.34E-10	Low U conc aragonite
9	N3Blank3	14/10/2015					Low U conc aragonite, blank lost during measurement on MCICPMS
10	N3Blank4	26/10/2015	6	1.10E-15	6.37E-15	1.12E-10	High U conc clean calcite
11	N3Blank5	2/11/2015	197	1.96E-14	3.89E-12	4.50E-10	Dirty calcite, multiple dissolution steps
12	N3Blank6	26/10/2015	868	5.48E-16	4.80E-13	3.10E-10	High U conc clean calcite

Table 3.5: Blank measurements of various sets of column chemistry. Every column set had at least one and sometimes two blank measurements. Columns were run in batches in such a way that all ‘dirty’ calcite subsamples were paralleled by a blank that was treated like the subsamples. For example N3Blank5, was run with ‘dirty’ calcite subsamples that required dissolution by multiple acid steps including aqua regia, HCl and HF. N3Blank5 has been subject to all these dissolution steps, eluted in the same batch of column chemistry and measured in the same run in the instrument as the other dirty calcite subsamples. This blank was used to correct the ‘dirty’ calcite subsamples.

1 or 2 blanks were included in each batch of U-Th analyses to monitor potential contamination with U and Th that could affect ages. The blanks comprised a clean Teflon beaker and went through all the steps as a sample including spike addition. Where additional acids were required for specific subsample dissolution, 1 or 2 blanks were treated similarly. Subsamples and their blanks were run in the same batch in the MCICPMS as far as possible. Procedural blanks of this thesis are largely consistent with blanks of other researchers using the same laboratories and MCICPMS and have been given in table 3.5.

j) U-Th analysis on the MCICPMS

U-Th analysis was performed on a Nu plasma (P2) MCICPMS at the University of Oxford following the procedures detailed in *Robinson et al, 2004* and *Thomas, 2006*. P2 is coupled with a DSN100 desolvator and a collector array of 12 Faraday collectors and 3 ion counters (figure 3.4). The ion counters are fitted with dynodes which amplify the arriving signal.

step	F(+8)	F(+6)	F(+4)	F(+3)	F(+2)	F(+1)	AXIAL	F(-1)	F(-2)	IC(-3)	F(-4)	IC(-5)	F(-6)	IC(-7)	F(-8)
<i>Uranium</i>															
<i>Ion counter gain and mass bias</i>															
A1							^{238}U			^{235}U					
A2									^{238}U			^{235}U			
A3											^{238}U				^{235}U
A4						^{238}U			^{235}U						
B1								^{238}U			^{235}U		^{234}U		
<i>Thorium</i>															
1		^{238}U				^{235}U			^{232}Th	X			^{229}Th		
2				^{238}U			^{235}U			X			^{230}Th		

Figure 3.4: A table showing the array of collectors in 'P2'. F refers to Faraday collectors and IC to Ion Counters. The number in brackets is the mass between each collector and the axial Faraday collector. The measurement configurations for measuring different solutions has been shown below. The figure and description are from Thomas, 2006.

The subsamples are transferred from Teflon beakers to 2 ml centrifuge tubes for measurements on the MCICPMS. The current produced by the arrival of ions in the instrument is amplified by a high impedance operational amplifier using a $10^{11}\Omega$ resistor. The Faraday collectors have a dynamic range from $\sim 10^{18}\text{A}$ to $\sim 10^{-10}\text{A}$ which is measured as a voltage of $\sim 0.1\text{mV}$ to 10V across the resistor. The ion counters have the sensitivity to register the arrival of a single ion and are used to measure up to 500,000 cps or 8 mV.

The configuration of 'P2' is such that the ion counters are two masses apart which means ^{229}Th and ^{230}Th cannot be measured simultaneously. To accommodate for this, Th is measured dynamically in two steps i.e. the beam is shifted so that both ^{230}Th and ^{229}Th can be measured in the same ion counter but in successive steps. Since this means that $^{230}\text{Th}/^{229}\text{Th}$ cannot be directly measured, each is measured relative to the larger beam of ^{235}U that is measured in a Faraday cup in both steps. The ^{235}U measurement is used to step normalise and calculate $^{230}\text{Th}/^{229}\text{Th}$. Th samples are doped with CRM-145, a uranium standard, for this step normalization.

All uncertainties are reported as 2 standard error (2 se), which is twice the standard deviation divided by the square root of the number of measurements. Since uncertainty reduces with number of measurements, U ratios were typically measured 50 or more times (i.e. 50, 10second integrations) and Th ratios were measured 75 or more times (2.5 second integrations for the first step to measure ^{229}Th and 4.5 second integrations for the second step to measure ^{230}Th) in each step. The balance lies between the dilution required to make a large number of measurements to reduce the error and yet running the sample at sufficient concentrations to yield a readily measurable signal.

It takes an hour for the U measurement of a single subsample including measurements of subsample itself and associated abundance sensitivity corrections, bracketing standards and the washing cycle before the next subsample measurement. A single Th subsample

measurement takes 45 minutes and includes measurement of the gain and memory and the washing cycle before the next sample measurement.

k) Corrections

All data corrections are performed by the in-house software called Donkey developed by Andrew Mason at Oxford. The corrections are detailed in Thomas, 2006 and *Mason and Henderson, 2010*.

- i) Mass bias corrections arise from differences in the transmission of ions in the plasma with heavier ions preferentially going into the mass spectrometer. This is internally corrected using the $^{238}\text{U}/^{235}\text{U}$ ratio of the U standard, CRM-145, (137.849) (*New Brunswick Laboratory – Certificate of Analysis, 2010*).
- ii) Ion counter gain corrections arise from the difference in ion counter measurement of an ion beam and the more accurate measurement of Faraday cup measurements. This is monitored and corrected using the $^{238}\text{U}/^{235}\text{U}$ ratio of CRM-145 where ^{238}U is measured in the Faraday cup while ^{235}U is measured in an ion counter. The natural $^{238}\text{U}/^{235}\text{U}$ ratio then allows an assessment of the ion counter ‘gain’, which is typically 90%, this allows as large a signal to register as possible without creating any ‘false’ signal greater than caused by genuine ion arrival (Thomas, 2006).
- iii) Abundance sensitivity corrections arise when the tail of a particularly strong beam contributes to the signal of an adjacent collector. These are corrected by measuring half masses and modelling expected tails away from the main beam assuming an exponential decay curve.

l) Age calculations

All U-Th measurements are processed using Donkey, developed by Andrew Mason at the University of Oxford. Donkey allows for sophisticated uncertainty propagation (such as the instrumental errors mentioned in the corrections subsection) using Monte Carlo

simulations. The uncertainty has been calculated on 95% of the total number of measurements lying within a 2σ confidence interval.

Corrections are also made for initial thorium. Thorium is insoluble in water and it is assumed that there is little to no thorium in drip waters. The process of dissolution isolates thorium from uranium. The only thorium measured in the stalagmite should be derived from the decay of uranium and is the basis of U-Th dating method. However, Th can be carried as detrital material by drip waters and incorporated into the stalagmite resulting in age errors. There are three main methods for constraining initial $^{232}\text{Th}/^{230}\text{Th}$ ratio: isochrons, sequential leaching and the *a priori* estimate (Hellstrom, 2006). *A priori* estimation has been used for initial thorium correction in this thesis using a bulk detrital value of $^{232}\text{Th}/^{230}\text{Th}$ with generous estimates of uncertainty (5.38E-06, +5.38E-06, -4.84E-06) (Richards and Dorale, 2003; Hellstrom, 2006).

For example, for a 'dirty' calcite subsample with an exceptionally high ^{232}Th concentration of 383 ppb, the raw age (without correction for detrital Th) is 89,568 years, +640 years and -570 years and with the detrital Th correction mentioned above, the uncertainty increases to 61,568 years, +24809 and -28693 years (see Appendix II). Whereas for a 'clean' aragonite subsample with a low ^{232}Th concentration of 0.7 ppb, there is a smaller age correction from (20688 to 20620) and an additional uncertainty of just one year due to detrital Th enabling much tighter age control of 20620 years, +78 and -84 years (see Chapter 8). The uncertainty in this case is due to counting statistics and chemistry blanks (see Thomas, 2006).

m) Age Modelling

Age model for one sample (from Kotumsar Cave) has been developed using the StalAge software developed by Scholz and Hoffmann, 2011. The software identifies major outliers, then age data are screened for minor outliers and age inversions. The uncertainty of

potential outliers is increased using an iterative procedure. Finally the age model and corresponding 95% confidence limits are calculated by a Monte-Carlo simulation. An age and error for each individual sub-sample was obtained by inputting the subsampling interval.

Chapter 4

Testing for Equilibrium Precipitation in an Aragonite Stalagmite

Abstract

Aragonite stalagmites can be fast growing, often allowing for preservation of annual laminae, and have high concentrations of uranium that allow precise age measurements. Consequently, they are increasingly being used to derive paleoclimate information. However, there is debate about whether the stable isotopes of oxygen and carbon precipitate under equilibrium conditions in this fast-growing aragonite. Hence a question arises about their fidelity as recorders of paleoclimate information.

This chapter reports results from a variety of tests to check for equilibrium calcium carbonate precipitation in an aragonite stalagmite collected from the west coast of India. Tests applied include those based on along-growth-layer and along-growth-axis relationships between carbon and oxygen isotopes, and a check against previously published equilibrium fractionation equations for the water-aragonite system. I find that there appears to be equilibrium precipitation in modern carbonate growth and specific subsamples from the sample stalagmite. 'Ponding' of drip water on the growth surface results in precipitation that has departed most from oxygen isotopic equilibrium. Changes in the growth surface of the stalagmite, so that the angle relative to horizontal changes, may also alter fractionation processes by changing the time available for carbonate removal. This process may also be significant for other samples, particularly those with changing angles of growth surface, and in caves with a high temperature ($>25^{\circ}\text{C}$) and low humidity ($<70\%$). Further information about past rainfall oxygen isotopic measurements, and a

tighter control on the actual isotope fractionation for equilibrium, are required to understand whether older portions of the sample formed in equilibrium.

4.1 Introduction

$\delta^{18}\text{O}$ records of past precipitation as recorded in ice, lakes, and speleothems, are widely used as a paleo-proxy for climate, and can provide information about temperature, rainfall amount, and/or the source of moisture. For stalagmites to be useful as records of rainfall $\delta^{18}\text{O}$, they must form with a predictable $\delta^{18}\text{O}$ relationship to rainfall $\delta^{18}\text{O}$. This relationship is often referred to as 'isotopic equilibrium' and assumes a constant and predictable change in fractionation between water and carbonate with temperature. The precise nature of this equilibrium is not straightforward, and a number of studies have suggested somewhat different equilibrium relationships for calcite (for example, *Hendy, 1971; Mickler et al, 2004; Mickler et al, 2006; Dreybrodt and Scholz, 2011; Day and Henderson, 2011; Hansen et al, 2013*). Nevertheless, in the specific environment of the cave, there appears to be a reasonably consistent relationship between $\delta^{18}\text{O}$ fractionation and cave temperature, where there is an inverse relationship between cave temperature and calcite $\delta^{18}\text{O}$ (*Duplessy et al, 1970; Schwarcz, 1986; Gascoyne, 1992*). To the extent that this is true, it is possible to use stalagmite $\delta^{18}\text{O}$ to assess past rainfall. It is therefore important to evaluate whether a particular sample follows the expected 'equilibrium' relationship. Deviations from equilibrium are known to be caused in some samples by rapid depletion of the Dissolved Inorganic Carbon (DIC) pool in the drip-waters during speleothem growth (*Hendy, 1971*).

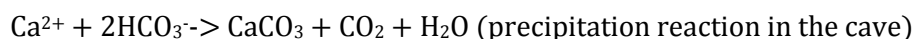
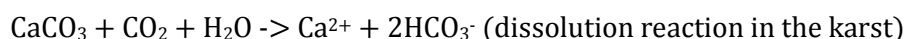
Aragonite speleothems have been much less widely studied than calcite examples. Aragonite speleothems typically form rather rapidly, so it has commonly been assumed that they may be more prone to non-equilibrium behaviour. Few studies have systematically assessed whether aragonite samples have grown under equilibrium or kinetic conditions using methods such as comparison of measured $\delta^{18}\text{O}$ values of the stalagmite with expected $\delta^{18}\text{O}$ value from published equilibrium fractionation equations for the water-aragonite

system (*Li HC et al, 2011; Li TY et al, 2011; Lachniet, 2015*) and comparison with coeval stalagmite $\delta^{18}\text{O}$ records from the same or nearby caves (*Denniston et al, 2013; Lachniet, 2015*).

Here I conduct a comprehensive study of an aragonite stalagmite from west India to assess whether it formed in equilibrium, or with a kinetic overprint. This study will enable data from this sample to be assessed i.e. can it be used for paleoclimate work? And will have wider implications for the use of $\delta^{18}\text{O}$ in other aragonite samples.

4.2 Equilibrium and kinetic isotopic effects on $\delta^{18}\text{O}$ composition

The normal chemical pathway leading to speleothem formation is,



The partial pressure of CO_2 in drip waters is usually many times higher than the partial pressure of CO_2 in the cave atmosphere so CO_2 from drip water is expelled to the cave and calcium carbonate is precipitated. The process of precipitation can be at equilibrium or involve a kinetic overprint.

Isotopes have different masses so there is a subtle preference for the heavier isotope to be preferentially partitioned into one phase relative to the other. This fractionation for most materials, including the water-calcium carbonate system varies regularly as a function of temperature (*Sharp, 2007*). In a cave system, if CaCO_3 is precipitated by equilibrium fractionation, the oxygen isotope partitioning into CaCO_3 should mainly be a function of drip water oxygen isotope composition and temperature of the cave (*Hendy, 1971; Kim and O'Neil, 1997*). Several papers have reported that calcium carbonate precipitation in caves can deviate from equilibrium and show a kinetic overprint due to various debated factors involving rapid DIC (Dissolved Inorganic Carbon) depletion and evaporation. Kinetic

isotopic effects attendant on diffusion and evaporation are explained by different translational velocities of different isotopologues as they move across a phase boundary such that *regardless of temperature*, the lighter isotopologue will have greater velocity than the heavier isotopologue. Another process that factors in kinetic isotopic effects is that heavier isotopologues will have higher dissociation energies making bonds between the atoms such as $^{13}\text{C-O}$ harder to break (*Sharp, 2007*).

Rain water is by far the dominant source of oxygen in drip waters. Other sources are carbon dioxide dissolved from the soil horizon, and limestone, but these are much less significant contributions (*Hendy, 1971; Dreybrodt and Scholtz, 2011*). There are two reservoirs for oxygen in drip water; the H_2O reservoir, and the $(\text{CO}_3^{2-} + \text{HCO}_3^-)$ reservoir, with speleothems forming from the latter. Oxygen isotopic exchange takes place between the water and $(\text{CO}_3^{2-} + \text{HCO}_3^-)$ reservoirs, through hydration and hydroxylation reactions (*Hendy, 1971*).



These hydration and hydroxylation reactions are the slowest reactions taking place in solution during precipitation (*Faurholt, 1924; Roughton and Booth, 1938; Mills and Urey, 1940; Pinsent and Roughton, 1951; Pinsent et al, 1956; Himmelblau and Babb, 1958*). As long as the hydration/hydroxylation reactions for $\text{CO}_{2(\text{aq})}$ are able to keep pace with precipitation, oxygen will be buffered and there should be no change in the oxygen isotopic composition of the $(\text{CO}_3^{2-} + \text{HCO}_3^-)$ reservoir as precipitation proceeds on the stalagmite growth surface. On the other hand, $(\text{CO}_3^{2-} + \text{HCO}_3^-)$ is the only reservoir of carbon so carbon will not be buffered (*Mickler et al, 2006*). In this case, the oxygen in the stalagmite is related to the oxygen in the drip water as a function of temperature (*Hendy, 1971; Kim and O'Neil, 1997*) and drip rate (*Day and Henderson, 2011*).

Calcium carbonate precipitation in caves can deviate from equilibrium due to rapid depletion of DIC pool in the drip waters (for example, *Hendy, 1971; Mickler, 2006; Day and Henderson, 2011; Hansen et al, 2013*) and evaporation (*Hendy, 1971; Day and Henderson, 2011*). Both processes cause a shift towards higher $\delta^{18}\text{O}$ in the speleothem than that predicted from equilibrium.

4.3 Tests for identifying kinetic effects on calcium carbonate precipitation

An advantage of isotopic systems is that the processes described above will affect the carbon and oxygen isotopes in specific ways and this will be reflected in the precipitated calcium carbonate. Various tests have been suggested and debated in past publications to identify kinetic effects in $\delta^{18}\text{O}$ records; these are described below.

4.3.1 Growth layer $\delta^{18}\text{O}$ - $\delta^{13}\text{C}$ variation

If kinetic isotopic effects in CaCO_3 precipitation are caused by evaporation of H_2O , there will be enrichment in oxygen isotopic composition along the growth layer since lighter isotopes will be preferentially lost as vapour while carbon isotopic composition will be close to its equilibrium value (*Hendy, 1971*). If kinetic isotopic effects are caused by rapid degassing, this will be reflected by simultaneous enrichment in carbon and oxygen isotopes along the growth layer of a stalagmite, since lighter isotopes will preferentially escape as gas and the oxygen and carbon isotopes will be positively correlated (*Hendy, 1971*). If the oxygen is buffered through hydration and hydroxylation reactions between the DIC reservoir ($\text{CO}_3^{2-} + \text{HCO}_3^-$) and water keeping pace with DIC depletion, there will be no change in the oxygen isotopic composition along the growth layer. While the carbon isotopic composition, which has no such buffer, will progressively evolve and get heavier away from the growth axis. On a graph of carbon versus oxygen isotopic values measured along the growth layer, a vertical line will indicate conditions closer to equilibrium for oxygen, and departure towards more

kinetic values would be indicated by a slope away from the vertical (figure 4.1) (Mickler, 2006).

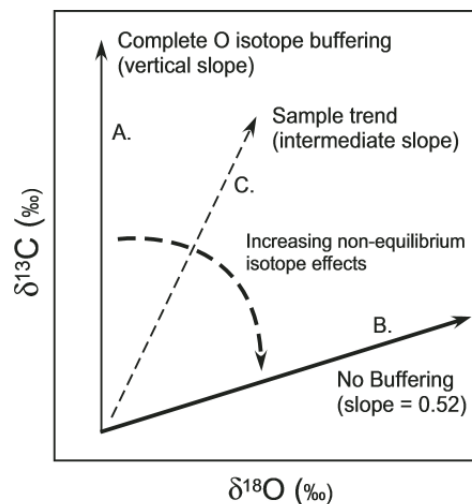


Figure 4.1: Oxygen and carbon isotope effects of progressive loss of HCO_3^- during CO_2 degassing and calcite precipitation on the $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values of speleothem calcite. Line A: maintenance of oxygen isotopic equilibrium between DIC through CO_2 hydration-hydroxylation reactions. Line B: absence of any oxygen isotopic exchange between DIC and H_2O . Line C: intermediate path of isotope evolution in which incomplete oxygen isotopic buffering occurs. The figure and description are from Mickler *et al*, 2006.

The slope of the growth layer may effect precipitation through influencing the time available for carbonate removal before the drop roles off and is replaced by or joined by a new drop. The longer the time that a drop spends on the stalagmite surface before precipitation, the longer time there is for CO_2 degassing/DIC depletion and evaporation. At higher temperatures this effect is more because both CO_2 degassing and evaporation rates increase with temperature (Day and Henderson, 2011). Day and Henderson, 2011 conducted laboratory analogue studies of calcite precipitation under controlled conditions at temperatures of 7°C, 15°C, 25°C and 35°C and drip rates of 1.6 drops per minute (dpm), 5.8 dpm and 10.4 dpm. They find that for slower drip rates and higher temperatures, the $\delta^{18}\text{O}$ is heavier by 1‰ than that expected from calcite equilibrium fractionation factor (compared to the fractionation factor from Kim and O'Neil, 1997). Drip rate measurements give an indication of the time available for DIC depletion before the reservoir on the surface of the

stalagmite is replaced/replenished by the next drop. If the angle of the growth surface, rather than the drip rate, results in the drip staying for longer, it will be reflected by significant correlation between the angles of the growth surfaces with respect to horizontal and their respective oxygen and, particularly, carbon isotopic compositions.

4.3.2 Along axis $\delta^{18}\text{O}$ - $\delta^{13}\text{C}$ variation

Kinetics caused by rapid degassing will result in carbon and oxygen enrichment along the growth layer and will be reflected by positive correlation in the isotopes measured along the growth axis (*Goede et al, 1986; Goede, 1994; Desmarchelier et al, 2000*). However, similar to the growth layer measurements, it is possible that there is correlation between carbon and oxygen isotopes along the growth axis but that the oxygen isotopes are in fact buffered i.e. the same mechanism causing correlation in the isotopes along the growth layer may reflect in a correlation along the growth axis as well. Thus a vertical slope on a plot of growth axis oxygen versus carbon isotopes would indicate conditions closer to equilibrium while a slope away from the vertical would indicate precipitation away from equilibrium (*Mickler et al, 2006*). In fact, *Mickler et al, 2006* found that most stalagmites (55% of 128 studies that presented both $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values of stalagmite calcite sampled along growth axes) exhibit positive $\delta^{18}\text{O}$ versus $\delta^{13}\text{C}$ covariation.

4.3.3 Comparison with expected equilibrium relationships

The along-growth layer and along-growth-axis tests help to understand fractionation during precipitation but have certain drawbacks as well,

- i) It is difficult to ensure that all sub-samples from the growth layer have been milled from the same growth lamina (*Dorale et al, 2002*).
- ii) The tests are based on the relative differences in $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ and therefore have no concept of whether growth axis carbonate is in equilibrium (*Day and Henderson,*

2011) i.e. the tests do not look at the relationship between drip water $\delta^{18}\text{O}$ and precipitated carbonate $\delta^{18}\text{O}$ compositions.

Laboratory experiments and natural samples provide reasonable estimates of the apparent oxygen isotopic fractionation between waters and carbonate, and samples falling within the range of published fractionation factors can be plausibly considered to be in apparent isotopic equilibrium. If the $\delta^{18}\text{O}$ of drip water and modern carbonate can be measured in addition to the temperature of the cave, the expected carbonate $\delta^{18}\text{O}$ value can be compared to the measured value to check for equilibrium (for discussion see *Lachniet, 2009*).

4.3.4 Replication test

Equilibrium tests presume that equilibrium conditions hold for the past as well, which may not necessarily be true. A $\delta^{18}\text{O}$ record from one stalagmite sample can be compared against another stalagmite sample from the same region to ensure that the $\delta^{18}\text{O}$ is recording regional climate rather than local cave effects. This is referred to as a replication test (for example, *Cheng et al, 2009* and *Denniston et al, 2013*).

Usually a combination of the tests mentioned above can give an idea of controls on isotopic composition of the stalagmite.

4.4 Formation of aragonite stalagmites

The tests described above have normally been made on calcium carbonate precipitating as calcite rather than aragonite. Aragonite speleothems typically have fast growth rates (*Railsback et al, 1994; Brook et al, 1999; Denniston et al, 2000; Bertaux et al, 2002; Shen et al, 2013*) and can have high Mg/Ca ratios where Mg blocks calcite nucleation and precipitation of aragonite is favoured (*de Choudens-Sanchez and Gonzalez, 2009; Spotl et al, 2016*). Caves hosted in dolomitic bedrock (*Duan et al, 2012*), evaporation (*Bar-Matthews et al, 1991; Railsback et al, 1994*) and prior calcium carbonate precipitation (*Bar-Matthews et*

al, 1991; Wassenburg et al, 2012) are factors that can increase concentration of Mg in drip waters resulting in aragonite precipitation.

4.5 Location and climate

Akalagavi cave ($14^{\circ} 59' \text{ N}$, $74^{\circ} 31'$, 521 m asl) is 30 km away from the Arabian Sea (figure 2.8) and is located in limestone and dolomite formations. Further information on the geology of the area and the cave has been given in section 2.5. The sample was removed by PRL (Physical Research Laboratory) in 1997 from a sloping ledge in a chimney like cavity extending ~ 5 m above it. It is fed by two drips, falling from the roof, over the surface of a large stalactite (figure 4.2).

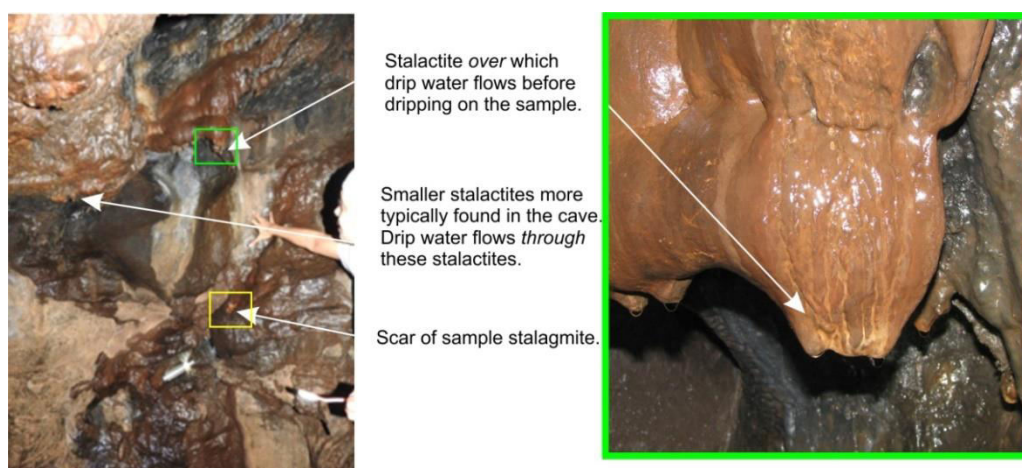


Figure 4.2: Sample location within the cave. The yellow box indicates the scar from where the stalagmite sample was removed. The sample was precipitating on a sloping surface. The green box shows the stalactite over which the drip water flows before dripping on the sample.

The locations of weather stations and regional grids are shown in figure 4.3. The closest weather station for temperature data is at Belgaum, located 100 km to the northeast of the cave. Long term temperature data has been obtained from Poona, located 400 km to the northeast of the cave, and parallels the CRUTEM4 temperature anomaly dataset for this region. Long term rainfall data for this region is available from the CRU TS 3.23 database. All datasets have been sourced from KNMI explorer. The closest GNIP station is located at

Mumbai, 470 km to the northwest of the cave and the $\delta^{18}\text{O}$ composition of rainfall in Mumbai has been accessed from WISER. Both the cave site and Mumbai are situated on the windward side of the Western Ghats with similar moisture sources and trajectories. Moreover, they have a similar pattern of rainfall i.e. the same months of monsoon rainfall (figure 4.7). Therefore, Mumbai is found to be the most suitable of the available GNIP sites in the area and data from Mumbai has been used to understand variation in the $\delta^{18}\text{O}$ composition of rainfall at the Akalagavi cave site.

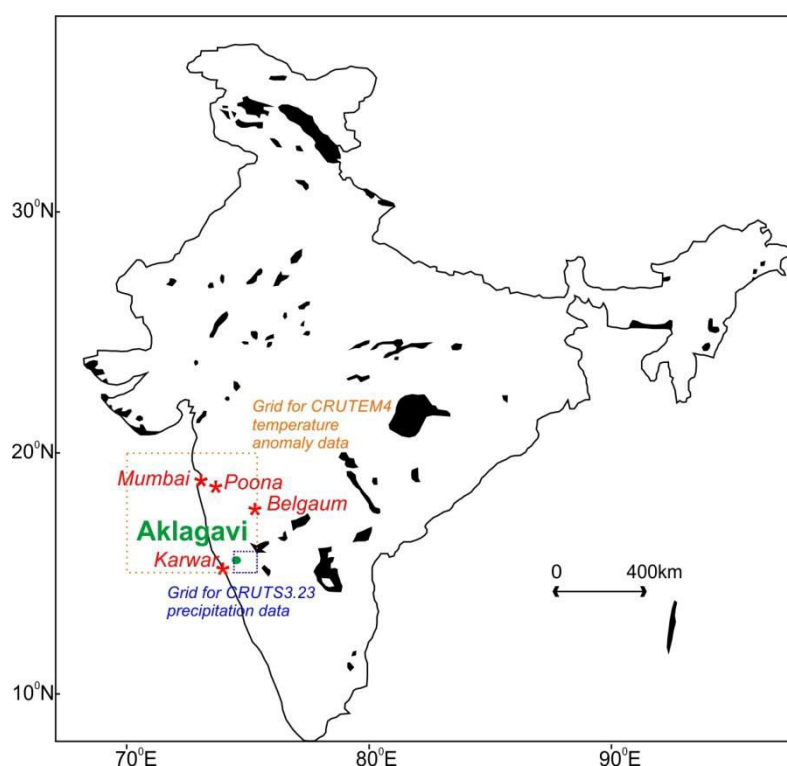


Figure 4.3: Location map. The black patches mark the location of limestone in India. Belgaum and Poona are the weather station locations from which temperature data has been retrieved. The orange dotted box marks the grid for which CRUTEM4 temperature anomaly data has been retrieved. The blue dotted box marks the grid for which precipitation data has been retrieved. Mumbai is the GNIP station close to Akalagavi cave that is similarly located close to the coast and has long term rainfall oxygen and deuterium measurements. Karwar is the meteorological station located closest to the cave site with rainfall amount data.

The cave region shows typical monsoon climate with a single rainy season lasting from June till September. Summer season lasts from February to May and winter from October to January. The mean monthly variation in temperature ranges from 22° to 28°C (1976 – 2016

AD) (figure 4.4) in Belgaum. The long term annual average temperature of Belgaum (1976 – 2016 AD) is 24.4°C. There is an increasing trend in temperature of ~0.6°C from 1880 till 2016 AD in temperature measurements for Poona and from the CRUTEM4 database (figure 4.5) (data tables 1, 2 and 3 of Appendix III).

The cave is on the windward side of the Western Ghats and receives nearly 2000 mm of total rainfall each year (figure 4.6). More than 80% of the rain falls from June till September when the monsoon winds carry moisture from the Arabian Sea and travel eastward into peninsular India.

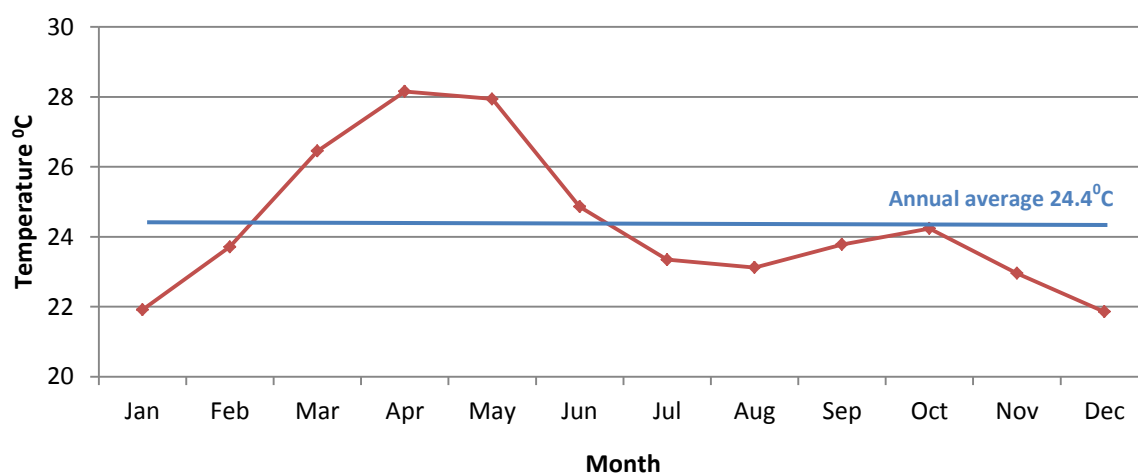


Figure 4.4: Monthly mean temperatures for Belgaum. Data is monthly means for the years 1976-2016. Data from GHCNM sourced from KNMI Explorer.

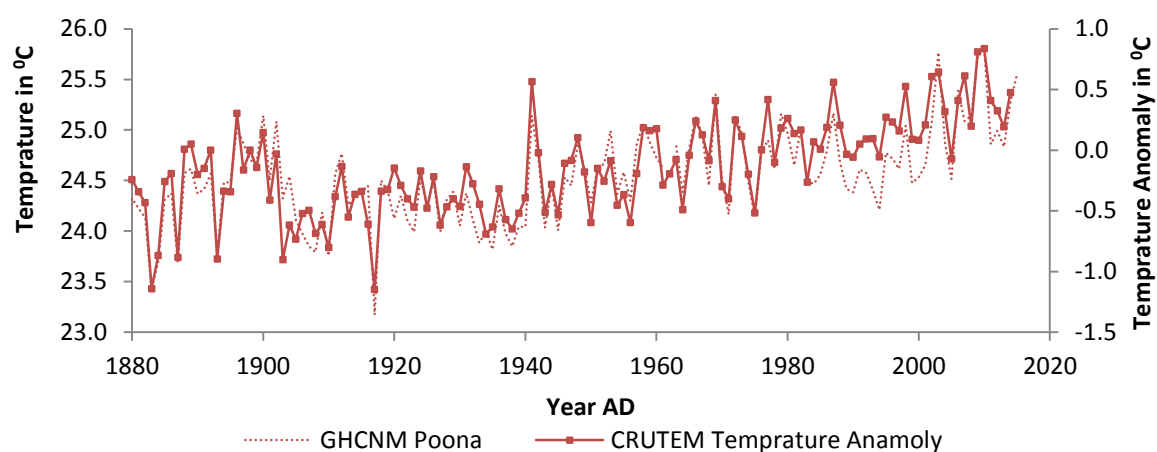


Figure 4.5: The longest mean temperature record from this region (Poona) from the GHCNM database and the temperature anomaly from CRUTEM4 database. Both datasets have been sourced from KNMI explorer.

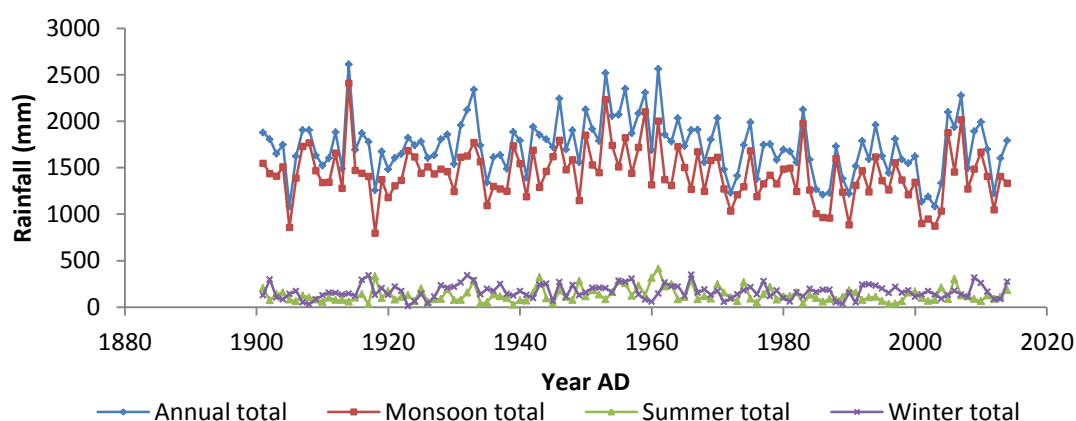


Figure 4.6: Annual and seasonal rainfall in the Akalagavi area. Data from CRU TS3.23 sourced from KNMI explorer. Monsoon total is sum of June, July, August and September. Summer total is sum of February, March, April and May. Winter total is sum of October, November, December, and January.

$\delta^{18}\text{O}$ composition of rainfall collected at Mumbai indicates that the monthly $\delta^{18}\text{O}$ ranges from -0.20 to -4.51‰ vSMOW (table 4.1, figure 4.8). Weighted $\delta^{18}\text{O}$ of monsoon rainfall for 8 years ranges from -0.39 to -2.45‰ vSMOW (table 4.2). (Raw data in tables 4 and 5 of Appendix III).

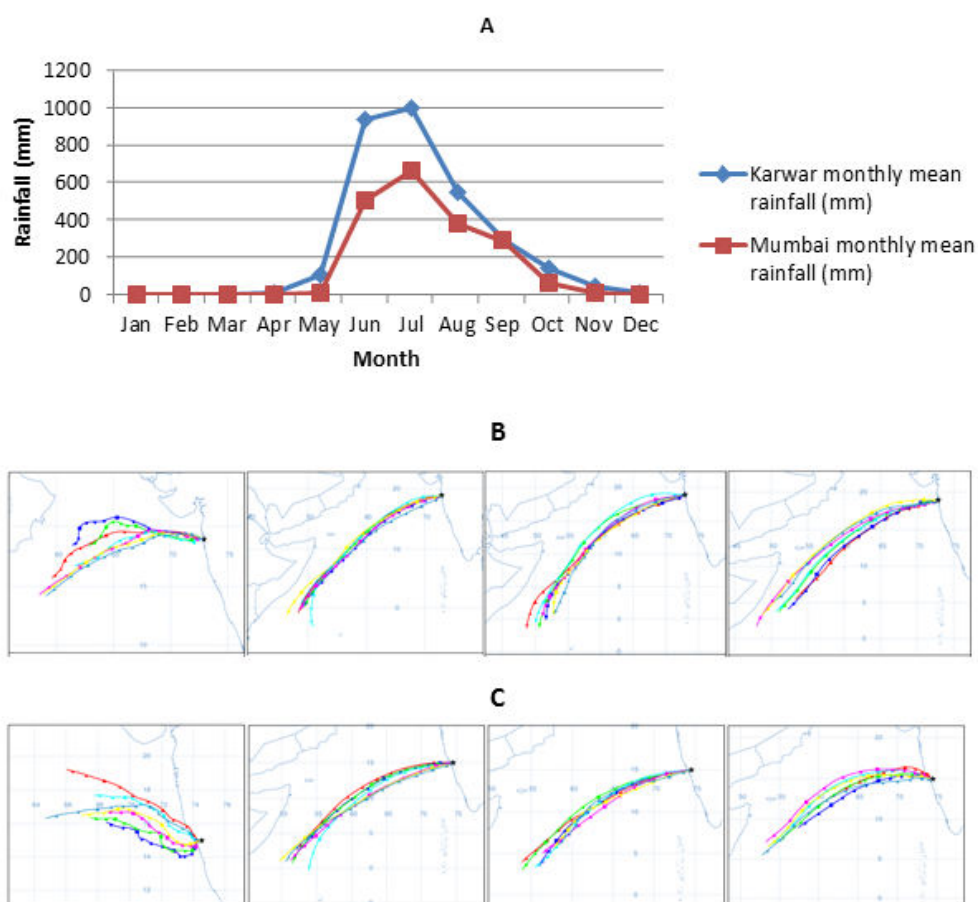


Figure 4.7: (A) Comparison of rainfall patterns and amounts in Mumbai and Karwar. Rainfall amounts are monthly averages from years 1871 to 1984. GHCNM data sourced from KNMI Explorer (B) Nine days of backward wind trajectories for Mumbai for the monsoon rainfall months of June, July, August and September (from left to right) of 2016. (C) The same nine days of backward wind trajectories for Akalagavi for the monsoon rainfall months of June, July, August and September (from left to right) of 2016. Wind trajectories plotted using Hysplit.

Month	No. of samples	Average $\delta^{18}O\%$	Average $\delta D\%$	Average rainfall (mm)	Rainfall %	Average Temperature ($^{\circ}C$)
January	1	-0.70	4.40	397.00	10.32	27.50
February	1	-2.20	-8.10	341.00	8.87	27.70
March	No rain					
April	No rain					
May	1	-0.20	6.20	51.00	1.33	26.60
June	10	-1.43	-3.40	386.90	10.06	29.14
July	9	-1.64	-2.64	874.89	22.75	27.53
August	10	-0.95	0.19	458.50	11.92	27.42
September	9	-1.65	-5.94	276.11	7.18	27.14
October	5	-4.51	-28.36	75.20	1.96	28.60
November	2	-2.62	-9.20	233.50	6.07	29.30
December	1	-1.20	-6.90	751.00	19.53	27.30

Table 4.1: Average monthly rainfall percentages and associated rainfall oxygen isotopic composition for Mumbai.

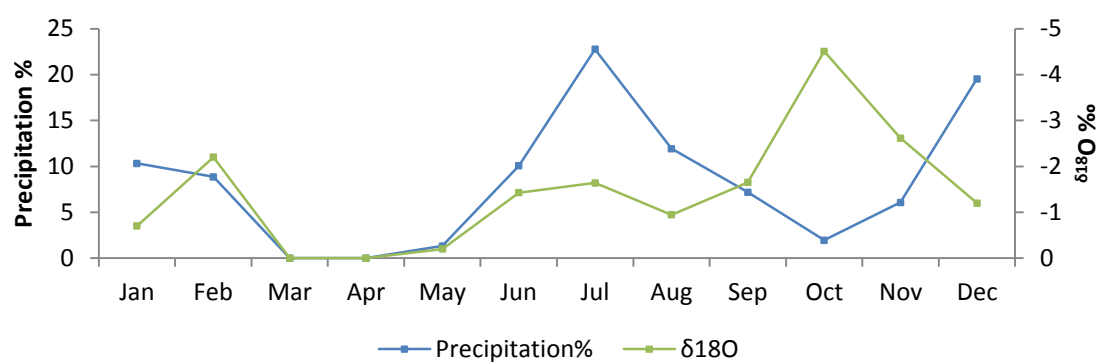


Figure 4.8: Monthly average rainfall percentage plotted against $\delta^{18}\text{O}$ ‰ vSMOW for Mumbai. Data from WISER. See table 4.1 for details.

Number	SampleDate	O18	H2	Rainfall (mm)	AirTemp	Total monsoon precipitation (mm)	Rainfall %	Weighted $\delta^{18}O$	Monsoon weighted $\delta^{18}O$
1	1961-06-15	-1.5	-10	393	29.4	2072	19	-0.28	-1.59
	1961-07-15	-2.1	-11.8	1110	26.9		54	-1.13	
	1961-08-15	-0.2	3.7	299	27.5		14	-0.03	
	1961-09-15	-1.2	-3.1	270	27.6		13	-0.16	
2	1962-06-15	-0.3	1.8	370	29.1	2501	15	-0.04	-0.76
	1962-07-15	-0.9	1.2	797	27.7		32	-0.29	
	1962-08-15	-1	1.8	1004	26.7		40	-0.40	
	1962-09-15	-0.2	1.8	330	27.6		13	-0.03	
3	1963-06-15	-2	-6.2	655	28.9	1848	35	-0.71	-1.84
	1963-07-15	-1.1	1.8	471	27.7		25	-0.28	
	1963-08-15	-2	-6.9	464	27.1		25	-0.50	
	1963-09-15	-2.5	-11.2	258	27.1		14	-0.35	
4	1965-06-15	0.3	7.3	342	29.2	1540	22	0.07	-1.26
	1965-07-15	-2.1	-9.2	884	27.8		57	-1.21	
	1965-08-15	0	8.6	131	27.5		9	0.00	
	1965-09-15	-1	2.7	183	28.1		12	-0.12	
5	1973-06-15	-0.98	1.8	85	29.6	2207	4	-0.04	-1.81
	1973-07-15	-2.55	-13.2	1441	27.5		65	-1.66	
	1973-08-15	0.06	8	533	27.3		24	0.01	
	1973-09-15	-1.89	-8.5	148	28.1		7	-0.13	
6	1974-06-15	-1.62	-6.2	539	28.7	2617	21	-0.33	-2.45
	1974-07-15	-1.24	1.7	910	27.7		35	-0.43	
	1974-08-15	-2.66	-13.7	715	27		27	-0.73	
	1974-09-15	-5.52	-40.6	453	27.3		17	-0.96	
7	1975-06-15	-3.58	-18.5	2	28.7	1429	0	-0.01	-0.39
	1975-07-15	-0.49	5.2	696	27.8		49	-0.24	
	1975-08-15	-0.23	3.9	332	27.6		23	-0.05	
	1975-09-15	-0.32	6.5	399	27.3		28	-0.09	
8	1976-06-15	-1.37	-1.2	463	29.3	1475	31	-0.43	-0.94
	1976-07-15	-0.88	3.7	647	27.7		44	-0.39	
	1976-08-15	-0.06		272	29		18	-0.01	
	1976-09-15	-1.81	-5.4	93	24.5		6	-0.11	

Table 4.2: Monsoon rainfall percentages and associated weighted rainfall oxygen isotopic composition for Mumbai. GNIP data from WISER.

4.6 Previous work on the sample

The stalagmite was collected in 1997 by scientists from the Physical Research Laboratory (PRL). Details of initial sample treatment and results are in *Yadava et al, 2004* and are briefly summarised here (figure 4.9). A combination of radiocarbon dating, lamina counting and ^{14}C bomb-spike measurements provides chronology for the sample. The sample grew for 331 years from 1666 to 1997 AD with a maximum lamina counting error of ± 7 years. The speleothem has a growth rate of 1.34 mm/year. The sample shows alternating white (compact) and dark (porous) layers. The white layers are considered to have been precipitated during the monsoon rainfall season while the dark layers represent non-monsoon rainfall season growth. The seasonal variation in layers is thought to be caused by a seasonal drip rate control which allows for entrapment of fine detrital material during the slower-dripping non-monsoon-rainfall seasons.

Stable isotope measurements were made by PRL on 5-10 mg subsamples from the compact (white) along the growth axis using a 0.5-0.8 mm drill bit to obtain a monsoon season signal of stable isotopes. Precision of $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ are 0.1‰ and 0.15‰ respectively. They conducted Hendy tests on two layers and found no progressive enrichment along the two growth layers (figure 4.9). XRD (X-Ray Diffraction) analysis on two spots, one where $\delta^{18}\text{O}$ is most depleted (~ 1666 AD) and the second where it is most enriched (~ 1900 AD) showed that the stalagmite is more than $\sim 98\%$ aragonite. The isotope records have been interpreted in terms of the amount of precipitation in the region and have been used to quantify the amount of rainfall going back in time.

In this thesis, the previous XRD analysis has been taken as conclusive evidence of aragonite mineralogy and no further tests have been made. The growth axis and Hendy test layer $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ measurements from compact (white) layers as well as lamina width measurements

as measured by *Yadava et al, 2004* were used. Further sampling and analytical methods, made as a part of this thesis, are described in section 4.7.

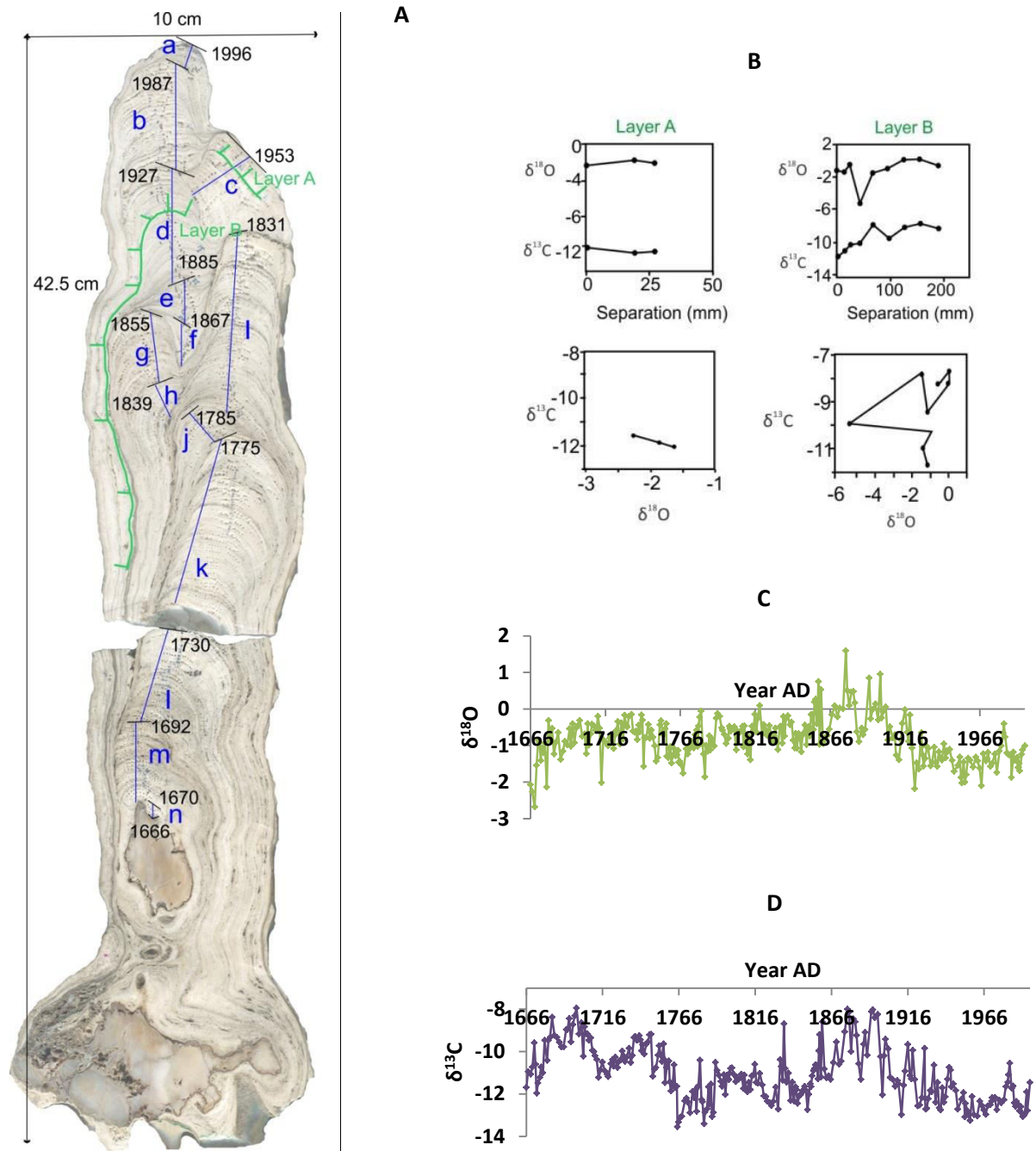


Figure 4.9: The panel shows previous work done on the sample and published by *Yadava et al, 2004*. (A) The sample has been shown with dimensions, growth axis, chronology and location of Hendy test layers A and B. (B) Oxygen and carbon stable isotopic composition of Hendy Test layer subsamples (Raw stable isotopic data in table 10 of Appendix III). The separation represents distance of subsample point from the growth axis. (C and D) The oxygen and carbon isotopic measurements along the growth axis have been plotted against age in years AD (Raw stable isotopic data in table 6 of Appendix III).

4.7 Further sampling and analytical methods

Modern carbonate growing in the cave over the sample scar was collected as chips in January, 2015. Subsamples were milled from the thickest chip. Continuous milling of the modern carbonate chip was preferred to capture both layers providing seasonal resolution stable isotope measurements (figure 4.11). As mentioned in section 4.6, the sample stalagmite has been milled by PRL to obtain subsamples from every white (compact) layer. To capture the variation in stable isotopic composition from both the white and dark layers of the sample stalagmite, a small 2 cm section of the sample stalagmite has been continuously milled to give seasonal resolution subsamples and includes both the dark and white layers (figure 4.11).

Rainwater, groundwater and drip water collection and measurements were also made as a part of this thesis. Together with the carbonate stable isotopic measurements, they can be used to test measured $\delta^{18}\text{O}$ values of precipitated carbonate against expected $\delta^{18}\text{O}$ values based on published fractionation equations for the aragonite-water system. To ensure that differences in $\delta^{18}\text{O}$ measurements are not a result of inter-laboratory measurement differences, aliquots of the same calcite subsamples have been measured in both laboratories (table 7 and figure 1 of Appendix III). In addition, mapping of the cave, measurements of humidity, drip rate and temperature have been done as a part of this study. The methodologies have been described in brief below and in detail in Chapter 3.

4.7.1 Field and monitoring work

Three well water samples were collected by collaborators at Mhadei Research Centre (MRC) and by Girish Punjabi in May, 2014. Ten drip water samples from different drip sites were collected on three different occasions; in the pre-monsoon period of May, 2014 and in the post monsoon periods of January, 2015 and May, 2015. Access to the cave is restricted in the monsoon. The samples of May, 2014 (2 samples) and May, 2015 (2 samples) were collected

by collaborators from MRC and by Girish Punjabi. The exact locations of the samples within Akalagavi cave are not known. The samples of January 2015 (6 samples) were collected by me and a team from Oxford and PRL, the precise locations of the samples within Akalagavi cave are known and have been plotted on the cave map (figure 4.10). One spring water sample was also collected during the same field work session of January, 2015. The spring is located ~ 1 km from the cave.

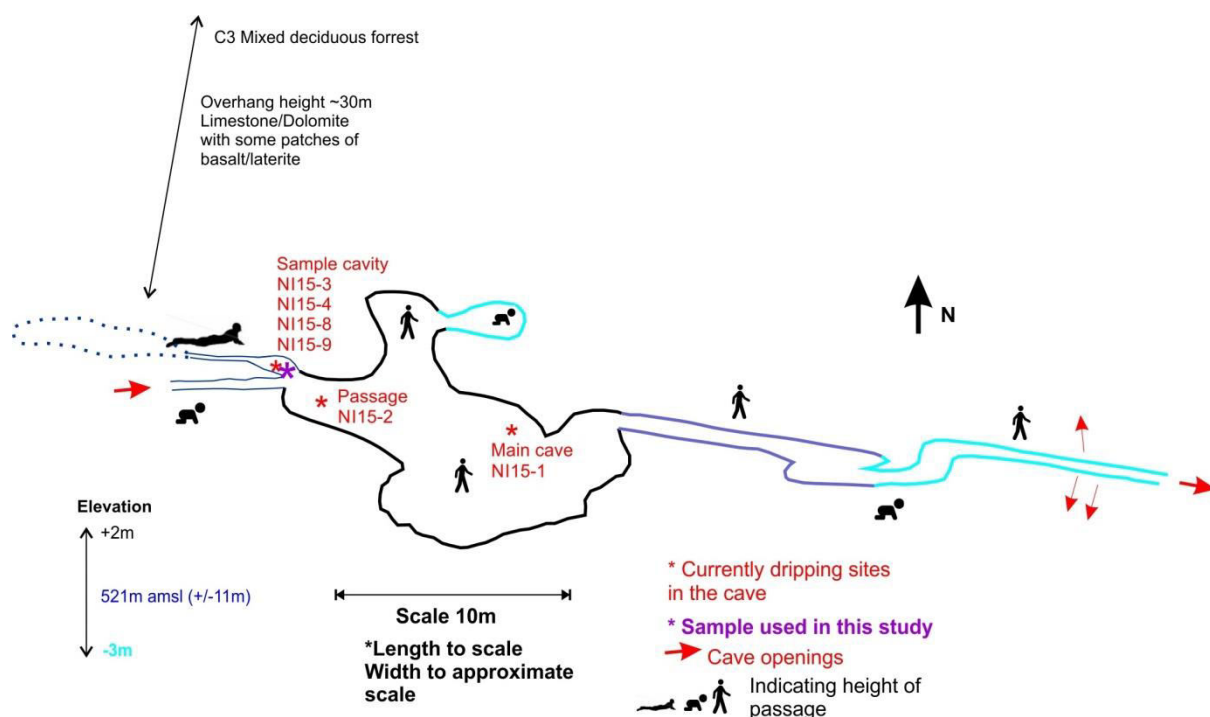


Figure 4.10: Akalagavi cave map with drip water sample locations (Drip water samples: NI15-3, NI15-4, NI15-8, NI15-9, NI15-2, NI15-1). Cave size parameters were measured with a DistoX instrument, which allows distances to be measured using a laser pointer, combined with a compass/clinometer. The map was produced using the software Survox and modified using CorelDRAW. The dashed line indicates a chamber that was seen but which could not be entered because of the very narrow passage that led to it.

During the January, 2015 fieldwork, temperature and humidity measurements in the cave were made using hand held devices and a HOBO temperature data logger was left in the cave. I visited the cave again in April, 2016 to retrieve the logger. The logger recorded data every 2 hours from the 16th of January, 2015 till the 31st of October, 2015, with an accuracy

of 0.53°C. 3 temperature data loggers were strategically hidden in the cave but only this one was found at the end of the year.

Rain water was collected by the MRC field team approximately once a week for a 24 hour period each time for the 2015 monsoon season. MRC is located ~120 km to the north of the cave site and is a part of the same forest corridor.

4.7.2 Analytical methods

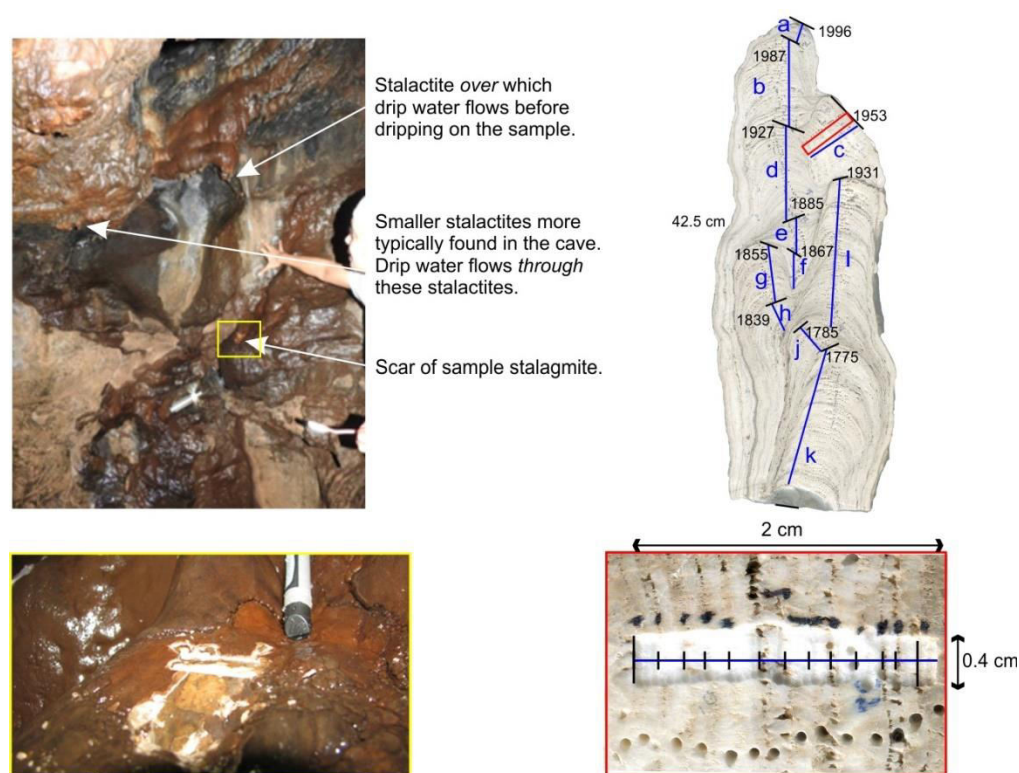


Figure 4.11: The panel to the left shows chips taken of modern carbonate growth formed on the sample scar (yellow box) for seasonal resolution oxygen and carbon stable isotope measurements. The panel to the right shows the sample stalagmite section (red box) milled continuously for seasonal resolution oxygen and carbon stable isotope measurements.

The thickest chip of modern carbonate material collected in the cave was washed with DI water, dried in a flow hood, mounted in playdough lined with aluminium foil and subsampled using a New Wave Micromill. Thirteen subsamples of ~0.3 mg were taken using a 0.8 mm drill bit at a resolution of 0.2 mm. Seasonal resolution milling of a ~2 cm long, 0.4

cm wide section of the sample (figure 4.11) was done with the same drill bit but at a resolution of 0.6 mm. 38 subsamples were collected.

Stable isotopes for water and carbonate samples were measured on a Delta V advantage isotope ratio mass spectrometer attached to a Gas Bench II (water samples) and a Kiel IV carbonate device respectively. Further analytical methods and standards have been described in *Day and Henderson, 2011*. External error for $\delta^{18}\text{O}$ is $\pm 0.14\text{‰}$ ($n=21$) for water isotopic measurements and $\pm 0.08\text{‰}$ ($n=62$) for carbonate powder measurements.

4.8 Results

4.8.1 Cave temperature and humidity

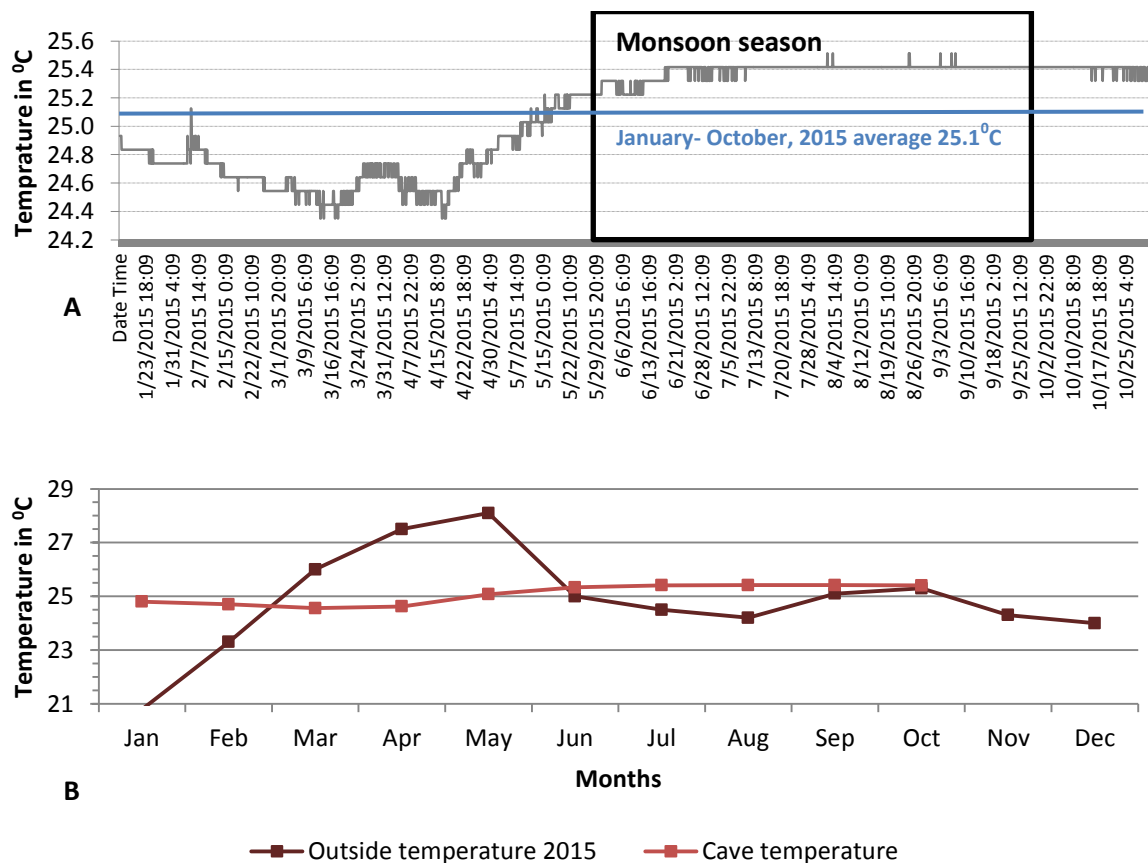


Figure 4.12: (A) Akalagavi cave temperature data recorded by the HOBO data logger plotted against date and time. (B) The cave temperature plotted against monthly average outside temperature (temperature for the year 2015 from Belgaum. GHCNM database sourced from KNMI explorer).

The average temperature recorded by the HOBO data logger for January to October is 25.1°C (figure 4.12). The outside temperature for Belgaum for 2015 was 25°C (January to October) and 24.8°C (January to December) (table 1 of Appendix III). Thus the cave is consistently at the average annual outside temperature (within error). HOBO data shows that the temperature increases in April and May from 24.4°C to 25.5°C and stays steady at this temperature till the end of October. It varies within a narrow range of 0.8°C in the non-monsoon period and 0.2°C during the monsoon period.

Humidity measured by a hand held Hanna portable Thermo-Hygrometer gave a reading of 70% in January, 2016.

4.8.2 Rain water, groundwater and drip water $\delta^{18}\text{O}$ measurements

To understand variation in $\delta^{18}\text{O}$ in the stalagmite with respect to rainfall, $\delta^{18}\text{O}$ measurements of rainwater and drip water are required. Ideally, they should be monitored for an extended period (i.e. more than one monsoon season) since there is usually some mixing of groundwater.

Tables 4.3, 4.4 and figure 4.13 show results of rainwater, groundwater and drip water measurements. $\delta^{18}\text{O}$ *variation* reduces from 5.14‰ in rainfall to 0.64‰ in groundwater and 0.40‰ in drip-waters. This is not surprising considering 658 mm of rainfall collected for $\delta^{18}\text{O}$ measurements has a $\delta^{18}\text{O}$ value between 0‰ and -2.06‰ while only 75 mm of rainfall had a value lighter than -2.06‰.

Drip rates were measured during spot collections of drip water. The drip rates of the two drip sites feeding the stalagmite were 122 dpm (drops per minute) and 68 dpm respectively in January, 2015. They showed nearly the same drip rates in April, 2016. In Chapters 4, 5 and 6 pertaining to this sample the drip sites feeding the sample will be referred to as the fast drip and slow drip respectively.

Serial number	Sample	Collection date	Location	$\delta^{18}O$	δD	Comments
1	NAW5	May, 2014	Well water	-1.28	0.17	Ulavi village
2	NAW6	May, 2014	Well water	-1.13	-0.50	Ulavi village
3	NAW7	May, 2014	Well water	-1.78	-0.60	Ulavi village: Slimy water
4	NAW2	May, 2014	Drip water	-1.46	-1.00	Chimney-like cavity
5	NAW3	May, 2014	Drip water	-1.30	2.16	Main cave
6	NI15-12	Jan, 2015	Spring water	-1.78	-3.87	Spring close to cave.
7	NI15-3	Jan, 2015	Drip water	-1.06	-0.02	Fast drip feeding sample
8	NI15-4	Jan, 2015	Drip water	-1.12	0.13	Slow drip feeding sample
9	NI15-5	Jan, 2015	Drip water	-1.07	-0.25	Fast drip feeding sample
10	NI15-8	Jan, 2015	Drip water	-1.21	-0.12	Chimney-like cavity
11	NI15-9	Jan, 2015	Drip water	-1.22	-0.39	Chimney-like cavity
12	NAWR1	May, 2015	Drip water	-1.06	-1.33	Not known
13	NAWR2	May, 2015	Drip water	-0.98	-2.99	Not known
				Mean = -1.27		
				Drip water mean = -1.23		

Table 4.3: Oxygen and hydrogen stable isotopic measurements of spring water, well water and drip water samples have been given in the table.

Number	Sample	Location	Water collection	Water collection	Rainfall amount	Rainfall amount	$\delta^{18}O$	δD
			Date and time from	Date and time to	(ml)	mm		
						$V = 3.14r^2 h$		
1	MP1	MRC	18/06/2015 9:30am	19/06/2015 9:30am	210	41.80	-3.62	-15.32
2	MP2	MRC	20/06/2015 9:15am	21/06/2015 9:15am	580	115.45	-1.63	0.84
3	MP3	MRC	22/06/2015 5:30pm	23/06/2015 5:30pm	300	59.71	-2.06	-7.28
4	MP4	MRC	25/06/2015 4:45pm	26/06/2015 4:45pm	180	35.83	-1.44	1.32
5	MP5	MRC	29/06/2015 5:00pm	30/06/2015 5:00pm	250	49.76	-1.39	-2.49
6	MP6	MRC	05/07/2015 9:30am	06/07/2015 9:30am	122	24.28	-1.14	1.22
7	MP7	MRC	07/07/2015 10:00pm	08/07/2015 10:00pm	280	55.73	-1.16	2.34
8	MP8	MRC	11/07/2015 9:00am	12/07/2015 9:00am	105	20.90	-0.97	1.90
9	MP9	MRC	13/07/2015 3:00pm	14/07/2015 3:00pm	400	79.62	-1.40	-0.53
10	MP10	MRC	18/07/2015 5:00pm	19/07/2015 5:00pm	350	69.67	-0.76	3.15
11	MP11	MRC	06/08/2015 5:30pm	07/08/2015 5:30pm	100	19.90	-1.06	1.10
12	MP12	MRC	08/08/2015 3:00pm	09/08/2015 3:00pm	110.3	21.95	-0.78	3.88
13	MP13	MRC	12/08/2015 5:00pm	13/08/2015 5:00pm	140	27.87	-0.86	2.97
14	MP15	MRC	22/08/2015 12:00noon	23/08/2015 12:00noon	110.5	21.99	-0.91	1.85
15	MP16	MRC	27/08/2015 4:00pm	28/08/2015 4:00pm	70	13.93	-1.69	-4.40
16	MP17	MRC	29/08/2015 3:00pm	30/08/2015 3:00pm	80.2	15.96	-1.77	-4.68
17	MP18	MRC	01/09/2015 4:00pm	02/09/2015 4:00pm	60.5	12.04	-5.90	-35.59
18	MP19	MRC	03/09/2015 2:00pm	04/09/2015 2:00pm	100	19.90	-5.90	-36.16
19	MP20	MRC	07/09/2015 5:00pm	08/09/2015 5:00pm	130.3	25.94	-1.76	-3.18

Table 4.4: Rainfall amount, oxygen and hydrogen stable isotopic composition of rainfall collected at Mhadei Research Centre (MRC) during monsoon rainfall season of 2015.

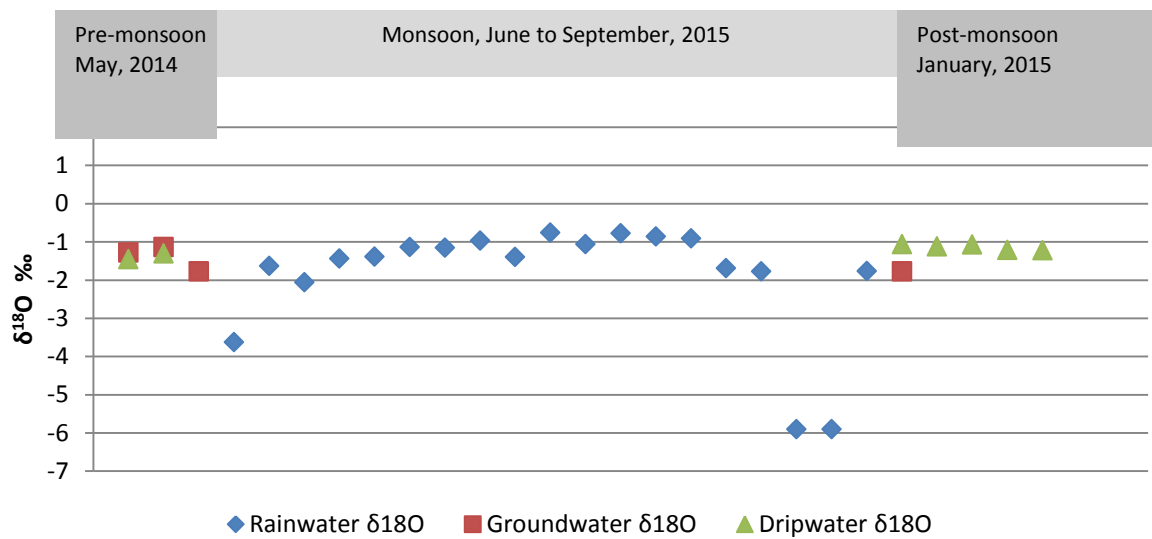


Figure 4.13: The figure shows rainwater, groundwater and drip water $\delta^{18}\text{O}$ composition for pre-monsoon, monsoon and post-monsoon periods.

Figure 4.14 shows a plot of rainwater, groundwater and drip water measurements made as a part of this study as well as the Mumbai GNIP rainwater measurements compared to the Global Meteoric Water Line (GMWL). The linear correlation of $\delta^{18}\text{O}$ and δD values in global precipitation defines the GMWL and was originally defined as $\delta\text{D} = 8 \times \delta^{18}\text{O} + 10$ (Dansgaard, 1964). A later, more comprehensive analysis indicates $\delta\text{D} = (8.20 \pm 0.7) \times \delta^{18}\text{O} + (11.27 \pm 0.65)$ for weighted mean annual precipitation (Rozanski et al, 1993). If waters are evaporated at relative humidity less than saturation, both $\delta^{18}\text{O}$ and δD values will increase in the remaining water, plotting to the right of the GMWL with slopes of less than 8 (Gat, 1996). Condensation produced under very low relative humidity and high evaporation, to maintain mass balance, will plot to the left of the GMWL, and have high deuterium excess values. Figure 4.14 indicates that the cave and Mumbai GNIP waters plot along the GMWL.

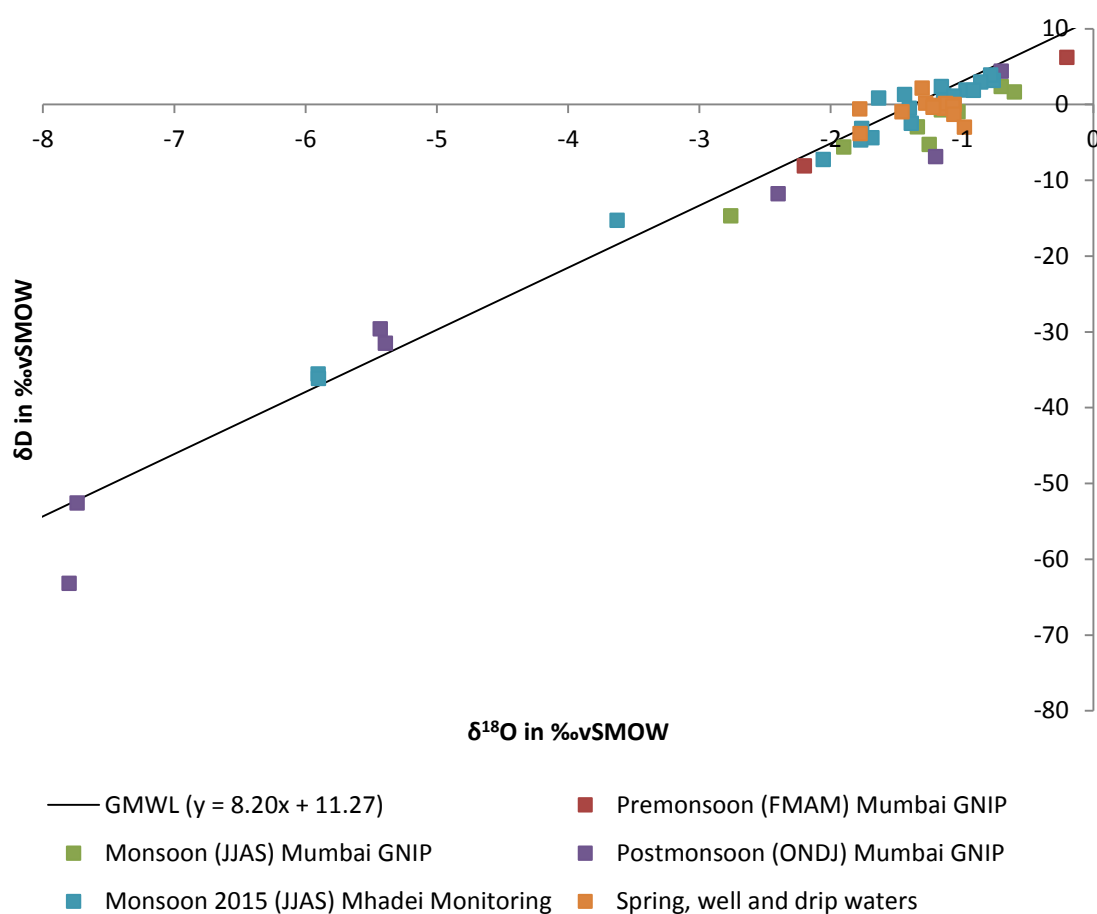


Figure 4.14: Rainwater, groundwater and drip water measurements plotted against the Global Meteoric Water Line (GMWL). The plots are of individual water sample measurements as described in section 4.7.1.

4.8.3 Carbonate $\delta^{18}\text{O}$ measurements

The $\delta^{18}\text{O}$ composition of subsamples obtained from continuous milling at a seasonal resolution from the sample stalagmite section and from the modern carbonate chip show similar magnitudes of variation between white and dark layers of $\sim 0.5\text{‰}$ although the sample stalagmite is enriched by 1‰ compared to modern carbonate (figure 4.15 and tables 8 and 9 of Appendix III).

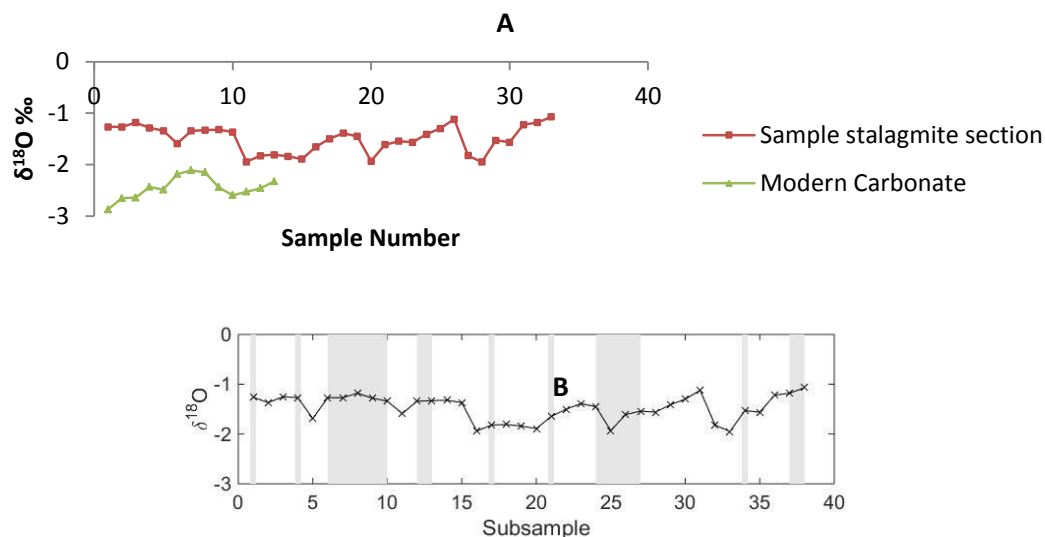


Figure 4.15: (A) $\delta^{18}\text{O}$ of a modern carbonate chip and subsamples from the sample stalagmite section plotted against subsample numbers. Modern carbonate shows similar magnitude of $\delta^{18}\text{O}$ variation between compact (white) and porous (dark) layers as seen in the sample but with lighter $\delta^{18}\text{O}$ values. (B) $\delta^{18}\text{O}$ from sample stalagmite section milled seasonally plotted on white and dark layers (based on milling observations). The figure shows that there is seasonal variation in $\delta^{18}\text{O}$ of $\sim 0.5\text{‰}$ between layers. In general, $\delta^{18}\text{O}$ is less enriched in the white layers.

4.8.4 Along-growth-layer and along-growth-axis $\delta^{18}\text{O}$ - $\delta^{13}\text{C}$ variation

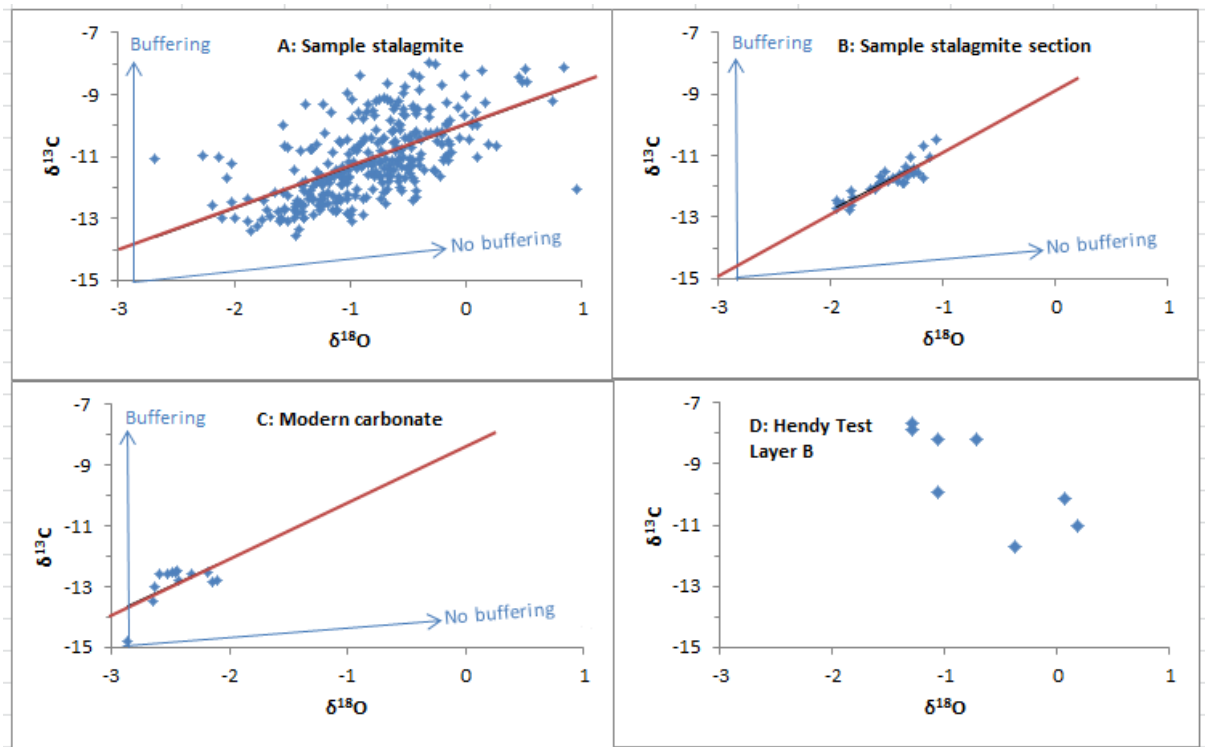
Hendy test Layer A (figure 4.9) shows no enrichment in carbon or oxygen isotopes along this growth layer. They are negatively correlated but since this is based only on 3 subsamples, this is not statistically significant. The nine subsamples of Layer B show 1‰ enrichment in oxygen and nearly 4‰ enrichment in carbon isotopes. After, *Mickler et al, 2006*, figure 4.16 indicates that the oxygen isotopes are buffered by hydration and hydroxylation reactions keeping pace with degassing.

There is significant positive correlation between $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ of subsamples measured along the growth axes of the sample stalagmite, seasonally milled sample stalagmite section and modern carbonate (figure 4.16). Slopes and intercepts on the Y axis for all three sets of subsamples measured along the growth axes are similar suggesting that they are evolving from a similar initial carbon isotopic composition. However, modern growth subsamples are less enriched in carbon and oxygen isotopes compared to most others measured along the sample stalagmite and seasonally milled stalagmite section growth axes.

The sample stalagmite shows variation in growth direction and angle at which layers are precipitating. Figure 4.17 shows that:

- (i) The most enriched oxygen and carbon isotopes can be found in the 'ponded' zone of the stalagmite i.e. in sections 'e' and 'f' where the growth layers concave inward and the drop does not flow away as quickly as in the rest of the stalagmite.
- (ii) The most depleted oxygen and carbon isotopes can be found where the slope angle of the growth layer is the steepest i.e. in sections 'a', 'c' and 'n' where the drop flows away quickly.

The figure also plots average oxygen and carbon stable isotopes against the average angle of growth sections, there appears to be some control and significant correlation. Sections 'e' and 'f' have been plotted separately.



Plot Code	Subsamples	Line equation	R^2	p value
A	Along growth axis of sample stalagmite: white layers only	$y = 1.4x - 10$ Std dev on slope = 0.1	0.4	1.03E-32
B	Along growth axis of seasonally milled stalagmite section: white and brown layers	$y = 1.9x - 9$ Std dev on slope = 0.2	0.8	9.70E-13
C	Along growth axis of modern carbonate chip: white and brown layers	$y = 1.8x - 8.4$ Std dev on slope = 0.7	0.4	0.021
D	Along growth layer of Hendy test layer B	$y = -2.0x - 9.6$ Std dev on slope = 0.7	0.1	0.4

Figure 4.16: Panel show A, B, C and D plots of $\delta^{18}\text{O}\text{‰ vPDB}$ against $\delta^{13}\text{C}\text{‰ vPDB}$ for various sets of subsamples indicated on the respective panels. The line equations, correlation coefficients and p values for the plots have been given in the table. On the plots, a vertical slope indicates that the oxygen has been buffered and conditions are close to equilibrium (after *Mickler et al, 2006*). Departure from equilibrium is indicated by the slope of 0.34 ($\Delta\delta^{13}\text{C}/\Delta\delta^{18}\text{O}$ of the Hendy test layer B, measured along the Rayleigh distillation model published in *Mickler et al, 2006*). The along-growth-layer Hendy test layer B subsamples show no correlation. Subsamples measured along the growth axes show significant correlations and similar slopes. The slopes of growth axes subsamples indicate that there is incomplete buffering of oxygen during precipitation. Modern growth subsamples are less enriched compared to most of the subsamples measured along the sample stalagmite and along the sample stalagmite section. (Hendy test layer stable isotopic data in table 10 of Appendix III).

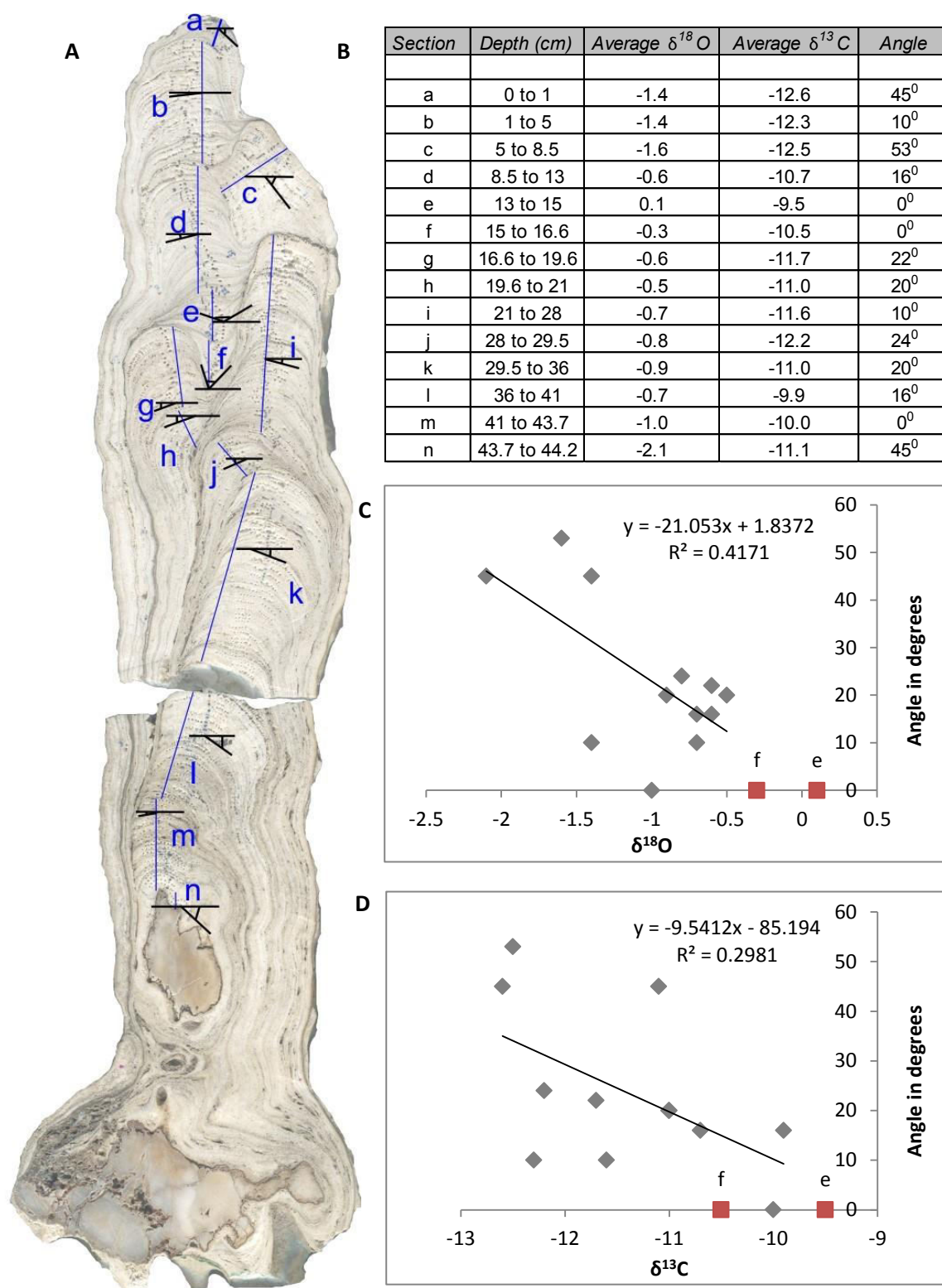


Figure 4.17: Figure A shows the change in growth axis on the sample, each change marks a different section (for example a, b, c etc.) and the associated angles that growth layers make with the horizontal. Figure B shows average angles, stable oxygen and carbon isotopic compositions of each section. Figures C and D plot average oxygen and carbon isotopic compositions, respectively, against average angles of growth surfaces in each growth section. The line equation and R^2 values have also been given. Sections e and f have been plotted separately since the growth layers are precipitating in 'ponded' sections of the sample.

4.8.5 Comparison with expected equilibrium relationships

Measured $\delta^{18}\text{O}$ for the stalagmite and modern growth subsamples can be compared with values expected for equilibrium precipitation, given the cave temperature and the $\delta^{18}\text{O}$ composition of drip water, to assess whether the sample is likely to have precipitated in equilibrium. This comparison is made complicated because there are differences in the published fractionation factors in different studies (table 4.5 and figure 4.18). Some of this difference is due to errors associated with oxygen isotopic measurements of water and carbonate (including acid fractionation factors) while other differences are associated with different laboratory set-ups and natural cave conditions (see *Lachniet, 2009* and *Lachniet, 2015*). Of these equations, *Zhou and Zheng, 2003* has been debated in *Kim and O'Neil, 2005*; *Horita and Clayton, 2007* and *Zheng and Zhou, 2007* and it is not discussed any further since it is markedly different from the other equations.

Number	Equation	Reference	Material
1	$10^3 \ln \alpha = 28.7$ at 25°C	<i>Tarutani et al, 1969</i>	Inorganically precipitated aragonite
2	$10^3 \ln \alpha = 18.34 \times 10^3 \times T_K^{-1} - 31.954$	<i>Grossman and Ku, 1986</i>	Biogenic aragonite: foraminifera and molluscs
3	$10^3 \ln \alpha = 18.56 \times 10^3 \times T_K^{-1} - 33.49$	<i>Patterson et al, 1993</i>	Otoliths of freshwater fish
4	$10^3 \ln \alpha = 18.56 \times 10^3 \times T_K^{-1} - 32.54$	<i>Thorrold et al, 1997</i>	Otoliths of marine fish
5	$10^3 \ln \alpha = 20.44 \times 10^3 \times T_K^{-1} - 41.48$	<i>Zhou and Zheng, 2003</i>	Inorganically precipitated aragonite
6	$10^3 \ln \alpha = 17.88 \times 10^3 \times T_K^{-1} - 30.76$	<i>Kim et al, 2007</i>	Inorganically precipitated aragonite

Table 4.5: Published aragonite equilibrium fractionation equations.

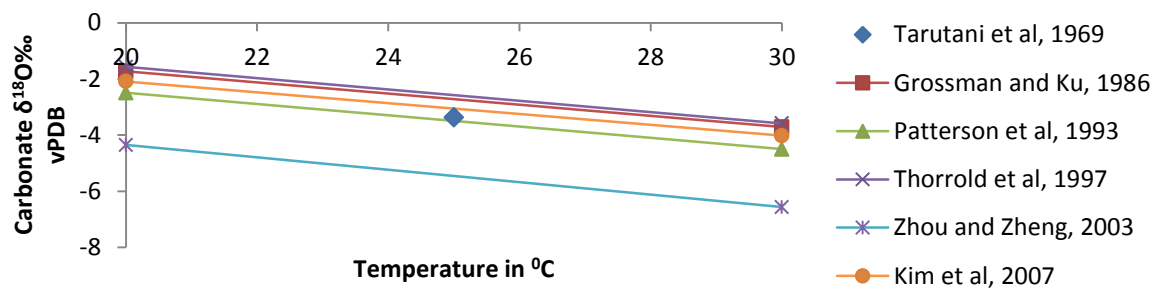


Figure 4.18: Coloured lines mark $\delta^{18}\text{O}$ values that sample aragonite is expected to have with a drip water $\delta^{18}\text{O}$ of -1.2‰ (table 4.3) which is the average of all the drip waters measured in the cave over the temperature range from 20 to 30°C shown on X axis. *Tarutani, et al, 1969* has been marked as a single point as given in their paper for 25°C . A full fractionation equation has not been shown in the paper.

In figure 4.19, measured sample stalagmite and modern carbonate $\delta^{18}\text{O}$ values (along-growth-axis) have been plotted on expected equilibrium precipitation $\delta^{18}\text{O}$ values. The temperature range used in the calculation of equilibrium fractionation equations is $25^{\circ}\text{C} \pm 0.6^{\circ}\text{C}$ which encompasses the measured cave temperature for the year 2015 (section 4.8.1) and includes a range of variation based on the rising trend measured since 1880 (section 4.5). The $\delta^{18}\text{O}$ range (-0.39 to -2.45‰ vSMOW) of weighted average monsoon rainfall $\delta^{18}\text{O}$ measured for Mumbai has been used in the equilibrium fractionation equations (section 4.5). This range of $\delta^{18}\text{O}$ encompasses all the drip water $\delta^{18}\text{O}$ measurements. Sample stalagmite and modern carbonate measured $\delta^{18}\text{O}$ values in the range from -1.63 to -4.85 ‰ vPDB can be considered to have precipitated in equilibrium (see table 11 in Appendix III for calculations). The measured sample stalagmite and modern carbonate values have been plotted in figure 4.19 at a temperature of 25°C . The figure suggests that all the modern carbonate and a few of the stalagmite subsamples have precipitated in equilibrium.

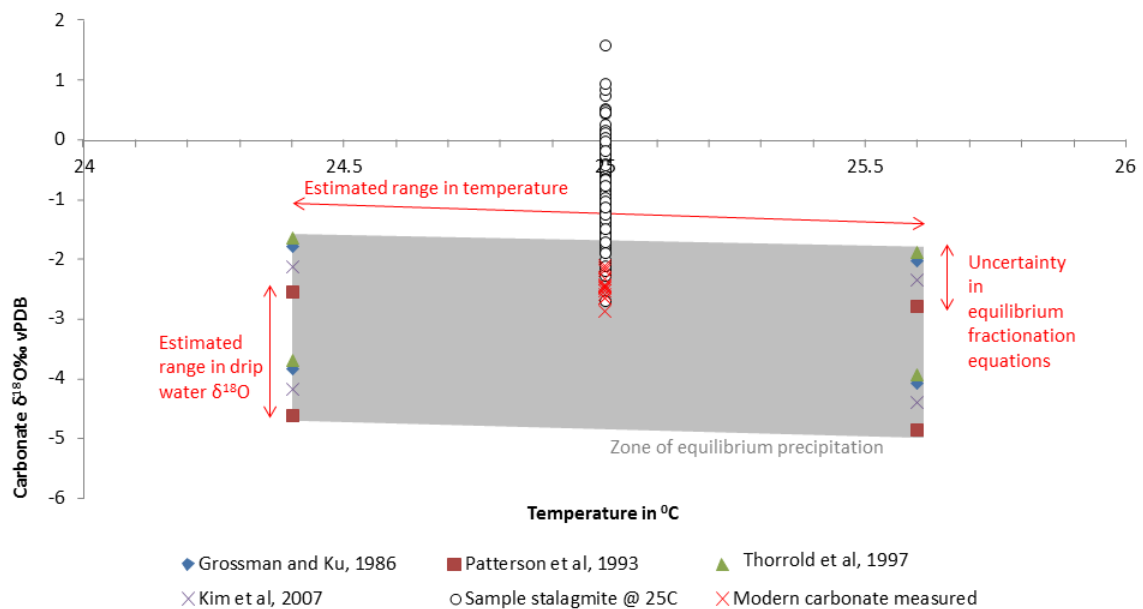


Figure 4.19: Measured carbonate $\delta^{18}\text{O}$ values compared to expected carbonate $\delta^{18}\text{O}$ values, plotted on a temperature axis. Calculations have been made for a temperature range from 24.4 to 25.6°C and drip water $\delta^{18}\text{O}$ range from -0.39 to -2.45 ‰. The uncertainty due to range of temperature and drip water $\delta^{18}\text{O}$ have been shown along with the uncertainty in equilibrium fractionation equations. The grey marks the resulting zone of plausible equilibrium precipitation. The black 'o' markers mark the measured $\delta^{18}\text{O}$ values of sample stalagmite (along-growth-axis). Similarly the red 'x' markers mark modern carbonate (along-growth-axis) measured $\delta^{18}\text{O}$ values.

4.8.6 Replication test

No other stalagmites were found in the same or surrounding caves so replication tests could not be performed.

4.9 Discussion

There is some enrichment in oxygen isotopes along the growth layer of Hendy Test Layer B but there is no significant correlation in the oxygen and carbon isotopes along the growth layer suggesting that this layer, at least, has precipitated in oxygen isotopic equilibrium (figure 4.16). There is significant positive correlation between oxygen and carbon isotopes along the growth axes of sample stalagmite and seasonally milled sample stalagmite section. The correlation suggests a strong kinetic impact on both the sample stalagmite and modern carbonate datasets (due to insufficient buffering of the DIC pool by water). However, along growth axis positive correlation can also be caused by oxygen and carbon isotopes, both responding to the same climate or environmental forcing. There are other studies that have found a positive correlation to result from environmental factors. For example, in tropical and monsoonal climates that affects the $\delta^{18}\text{O}$ value of precipitation (rainfall) such that an increase in the amount of precipitation will result in precipitation with lower $\delta^{18}\text{O}$ values (*Dansgaard, 1964; Rozanski et al, 1993*). The effect is a manifestation of preferential removal of ^{18}O as rainout continues as well as the saturation of the air mass below the cloud base as precipitation proceeds, an effect that diminishes any shift to higher ^{18}O values caused by evaporation during precipitation. This increase in precipitation could also result in lower $\delta^{13}\text{C}$ value of speleothem calcite by increasing soil moisture content and soil respiration rates (*Raich and Sclesinger, 1992; Lachniet et al, 2004*) or by reducing water-rock interactions and in turn reducing the contribution of heavier $\delta^{13}\text{C}$ from host limestone (*Paulsen et al, 2003*), resulting in a positive correlation between $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values of speleothem calcite (for example, *Li et al, 2000*). Thus a positive correlation between oxygen

and carbon isotopes along the growth axis, in this setting, does not necessarily indicate kinetic precipitation.

Based on the published equilibrium fractionation equations, while most of the modern aragonite precipitation is in equilibrium, only a few stalagmite subsamples have precipitated in oxygen isotopic equilibrium. There may be several reasons for this,

- i) Change in drip water $\delta^{18}\text{O}$ composition: Subsamples are closer to oxygen isotopic equilibrium when they have precipitated from more enriched drip waters. However, even the most enriched drip waters of $\delta^{18}\text{O} = -0.39\text{‰}$ of rainfall would not give the full range of measured $\delta^{18}\text{O}$ values of the sample stalagmite. In fact, even a drip water $\delta^{18}\text{O}$ value of -0.01‰ would not give the range of measured $\delta^{18}\text{O}$ values of the sample stalagmite or modern carbonate. Such enriched $\delta^{18}\text{O}$ values of carbonate requires a change in temperature. There is seasonal variation in $\delta^{18}\text{O}$ of precipitated carbonate of $\sim 0.5\text{‰}$. A seasonal temperature variation of 0.8°C measured in the cave would give a variation of 0.2‰ . The remaining variation may be caused by a seasonal kinetic overprint or lighter $\delta^{18}\text{O}$ drip water composition in the monsoon season through fracture flow, which was not captured during field work. Evaporation of water on its path from the surface into the soil and to the drip site combined with groundwater mixing can result in higher $\delta^{18}\text{O}$ values of drip water. Conversely, fracture flow that is particularly active during the high rainfall period through fluid pressure, provides a faster conduit for water from the surface to the drip site, reducing the evaporative and mixing effects, resulting in lower $\delta^{18}\text{O}$ values of drip water. This suggests that the white layers with lighter $\delta^{18}\text{O}$ have precipitated during the monsoon season.
- ii) Change in cave temperature: Subsamples are closer to oxygen isotopic equilibrium when they have precipitated at lower temperatures. For a drip water $\delta^{18}\text{O}$ of -

0.39‰, a temperature as low as 12°C would be required to result in the most enriched measured $\delta^{18}\text{O}$ values to have precipitated in equilibrium precipitation. However, no such temperature change has been measured in the region since 1880.

- iii) Change in local cave conditions: There have been no changes reported in the local cave conditions in the recent past which may alter drip water $\delta^{18}\text{O}$ (such as agriculture) or humidity and temperature conditions in the cave such as opening or closing entrances to the cave .
- iv) Change in the growing surface of the sample effects rate of DIC removal: It was found that the least and most enriched subsamples are from specific parts of the stalagmite. The most enriched oxygen and carbon isotopes are from the 'ponded' zone of the stalagmite. The longer the time that a drop spends on the stalagmite surface before precipitation, the longer time there is for CO_2 degassing/DIC depletion and evaporation (*Day and Henderson, 2011*). At higher temperatures this effect is more because both CO_2 degassing and evaporation rates increase with temperature (*Day and Henderson, 2011*) i.e. there is some control of the growing surface of sample on the rate of DIC removal. The steeper the growth layer, the less enriched the oxygen and carbon isotopic composition of the growth axis subsample. It may explain why the subsamples that have precipitated in equilibrium are the oldest ones of the sample stalagmite (facilitated by the sloping ledge) and all the modern carbonate (where the slope of the ledge was once again made available through sample removal). Although there is significant correlation between the angle of growth layers and the oxygen and carbon isotopic compositions (figure 4.17); the control is small.

This study finds that aragonite stalagmites can precipitate in equilibrium conditions similar to findings of *Li TY et al, 2011* and *Lachniet, 2015*. However, the sample stalagmite from

Akalagavi cave shows a kinetic overprint in certain parts which may be caused by a change in the surface of the growth layer.

4.10 Conclusion

We find evidence to suggest that aragonite stalagmites can precipitate in equilibrium. However, given the complexity of ensuring equilibrium precipitation, replication of $\delta^{18}\text{O}$ record either with other $\delta^{18}\text{O}$ records from the same region or other proxies from the same sample must be produced before making any paleoclimatic interpretations. Changes in the growth surface can alter fractionation processes through time available for carbonate removal. This implies that the time available for CO_2 degassing and DIC depletion is not only controlled by the drip rate but may also be controlled by angle of growth surface. This control is more effective at high temperatures where reactions are faster. A sample with a sloping growth surface may provide better conditions for equilibrium precipitation of CaCO_3 than a sample with a horizontal growth surface, particularly in caves with temperatures higher than 25°C and humidity less than 70%. A sample with changing angles of growth surface should be investigated for control of growth surface on $\delta^{18}\text{O}$ composition.

Reconstructing rainfall precisely and quantitatively is one of the major aims of studying $\delta^{18}\text{O}$ in speleothems. Even without precise quantitative reconstructions, oxygen is a part of the global hydrological cycle and can be studied from many sources on land and in water across the globe. As such, $\delta^{18}\text{O}$ values are an invaluable source of information regarding the triggers and pathways of global changes in climate. It is worth knowing if the changes in $\delta^{18}\text{O}$ are due to a global change in climate or a just a change in the sample precipitation site. Along-growth-layer and along-growth-axis tests are important because they give indications of kinetic isotopic effects in carbonate precipitation. But they should be supported by additional information. It is useful to visit the cave site and observe the physical site of

precipitation. If possible and applicable, equilibrium fractionation equations form an additional check. This still ensures only that modern precipitation is in equilibrium.

An interesting future direction to try is if there is a consistent relationship between $\delta^{18}\text{O}$ and trace element ratios in the same subsample powders, it could indicate that $\delta^{18}\text{O}$ is being controlled by climatic or environmental factors rather than kinetics of oxygen precipitation alone. Multiple proxies from the same stalagmite, such as trace elements, can also be used to derive and internally confirm paleoclimatic information, especially where replication tests are not possible.

Chapter 5

Seasonally Resolved Trace Element Studies in an Aragonite Stalagmite

Abstract

Aragonite speleothems can be fast growing, allowing for preservation of annual laminae with seasonal paleoclimate signals but there is debate about whether they capture oxygen and carbon in equilibrium, making them problematic for such work. Trace element measurements from speleothems can be used to corroborate interpretations of oxygen and carbon stable isotopic data, and to give independent paleoclimatic information, but there are few studies investigating the controls on trace elements in aragonite speleothems.

This study presents a seasonal resolution time series capturing 12 annual growth bands from a rapidly forming aragonite stalagmite to assess the utility of trace elements in aragonite samples for paleoclimate work. Subsampling (2 to 4 subsamples per year) appears to capture a seasonal signal. High Mn/Ca forms a distinct seasonal marker in the sample. Trace element compositions of bed rock, well water and drip water have been measured. These measurements in addition to the consistent aragonite mineralogy in the stalagmite sourced from a high rainfall region indicates that the mineralogy is controlled by the lithology rather than the climate. Calculation of empirical partition coefficients show that Sr, U, and P are preferentially incorporated into aragonite relative to Ca, which may allow the use of these elements as paleo-aridity indicators in aragonite speleothems through the process of prior aragonite precipitation. The water and bed rock trace element measurements provide constraints on the sources of trace elements. Sea water is likely to be the main source for Na and S in this stalagmite with the sea located only 30 km from the

cave. These elements thus form a potential proxy for strength of onshore winds i.e. a proxy for monsoon circulation that may be independent of the amount of rainfall.

5.1 Introduction

Trace element proxies have been widely applied to calcite speleothems to corroborate the fidelity of oxygen and carbon isotopes as recorders of paleoclimate information and to derive paleoclimate information (*Fairchild and Treble, 2009; Fairchild and Baker, 2012*). Trace elements have also been applied to aragonite speleothems but less commonly. A key limitation is the non-thermodynamic nature of partition coefficients (term explained later in text) during calcium carbonate precipitation in most natural contexts (*Morse and Bender, 1990*). Element partitioning is made particularly complicated by the orthorhombic structure of aragonite which leads to a variety of forms whose crystal faces can have different trace element affinities (*Finch et al, 2003; Fairchild and Treble, 2009*). This requires partitioning behaviour to be established for speleothem specific conditions, yet for many elements, partition coefficients are only available from marine contexts or from caves in non-controlled growth conditions (*Day and Henderson, 2013*). There are only two cave analogue laboratory studies on calcite partition coefficients (*Huang and Fairchild, 2001; Day and Henderson, 2013*) and none on aragonite. To minimize resulting uncertainty in controls on trace element partitioning into aragonite, study is required of the key processes that control concentrations of trace elements in aragonite speleothems at particular sites (*Fairchild and Treble, 2009*).

Finch et al, 2001 conducted the first study of the controls on trace elements in aragonite speleothems and find spectral evidence for significant regular oscillations in Sr and Ba concentrations at a scale which matches the scale of the annual laminae. *McMillan et al, 2005* find pronounced covariation of Sr, Ba and U in the discrete aragonite layers of calcite stalagmites. The mean peak spacing of trace elements show annual cyclicity based on long

term mean growth rates determined by U-series ages. *Finch et al, 2003* compared a 40-year averaged trace element record from two proximal aragonite stalagmites from South Africa with instrumental records (1955 to 1996 AD). They found poor correlation with temperature and annual rainfall magnitude does not correlate directly with trace element ratios. However, droughts corresponded to minima in trace element ratios and peaks corresponded to annual maxima in rainfall. *Wassenburg et al, 2012* measured trace elements in aragonite-to-calcite transitional speleothems to shed light on factors controlling variable aragonite and calcite precipitation in the same speleothem. *Wassenburg et al, 2016* gave the first quantitative estimates of partition coefficients for speleothem aragonite. The partition coefficient values were derived from ten transitions between calcite and aragonite, from seven speleothems from Morocco, Germany, Spain, France and India. Evidence for seasonal prior aragonite precipitation as a process controlling U/Ca and $\delta^{13}\text{C}$ ratios in a Belizean aragonite stalagmite has been shown by *Jamieson et al, 2016*.

Most trace element studies for carbonates focus on elements which form divalent cations in solution and which substitute for calcium in a carbonate crystal lattice particularly Mg, Sr and Ba (*Fairchild and Treble, 2009*). For such elements, a simple equation defining a distribution or partition coefficient (*Morse and Bender, 1990*) can be used to relate solution and mineral composition. A similar relationship applies to sulphate substitution for carbonate ions (*Busenberg and Plummer, 1985*). Other elements may be incorporated in CaCO_3 by different mechanisms, for example, carried by water as detrital particles or as colloids. Elements such as Na tend to be incorporated at defects in crystals (*Busenberg and Plummer, 1984*) and phosphate absorbs strongly to these sites (*Meyer, 1984*). Single or triply charged ions (Y^{3+} , Na^+ , PO_4^{3-} , Br^-) substitute as couples to preserve charge balance (*Fairchild and Treble, 2009*).

The partition coefficient or distribution coefficient is described by the formula:

$$\text{Tr}/\text{Ca}_{\text{CaCO}_3} = k_{\text{Tr}} (\text{Tr}/\text{Ca})_{\text{solution}}$$

Where,

Tr = Trace ion

k_{Tr} = Distribution or partition coefficient

Partition coefficients cannot be directly measured at the point of mineral growth because $(\text{Tr}/\text{Ca})_{\text{solution}}$ values of individual areas of sample at different times are not known in a rapidly developing chemical environment, instead calculations are generally based on the initial solution composition i.e. trace element composition of drip waters (*Day and Henderson, 2013*), and the assumption that solution composition has not evolved significantly.

The partition coefficients may vary to a greater or lesser degree with temperature, precipitation rate, crystal morphology or other aspects of solution composition (*Lorens, 1981; Gascoyne, 1983; Pingitore and Eastman, 1986; Morse and Bender, 1990; Paquette and Reeder, 1995; Fairchild and Treble, 2009*). In speleothems, they are essentially empirical, although values can be theoretically predicted using thermodynamic and kinetic theory (*Rimstidt et al, 1998; Curti, 1999; Watson, 2004*). Trace element trends will be transferred to speleothems given relatively constant partition coefficients and indications are that they are quite consistent in cave environment and experimental analogues (*Fairchild and Treble, 2009*).

A Rayleigh distillation model for speleothem precipitation has been considered in several previous studies (for example, *Day and Henderson, 2013*). The model considers a reservoir of solution with dissolved Ca, Dissolved Inorganic Carbonates (DIC) and trace elements and a calcite product with precipitation from solution depleting elements from the reservoir such that calculations are based on the fraction of Ca remaining in solution. In some

examples, $\text{Tr}/\text{Ca}_{\text{CaCO}_3}$ measurements do not fall on Rayleigh fractionation curves (*Day and Henderson 2013*) but also require mixing of two forms, either (i) solution mixing between the evolved solution layer and new drip solution (*Muhlinghaus et al, 2007; Muhlinghaus et al, 2009; Deininger et al, 2012*) or (ii) mixing between solids formed from solutions at different stages of Ca precipitation (*Muhlinghaus et al, 2007; Muhlinghaus et al, 2009*).

In this chapter, I report the behaviour of various trace elements in an aragonite stalagmite collected from the west coast of India. The behaviour is interpreted based on chemical analysis of the sample, drip water and bed rock, as well as physical observations of the cave site and findings from previous publications on trace elements from speleothems as paleoclimate proxies.

5.2 Location and Climate

Location and climate information of the Akalagavi cave region have been previously described in section 4.5.

5.3 Previous work

Results and paleoclimate interpretation of annual resolution $\delta^{18}\text{O}$ analysis of the sample have been published in *Yadava et al, 2004*. They use a combination of radiocarbon dating, layer counting and C-14 bomb spike measurements show that the sample grew for 331 years from 1666 to 1997 AD with an age error of ± 7 years.

In chapter 4, I have reported findings on tests to assess whether the sample formed in oxygen isotope equilibrium with the drip-waters. In this chapter, I will explore the sources and behaviour of trace element ratios from the same sample to support and add to paleoclimate information that can be derived from $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$. This initial study has been made on a ~ 2 cm section that is less porous compared to the rest of the sample, such that continuous high resolution milling was readily possible.

5.4 Sampling and analytical methods

Trace elements measurements were made of bed rock, well water, spring water, drip water and a section of the sample stalagmite in order to understand the sources of trace element and controls on trace element distribution in the stalagmite.

5.4.1 Field and monitoring work

One bed rock sample from the cliff above the cave was collected during field work conducted by me and a team from Oxford and PRL in January, 2015. The remaining details of water sample collection, temperature and humidity measurements are given in section 4.7.

5.4.2 Analytical Methods

Seasonal-scale milling of a sample stalagmite section with low porosity selected for this high resolution work has been previously described in section 4.7 and shown in figure 4.11. The wide sampling trench of 0.4 cm serves to average lateral variation (for example, *Finch et al, 2003*). Notes were made during high resolution milling of the sample of whether a white or a dark layer was being milled. Milling was done at a resolution of 0.6 mm (see section 4.7.2). Grey level was measured at the same resolution using ImageJ software. Aliquots of the subsamples were subjected to trace element analysis on a Thermo-Finnigan Element 2 ICPMS at Oxford. Water samples for trace element analysis were collected in polypropylene bottles, acidified in the laboratory and measured on the Thermo-Finnigan Element 2 ICPMS. Further details of analytical procedures and trace elements measured have been given in section 3.3.9.

5.5 Results

5.5.1 Spring water, well water and drip water trace element measurements

The following results were obtained from bedrock and water trace element ratio measurements (table 5.1, table extends across two pages):

- i) There is no drip rate control on trace element ratios measured at different drip sites with varying drip rates (figure 5.1).
- ii) Keeping in mind that seasonal measurement of drip water compositions at the same drip locations have not been made, in the data measured above, there is no seasonal control on drip water ratios i.e. drip waters collected in May do not necessarily have higher or lower trace elements ratios compared to those collected in January (figure 5.2).

Number	Sample	Parameter	Drip Rate	$\delta^{18}O$	δD	Mg/Ca	Sr/Ca	Ba/Ca	Mn/Ca
			dpm	‰ vSMOW	‰ vSMOW	mmol/mol			
		Detection Limit				1.3E-01	9.7E-06	5.1E-03	1.7E-02
		Repeat Standard Precision %		0.14‰	0.14‰	1.74	1.09	1.01	16.44
1	NI15-11	Bed Rock	-			4.2E+02	8.3E-01	8.5E-02	1.0E+02
2	NAW5	WW May'14	-	-1.28	0.17	3.9E+02	1.7E+00	4.9E-01	2.4E-01
3	NAW6	WW May'14	-	-1.13	-0.50	3.3E+02	1.4E+00	2.5E-01	1.8E-01
4	NAW7	WW May'14	-	-1.78	-0.60	5.3E+02	2.8E+00	8.40E+00	1.2E+03
5	NI15-12	SW Jan'15	-	-1.78	-3.87	8.0E+02	4.2E-01	2.5E-04	2.7E-03
6	NAW2	DW May'14	-	-1.46	-1.00	1.3E+03	2.0E-01	4.6E-04	1.2E-03
7	NAW3	DW May'14	-	-1.30	2.16	1.3E+04	3.0E-01	2.2E-04	3.4E-03
8	NI15-1	DW Jan'15 Main Cave	-	-0.48	4.74	5.2E+02	3.1E-01	1.4E-03	2.1E+00
9	NI15-2	DW Jan'15 Passage	38	-0.54	error	8.8E+03	2.8E-01	1.6E-03	3.9E-02
10	NI15-3	DW Jan'15 122dpm	122	-1.06	-0.02	1.3E+03	1.8E-01	6.1E-04	3.6E-02
11	NI15-4	DW Jan'15 68dpm	68	-1.12	0.13	1.4E+03	1.9E-01	5.7E-04	5.5E-03
12	NI15-5	DW Jan'15 Sample Cavity	10	-1.21	-0.12	1.5E+03	1.8E-01	2.5E-04	6.4E-02
13	NI15-6	DW Jan'15 Sample Cavity	9	-1.22	-0.39	3.9E+03	1.5E-01	2.8E-04	7.4E-02
14	NAWR1	DW May'15	-	-1.06	-1.33	1.2E+03	1.8E-01	2.9E-02	-
15	NAWR2	DW May'15	-	-0.98	-2.99	1.2E+03	1.8E-01	1.8E-03	-

Number	Sample	Fe/Ca	Na/Ca	S/Ca	Y/Ca	U/Ca	P/Ca	Co/Ca	Cd/Ca	Th/Ca	Zn/Ca	Rb/Ca	Pb/Ca	K/Ca
		1.1E-02	1.1E+00	3E-01	5.7E-05	5.2E-05	1E-02	7.8E-05	3.2E-04	1.7E-04	1.4E-02	3E-04	9.7E-06	2.0E-01
		33.86	6.44	1.09	3.55	1.56	1.56	1.58	2.81	4.64	5.01	1.32	1.02	2.80
1	NI15-11	4.1E+02	1.7E+02	2.0E+01	1.8E-02	1.2E-03	2.2E+01	1.1E+01	2.4E-03	4.0E-04	2.4E+01	1.2E-01	1.6E-01	2.8E+02
2	NAW5	1.3E+00	9.7E+02	7.0E+01	2.2E-04	4.9E-05	1.2E+00	9.2E-04	-5.4E-05	-5.9E-06	2.8E-02	1.6E-01	3.6E-05	2.4E+02
3	NAW6	1.4E+00	5.3E+02	1.1E+02	4.4E-04	1.3E-04	1.8E-01	7.0E-04	-8.4E-05	-3.0E-06	1.3E-02	7.3E-02	1.3E-04	6.1E+01
4	NAW7	2.4E+02	1.6E+03	5.1E+00	2.9E-03	8.9E-05	2.4E+00	7.6E-01	3.9E-04	-1.7E-07	5.8E-01	2.5E-01	4.6E-04	1.8E+02
5	NI15-12	4.9E-03	1.9E+02	3.5E+00	8.3E-05	3.8E-05	7.0E-02	8.1E-06	7.0E-06	2.9E-04	9.4E-03	7.8E-03	4.7E-05	7.6E+00
6	NAW2	2.3E-02	1.9E+02	1.8E+01	1.5E-05	9.3E-05	2.6E-01	2.0E-05	-7.0E-05	-8.7E-06	4.2E-02	9.4E-04	9.3E-06	2.1E+00
7	NAW3	3.8E-03	1.2E+03	6.8E+01	6.5E-06	1.7E-03	1.1E+00	4.8E-05	-7.8E-05	-9.7E-06	7.6E-03	1.5E-02	2.0E-05	2.3E+01
8	NI15-1	2.9E+00	2.2E+02	1.0E+01	1.3E-04	3.5E-04	7.1E+00	1.6E-03	8.3E-05	-3.6E-05	2.5E-01	4.6E-03	5.0E-04	8.9E+00
9	NI15-2	2.9E-01	1.0E+03	1.5E+02	4.3E-04	4.7E-04	1.0E+01	1.3E-03	1.1E-04	-7.7E-05	2.8E-01	1.3E-02	1.1E-04	2.9E+01
10	NI15-3	1.8E-01	2.2E+02	2.5E+01	1.3E-05	1.0E-04	2.1E-01	1.8E-04	1.2E-05	-8.1E-05	3.6E-02	9.2E-04	6.8E-05	2.3E+00
11	NI15-4	2.9E-02	2.2E+02	2.6E+01	2.5E-05	1.0E-04	2.4E-01	1.0E-05	1.3E-05	-9.0E-05	5.6E-02	1.3E-03	1.7E-04	3.4E+00
12	NI15-5	8.0E-02	2.4E+02	2.8E+01	3.7E-05	1.1E-04	1.1E+00	8.4E-05	1.4E-05	-9.8E-05	3.1E-02	1.2E-03	6.3E-05	2.7E+00
13	NI15-6	8.1E-02	5.5E+02	2.5E+01	2.7E-05	1.1E-04	1.3E+00	8.2E-05	3.4E-05	-1.1E-04	4.6E-02	6.7E-03	1.2E-04	8.1E+00
14	NAWR1	-	2.0E+02	2.5E+01	-	6.5E-05	1.2E+00	-	3.3E-05	-	-	-	-	-
15	NAWR2	-	2.0E+02	2.4E+01	-	5.7E-05	8.6E-01	-	2.5E-05	-	-	-	-	-

Table 5.1: Akalagavi cave trace element ratio measurements for a single bed rock sample and all collected waters have been given in the table. The drip rate and stable isotope measurements have also been given for reference. Subsamples below detection limit are in grey. WW-well water, SW-spring water, DW-drip water, DW 122 dpm and 68 dpm-drip waters feeding the sample with drip rates of 122 drops per minute and 68 drops per minute, Sample cavity-drip waters from stalactites located ~15 cm away from those feeding the sample. Where the location is unspecified, the drip waters have been collected by field staff and the location has not been clearly defined at the time of collection. '-' indicates value not measured.

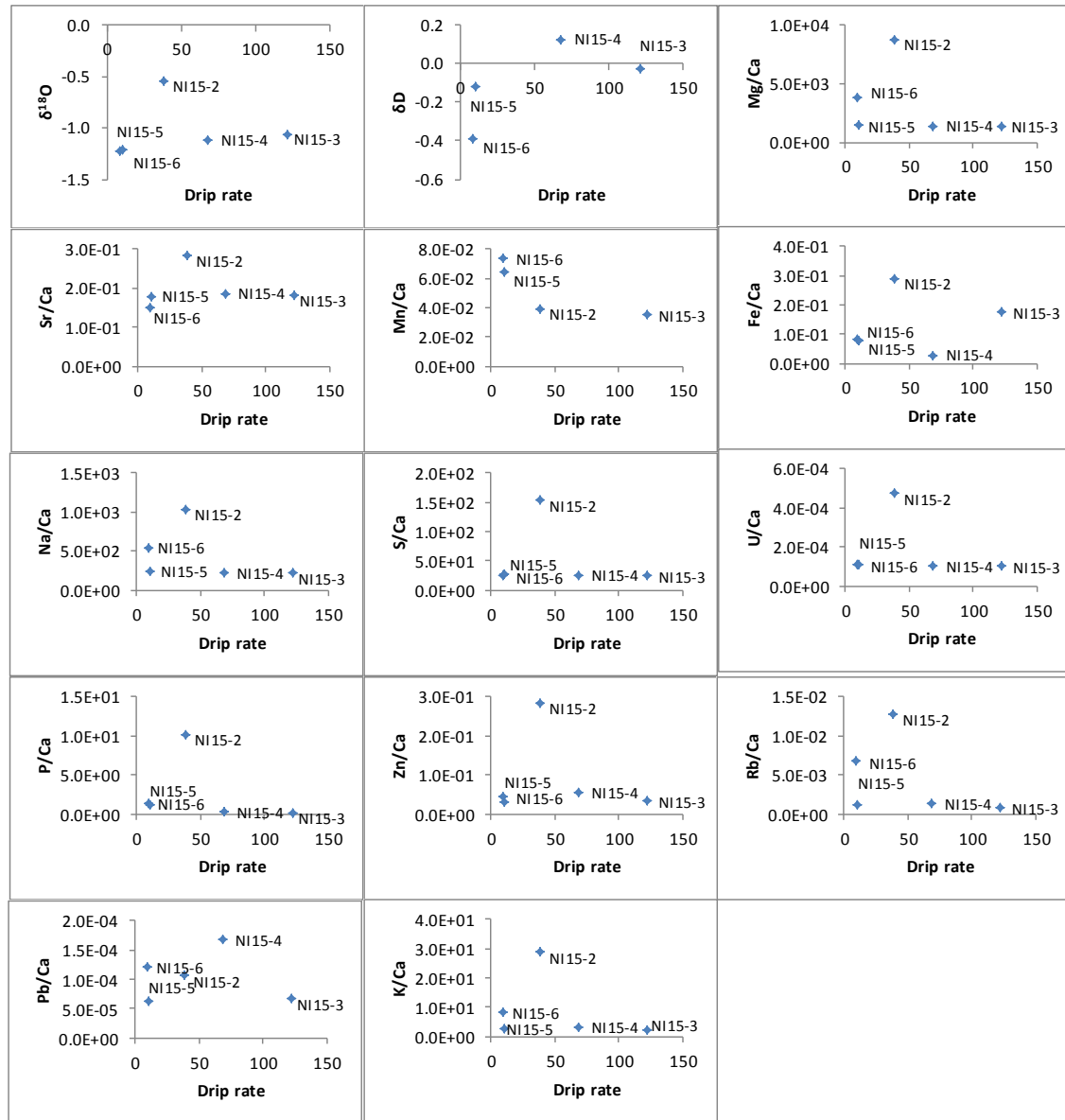


Figure 5.1: Variation in stable isotope and trace element geochemistry with respect to drip rate of 5 drip water measurements from Akalagavi cave. On the X axes is the drip rate in drops per minute (dpm). Respective trace element ratios in mmol/mol have been given on Y axes. $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ in ‰ vSMOW have been given on the Y axes. Data labels are of sample numbers. Data is given in table 5.1.

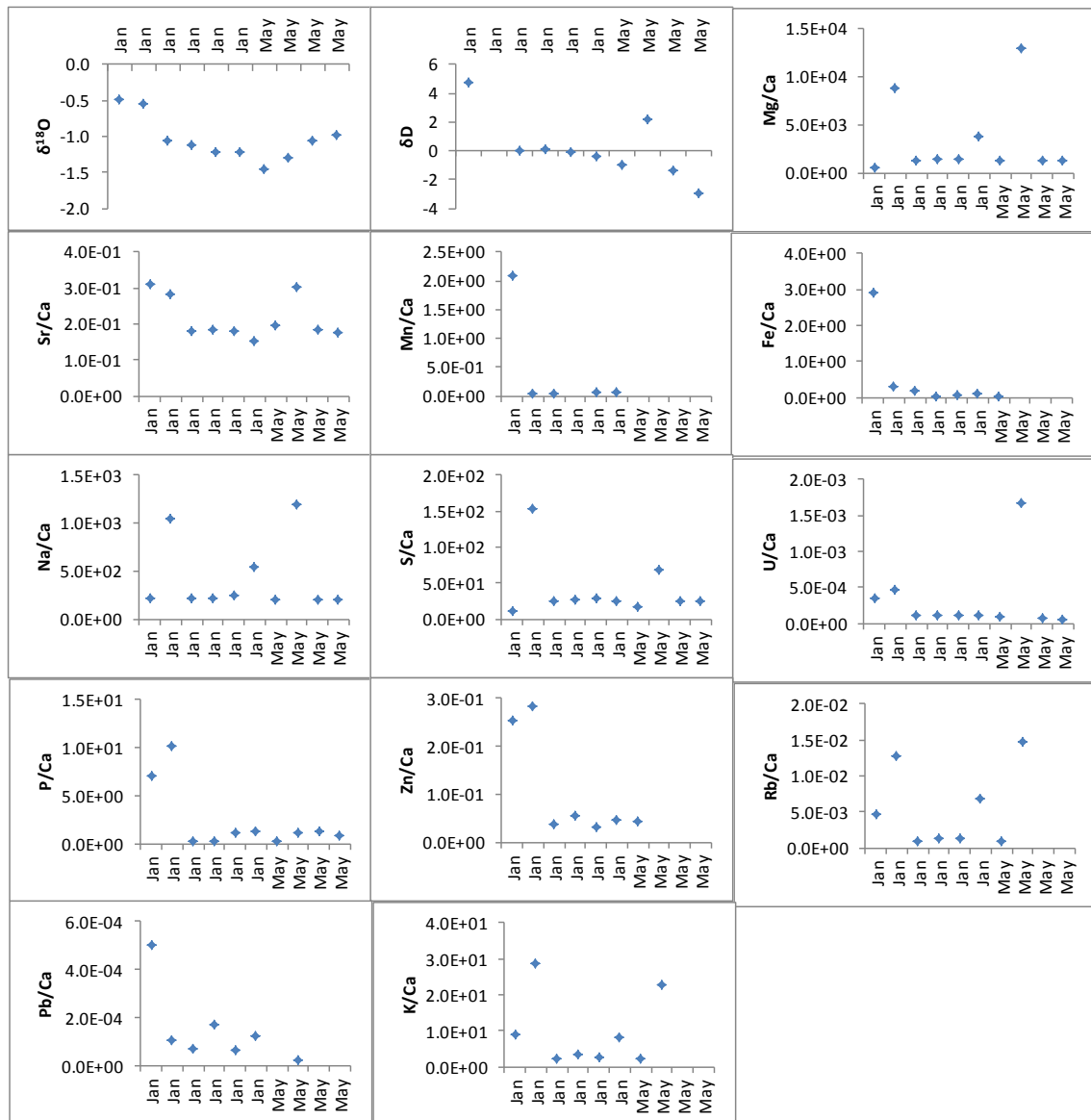


Figure 5.2: Variation in stable isotope and trace element geochemistry with respect to season of 10 drip water measurements from Akalagavi cave. On the X axes is the month in which the drip water was collected. Respective trace element ratios in mmol/mol have been given on Y axes. $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ in ‰ vSMOW have been given on the Y axes. Data is given in table 5.1.

5.5.2 Sample stalagmite seasonally milled section trace element measurements

The seasonally milled section of the stalagmite was used to test the behaviour of trace elements over multiple white and dark layers (figure 5.3 and tables 5.2 and 5.3). The following results were obtained:

- i) Mg/Ca, Mn/Ca and Fe/Ca peak in the dark layers.
- ii) K/Ca, S/Ca, Zn/Ca and Y/Ca also peak in the dark layers but the relationship of these trace element ratios with dark layers is more variable i.e. they do not peak in all dark layers.
- iii) Strong and significant correlations (p value < 0.05) are seen between
 - Mn/Ca and grey level (measured using ImageJ software) and Mn/Ca and Fe/Ca. They have been plotted in figure 5.4.
 - U/Ca, $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$. They have been plotted in figure 5.5.
 - Na/Ca, Rb/Ca and K/Ca. They have been plotted in figure 5.6.
 - S/Ca and Zn/Ca. They have been plotted in figure 5.7.

Number	Sample code	Width of subsample milled mm mm	Milling notes White or dark layer milled?	Milling notes dark (0), mixture (0.5), white (1)	Grey level: Image J 0-255 from black to white	$\delta^{18}O$ ‰	$\delta^{13}C$
1	NA43	0.8	top end of dark layer	0	197	-1.26	-11.59
2	NA44	0.6	mixture: top end of dark layer + white layer	0.5	232	-1.37	-11.99
3	NA45	0.6	mixture: top end of white layer + very little dark layer	0.5	246	-1.25	-11.35
4	NA46	0.6	top end of dark layer	0	249	-1.27	-12.14
5	NA47	0.6	beginning of white layer	1	242	-1.69	-12.49
6	NA48	0.6	beginning of thick dark layer	0	209	-1.27	-11.56
7	NA49	0.6	dark layer	0	183	-1.27	-11.39
8	NA50	0.6	dark layer	0	188	-1.18	-11.74
9	NA51	0.6	dark layer	0	208	-1.28	-11.52
10	NA52	0.6	dark layer	0	227	-1.34	-11.49
11	NA53	0.6	beginning of white layer	1	245	-1.59	-11.99
12	NA54	0.6	mixture: end of white + beginning of dark layer	0.5	230	-1.34	-11.86
13	NA55	0.6	mixture: end of dark + beginning of white layer	0.5	241	-1.33	-11.37
14	NA56	0.6	white layer	1	241	-1.32	-11.68
15	NA57	0.8	white layer	1	208	-1.37	-11.86
16	NA58	0.6	white layer	1	107	-1.94	-12.47
17	NA59	0.6	dark layer	0	124	-1.82	-12.62
18	NA60	0.6	white layer	1	166	-1.81	-12.33
19	NA61	0.6	white layer	1	149	-1.84	-12.79
20	NA62	0.6	mixture: white + dark layers	0.5	210	-1.89	-12.56
21	NA63	0.6	dark layer	0	237	-1.65	-12.07
22	NA64	0.6	beginning of white layer	1	240	-1.50	-11.82
23	NA65	0.6	white layer	1	234	-1.39	-11.62
24	NA66	0.6	beginning of dark layer	0	245	-1.45	-11.70
25	NA67	0.6	mixture: porous white and dark layers	0.5	211	-1.93	-12.56
26	NA68	0.6	top end of dark porous layer	0	210	-1.61	-12.08
27	NA69	0.6	mixture: dark + white layers	0.5	245	-1.54	-11.83
28	NA70	0.6	white layer	1	223	-1.56	-11.90
29	NA71	0.6	Pale dark layer. Beware of pen marking contamination	0	240	-1.41	-11.83
30	NA72	0.6	Pale dark layer. Beware of pen marking contamination	0	227	-1.30	-11.05
31	NA73	0.6	Pale dark layer	0	202	-1.12	-11.04
32	NA74	0.6	dark porous layer	0	148	-1.82	-12.15
33	NA75	0.6	white layer between two porous layers	1	223	-1.95	-12.69
34	NA76	0.6	mixture: top of dark porous layer + white layer	0.5	206	-1.53	-11.50
35	NA77	0.6	white layer	1	220	-1.56	-11.65
36	NA78	0.6	white layer	1	211	-1.22	-11.59
37	NA79	0.6	edge pale dark layer	0	201	-1.18	-10.70
38	NA80	0.6	edge pale dark layer	0	213	-1.07	-10.46

Number	Sample code	Y/Ca mmol/mol	U/Ca	Na/Ca	Mg/Ca	P/Ca	S/Ca	Mn/Ca	Fe/Ca	Zn/Ca	Rb/Ca	Sr/Ca	Pb/Ca	K/Ca
1	NA43	2.7E-05	9.6E-04	1.6E+00	4.5E-01	4.0E-01	2.0E-01	5.8E-03	1.4E-01	2.4E-02	1.3E-04	4.9E-01	8.4E-04	2.7E-01
2	NA44	1.2E-05	1.3E-03	1.3E+00	3.6E-01	4.7E-01	1.6E-01	1.4E-03	3.3E-02	2.7E-02	8.5E-05	4.8E-01	3.8E-04	2.0E-01
3	NA45	2.4E-05	1.0E-03	1.4E+00	4.4E-01	4.2E-01	2.0E-01	7.4E-01	2.2E-01	5.4E-02	1.1E-04	4.9E-01	4.0E-04	2.8E-01
4	NA46	4.7E-05	8.5E-04	1.5E+00	5.3E-01	4.6E-01	2.0E-01	1.1E-02	4.6E-01	7.4E-02	2.1E-04	4.6E-01	5.9E-04	3.3E-01
5	NA47	1.3E-05	1.8E-03	1.3E+00	3.7E-01	4.2E-01	2.5E-01	2.3E-03	8.1E-02	7.9E-02	7.5E-05	4.7E-01	1.7E-04	3.9E-01
6	NA48	4.9E-05	1.0E-03	1.5E+00	4.3E-01	3.0E-01	2.5E-01	1.2E-02	6.6E-01	6.2E-02	1.6E-04	5.1E-01	5.6E-04	3.2E-01
7	NA49	5.9E-05	8.2E-04	1.2E+00	4.2E-01	3.3E-01	1.6E-01	1.5E-02	7.7E-01	4.4E-02	1.9E-04	5.0E-01	3.3E-04	2.8E-01
8	NA50	3.3E-05	1.1E-03	1.2E+00	3.6E-01	4.8E-01	1.1E-01	8.9E-03	4.3E-01	7.1E-03	9.0E-05	5.1E-01	1.4E-04	9.5E-02
9	NA51	2.6E-05	9.9E-04	1.4E+00	4.2E-01	5.3E-01	1.6E-01	1.6E-02	3.9E-01	2.9E-02	1.2E-04	5.2E-01	2.1E-04	2.5E-01
10	NA52	2.0E-05	7.4E-04	1.5E+00	3.5E-01	4.5E-01	2.3E-01	6.4E-03	1.9E-01	1.1E-01	1.6E-04	5.0E-01	3.0E-04	4.7E-01
11	NA53	1.4E-05	1.2E-03	1.6E+00	4.4E-01	5.7E-01	2.2E-01	2.7E-03	1.0E-01	6.1E-02	2.8E-04	4.9E-01	1.9E-04	8.4E-01
12	NA54	1.3E-05	1.3E-03	2.0E+00	5.7E-01	5.4E-01	3.9E-01	2.8E-03	8.7E-02	1.5E-01	1.4E-04	5.1E-01	1.9E-04	5.9E-01
13	NA55	1.2E-05	9.1E-04	1.3E+00	3.5E-01	4.7E-01	1.5E-01	2.5E-03	1.0E-01	2.5E-02	1.3E-04	5.2E-01	1.7E-04	3.1E-01
14	NA56	1.5E-05	9.5E-04	1.6E+00	3.6E-01	5.1E-01	2.5E-01	1.8E-03	2.8E-02	6.5E-02	2.9E-04	5.0E-01	4.8E-03	9.2E-01
15	NA57	1.1E-05	1.3E-03	1.7E+00	4.7E-01	6.6E-01	2.0E-01	3.7E-03	4.4E-02	3.2E-02	2.3E-04	5.2E-01	2.6E-04	6.9E-01
16	NA58	3.6E-05	2.3E-03	1.6E+00	6.7E-01	6.6E-01	1.9E-01	1.8E-02	2.5E-01	4.5E-02	1.0E-04	5.4E-01	2.5E-04	2.3E-01
17	NA59	9.6E-05	3.2E-03	2.9E+00	9.1E-01	5.6E-01	3.4E-01	2.6E-02	7.1E-01	1.4E-01	5.0E-04	5.4E-01	5.9E-04	1.3E+00
18	NA60	4.7E-05	2.0E-03	2.0E+00	5.1E-01	4.6E-01	2.3E-01	1.9E-02	4.1E-01	4.7E-02	2.3E-04	5.7E-01	3.4E-04	5.2E-01
19	NA61	5.2E-05	2.1E-03	2.0E+00	6.3E-01	4.8E-01	2.0E-01	2.1E-02	4.2E-01	3.8E-02	2.5E-04	5.6E-01	3.7E-04	5.5E-01
20	NA62	1.1E-04	2.9E-03	1.9E+00	3.4E+00	5.0E-01	2.0E-01	3.0E-02	1.5E+00	3.5E-02	2.8E-04	4.8E-01	1.2E-03	4.1E-01
21	NA63	8.2E-05	1.7E-03	2.3E+00	1.0E+00	5.3E-01	3.5E-01	1.8E-02	8.9E-01	1.3E-01	4.9E-04	5.4E-01	4.9E-04	1.2E+00
22	NA64	4.8E-05	1.1E-03	1.7E+00	5.8E-01	4.5E-01	1.9E-01	5.1E-03	3.1E-01	2.7E-02	1.5E-04	5.3E-01	3.3E-04	3.5E-01
23	NA65	1.8E-05	1.3E-03	3.0E+00	5.0E-01	5.1E-01	2.0E-01	4.2E-03	2.4E-01	3.9E-02	9.9E-04	5.3E-01	2.8E-04	2.6E+00
24	NA66	1.9E-05	1.3E-03	1.6E+00	4.3E-01	5.4E-01	2.4E-01	4.6E-03	2.5E-01	1.1E-02	1.3E-04	5.3E-01	1.7E-04	3.0E-01
25	NA67	6.1E-05	2.5E-03	1.8E+00	8.8E-01	6.2E-01	1.8E-01	1.4E-02	4.0E-01	2.8E-02	3.1E-04	5.2E-01	3.3E-04	6.7E-01
26	NA68	9.8E-05	1.9E-03	1.9E+00	7.1E-01	4.0E-01	1.6E-01	2.0E-02	7.8E-01	1.8E-02	2.4E-04	5.2E-01	5.1E-04	3.4E-01
27	NA69	3.5E-05	1.1E-03	1.9E+00	3.8E-01	3.5E-01	1.9E-01	7.5E-03	2.5E-01	3.6E-02	3.5E-04	5.1E-01	2.3E-04	7.7E-01
28	NA70	9.3E-06	1.3E-03	2.1E+00	3.4E-01	4.4E-01	2.1E-01	1.1E-03	4.3E-02	2.6E-02	4.6E-04	5.1E-01	1.5E-04	1.1E+00
29	NA71	1.3E-05	1.5E-03	1.7E+00	7.0E-01	5.7E-01	2.0E-01	1.8E-03	6.9E-02	2.1E-02	8.8E-05	5.2E-01	1.2E-04	2.4E-01
30	NA72	1.9E-05	7.2E-04	1.5E+00	4.7E-01	4.2E-01	1.6E-01	3.7E-03	1.7E-01	2.4E-02	9.9E-05	5.1E-01	1.8E-04	2.3E-01
31	NA73	5.2E-05	1.1E-03	1.7E+00	8.8E-01	5.7E-01	1.9E-01	1.3E-02	3.6E-01	4.5E-02	1.9E-04	5.3E-01	3.2E-04	4.5E-01
32	NA74	5.7E-05	1.6E-03	2.0E+00	7.6E-01	7.4E-01	2.1E-01	1.5E-02	6.2E-01	4.2E-02	3.0E-04	5.3E-01	3.4E-04	6.5E-01
33	NA75	9.5E-05	2.8E-03	1.9E+00	1.3E+00	5.8E-01	2.4E-01	2.4E-02	1.0E+00	2.7E-02	2.3E-04	5.0E-01	5.3E-04	3.6E-01
34	NA76	8.6E-05	1.5E-03	3.7E+00	1.0E+00	4.2E-01	2.7E-01	1.7E-02	7.9E-01	3.5E-02	1.6E-03	5.1E-01	4.5E-04	2.6E+00
35	NA77	1.3E-05	1.3E-03	1.6E+00	5.6E-01	4.6E-01	1.9E-01	2.7E-03	1.3E-01	2.4E-02	1.7E-04	5.2E-01	1.5E-04	4.4E-01
36	NA78	5.7E-04	2.7E-03	2.0E+00	1.2E+00	7.4E-01	2.9E-01	1.0E-02	3.5E-01	6.4E-02	2.4E-04	5.2E-01	3.4E-04	5.0E-01
37	NA79	8.6E-05	1.0E-03	3.0E+00	1.6E+00	5.0E-01	4.9E-01	2.0E-02	8.5E-01	1.7E-01	3.8E-04	5.0E-01	5.0E-04	1.2E+00
38	NA80	5.5E-05	7.9E-04	2.1E+00	1.4E+00	5.6E-01	2.3E-01	1.2E-02	5.4E-01	3.9E-02	3.9E-04	5.1E-01	2.7E-04	9.5E-01

Table 5.2: Sample stalagmite seasonal milled section trace element ratios have been given in the table. 1 represents the oldest sample. Stable isotope measurements have also been given for reference.

	Milling notes	Image J	δ^{180}	δ^{13C}	Y/Ca	U/Ca	Na/Ca	Mg/Ca	P/Ca	S/Ca	Mn/Ca	Fe/Ca	Zn/Ca	Rb/Ca	Sr/Ca	Pb/Ca	K/Ca
Milling notes	1																
Grey level	0.00	1															
δ^{180}	-0.16	0.16	1														
δ^{13C}	-0.16	0.09	0.74	1													
Y/Ca	0.01	-0.02	0.00	-0.0001	1												
U/Ca	0.10	-0.22	-0.58	-0.54	0.21	1											
Na/Ca	0.00	-0.05	-0.03	0.00	0.04	0.09	1										
Mg/Ca	-0.003	-0.02	-0.07	-0.01	0.14	0.27	0.13	1									
P/Ca	0.03	-0.08	-0.06	-0.04	0.14	0.20	0.02	0.06	1								
S/Ca	-0.004	-0.002	0.00	0.01	0.06	0.04	0.36	0.09	0.03	1							
Mn/Ca	-0.04	-0.36	-0.23	-0.12	0.08	0.40	0.16	0.41	0.02	0.06	1						
Fe/Ca	-0.09	-0.08	-0.09	-0.03	0.08	0.20	0.15	0.58	-0.001	0.07	0.76	1					
Zn/Ca	-0.03	-0.01	0.00	0.00	0.01	0.01	0.14	0.02	0.01	0.75	0.04	0.03	1				
Rb/Ca	0.01	0.00	-0.01	0.00	0.01	0.01	0.73	0.04	-0.002	0.06	0.04	0.08	0.01	1			
Sr/Ca	0.02	-0.27	-0.14	-0.05	0.01	0.11	0.08	-0.01	0.08	0.00	0.09	-0.002	-0.002	0.02	1		
Pb/Ca	0.02	0.01	0.00	-0.001	-0.0002	-0.0004	0.00	0.01	-0.001	0.01	-0.0001	0.00	0.01	0.00	-0.02	1	
K/Ca	0.03	0.00	-0.004	0.01	0.00	0.00	0.77	0.02	0.00	0.15	0.01	0.02	0.06	0.88	0.03	0.01	1

Table 5.3: Correlation coefficients (R^2) between grey level observations (milling notes) and measurements (using Image J software), trace element ratios and stable isotope measurements have been shown in the table. R^2 values above 0.7 have been highlighted in bold.

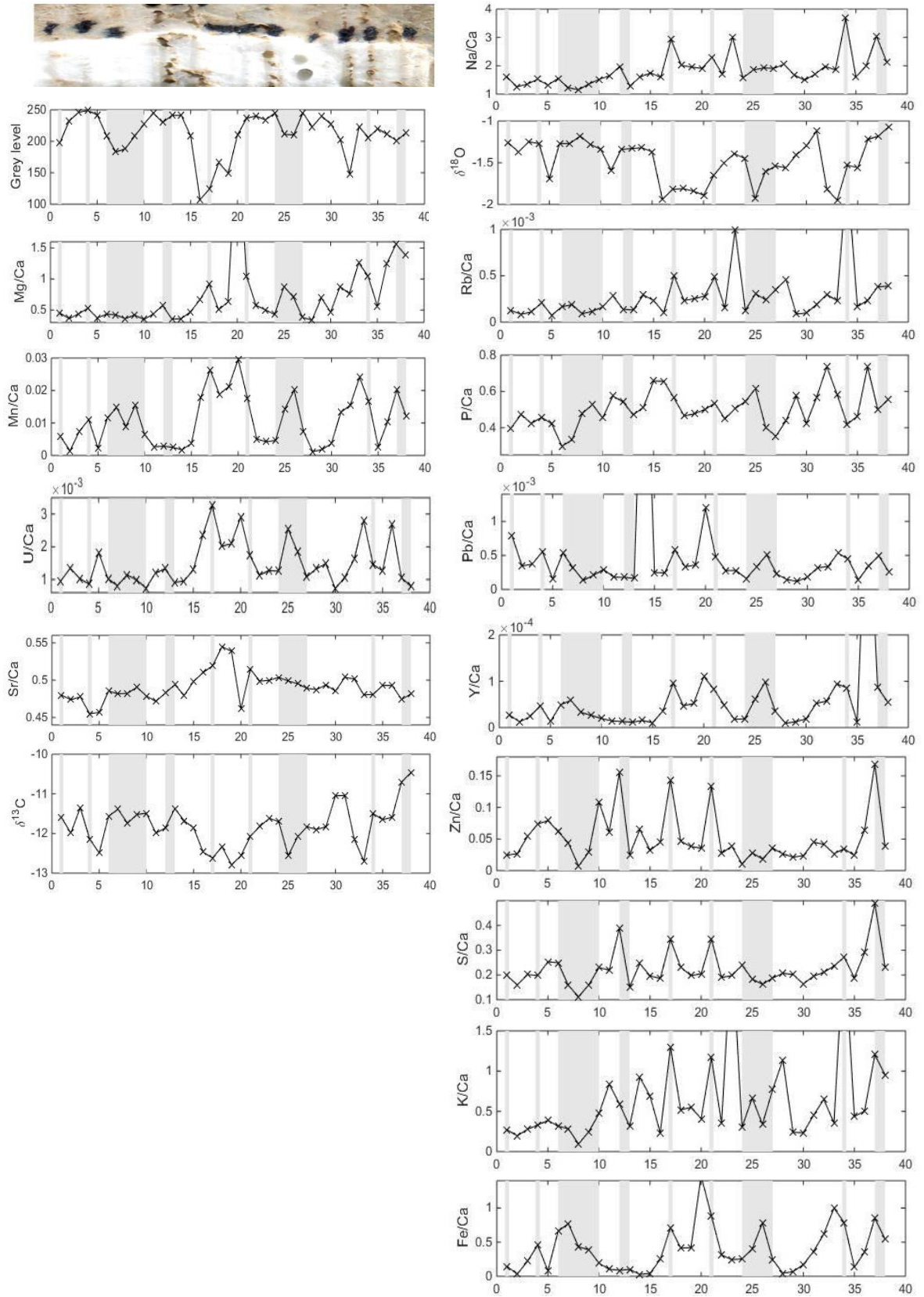
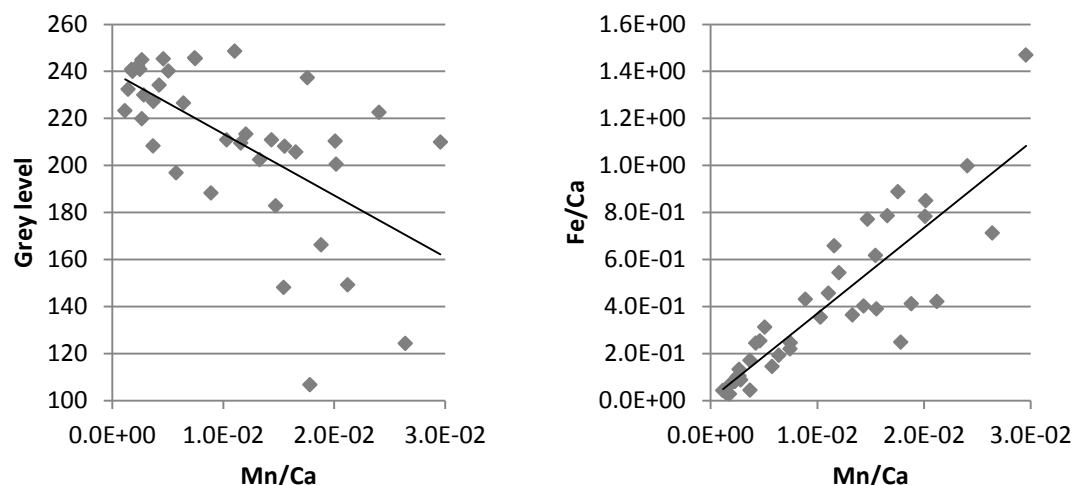
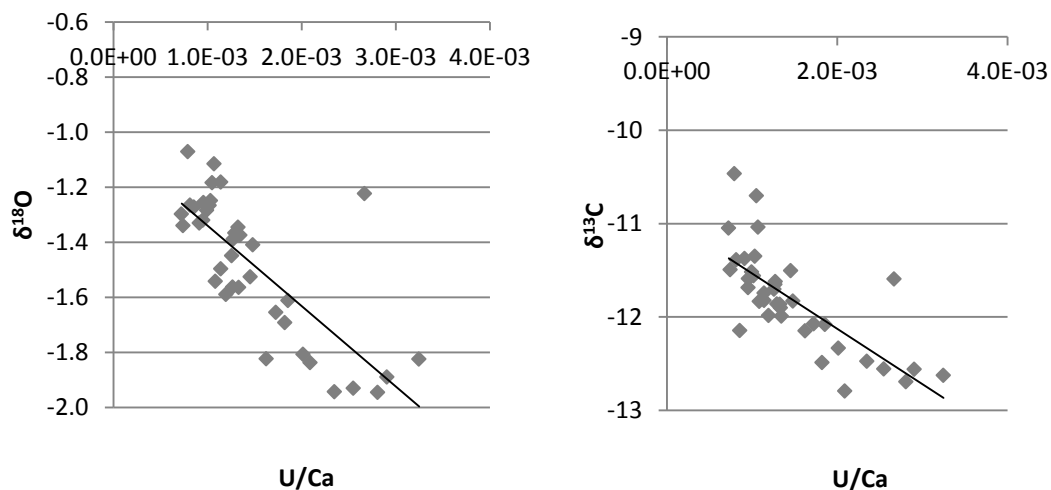


Figure 5.3: Grey level measurements and observations and trace element ratios of 38 subsamples milled from sample stalagmite section have been plotted. On the X axes is the subsample number with the oldest being 1. Grey level measurements are on a grey scale of 0-255 representing the range from black-white. The grey bars on all graphs are observed dark layers during milling of subsamples. Respective trace element ratios in mmol/mol have been given on Y axes. $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ in ‰V-PDB.



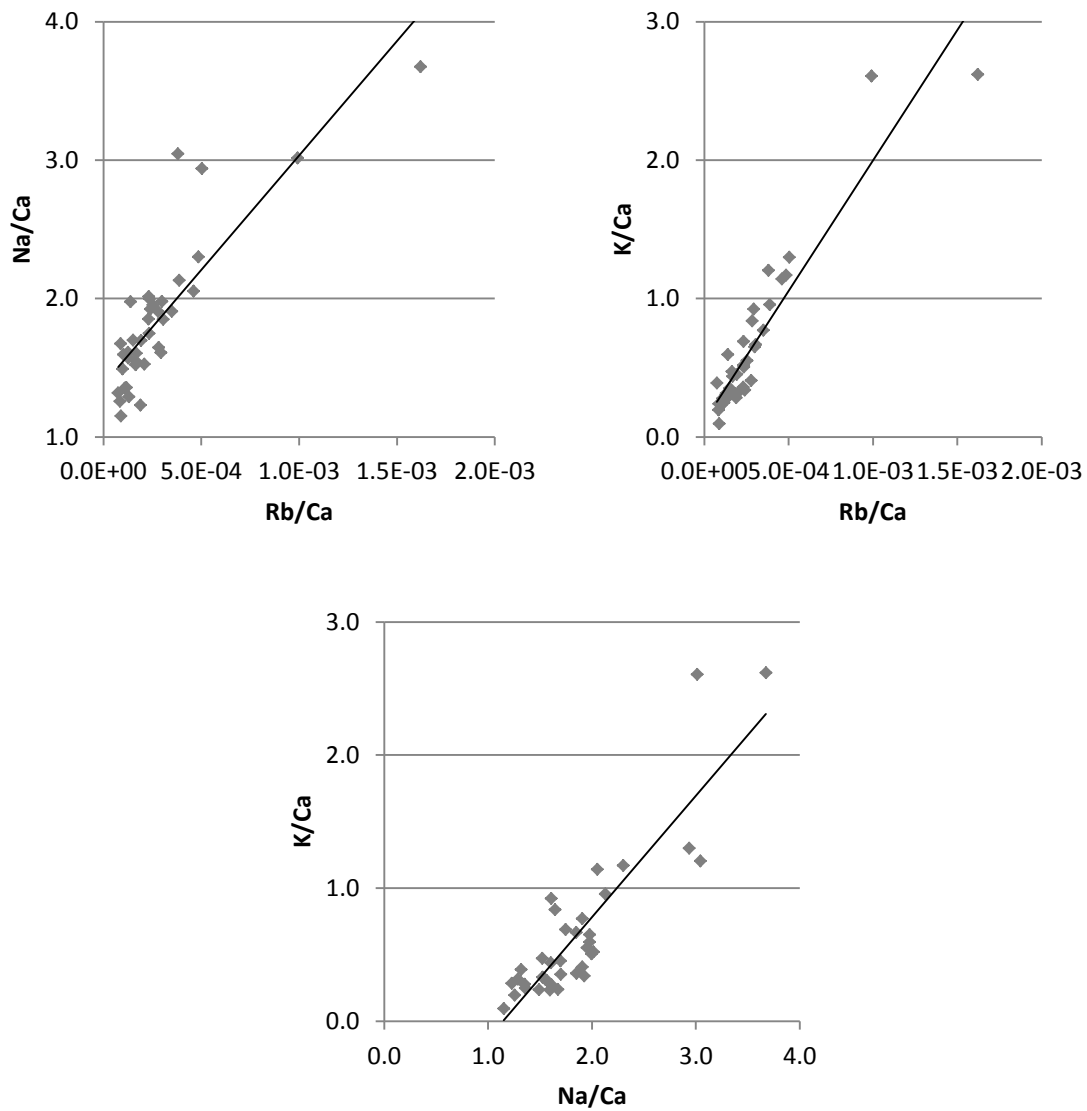
Panel	X axis	Y axis	Line equation	R^2	p value
A	Mn/Ca	Grey level scale	$y = -2620.4x + 239.62$	-0.36	2.80E-05
B	Mn/Ca	Fe/Ca	$y = 0.02x + 0.0024$	0.76	2.46E-13

Figure 5.4: Mn/Ca vs grey level and Mn/Ca vs Fe/Ca have been plotted in the two panels and associated line equations, R^2 and p values have been given in the table.



Panel	X axis	Y axis	Line equation	R^2	p value
A	U/Ca	$\delta^{18}\text{O}$	$y = 292.36x - 1.04$	-0.58	8.80E-09
B	U/Ca	$\delta^{13}\text{C}$	$y = -593.06x - 10.9$	-0.54	4.80E-08

Figure 5.5: U/Ca vs $\delta^{18}\text{O}$ and U/Ca vs $\delta^{13}\text{C}$ have been plotted in the two panels and associated line equations, R^2 and p values have been given in the table.



Panel	X axis	Y axis	Line equation	r^2	p value
A	Rb/Ca	Na/Ca	$y = 1654.3x + 1.38$	0.73	8.18E-08
B	Rb/Ca	K/Ca	$y = 1885x + 0.11$	0.88	1.04E-13
C	Na/Ca	K/Ca	$y = 0.91x - 1.04$	0.77	5.04E-09

Figure 5.6: Rb/Ca vs Na/Ca, Rb/Ca vs K/Ca and Na/Ca vs K/Ca have been plotted in the three panels and associated line equations, R^2 and p values have been given in the table.

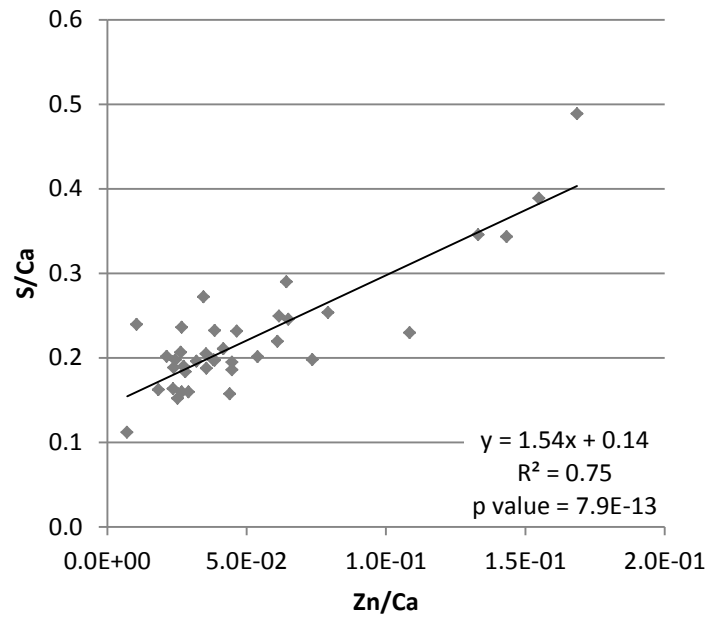


Figure 5.7: Zn/Ca vs S/Ca has been plotted in the panel and associated line equation, R^2 and p values have been given in the figure.

5.5.3 Partition coefficients

Empirical partition coefficients (k) have been calculated for elements known to replace Ca in a CaCO_3 structure (Mg, Sr, Mn, Na, U, P, Rb, K) using measurements from seasonally milled subsamples of the sample stalagmite section and drip waters feeding the sample stalagmite (table 5.4 and calculations in table 12 of Appendix 3) where $k = (\text{trace element}/\text{Ca})_{\text{CaCO}_3}/(\text{trace element}/\text{Ca})_{\text{dripwater}}$. Ba can also replace Ca in aragonite but since drip water Ba values are below detection limit, k_{Ba} values could not be calculated. Two drip sources feed the sample stalagmite, ‘the fast drip’ and ‘the slow drip’ respectively. The partition coefficients and standard deviations have been calculated for each drip separately and then averaged. k_{Sr} , k_{P} and k_{U} are more than 1 i.e. these trace elements are compatible with the aragonite structure. Conversely, k_{Mg} , k_{Mn} , k_{Na} , k_{Rb} and k_{K} are less than 1 and are incompatible. In all cases (except Mn where the slow drip measurement is below detection limit), the difference between k values calculated based on fast drip measurements and k

values based on slow drip measurements are within 1sd and no comparison can be made between them.

<i>Trace Element Ratio</i>	<i>Partition Coefficient (k)</i>	<i>k +/- (1sd)</i>	<i>Previously Published k Values</i>
	<i>Sample stalagmite section</i>		<i>Wassenburg et al, 2016</i>
Mg/Ca	5.3E-04	4.1E-04	
Sr/Ca	2.80	0.12	1.38 +/- 0.53
Mn/Ca	0.30	0.22	
Na/Ca	8.4E-03	2.5E-03	
U/Ca	14.39	6.45	6.26 +/-4.53
P/Ca	2.24	0.44	
Rb/Ca	0.26	0.26	
K/Ca	0.23	0.21	

Table 5.4: Empirical partition coefficients from this study compared with previously published values reported by *Wassenburg et al, 2016* (they use the term distribution coefficient rather than partition coefficient).

5.6 Discussion

5.6.1 Sources of trace elements in the Akalagavi cave system

Trace elements may, in general, be derived from the atmosphere (dissolved or aerosol), from dissolution of overlying soil and rock, or in a colloidal/particle phase from the soil or rock. Assessment of typical geochemistry of each element in the cave environment, and the relationships between the elements measured here, allow some assessment of the likely sources of each trace element in the Akalagavi stalagmite.

Table 5.5 compares the drip water composition with that of the ocean and the Akalagavi bed rock sample.

Element	Ocean water (g/g)	Ocean water Element/Na (g/g) %	Dripwater Element/Na (mg/mg) %	Bedrock Element/Ca (g/g) %	Dripwater Element/Ca (g/g) %
Ca	4.13E-04				
Na	1.08E-02	100			
Mg	1.29E-03	12	700	26	206
S	9.00E-04	8	14	2	3
K	3.99E-04	4	3	27	1
Sr	7.60E-06	0.07	0.3	0.18	0.05
Ba	1.40E-08	1.30E-04	1.03E-02	2.92E-02	1.25E-03
Mn	3.00E-10	2.78E-06	3.05E-01	14	3.96E-02
Fe	6.00E-11	5.56E-07	4.62E-01	57	6.27E-02
Y	7.00E-12	6.48E-08	6.99E-05	4E-03	1.88E-05
U	3.10E-09	2.87E-05	6.35E-04	7E-04	1.86E-04
P	7.10E-08	6.57E-04	8.66E-01	2	0.2
Zn	4.00E-10	3.70E-06	8.13E-02	4	0.02
Rb	1.20E-07	1.11E-03	3.63E-03	2.7E-02	1.15E-03
Pb	2.00E-12	1.85E-08	4.51E-04	8.2E-02	6.80E-05

Table 5.5: The table compares drip water values with ocean water composition (*Taylor and McLennan, 1985*) and Akalagavi bed rock values with drip water composition. Drip water values are averages of all drip waters measured in the cave.

Comparison of Akalagavi bed rock ratios with well water and drip water ratios shows that (schematically shown in figure 5.8):

- i) Na/Ca and S/Ca are higher in most well and drip waters compared to bedrock values. This suggests that sea water, which has comparably high Na/Ca and S/Ca ratios, is a likely source for these trace elements. Akalagavi cave is located 30 km away from the Arabian Sea and receives strong onshore winds and so one of the sources of trace elements is likely to be aerosol from the sea. Na is the second largest constituent of sea water (apart from Cl). If we consider all the Na in well and drip waters to have been sourced from the sea, we can estimate the contribution of sea water to other trace element concentrations. Table 5.5 shows that Mg, S and K may also be sourced from ocean water. This is similar to results obtained by *Fairchild et al, 2000*. In addition to Mg, S and K, they suggest that 2% of Sr in their cave site may also be sourced from ocean water.
- ii) Mg/Ca is lower in well waters compared to bedrock values and higher than bedrock values in almost all drip waters except NAW7, which has higher Mg/Ca than bedrock

values. This suggests that potentially in addition to sea water, the bed rock is a major source for Mg.

- iii) Sr/Ca, Ba/Ca, Rb/Ca, Mn/Ca, Fe/Ca, Y/Ca, U/Ca, P/Ca, Zn/Ca, Pb/Ca and K/Ca are consistently below bedrock values indicating that the bedrock is a likely source for these trace elements.

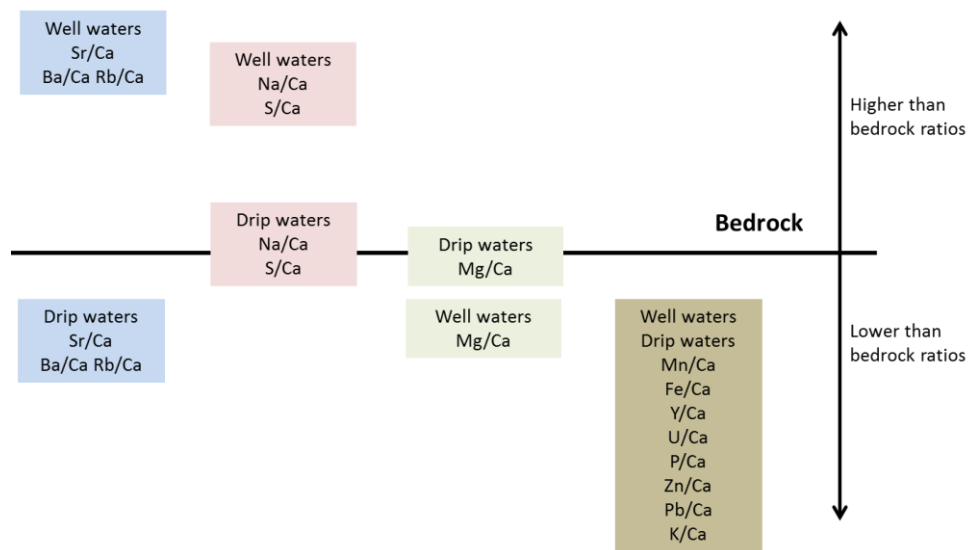


Figure 5.8: Schematic figure of trace element ratios in well, spring and drip waters in comparison to bedrock values. For example, drip waters have Mg/Ca ratios similar to or lower than bedrock Mg/Ca ratio. And well waters have higher Na/Ca and S/Ca ratios than the bedrock. Spring water behaves similar to drip water and has not been shown separately.

5.6.2 Prior Aragonite Precipitation (PAP)

The sample drip waters have resulted in the precipitation of aragonite (rather than calcite) mineralogy for the last ~300 years. Drip waters feeding the sample have high Mg/Ca ratio of ~1300 mmol/mol. Previous studies have shown that aragonite speleothems often precipitate when the Mg/Ca ratio is above 1100 mmol/mol (*Gonzalez and Lohmann, 1988; Frisia et al, 2002; de Choudens-Sanchez and Gonzalez, 2009*). Since the precipitation of aragonite versus calcite is due to consistently high Mg/Ca ratios in drip waters rather than seasonally high Mg/Ca ratios in drip waters, it is unlikely that calcite will precipitate from this water making prior calcite precipitation unlikely.

U/Ca has the highest partition coefficient measured from this stalagmite (table 5.4) and significantly correlates with $\delta^{13}\text{C}$ (figure 5.5). During drier periods, low pCO_2 air pockets may be present in the epikarst (*Fairchild et al, 2000*). If saturated ground waters, in equilibrium with soil pCO_2 encounter these air pockets, the solution may degas resulting in the precipitation of aragonite upstream of the cave environment. This is commonly referred to as Prior Aragonite Precipitation (PAP). Aragonite precipitation in these pockets will preferentially incorporate U which has a partition coefficient significantly above 1 in aragonite (table 5.4), resulting in lower concentration of U/Ca in the remaining solution and the stalagmite that precipitates from it. Similarly, CO_2 degassing leads to increase in solution and carbonate $\delta^{13}\text{C}$ due to preferential loss of ^{12}C in degassed CO_2 . During dry periods, the stalagmite precipitating from this solution would have lower U/Ca ratios and higher $\delta^{13}\text{C}$. There may also be PAP on the cave ceiling (for example, on the stalactite) where seasonally lower drip rates may allow CO_2 degassing and aragonite precipitation on the cave ceiling (*Johnson et al, 2006*). An additional drip rate control may be through increased residence time on the growth surface allowing for more CO_2 degassing (*Johnson et al, 2006*). The high drip rates measured in the non-monsoon months of January and May suggest that even in the non-monsoon (dry) months, the residence time for drip water on the stalagmite surface is minimal so this is unlikely to be a dominant control. This stalagmite shows seasonal cyclicity in U/Ca and $\delta^{13}\text{C}$, indicating that there is seasonal PAP. A seasonal PAP cyclicity in U/Ca and $\delta^{13}\text{C}$ controlled by PAP has also been found by *Jamieson et al, 2016* for a Belizean aragonite stalagmite.

However, other element partition coefficients would also indicate that if there is precipitation of aragonite prior to drip waters reaching the stalagmite; for example P and Sr, which both have partition coefficients above 1 in aragonite, would have also been preferentially removed by any PAP (after *Fairchild et al, 2000; McMillan et al, 2005; Johnson et al, 2006; Fairchild and Treble, 2009*). There is little correlation between P/Ca, Sr/Ca and

U/Ca in the time series generated by seasonal resolution milling of the sample stalagmite section. It is possible that there is a stronger control of PAP on U/Ca ratios in comparison to Sr/Ca and P/Ca ratios at a seasonal scale such that even a small percentage of aragonite removed may reflect in the U/Ca system but not in the Sr/Ca or P/Ca systems (see table 5.4). Further, although both studies, this study and that of *Wassenburg et al, 2016*, indicate that the partition coefficient for U/Ca is above 1, there is significant variation in the values of K_U . Similarly, this study indicates that Sr/Ca has a partition coefficient value of more than 1 but the *Wassenburg et al, 2016* study finds that K_{Sr} may or may not be above 1. Cave analogue studies on trace element distribution in aragonite are required to get a better control on these partition coefficients. Cave analogue studies can also determine the sensitivity of trace elements to additional controls such as temperature and growth rate, further increasing confidence in the control of percentage PAP on these trace element ratios.

5.6.3 Seasonal variation in Mn/Ca ratios

Demarcations of grey layers from white layers (based on observations made during milling and using Image J software) indicate that Mn/Ca is significantly correlated and higher in concentration in dark layers (figure 5.4) ($R^2 = -0.36$ Mn/Ca – Image J grey layers). This thus provides a distinct seasonal marker in this annually layered stalagmite. Since the dark layer was precipitating during the visit to the cave in January, 2015, there appears to be higher Mn/Ca during the non-monsoon period.

Mn/Ca may be sourced from the soil or the host rock. The narrow nature of cave entrances, humidity of 70% in the cave and the lack of air flow observed in the cave during the field work in January, 2015 suggest that wind-blown material is an unlikely source for the Mn in the cave. Mn is a redox sensitive element indicating that its dissolution in water would be related to low-oxygen conditions (see *Perrett et al, 2000*). Low oxygen conditions in the soil or host rock can be caused by increased oxygen consumption by bacteriological activity

(more likely in the soil). Mn can be transported as organic complexes as indicated by *Richter et al, 2004*. In their study, *Zhou et al, 2008* filtered cave drip waters and found that the Mn concentration reduces with filtering from 0.3-2.9 ppb to 0.1-0.53 ppb suggesting that Mn can also be carried as a colloidal and/or in particle phase in drip waters. No filtering of drip waters or organic analysis of the drip waters or stalagmite sample was made so it is not possible to differentiate the form in which Mn occurs in this sample. In the fast flowing drip waters, it seems unlikely that the Mn will continue to be in a reduced form during its journey from the soil to the cave. Dilution and mixing with groundwater should provide the oxidizing conditions for precipitating Mn. Based on this line of evidence; it seems likely that Mn is carried in its particle/colloidal form. The correlation between Mn/Ca and Fe/Ca (figure 5.4) indicates that Fe may also be carried in the particle/colloidal form.

Seasonal variation in Mn/Ca ratios in the drip waters feeding the sample could not be measured so that seasonal variation in drip waters cannot be commented on. However, this is one possible source for the seasonal signal in Mn/Ca ratios in the stalagmite, and warrants further investigation.

The faster drip feeding the sample has a higher Mn/Ca ratio than the slower drip (Mn/Ca of slower drip was below detection limit) suggesting the pathway of drip water through the epikarst has some control over Mn/Ca composition of drip waters (*Perrette et al, 2000*). However, presumably since both drips feed the stalagmite through the year, this still does not explain why there is seasonal variation in the Mn/Ca ratios in the stalagmite itself unless there has been a variation in the drip water feeding the stalagmite in the past. Figure 4.9 shows the variation in growth axis seen in this stalagmite sample and change in drip water location/or change in the drip water reaching saturation and precipitating is the most likely cause for this variation in growth axis.

5.6.4 Controls on trace element relationships

Figure 5.6 indicates that Rb/Ca, Na/Ca and K/Ca are significantly correlated. Section 5.6.1 indicates that Na and some of the K found in drip waters maybe sourced from the sea while Rb and K are probably mainly sourced from the bedrock. The correlation of the three elements in the stalagmite is unlikely to do with them having a common source. Since Na, K and Rb are all Alkali metals, their correlation is more likely to be because they have similar chemical behaviour and atomic sizes thus easily replacing for each other in the calcium carbonate system.

Table 5.5 indicates that Zn maybe sourced from the carbonate host rock while S maybe sourced from sea water and from the host rock. In addition Zn may also be sourced from basalt found in the area (for example, *Beane et al, 1986*) and S may also be sourced from anthropogenic pollution (*Wynn et al, 2010*). S is found in the form of sulphate in speleothems (*Fairchild et al, 2010*) and it is likely that the correlation between Zn and S (figure 5.7) is because they have a common source and/or occur together in the stalagmite.

5.6.5 Use of trace elements in aragonite stalagmites

Mn/Ca ratios form a useful seasonal marker in the Akalagavi stalagmite although further work such as seasonal monitoring of the drip waters feeding this stalagmite is required to understand the pathway for seasonal variation in Mn/Ca in the stalagmite.

It is promising that U/Ca correlates with $\delta^{13}\text{C}$ since it indicates a seasonal PAP signal which can be a potential paleo-aridity indicator on longer time scales. However, in this stalagmite, Sr/Ca and P/Ca which are also expected to behave similar to U/Ca based on measured partition coefficients show little correlation with U/Ca. Laboratory analogue measurements of partition coefficients of U/Ca, Sr/Ca and P/Ca in aragonite are required to corroborate a seasonal PAP interpretation for this sample. If laboratory analogue experiments suggest that

partition coefficients for Sr and P are lower than 1, they may not be preferentially removed during PAP. In which case it is plausible that U/Ca ratios are indicating seasonal PAP in this stalagmite. However, uranium has not been extensively studied as a palaeo-environmental proxy and it is possible that there are other controls on its behaviour in stalagmites. *Bourdin et al, 2011* suggest that U in drip waters is mainly sourced from limestone at their cave site, *Frumkin and Stein, 2004* explore an external source such as Saharan dust, *Zhou et al, 2005* suggest overlying sediments. This suggests the possibility of source control on U/Ca ratios. Further work is required to understand controls on U/Ca.

Chapter 4 shows that there is likely to be a seasonal kinetic overprint on the $\delta^{18}\text{O}$ driving it to higher values or a seasonal control through more negative drip water $\delta^{18}\text{O}$ values during the monsoon. The significant negative correlation of $\delta^{18}\text{O}$ with U/Ca (if U/Ca is controlled by PAP) suggests that the sample section shows higher $\delta^{18}\text{O}$ values during seasonally dry periods. Significant correlation between the trace element ratios of U/Ca and the stable isotopic measurements of $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ suggests that they have a common dominant control other than the kinetics of oxygen isotopic precipitation since this will not affect U/Ca. Thus in the absence of replication tests, trace elements can be used to verify the stability and fidelity of oxygen isotopic records.

At this cave site, Na/Ca and S/Ca are likely to be sourced from the sea through sea surface aerosol particles. Increase in Na/Ca and S/Ca ratios in a stalagmite located close to the sea are likely to indicate a larger contribution of sea surface aerosol particles through strong onshore winds. Na/Ca and S/Ca can be measured in drip waters and the stalagmite and form a powerful potential proxy for onshore wind strength. This has the potential to enable us to decouple strength of atmospheric circulation from amount of precipitation. However, further empirical measurements and laboratory work is required to understand the controls on Na and S distribution in the stalagmite.

5.7 Conclusion

To the best of our knowledge, this is the first study on seasonal resolution trace element variation in aragonite speleothems. Based on drip water and seasonal resolution stalagmite subsample measurements, this study gives empirical partition coefficients for Sr/Ca, U/Ca, Mg/Ca, P/Ca, Na/Ca, Rb/Ca, K/Ca and Mn/Ca and provides evidence for the use of prior aragonite precipitation as a proxy for paleo-aridity. It indicates a marine source for Na/Ca, S/Ca and a marine and lithological source for Mg/Ca. It also shows a method for seasonal demarcation of layers based on concentration of detrital material (Mn/Ca). There is significant correlation between U/Ca and $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ giving a potential way to isolate kinetic control on $\delta^{18}\text{O}$ from a larger climatic/environmental control. There are several promising directions for further work on trace element distribution in aragonite speleothems, specifically since in these fast growing stalagmites where the equilibrium precipitation of oxygen isotopes is often debated, trace element distribution allows for a multi-proxy approach at identifying the climatic/environmental control.

Chapter 6

Annually Resolved Trace Element Studies in an Aragonite Stalagmite

Abstract

Trace element ratios of U/Ca, Na/Ca, Mg/Ca, P/Ca, Mn/Ca, Fe/Ca, Rb/Ca, Sr/Ca and Pb/Ca, measured at an annual resolution from an aragonite stalagmite, are reported in this Chapter. The stalagmite was collected from a tropical monsoon region, 30 km from the sea on the west coast of India.

Multiple proxies from the same stalagmite, such as trace elements, can be used to derive and internally confirm paleoclimatic information, especially where the equilibrium precipitation of $\delta^{18}\text{O}$ is debated. In this study, annual resolution trace element ratios are tested as proxies for paleoclimate information and are also compared to stable isotope measurements in order to elucidate what processes are influencing the $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ signals. P/Ca is found to significantly correlate with $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$, giving a potential way to isolate kinetic control on $\delta^{18}\text{O}$ from a larger climatic/environmental control.

Averaged (7 years) trace element ratios are compared to instrumental rainfall, land temperature and sea surface temperature (SST) records of the last ~100 years. Instrumental records show that there is an increasing trend in land temperature and SST from 1900 to 2000 AD. There are decadal periods of above and below average rainfall.

Temperature rather than rainfall amount is a greater influence on trace element and stable isotope distribution in this stalagmite. Rainfall amount dominantly influences only Fe/Ca ratios and lamina width. Distinct linear trends are seen in several trace element datasets.

Sr/Ca, shows a significant decreasing trend from 1900 to 1993. Results show significant correlation of Sr/Ca with SST ($R^2 = -0.80$, $p < 0.05$) and Sr/Ca with land temperature ($R^2 = -0.76$, $p < 0.05$). The control of SST on Sr/Ca concentration of the stalagmite is not straightforward. The correlation of Sr/Ca with land temperature indicates that there may be temperature control on the partitioning of Sr/Ca in this aragonite stalagmite. This suggests that in this sample, Sr/Ca can be used as a potential high resolution terrestrial temperature proxy but further laboratory work is required to corroborate this interpretation.

6.1 Introduction

There are few studies on trace elements from aragonite speleothems despite their fast growth and high uranium concentration. This is because it is believed that the fast growth and diagenesis to calcite will affect equilibrium oxygen isotopic conditions in the speleothem, and oxygen isotopes have to date formed the backbone of paleoclimate reconstructions using speleothems (*Hendy, 1971; McDermott, 2004*). With advances in instrumental capabilities, particularly mass spectrometers, trace element concentrations from speleothems are being used for a more robust multiproxy approach of interpreting paleoclimatic records (see *Fairchild and Treble, 2009*). Consequently, the number of studies on trace element proxies from aragonite speleothems has been increasing (for example, *Finch et al, 2001; Finch et al, 2003; McMillan et al, 2005; Wassenburg et al, 2016; Jamieson et al, 2016*). Of these studies, the *Finch et al, 2003* study investigates climatic/environmental control of trace element distribution (Sr and Ba) in an aragonite stalagmite from South Africa. It is a ~5 year averaged ~40 year trace element record. They find that trace element peaks correspond to rainfall maxima with notable inflexions in trace elements during drought periods. There is poor correlation with temperature. They suggest that speleothem growth rate plays a significant role in determining trace element uptake in aragonite stalagmites. Another study by *Jamieson et al, 2016* looking at an aragonite

stalagmite from Belize uses U/Ca ratios to understand past variation in rainfall amounts for the time period between 1669 and 1983 AD, through the process of prior aragonite precipitation. They calculate the partition co-efficient for U/Ca using U/Ca concentrations across primary calcite to aragonite mineralogical transitions. Since the partition coefficient of U/Ca is found to be considerable above 1, it is expected that prior aragonite precipitation due to increased karst water residence time will strongly control U/Ca ratios in the stalagmite. Lower rainfall periods are reflected by lower U/Ca ratios in the stalagmite.

In this Chapter, I compare annual resolution trace element ratios of U/Ca, Na/Ca, Mg/Ca, P/Ca, Mn/Ca, Fe/Ca, Rn/Ca, Sr/Ca and Pb/Ca from a modern aragonite stalagmite collected from the west coast of India with instrumental temperature and rainfall records. I further investigate if trace element measurements can be used to corroborate stable isotope measurements of $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$, which are often thought to have kinetic imprints in aragonite stalagmites due to their typically fast growth rates.

6.2 Location and Climate

In this Chapter, I will be comparing significant trends in instrumental records with trends in the trace element ratios. Location, rainfall and temperature information of the Akalagavi cave region have been previously described in section 4.5.

Chapter 5 shows that the sea can be a significant source of trace elements in this sample, specifically Na. Over the open ocean, the main physical driver of sea salt emissions is surface wind speed (*Blanchard, 1963*). A number of studies suggest that the emissions are also dependant on SST (*Martensson et al, 2003; Hultin et al, 2010*). The concentration of trace elements such as Na that are sourced from the sea and transported to the cave site may vary depending on the amount of sea salt aerosol particle production and the strength of onshore winds, so comparisons of speleothem trace element and stable isotope measurements have been made with Sea Surface Temperatures (SST) as well.

Land temperature and rainfall trends for the last 100 years from instrumental records have been shown in figure 6.1. The mean annual total rainfall amount for 1901-2000 AD for this region was 1732 mm. 1941-1968 AD is a distinct ~30 year period of above average rainfall. The annual total rainfall increased by up to 400 mm compared to the 1901-2000 average during this time period. 1969-2000 AD is a 30 years period of below average rainfall. The rainfall decreased up to 350 mm compared to the 1901-2000 AD average during this time period. The instrumental land temperature anomaly record shows a distinct increasing trend from 1900 to 2000 AD. The rate of temperature increase is 0.72 ± 0.31 °C per hundred years. The SST shows a rising trend from 1900 to 2000 AD. The rate of SST increase is 0.59 ± 0.06 °C per hundred years.

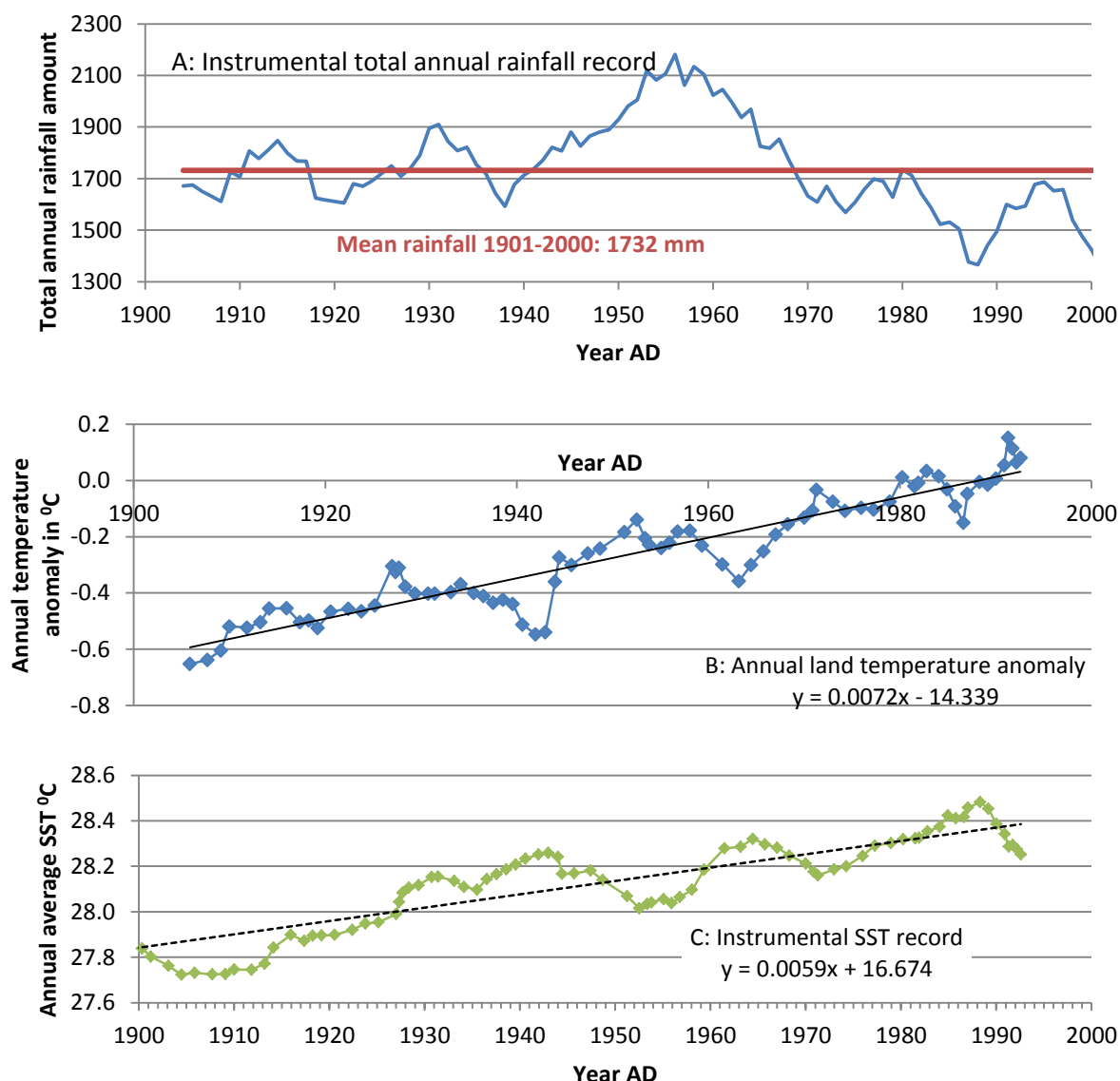


Figure 6.1: The figures plot instrumental records against time. Data are plotted on a 7 year running mean. Dashed lines are linear trend lines; respective line equations of the trend lines have been given. (A) The gridded CRU TS3.23 rainfall record for rainfall amount comparison (table 4 of Appendix III). (B) CRUTEM temperature anomaly dataset (table 3 of Appendix III). (C) HadISST record for SST comparison (table 13 of Appendix III).

6.3 Previous work

The sample was collected in 1997 AD by a team from the Physical Research Laboratory (PRL) and initial results have been published in *Yadava et al, 2004*. Their work has been summarised in section 4.6. Lamina width measurements and annual resolution $\delta^{18}\text{O}$ and

$\delta^{13}\text{C}$ measurements (as published by them) have been used in this Chapter. Since the Chapter compares annual resolution stable isotope and trace element record with instrumental records, the chronology established for the sample by *Yadava et al, 2004* has been explained in detail below, followed by a summary of the work done by me on the sample in Chapters 4 and 5 of this thesis.

When the sample was collected, it was actively growing. This ensures that the tip corresponds to the year of collection i.e. 1997 AD. Bomb ^{14}C measurements of the tip confirm that the sample was growing non-stop during the period when bomb ^{14}C was present in the atmosphere. A base ^{14}C age of 210 ± 100 years BP (corresponding to 1741 AD) suggests that stalagmite growth started recently. The stalagmite is well laminated, showing alternating white and brown layers. The sample precipitates in a region with strong annual climate cycles, with a single rainy season (figure 1.10), and the laminations are likely to be annual. A couplet of a white and brown layer represents a single years' precipitation. The white layers are thought to have precipitated during the rainfall months. The brown layers are thought to have precipitated during the other months of little to no rainfall such that the lower drip rates giving lower amount of carbonate precipitation allowed entrapment of detrital material that is otherwise washed away during the high drip rates of rainfall months. The total number of couplets counted using a travelling microscope was 331, giving a base age of 1666 AD. Since all distinct compact layers were counted, the error was assumed to be zero. However in some parts of the sample, where the layers are very thin, judgement of the observer is involved in the counting which may introduce an error. This error was expected to be no more than ± 7 years based on specific sections on the stalagmite where the laminae were particularly diffuse or where the brown layers were indistinct. Lamina width measurements were made using the same microscope with a linear movement platform with a resolution of 0.01 cm. Lamina width measurements for this sample are typically in the range of 1 to 2 mm for the time period of 1900 to 1996. Using an

average growth rate of 1.34 mm calculated based on lamina counting and lamina width measurements, *Yadava et al, 2004* provide an age depth relationship as shown in figure 6.2.

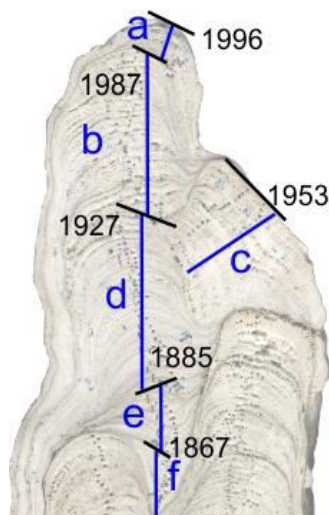


Figure 6.2: The part of the sample stalagmite that has been discretely milled at annual resolution. Sections a, b, c, d, e and f were milled. The base of 'f' corresponds to 1864 $\pm$ 7 years while the top of the stalagmite corresponds to 1997 which is the year in which it was collected.

In Chapter 4, I have reported findings on tests to assess whether the sample formed in oxygen isotope equilibrium with the drip-waters. In Chapter 5, I have explored the sources and partitioning behaviour of trace element ratios using seasonal resolution trace element data from a section of the sample stalagmite. In this Chapter, I look at trace element ratios milled from the white layers (expected to represent monsoon rainfall growth) of a section of the sample covering ~ 100 years and overlapping with instrumental records (figure 6.2).

6.4 Sampling and analytical methods

White layers of the Akalagavi sample stalagmite were discretely milled to get subsamples for trace element measurements. Only subsamples overlapping with instrumental records (i.e. covering the last ~ 100 years) were milled for this initial study, in order to understand the climatic and environmental control on trace element distribution in an aragonite stalagmite from a monsoonal setting.

Milling was done using a dentist's drill and a 0.8 mm tungsten carbide drill bit. 1-2 mg of subsample powder was collected from multiple lateral drill holes from the same white layer for trace element measurements (see section 3.3.4 and figure 3.3). 108 subsamples were milled. Care was taken to match the drill holes made by *Yadava et al, 2004* for stable isotope measurements in order to enable direct comparisons to be made between the stable isotope and trace element measurements.

Aliquots of the subsamples were analysed on a Thermo-Finnigan Element 2 ICPMS at Oxford. Trace element ratios of Y/Ca, Cd/Ca, Ba/Ca, Th/Ca, U/Ca, Na/Ca, Mg/Ca, P/Ca, S/Ca, Mn/Ca, Fe/Ca, Co/Ca, Zn/Ca, Rb/Ca, Sr/Ca, Pb/Ca and K/Ca were measured. Of these trace element ratios; Y/Ca, Cd/Ca, Ba/Ca, Th/Ca, S/Ca, Co/Ca, Zn/Ca and K/Ca have all or a significant number of measurements below detection limit and so have not been considered further. Details of analytical procedures and trace elements measured have been given in section 3.3.9. Detection limits and precision percentages have been specified in the result table (table 14 of Appendix III).

6.5 Results

6.5.1 Trace element measurements

Trace element measurements have been given in table 14 of Appendix III. Since there is an error of up to +/- 7 years in the sample stalagmite chronology, the trace element, stable isotope and instrumental records have been analysed at a 7 year running mean.

Table 6.1 gives the correlation coefficients (R^2) between the trace element ratios measured and the published lamina width and stable isotopic data. Highest correlation values are for P/Ca with $\delta^{18}\text{O}$ ($R^2 = 0.73$) and $\delta^{13}\text{C}$ ($R^2 = 0.71$) (figure 6.3).

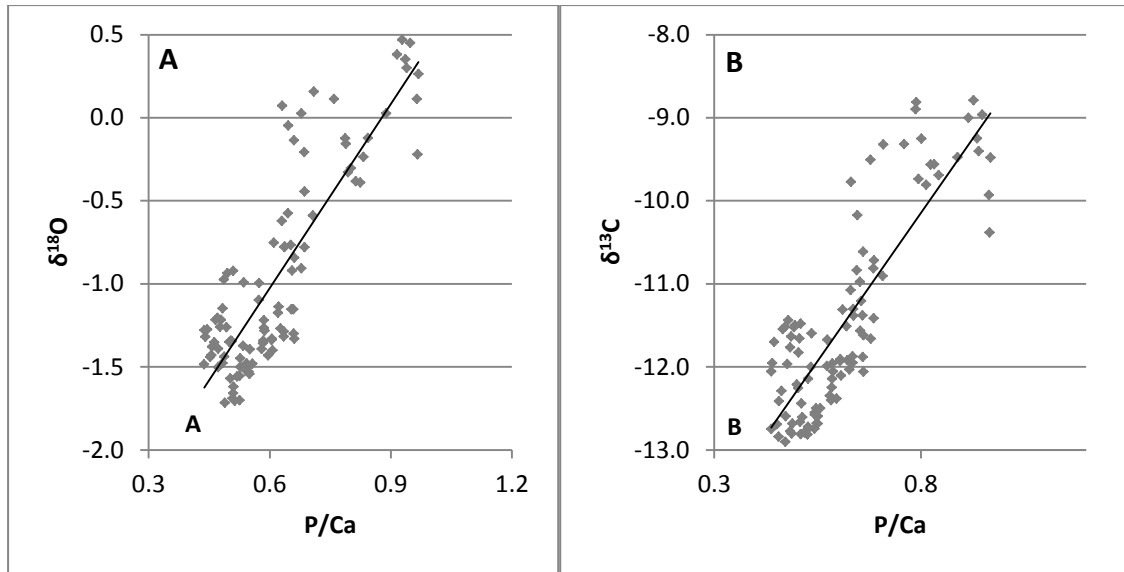
As discussed in Chapter 5, evidence for the process of Prior Aragonite Precipitation will be reflected by decrease in U/Ca and increase in $\delta^{13}\text{C}$ values, and a likely decrease in P/Ca and

Sr/Ca ratios as well. However, the correlation analysis in table 6.1 doesn't indicate any common influence on these ratios suggesting that Prior Aragonite Precipitation is not a dominant mechanism controlling trace element and stable isotope distribution during the monsoon period.

The trace element data has been plotted in figure 6.4. The stable isotope data as published by *Yadava et al, 2004* has also been plotted. The figure shows that there is a reducing trend in the P/Ca, Sr/Ca, Na/Ca, Fe/Ca, Mg/Ca, Mn/Ca, $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ records and an increasing trend in U/Ca record.

	U/Ca	Na/Ca	Mg/Ca	P/Ca	Mn/Ca	Fe/Ca	Rb/Ca	Sr/Ca	Pb/Ca	$\delta^{18}\text{O}$	$\delta^{13}\text{C}$	Lamina width
U/Ca	1											
Na/Ca	-0.28	1										
Mg/Ca	-0.08	0.08	1									
P/Ca	-0.10	0.51	0.10	1								
Mn/Ca	-0.43	0.02	0.37	0.09	1							
Fe/Ca	-0.03	0.36	0.13	0.50	0.08	1						
Rb/Ca	0.02	0.00	0.16	0.00	0.00	0.10	1					
Sr/Ca	-0.27	0.45	0.14	-0.42	0.16	0.19	-0.020	1				
Pb/Ca	0.01	0.18	0.02	0.06	-0.01	0.12	0.01	0.13	1			
$\delta^{18}\text{O}$	-0.20	0.58	0.03	0.73	0.08	0.26	-0.05	0.34	0.06	1		
$\delta^{13}\text{C}$	-0.17	0.59	0.02	0.71	0.05	0.23	-0.11	0.34	0.06	0.92	1	
Lamina width	0.14	0.00	-0.02	0.00	-0.06	0.03	-0.03	0.05	0.06	-0.05	-0.015	1

Table 6.1: Correlation coefficients (R^2) between the trace element ratios measured and published lamina width and stable isotopic data have been shown in the table. R^2 values above 0.7 are in bold.



Plot code	Subsamples	Line equation	R^2	p value
A	P/Ca - $\delta^{18}\text{O}$	$y = 3.7x - 3.2$ Std dev on slope = 0.22	0.73	1.7E-28
B	P/Ca - $\delta^{13}\text{C}$	$y = 7.1 - 15.9\text{Std dev on slope} = 0.14$	0.71	3.6E-28

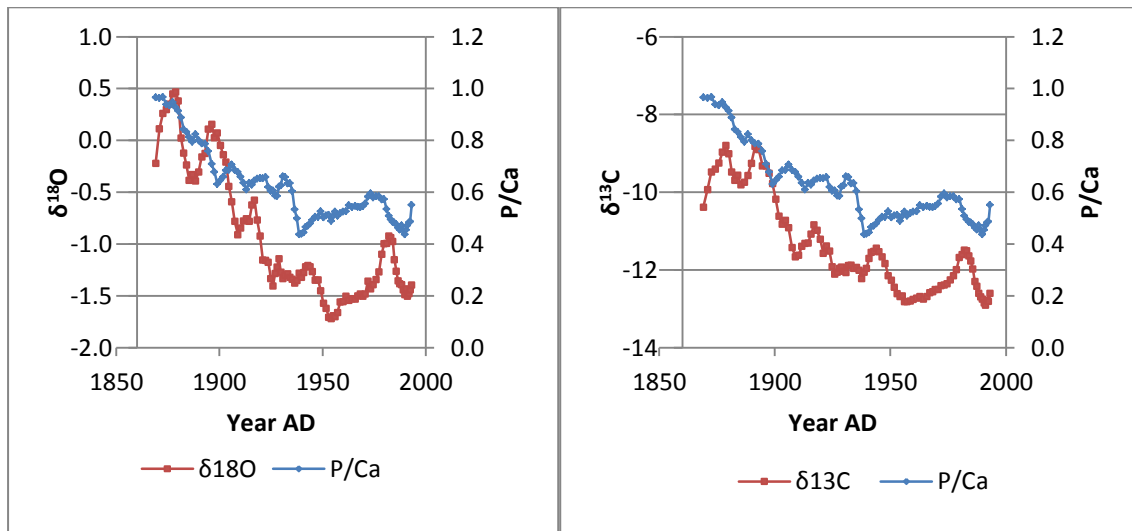


Figure 6.3: A and B plot P/Ca against $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ in ‰ vPDB respectively. The associated line equations, standard deviations on slope, R^2 and p values have been given in the table. The remaining two plots show variation of P/Ca- $\delta^{18}\text{O}$ and P/Ca- $\delta^{13}\text{C}$ against time.

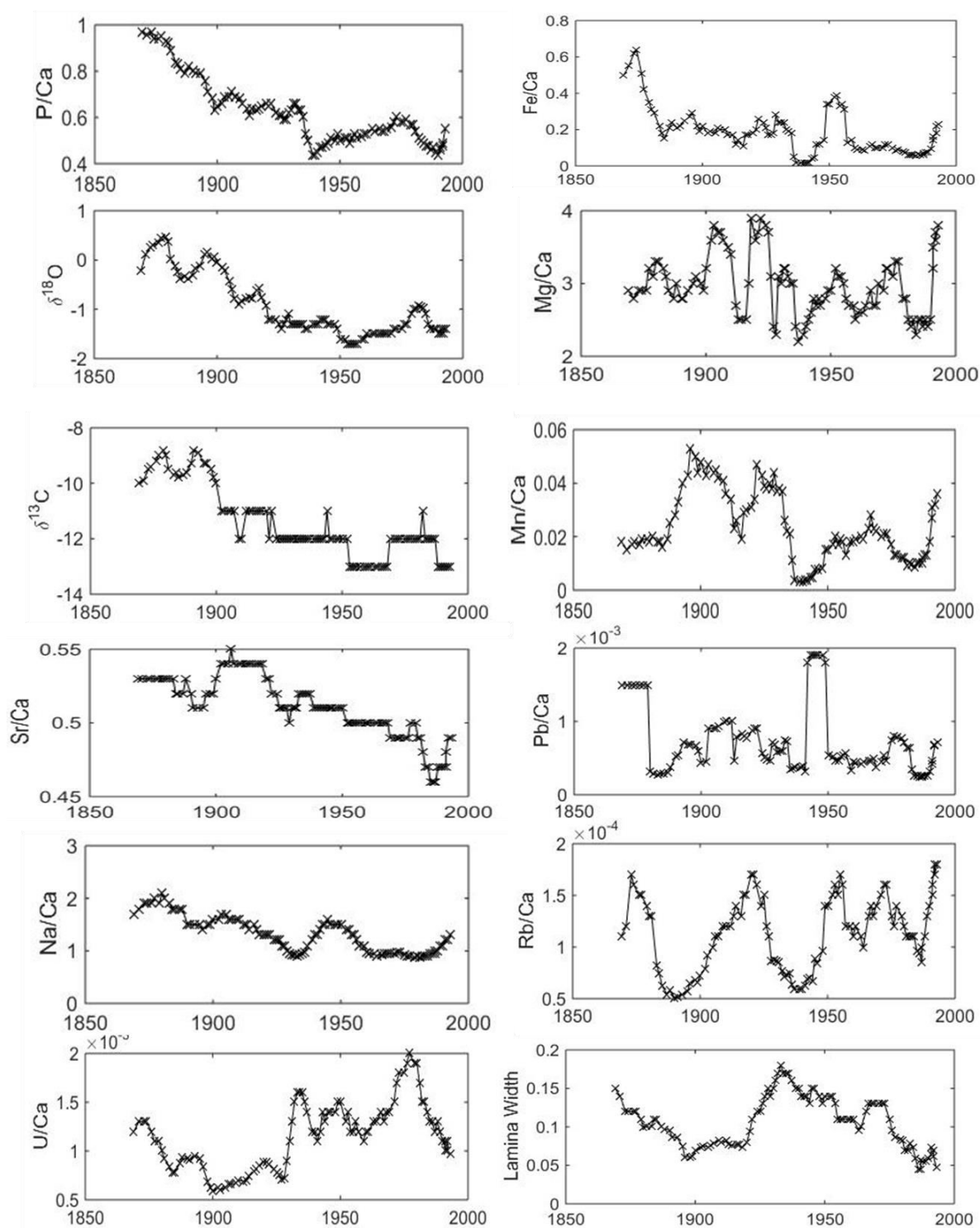


Figure 6.4: Trace element measurements (in mmol/mol), published stable isotope data (in ‰vPDB) and lamina width data (in mm) on the Y axis have been plotted against Year AD on the X axis.

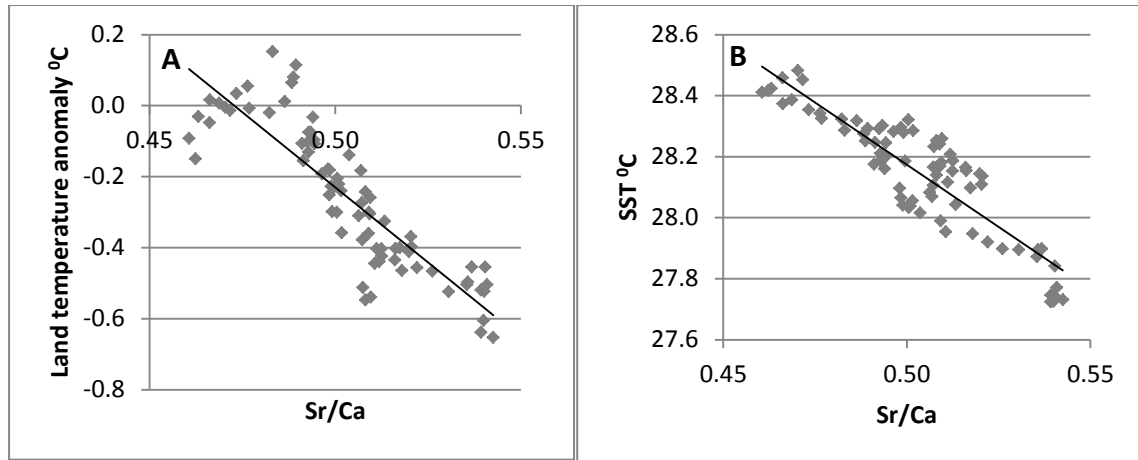
6.5.2 Trace element, stable isotope and lamina width measurements compared to lamina width, land temperature, rainfall and SST records

Table 6.2 shows results from correlation analysis of trace element, stable isotope and lamina width data and the temperature, rainfall and SST instrumental records. According to the correlation analysis, except Fe/Ca and lamina width, all other trace elements and stable isotope ratios indicate that SST and T have a generally stronger influence on their distribution than rainfall amount. Lamina width is not a strong influence on trace element partitioning in this stalagmite.

The strongest correlation is between Sr/Ca and SST ($R^2 = -0.80$) and Sr/Ca and land temperature anomaly ($R^2 = -0.76$). The relationships between Sr/Ca, land temperature anomaly and SST have been shown in figure 6.3.

	U/Ca	Na/Ca	Mg/Ca	P/Ca	Mn/Ca	Fe/Ca	Rb/Ca	Sr/Ca	Pb/Ca	$\delta^{18}O$	$\delta^{13}C$	Lamina width
Lamina width	0.07	0.00	-0.01	0.01	-0.01	0.03	-0.27	0.13	0.06	-0.10	0.00	1.00
Annual average land temperature anomaly °C	0.22	0.24	-0.01	-0.30	-0.07	-0.01	0.15	-0.76	-0.14	-0.20	-0.37	-0.18
Total rainfall (mm)	0.00	0.03	0.00	0.01	0.00	0.24	0.00	0.14	0.03	-0.12	-0.04	0.23
Annual mean SST	0.37	-0.34	-0.18	-0.57	-0.32	-0.23	-0.02	-0.80	-0.05	-0.22	-0.26	-0.02

Table 6.2: Correlation coefficients (R^2) between the trace element ratios measured, published stable isotopic data and lamina width with lamina width, annual average temperature, annual total rainfall and annual mean SST have been shown in the table. The data are on a 7 year running mean. Correlation coefficients higher than 0.7 have been highlighted in bold.



Plot code	Subsamples	Line equation	R^2	p value
A	Sr/Ca - land temperature anomaly	$y = -8.47x + 4.00$ Std dev on slope = 0.55	-0.76	2.0E-19
B	Sr/Ca - SST	$y = -8.2 + 32.1$ Std dev on slope = 0.005	-0.80	1.1E-34

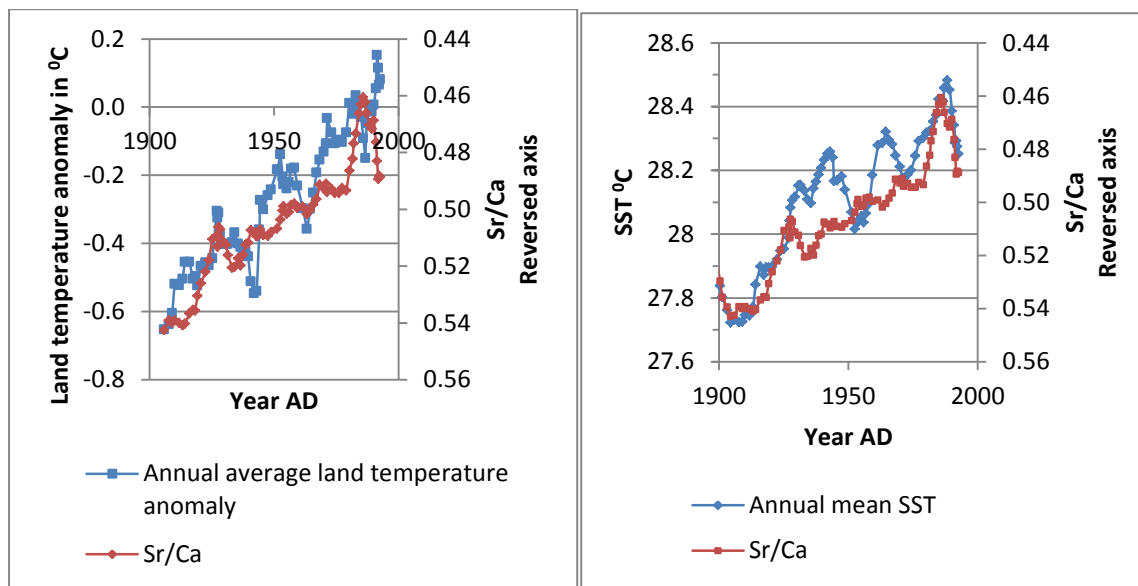


Figure 6.5: A and B plot Sr/Ca against land temperature anomaly and SST respectively. The associated line equations, standard deviations on slope, R^2 and p values have been given in the table. The remaining two plots show variation of Sr/Ca-land temperature and Sr/Ca-SST against time.

6.6 Discussion

The main aim of this study is to understand the relationship between proxy data and the instrumental record. The instrumental record is available for the last ~100 years. If a relationship can be established, the proxy data can be used to extend the climate information till 1666 AD i.e. it may provide climate information beyond that available from instrumental records for this region.

6.6.1 Trace element, stable isotope and lamina width measurements

Correlation analysis indicates that there is no strong relationship between the trace element ratios (table 6.1). The data also shows that growth rate (measured using lamina width) is not a strong control on trace element distribution in this sample (table 6.2).

The strongest correlation between trace elements, stable isotopes and lamina width measurements, is that of P/Ca with $\delta^{18}\text{O}$ ($R^2 = 0.73$) and $\delta^{13}\text{C}$ ($R^2 = 0.71$) (figure 6.3). This indicates that, although there may be control of kinetics of calcium carbonate precipitation on the $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ composition of the sample, $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ are also being controlled by larger climatic/environmental factors.

Soil is an important source of P (*Fairchild et al, 2001; Treble et al, 2003*) and is thought to be controlled in soil through seasonal vegetation uptake (*Heathwaite, 1997*) and decay (*Treble et al, 2003*). However the fate of P is complicated because analysis reveals that even the dissolved form of P in drip waters can occur in various inorganic and organic forms (*Chapman et al, 1997*). P has previously been linked to ‘flushing’ of colloidal soil organic matter into the cave during high infiltration and the P concentration of the stalagmite reflects the P concentration in drip waters (*Huang et al, 2001*). It is known that P is strongly scavenged from ground waters during calcite precipitation (*Huang et al, 2001*) so that Prior Calcite Precipitation during dry periods will result in lower P concentrations in the

stalagmite (*Johnson et al, 2006*). Similarly partition coefficients calculated for this sample in Chapter 5 suggest that Prior Aragonite Precipitation (PAP) during dry periods would preferentially incorporate P into the aragonite structure resulting in lower P/Ca in the stalagmite during dry episodes. However, the lack of correlation between U/Ca and P/Ca, suggests that PAP is not a significant control on trace element ratios in this sample during the monsoon period. An additional control on P is microbial mediation which may colonise pores during reduced drip rates. However, the drip rates for this stalagmite are high even during non-monsoon rainfall months (68 and 122 drops per minute for the two drip waters feeding this stalagmite, measured in January, 2015) so it seems unlikely that microbial mediation controls P partitioning in this stalagmite. The 'flushing' model, the PAP/PCP model and the microbial mediation model, all suggest higher P concentrations in the stalagmite during high rainfall periods. However, in this sample, correlation analysis indicates that rainfall is not a strong control on P/Ca.

No laboratory analogue experiments are available for controls on P/Ca partitioning into aragonite, to the best of our knowledge. Analysis on P partitioning into marine biological aragonite suggests that concentration of P is dependent on the P concentration of sea water and temperature of sea water does not influence P partitioning (*Montagna et al, 2006; Anagnostou et al, 2011*).

The previously published studies suggest that the concentration of P in drip waters is likely to be the main influence on P incorporation in the stalagmite. Drip water P measurements of multiple monsoon rainfall seasons from this cave will be required to understand the controls on P/Ca and hence $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$.

6.6.2 Sr/Ca and SST

The strongest relationship is seen between Sr/Ca and SST. To explain the strong influence of SST on Sr/Ca concentrations in this stalagmite, (i) the sea needs to be source for Sr (ii) there

should be decreasing sea salt aerosol production with increasing SST and/or there should be decreasing strength of onshore winds with increasing SST.

Chapter 5 shows that Sr is most likely sourced from the bedrock since the Sr/Ca ratios measured in drip waters are lower than the bedrock. Minor amounts of Sr may also be sourced from sea salt aerosol and dust (*Goede et al, 1998; Frumkin and Stein, 2004*). It seems unlikely that the minor amount of Sr/Ca sourced from the sea (Sr is 0.07% of the Na concentration of sea water) will dominate the variation in drip water and stalagmite Sr/Ca. Although *Fairchild et al, 2000* show that 2% of the Sr in the stalagmite may be sourced from the sea. Na which is dominantly sourced from the sea shows a much lower correlation coefficient with SST of $R^2 = -0.34$ (table 6.2). Similarly, a significant concentration of Mg may be sourced from the sea (Mg is 12% of the Na concentration of sea water) but shows a correlation coefficient with SST of $R^2 = -0.18$ (table 6.2). The controls on Na and Mg partitioning into aragonite are not well understood. Sr is known to be preferentially partitioned into aragonite since it easily replaces Ca in the aragonite structure (*Ortega et al, 2005*). Significant amounts of Na and Mg maybe sourced from the sea in comparison to Sr but Sr maybe preferentially incorporated into aragonite compared to Mg and Na. This line of evidence, although plausible is not very convincing.

Over the open ocean, the main physical driver of sea salt emissions is the surface wind speed (*Blanchard, 1963*). Because of shortcomings in observations, there is low confidence on the analysis of surface wind strengths (*IPCC, Fifth Assessment Report, Working Group I: The Physical Science Basis, 2013*). Sea salt emissions are also dependant on SST (*Martensson et al, 2003; Hultin et al, 2010*). A general increase in sea salt aerosol emissions from 1900 to 2000 have been suggested by a number of studies (*Latham and Smith, 1990; Penner et al, 2001; Mahowald et al, 2006*). However, the SST control on sea salt emissions is less well understood. SST is thought to influence the size of sea salt aerosol particle formation with reduction in sea salt aerosol particle formation, atleast in the smallest

(ultrafine) size range, with increasing SST (*Martensson et al, 2003; Hultin et al, 2010*). Since the Sr/Ca ratios in the stalagmite decrease with SST it implies that either (i) increasing SST is reducing sea surface aerosol particle formation and/or (ii) the strength of onshore winds bringing sea surface aerosol particles to the cave site have been decreasing from 1900 to 2000 years. Further work on controls of aerosol particle formation and measurements and analysis of wind speeds in this region are required to analyse these controls on Sr/Ca concentration in the stalagmite.

6.6.3 Sr/Ca and the land temperature record

Sr/Ca significantly correlates with the land temperature anomaly record (figure 6.5). Section 4.8.1 shows that the cave is consistently at the annual average outside temperature (accuracy of 0.53°C). This suggests that the cave air temperature may reflect the annual outside temperature variation.

Most studies on the temperature dependence of Sr partitioning into aragonite are based on biological precipitation of aragonite and the influence of temperature on Sr partitioning is still debated (for example, *Bath et al, 2000; Rosenthal et al, 2006*). *Kinsman and Holland, 1969* conducted laboratory experiments on the temperature dependence of Sr partitioning into inorganically precipitated aragonite.

Calcium carbonate was precipitated from seawater by the slow addition of dilute Na₂CO₃ solutions. The distribution coefficient was found to decrease linearly with increasing temperature from 1.7 +/-0.04 at 16°C to 0.88 +/-0.03 at 80°C. Up to 30°C a mixture of aragonite and calcite were precipitated, while above 30°C only aragonite was precipitated (figure 6.6).

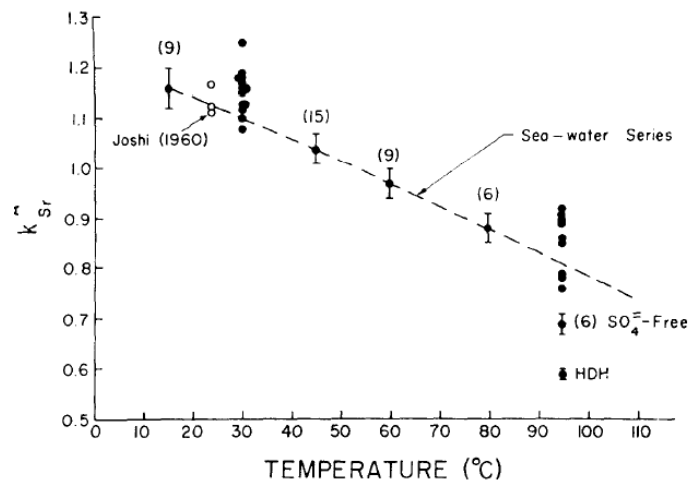


Figure 6.6: The distribution coefficient of strontium into aragonite between 16°C and 96°C: in runs marked 'sea water series' aragonite was precipitated from sea water; in runs marked 'SO₄²⁻ free' aragonite was precipitated from sulphate-free artificial sea water; in runs marked 'HDH' aragonite was precipitated from calcium-strontium-chloride-trichloroacetate solutions (see *Holland et al, 1963*). Numbers in parentheses indicate number of data points included in average value. Data points at 24°C from *Joshi, 1960*. (Figure and description are from *Kinsman and Holland, 1969*).

The distribution coefficient for Sr/Ca in this sample is 2.7 (see Chapter 5), which is higher than that suggested by the experiment of *Kinsman and Holland, 1969*. Furthermore, the slope of the line generated by the *Kinsman and Holland* study was -0.004 whereas for this sample, the slope is between -8 and -9. The trend of the slope is in the same direction for both studies but the slope magnitude for this study is several orders higher than predicted by the laboratory experiment (figure 6.5).

This difference may arise for several reasons:

- i) The solution chemistry used to precipitate aragonite in *Kinsman and Holland, 1969* does not mimic drip water.
- ii) The experiment has not been conducted in cave analogue conditions.
- iii) They get a mixture of calcite and aragonite till 30°C while the sample stalagmite is composed wholly of aragonite and has precipitated at 25°C.

No other laboratory experiments for Sr partitioning into inorganically precipitated aragonite by CO₂ degassing from solutions with ionic strengths typical of drip waters have

been published. Further laboratory analogue experiments are required to test if there is temperature dependent distribution of Sr/Ca in aragonite.

In addition to sea salt aerosol and the bed rock, dust maybe a source for Sr/Ca. The closest sources of dust to the west coast of India are the Thar Desert and the Arabian Peninsula to the northwest of India and parts of the African continent to the west of India. *Grini et al, 2005* use Dust Entrainment and Deposition (DEAD) models to shows that dust sourced from these regions can be deposited on the west coast of India through dry (wind carried) and wet (through rainout) depositions. Sr isotopic analysis can be used in the future to identify the source of Sr in this stalagmite (*Goede et al, 1998; Frumkin and Stein, 2004*).

There are other trace element ratios that also show correlation with land temperature, in as U/Ca, Mn/Ca and Na/Ca. Christopher Day (personal communication) finds that temperature shows a larger influence on Sr partitioning into aragonite than calcite from cave analogue laboratory experiments on aragonite.

6.6.4 Trace element and instrumental rainfall records

Finch et al, 2003 and *Jamieson et al, 2016* show that in aragonite stalagmites collected from South Africa and Belize, rainfall is the dominant control on trace elements in the stalagmite samples. Calcite stalagmite samples from China, i.e. regions with monsoonal climates, rainfall amount (usually defined as wet and dry periods) has been found to be the dominant control on trace element ratios (for example, *Johnson et al, 2008*). For these reasons, in this sample from Akalagavi cave, it was expected that rainfall would be a dominant control on trace element measurements.

The trace element measurements from calcite stalagmites from monsoonal climates show a dominant PCP control (for example, *Johnson et al, 2006; Cruz et al, 2007; Griffiths et al, 2010*), which effects trace elements ratios of Mg/Ca, and Sr/Ca. *Jamieson et al, 2016* use

U/Ca and $\delta^{13}\text{C}$ to show a PAP control on U/Ca in the aragonite stalagmite from Belize. However, no Prior Aragonite Precipitation control is observed for carbonate precipitation during the monsoon rainfall months in this stalagmite. It is unlikely that there is Prior Calcite Precipitation from the drip waters feeding this stalagmite (see section 5.6.2).

The lack of PCP/PAP control on the trace element ratios of this stalagmite may explain the lack of trace element response to rainfall amounts in this stalagmite.

Day and Henderson, 2013 measure temperature and growth rate controls on trace element ratios but they find that the fraction of Ca remaining in solution is likely to be the dominant control on Mg and other trace elements in their cave analogue laboratory experiment on calcite. Similar studies are required for aragonite.

6.7 Conclusion

This study gives annual resolution trace element ratios from an aragonite stalagmite. However, R^2 values indicate that no single process dominantly controls multiple trace element distribution. There is a strong relationship between P/Ca and stable isotope measurements showing that stable isotopes are controlled by processes other than the kinetics of oxygen isotope precipitation alone. Growth rate (measured through lamina width) is not a significant control on the trace element distribution in this sample; instead there is a stronger control of temperature on trace element ratios. SST and land temperature appears to be a dominant influence, particularly on Sr/Ca measurements. However, further laboratory studies on Sr isotopes and Sr partitioning into aragonite are required to understand the influence of source, SST and land temperature on Sr/Ca ratios.

Chapter 7

Stable Isotope and Trace Element Records from a Calcite Stalagmite

Abstract

Oxygen isotopes from speleothems in tropical regions are traditionally used to understand variation in past rainfall. However, there is increasing debate about the interpretation of oxygen isotope variation with respect to rainfall amount. In this study, I use trace element ratio measurements in a stalagmite from peninsular India to decouple local hydrological changes from the larger circulation pattern changes that are thought to be represented by oxygen isotopes.

Published speleothem records of $\delta^{18}\text{O}$ from peninsular India extend from the modern to 1200 years BP. This study extends that record, with coverage of a time period between 3130 years BP and 2100 years BP, combining trace element ratios and $\delta^{18}\text{O}$ as proxies for past rainfall.

Trace element measurements of Ba/Ca, Sr/Ca and S/Ca suggest that dissolution of sulphates in the epikarst may control their distribution in the stalagmite. However, drip water measurements are required to corroborate this interpretation. Higher P/Ca and U/Ca ratios have been interpreted to indicate discrete periods of high rainfall and two sustained periods of high rainfall between 3100 and 2900 years BP and between 2700 and 2400 years BP. Drip water P/Ca and U/Ca measurements are required to confirm this interpretation.

Correlation analysis between the P/Ca and U/Ca records and the $\delta^{18}\text{O}$ record suggest that rainfall amount is not the dominant influence on $\delta^{18}\text{O}$ ratios in this stalagmite. The

systematic offset in the mean $\delta^{18}\text{O}$ of this record and those from stalagmites from Oman and eastern China suggest that source of moisture and air mass trajectories are a likely long term control on $\delta^{18}\text{O}$ composition at these cave sites. This interpretation is supported by previously published modelling results.

7.1 Introduction

$\delta^{18}\text{O}$ records from speleothems in the Asian monsoon region are used to assess changes in past climate, such as: (i) drier and wetter periods in the past (ii) whether Asian Monsoon subsystems varied in phase, and (iii) the extent to which Asian Monsoon was affected by high Northern latitude climate (*He et al, 2004; Hong et al, 2005; Wang et al, 2005; Liew et al, 2006; Zhou et al, 2007; Fleitmann et al, 2007; Maher, 2008; Dong et al, 2010*).

There is, however, increasing debate about the interpretation of $\delta^{18}\text{O}$ records from speleothems in monsoon regions. They have been variously interpreted as recording the amount of rainfall (for example, *Yadava et al, 2004; Berkelhammer et al, 2010*), change in seasonality of precipitation (for example, *Wang et al, 2001*) and hence summer monsoon intensity (for example, *Cheng et al, 2009; Liu et al, 2014*), fraction of water vapour removed from air masses (for example, *Yuan et al, 2004*), and moisture source (for example, *Maher, 2008; Maher and Thompson, 2012*).

Oxygen in speleothems is derived from moisture that may have travelled several hundred kilometres before raining in the cave region, thus its isotopic composition is a result of a number of processes that are not restricted to the cave region being studied. In contrast, trace elements in speleothems are usually sourced from vegetation, soil and lithology of the immediate cave region, and variations in many trace elements in speleothems are thought to reflect variations in local hydrological conditions (see *Fairchild and Treble, 2009*). Combining stable isotopes and various trace element ratios from speleothems can help

understand variation in local and regional precipitation and give a more rigorous interpretation of $\delta^{18}\text{O}$ records.

Compared to $\delta^{18}\text{O}$, relatively few studies have measured trace element incorporation into speleothems in tropical monsoon regimes, but most of those that have, suggest that Prior Calcite Precipitation (PCP) is the dominant control on trace element concentration. PCP is considered to be a robust paleo-aridity indicator. For example, *Johnson et al, 2006* show that high values of Mg/Ca, Sr/Ca, Ba/Ca and $\delta^{13}\text{C}$ in speleothems values can be explained by two related processes that occur during dry periods (i) increased Prior Calcite Precipitation (PCP) in the epikarst or the cave ceiling and/or (ii) a greater degree of CO_2 degassing and calcite precipitation on stalagmite surfaces when drip rates are lower. The second process can occur even when the drip water chemistry is relatively invariant through the year. Similar to the *Johnson et al, 2006* study, other studies have compared annual to sub-annual changes in speleothem trace element composition to changes in climate or environmental parameters including hydrology (for example, *Fairchild et al, 2001 Treble et al, 2003; Treble et al, 2005; Borsato et al, 2007*).

Upscaling these processes to allow interpretation of these proxies over longer time scales has proven to be more difficult challenge. For example, Mg/Ca and Sr/Ca in speleothems are controlled by a number of variables that probably operate at different timescales, including composition of drip water (influenced by soil chemistry), cave air temperature and growth rates (*Huang and Fairchild, 2001; Treble et al, 2003*). Despite these studies, there are a number of examples of previous work that have successfully used stalagmite trace element ratios to assess long-term change in rainfall. For instance, a study by *Griffiths et al, 2010* extrapolated PCP control on Mg/Ca, Sr/Ca, $\delta^{13}\text{C}$ and their correlation with $\delta^{18}\text{O}$ on a longer time scale (last 12 kilo years BP) to reconstruct rainfall from a stalagmite from Indonesia. In another example, *Cruz et al, 2007*, explore trace element ratios in a stalagmite from Botuvera cave, Southern Brazil as a proxy for local rainfall recharge during the last 116 kilo

years BP. They found that higher Mg/Ca and Sr/Ca values are associated with lower levels of recharge into the karstic aquifer, resulting in PCP in the unsaturated zone above the cave during dry climate periods. These trace element ratios vary consistently with $\delta^{18}\text{O}$ in the same stalagmite during the last glacial period.

In this chapter, I measure stable isotope and trace element variations in a stalagmite from peninsular India that grew between 3130 years BP and 2100 years BP. I explore the possible climatological interpretations of $\delta^{18}\text{O}$ variations in the stalagmite and use trace element ratio measurements to tighten the interpretation of $\delta^{18}\text{O}$ and understand changes in peninsular Indian climate during this period.

7.2 Location and climate

The sample was removed from Kotumsar cave by collaborators from the Physical Research Laboratory (PRL, India). The cave entrance is at $18^{\circ} 52' 89''$ N and $81^{\circ} 56' 05''$ E and lies at an altitude of 560 m asl near Jagdalpur town, Bastar district, Chattisgarh state. Further details of the cave site are given in section 2.5.

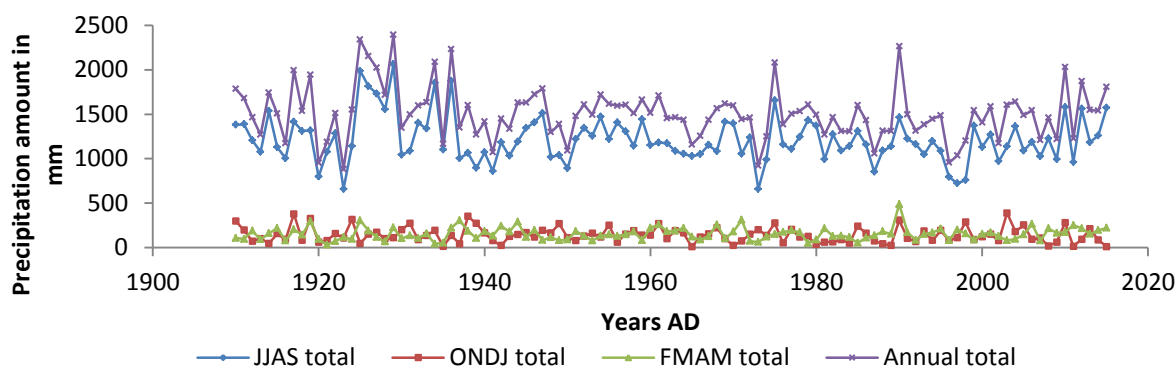


Figure 7.1: Monsoon (JJAS), Winter (ONDJ) and Summer (FMAM) total precipitation amount data in mm for Jagdalpur plotted against time. Data for Jagdalpur from GHCNM sourced from KNMI Explorer.

The cave receives nearly 1300 mm of total rainfall on average each year and shows typical monsoon climate with a single rainy season. More than 80% of the rain falls between June and September (figure 7.1; raw data in table 15 of Appendix III).

The average annual temperature is 25°C (figure 7.2, raw data in table 16 of Appendix III). The minimum to maximum temperature range in a single season, often between day and night temperatures, is 20°C for summer (February, March, April and May or FMAM) and winter (October, November, December and January or ONDJ) but reduces to 10°C during the rainy months (June, July, August and September or JJAS).

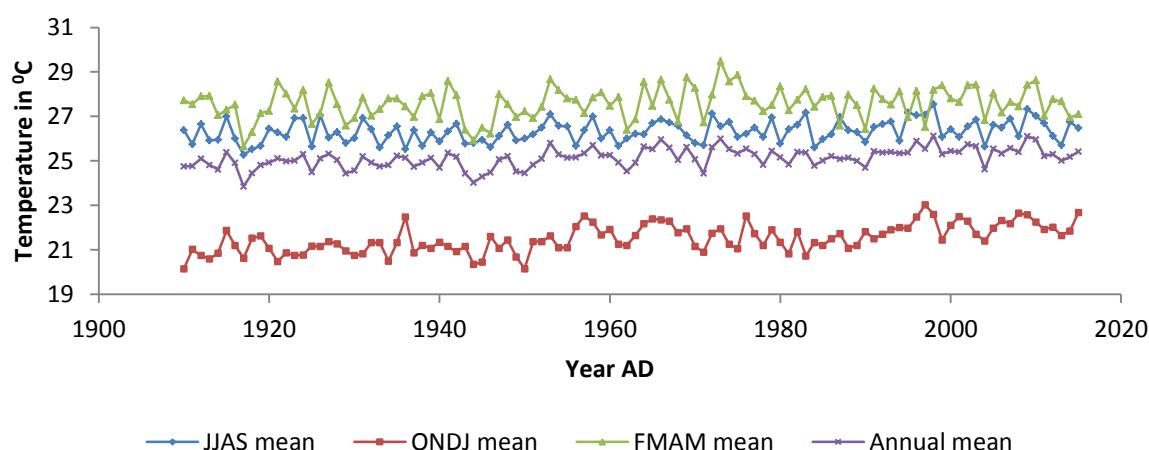


Figure 7.2: Monsoon (JJAS), Winter (ONDJ) and Summer (FMAM) temperatures in °C for Jagdalpur plotted against time. Data for Jagdalpur from GHCNM sourced from KNMI Explorer.

7.3 $\delta^{18}\text{O}$ in modern precipitation

Jagdalpur is the closest weather station to the cave, located ~30 km from the cave site, with rainfall amount data whereas Hyderabad, located 500 km to the southwest of the cave, is the closest GNIP station with both rainfall and $\delta^{18}\text{O}$ data (figure 2.8). Although Hyderabad GNIP station is located 500 km from the cave sit, figure 7.3 shows that the pattern of rainfall (i.e. months of rainfall) is similar in Jagdalpur and Hyderabad. Both locations also have similar moisture sources and trajectories. Therefore, GNIP data from Hyderabad has been used to understand variation in the $\delta^{18}\text{O}$ composition of rainfall at the Kotumsar cave site.

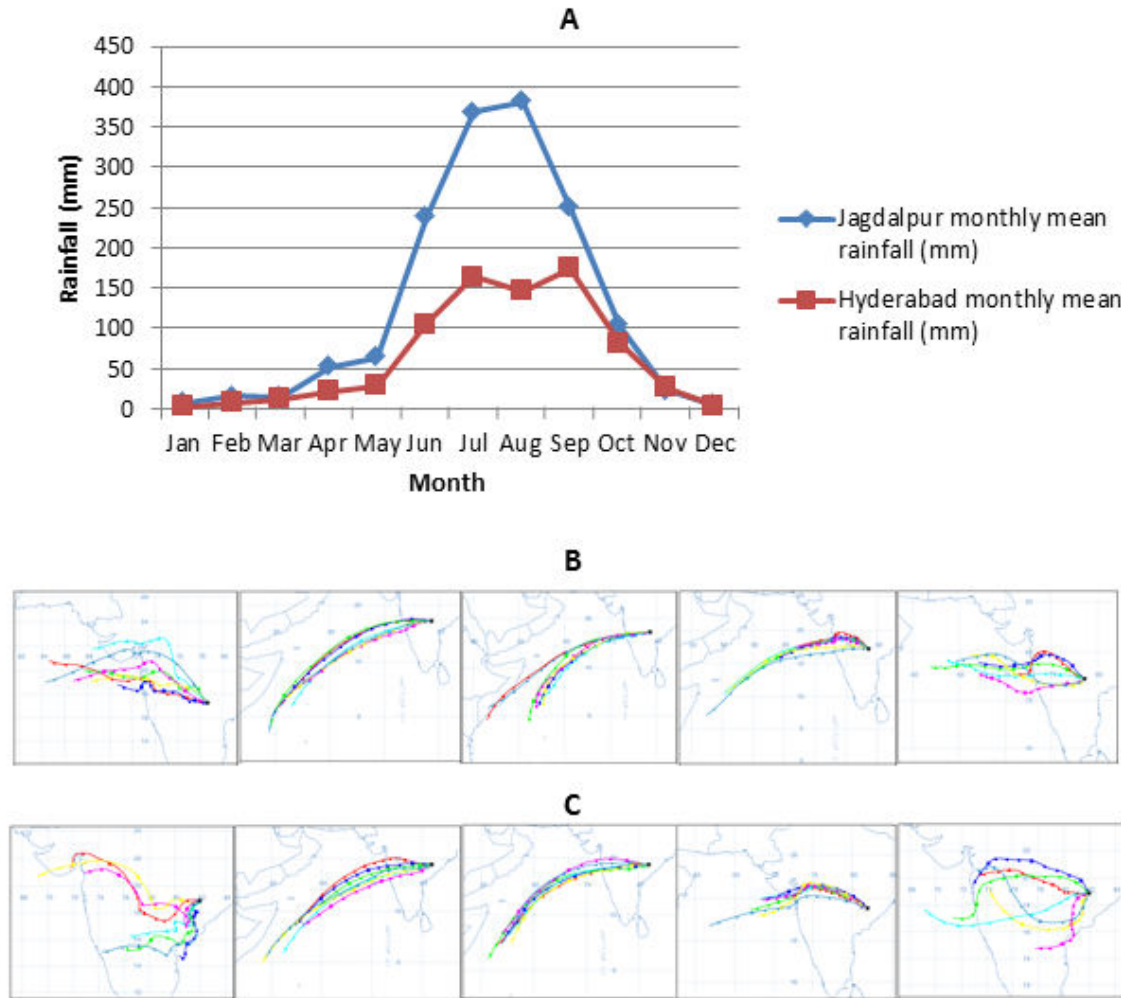


Figure 7.3: (A) Comparison of rainfall patterns and amounts in Jagdalpur and Hyderabad. Rainfall amounts are monthly averages from years 1910 to 1984. GHCNM data sourced from KNMI Explorer (B) Nine days of backward wind trajectories for Hyderabad for the monsoon rainfall months of June, July, August, September and October (from left to right) of 2016. (C) The same nine days of backward wind trajectories for Jagdalpur for the monsoon rainfall months of June, July, August, September and October (from left to right) of 2016. Wind trajectories plotted using Hysplit.

Figure 7.4 and table 7.1 show that,

- i) 65% of the rainfall is during the monsoon rainfall months of June, July, August and September (JJAS) with an average $\delta^{18}\text{O}$ of -3.23‰ vSMOW.
- ii) 35% of the rain falls during the non-monsoon rainfall months with an average $\delta^{18}\text{O}$ of -4.50‰ vSMOW.

- iii) Of the non-monsoon rainfall, ~20% of the rain falls during the months of May and October, immediately preceding and succeeding the monsoon months. The average $\delta^{18}\text{O}$ value of May to October rainfall is -3.60‰ vSMOW.
- iv) The remaining 15% precipitation occurs during months of January, February, March, April, November and December and has an average $\delta^{18}\text{O}$ of -4.56‰ vSMOW.

It is possible that the annual average rainfall $\delta^{18}\text{O}$ composition may reflect a change in the length of the monsoon season (lower $\delta^{18}\text{O}$ with increased rainfall in May and October) but it is likely that this signal, which is less than 1‰ vSMOW difference in $\delta^{18}\text{O}$ will be averaged by groundwater since it represents 20% of the rainfall compared to the 65% of rainfall during the monsoon months of JJAS. Similarly, it is unlikely that the remaining 15% of rainfall will affect the groundwater averaged-drip water signal, particularly since it is the December month rainfall $\delta^{18}\text{O}$ composition of -8.44‰ vSMOW driving the $\delta^{18}\text{O}$ composition to the negative value of -4.56‰ vSMOW but is only 5% of the total rainfall in Jagdalpur. Figure 7.5 shows that the monsoon, post-monsoon and pre-monsoon rainfall measurements from the Hyderabad GNIP station fall on the Global Meteoric Water Line (GMWL).

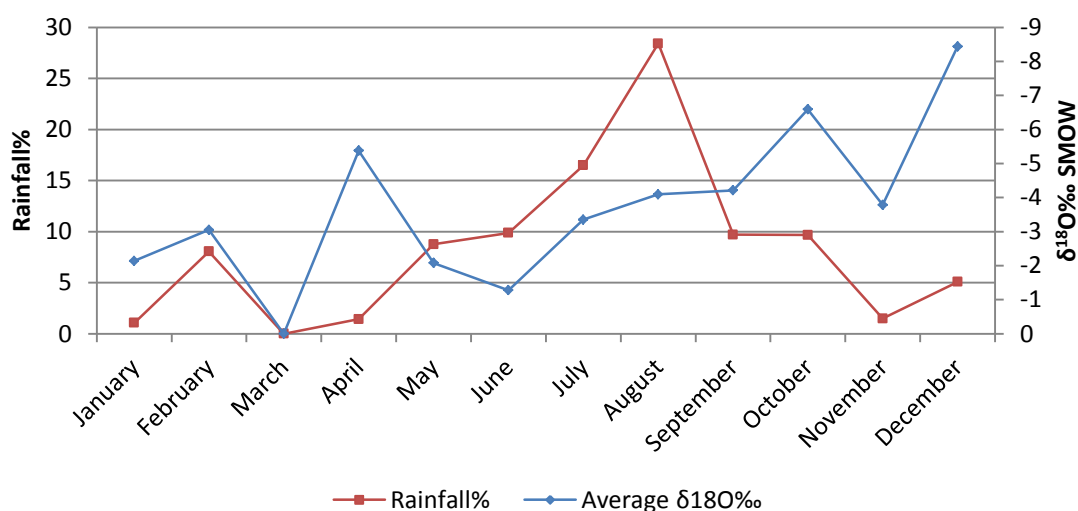


Figure 7.4: Monthly average rainfall, expressed as a percentage of annual rainfall, plotted against oxygen isotopic data for Hyderabad. Oxygen is on a reversed scale. Data is from WISER. See table 7.1 for details.

Month	No. of samples	Average $\delta^{18}\text{O}$ ‰	Average δD ‰	Average rainfall (mm)	Rainfall%	Average Temperature ($^{\circ}\text{C}$)
January	1	-2.14	-1.20	11	1.06	22.90
February	1	-3.05	-6.50	81	8.06	25.35
March	-	-	-	-	-	-
April	1	-5.38	-32.90	14	1.43	1.45
May	1	-2.08	-9.50	88	8.75	32.23
June	3	-1.28	-2.57	99	9.87	29.00
July	3	-3.35	-18.10	166	16.48	27.03
August	3	-4.09	-23.73	286	28.42	26.13
September	4	-4.21	-25.80	98	9.70	26.40
October	4	-6.59	-42.05	97	9.67	26.03
November	3	-3.79	-24.83	15	1.49	24.50
December	1	-8.44	-60.50	51	5.07	28.90

Table 7.1: Average monthly rainfall percentages and associated rainfall oxygen and deuterium isotopic compositions for Hyderabad.

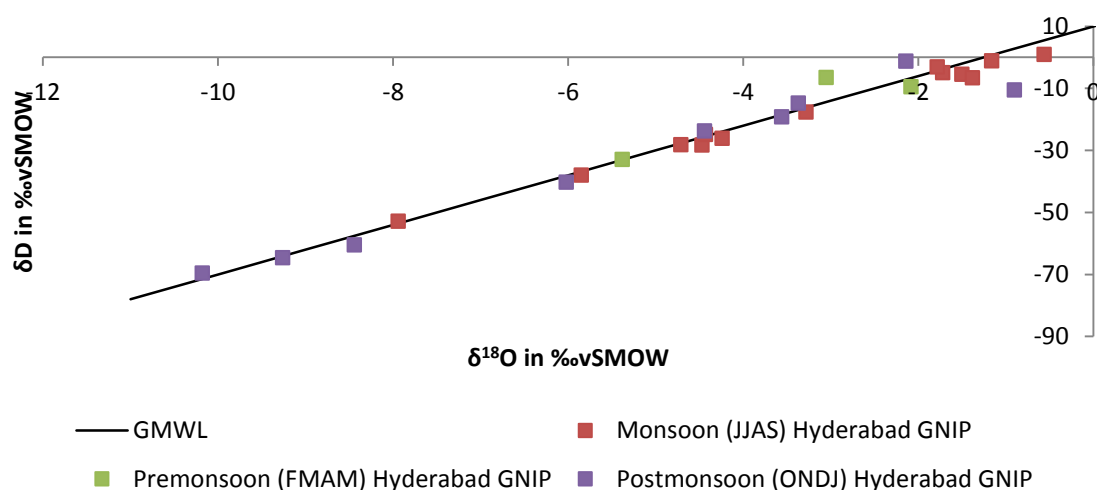


Figure 7.5: Rainwater stable isotope measurements plotted against the Global Meteoric Water Line (GMWL).

Discretely sampled monthly air parcel trajectories shown in figure 7.6 indicate that the moisture source for the rainfall months of June, July and August is the west i.e. the Arabian Sea and the western Indian ocean. The rainfall of these 3 months has an average $\delta^{18}\text{O}$ value of -3.89‰ vSMOW. For the remaining months, the moisture source is the east and the south. The sources of moisture for these months include continental recycling, Bay of Bengal and the Indian ocean. The rainfall for the remaining months has an average $\delta^{18}\text{O}$ value of -4.09‰ vSMOW. The difference between the $\delta^{18}\text{O}$ compositions of the two sources is less than 1‰ vSMOW and is unlikely to reflect in the ground water averaged-drip water signal.

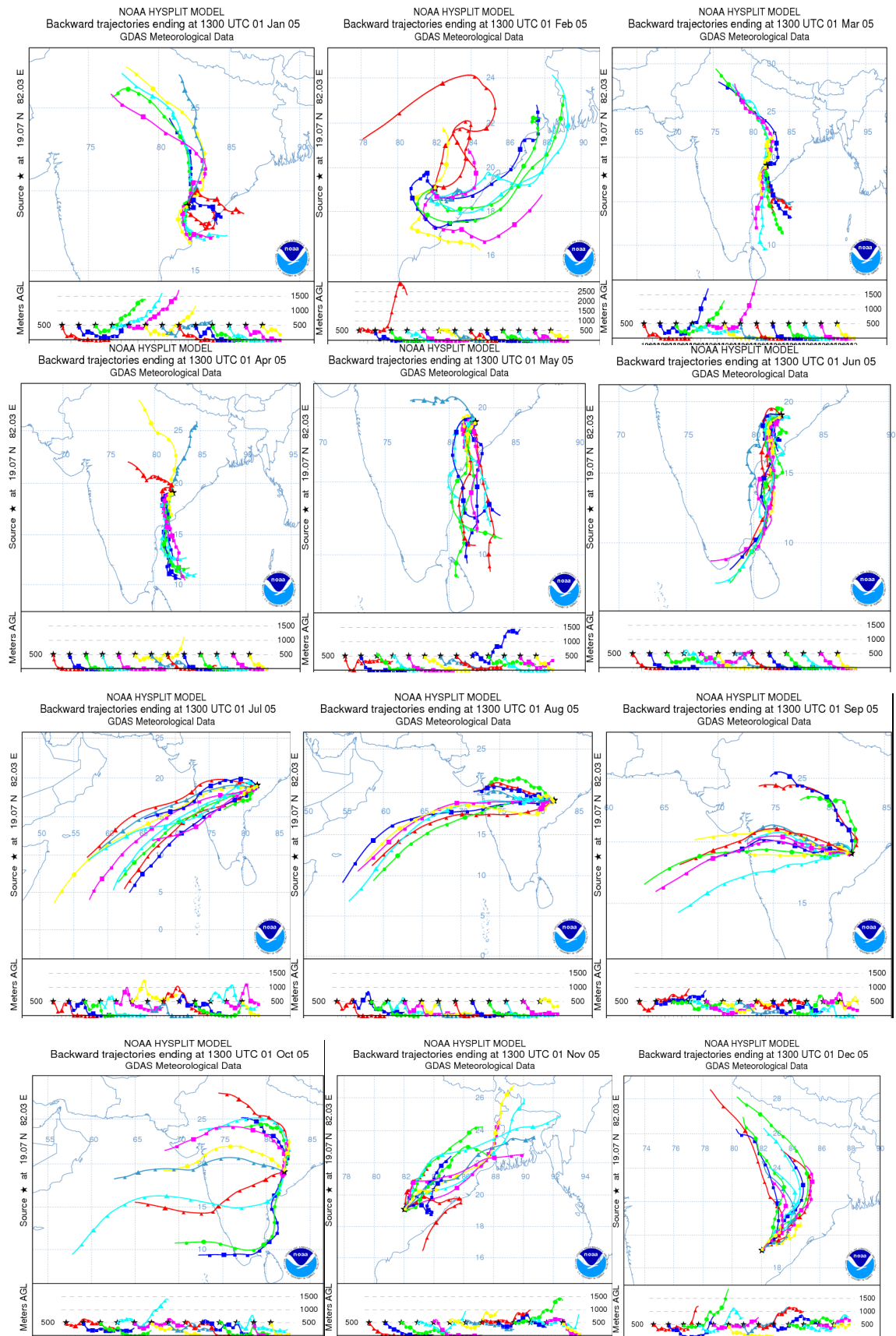


Figure 7.6: Backward air parcel trajectories for every month of the year 2005. Hysplit models run for 72 hours ending on 1300 hours of the 1st of the respective month.

The investigation of controls on the $\delta^{18}\text{O}$ composition of rainwater at the Kotumsar cave site indicates that the $\delta^{18}\text{O}$ signal of ground water is likely to be that of the monsoon months of JJAS and this moisture is predominantly sourced from the Arabian Sea and West Indian ocean.

7.4 Sample, subsampling and analytical methods

Subsections below describe methods used for subsampling and measurements of mineralogy, stable isotope and trace element geochemistry. The software and methods used for lamina count and lamina thickness measurements are also described.

7.4.1 Sample description

The sample was collected and cut into a slab ~2 inches thick by collaborators from PRL, India. The sample has not been polished. The cut sample slab was shipped to the University of Oxford and all further subsampling and measurements were made on this slab section. The sample is 28 cm long and 10 cm wide. It is beautifully laminated with alternating dark and light layers (figure 7.7).

- i) The sample shows 3 sections of texturally disturbed growth that have been shown with green boxes in figure 7.7.
- ii) Beyond subsample Nk162, there appears to be an increase in precipitation on the left hand flank of the sample, particularly the sections of the stalagmite between subsamples Nk162-Nk180, Nk233-Nk242 and Nk263-Nk270. This growth on the left hand flank results in a wider horizontal growth surface by Nk272.
- iii) There is a section of dark, nearly black, layers between subsamples Nk180 and Nk194, following which the instances of dark black layers increase.
- iv) The layers between Nk217 and Nk238 show diffuse layer boundaries along the left hand flank of the sample.

- v) Subsample Nk242 is from a layer of white opaque material that is different from the crystalline calcite seen in the non-texturally disturbed parts of the stalagmite. It shows increased growth and a diffuse growth boundary along the flank.

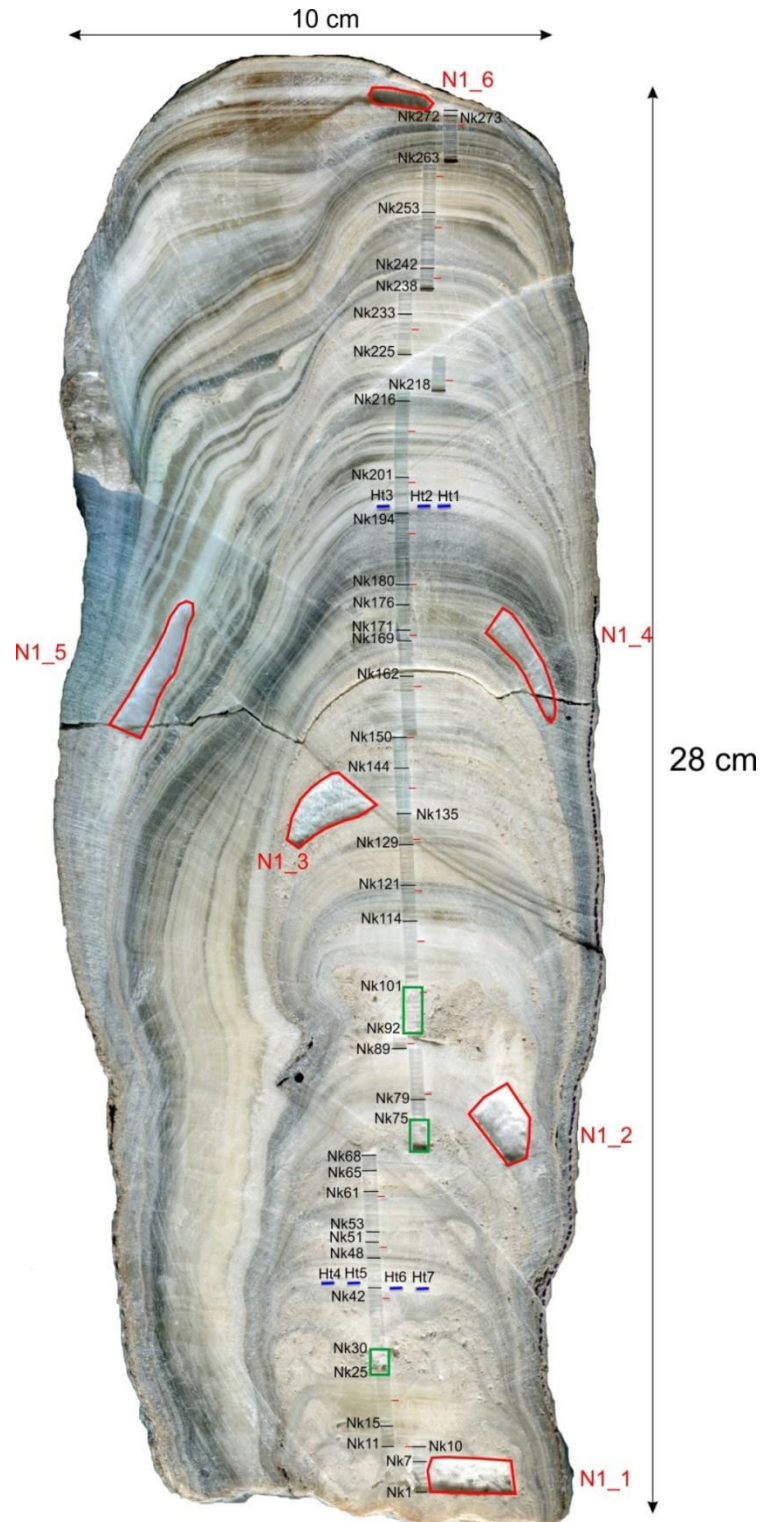


Figure 7.7: N1_1 to N1_6 in red mark the 6 subsamples milled for U-Th dating. Subsamples for stable isotopes and trace elements were milled at mm resolution. Sample numbers that mark significant changes in texture or growth axis are marked on the figure in black. Red lines on the trench mark every 10th sample. The blue lines indicate subsamples milled for 'Hendy' tests. The green boxes indicate zones of texturally disturbed growth.

7.4.2 Mineralogy

Three subsamples (NKF1, NKF2 and NKF3), one each from the bottom, middle and top of the sample, were measured using FTIR to determine their mineralogy (see section 3.3.6 for FTIR method). Since there is no visible indication of a change in mineralogy in the sample or in stable isotope and trace elements measurements, the three subsamples were sufficient to confirm the dominant mineralogy of the sample.

7.4.3 Lamina count and lamina thickness measurements

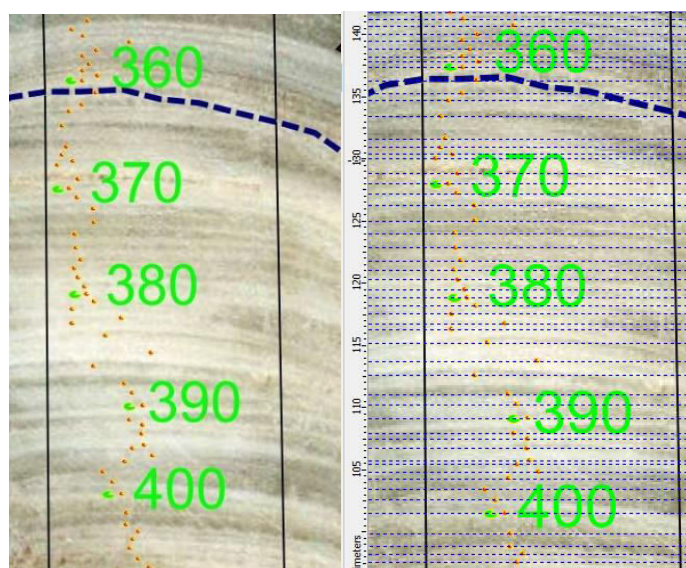


Figure 7.8: A section of the sample showing lamina counting and lamina thickness measurements using CorelDRAW. The green pointer and adjoining count mark every 10th lamina.

Lamina counting and lamina thickness measurements were made using CorelDRAW software and a high resolution scan of the sample. The base of every dark lamina was clearly marked with a flat marker point (figure 7.8). This gives the lamina count. Lamina thickness measurements were made using a feature of CorelDRAW that allows for lines to be dragged precisely to the top of the marker, the thickness can then be read off the scale to the left of

the software. The scale is then converted from an image scale to the sample scale to give actual lamina thickness measurements (figure 7.8).

7.4.4 U-Th dating

Six subsamples were dated using the U-Th method (see figure 7.7 for locations of these dates on the sample). ~ 300 mg of powder from each dating site on the stalagmite was extracted using a Dentist's drill and spiked with a ^{229}Th - ^{236}U mixed spike. The U and Th aliquots were separated broadly following the ion-exchange method of other carbonate samples handled at Oxford which is a modified version of the chemistry originally described by *Edwards et al, 1987*. The samples were analysed by a Nu Instruments MC-ICPMS at Oxford. Details of the instrument have been discussed in *Belshaw et al, 1998*. U concentrations were measured using a bracketing standard approach (*Robinson et al, 2002*). Th was measured against in-house Th standards (*Mason and Henderson, 2010*). The resulting U-Th concentration data was reduced to ages using an in-house software called Donkey. Half-lives, as assessed by *Cheng et al, 2013*, were used for calculations. The age data was further corrected for the presence of detrital Th using bulk detrital value of (5.38E-06, +5.38E-06, -4.84E-06; *Hellstrom, 2006*). Error propagation was done using Monte-Carlo simulations. The error has been calculated on 95% of the total number of measurements lying within a 2σ confidence interval. Further details of dating procedures are given in section 3.3.10. StalAge software was used to construct an age model for the sample (*Scholz and Hoffmann, 2011*).

7.4.5 Stable isotope and trace element measurements

Subsamples were milled from a trench ~3 mm in width using a New Wave Micromill. A total of 273 subsamples of ~1.5 mg were taken using a 0.8 mm drill bit at a resolution of 1 mm. Each subsample of 1 mm was taken in 4 increments of 0.25 mm each to reduce edge bias from the drill bit (see section 3.3.4). Stable isotope and trace elements were analysed from

aliquots of these subsample powders. This gives a subsampling resolution of 1 to 13 years per mm based on the variable growth rate of the sample.

Aliquots of the subsample powders were sent to PRL for stable isotope analysis, where $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values of carbonates were measured on Delta-plus Isotope Ratio Mass Spectrometer (IRMS) attached to Gas Bench II. For internal calibration, laboratory standard MMB (Makrana marble = 99.9% purity) was used. The values of MMB are $\delta^{18}\text{O} = -10.7\text{‰}$ and $\delta^{13}\text{C} = 3.9\text{‰}$. Several repeat measurements of random samples gave reproducibility of 0.04‰. The external precision of measurements were $\delta^{18}\text{O} = 0.06\text{‰}$ and $\delta^{13}\text{C} = 0.04\text{‰}$.

Trace elements on the subsample aliquots were measured on a Thermo Element 2 ICPMS (see section 3.3.9). Trace element ratios of Y/Ca, Ba/Ca, U/Ca, Na/Ca, Mg/Ca, P/Ca, S/Ca, Co/Ca, Rb/Ca and Sr/Ca were measured. Many subsample measurements of S/Ca and Co/Ca were below detection limit. Detection limits and precision percentages are given in the result table (table 20 of Appendix III).

7.5 Results

7.5.1 Mineralogy

The FTIR spectra of calcium carbonate phases of calcite and aragonite have been given in a paper by *Vagenas et al, 2003*. They find an absorption band for calcite at 713 cm^{-1} and for aragonite a double absorption peak at 700 cm^{-1} and 713 cm^{-1} respectively. These absorption bands have been used to assess the mineralogy of the 3 subsamples NKF1, NKF2 and NKF3 from the stalagmite. All three subsamples show a signal typical of calcite (figure 7.9). Since this specific instrument has not been tested and calibrated for speleothem calcite and aragonite powders, it remains possible that the sample is not pure calcite, but no evidence for a second phase is distinguished in the data.

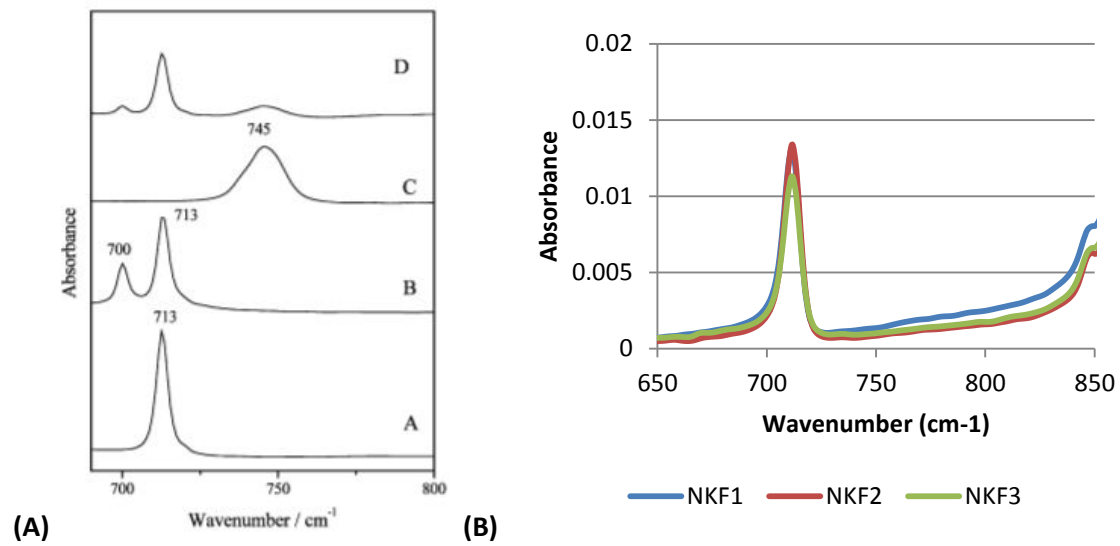


Figure 7.9: (A) Absorption FTIR spectra of (A) calcite; (B) aragonite; (C) vaterite (D) ternary mixture of 0.2 mg calcite, 0.1 mg aragonite and 0.15 mg vaterite (*Vagenas et al, 2002*). (B) Absorbance FTIR spectra for subsamples NKF1, NKF2 and NKF3 from this study. NKF2 targets the texturally disturbed part of the sample. All subsamples have conspicuous absorbance peaks at 713/cm⁻¹. The peaks at 700/cm⁻¹ (typical of aragonite) and the peak at 745/cm⁻¹ (typical of vaterite) are absent. Raw data in table 18 of Appendix III.

7.5.2 Lamina thickness measurement

Lamina thickness measurements have been given in figure 7.10 and table 19 of Appendix III. Every instance of disturbed growth has been considered to be one lamina. Lamina number was counted from the oldest part of the sample towards the younger part of the sample.

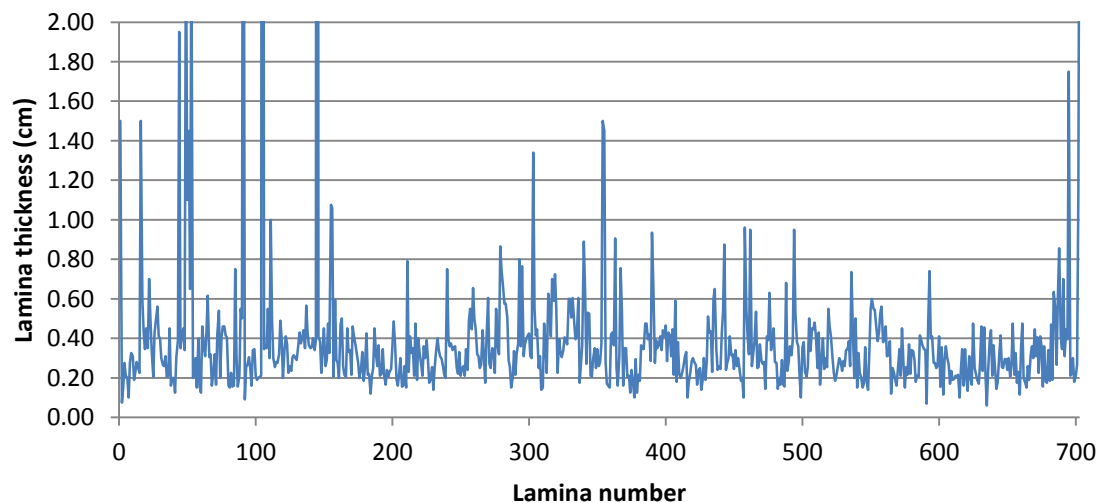


Figure 7.10: Lamina thickness (cm) has been shown against lamina count. Each section of texturally disturbed growth has been considered to be a single lamina.

7.5.3 Age model

Six subsamples were measured for U-Th ages. These indicate that the sample grew for a period of ~1200 years between 3218 and 1964 years BP.

Figure 7.11 and table 7.2 show that all ages except subsample N1_4 are in chronological order. The subsamples have low U concentrations of 58 to 109 ppb. The sample is young in age (~3000 years old) giving a short time for decay of ^{238}U to ^{230}Th and consequently low ^{230}Th concentrations. These factors combine with high detrital ^{232}Th content of 0.6 to 3.9 ppb to give age errors of 320 to 700 years for this stalagmite (see Appendix 1 for further work on age errors associated with this sample).

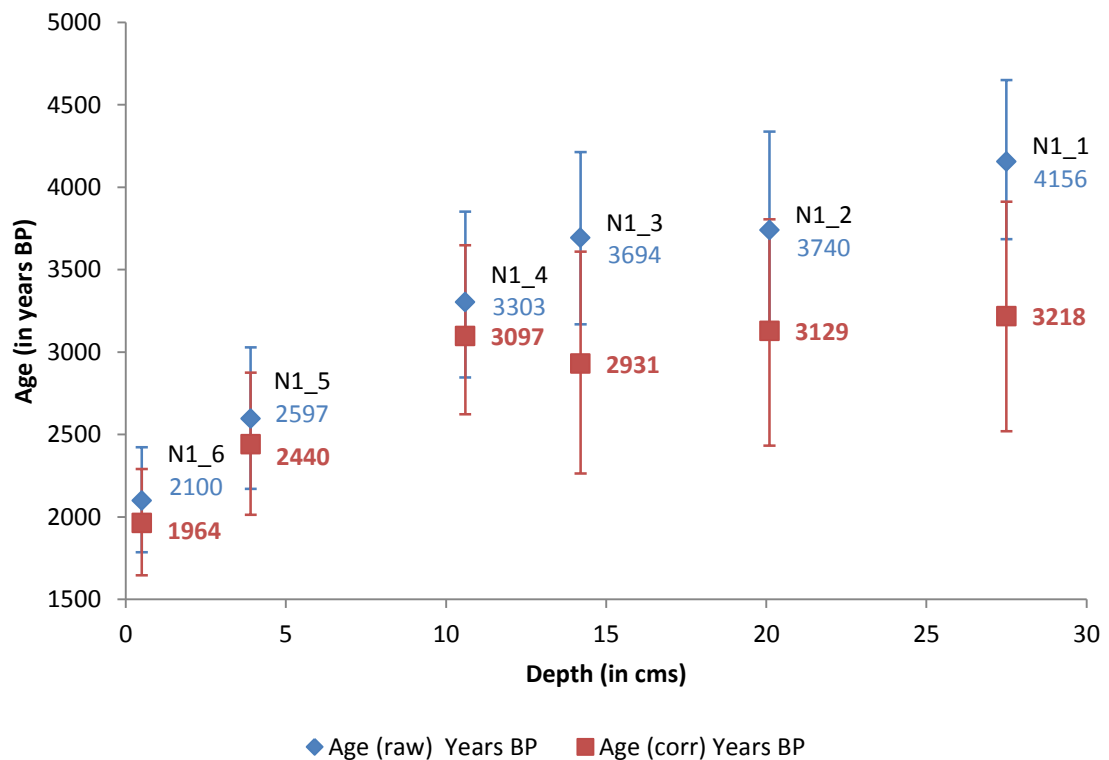


Figure 7.11: Raw and corrected ages plotted against depth in the stalagmite, with 95% confidence limits.

Sample	Depth cms	²³⁸ U ppb	²³² Th ppb	²³⁰ Th ppb	d ²³⁴ U	²³⁰ Th/ ²³² Th atomic	²³⁰ Th/ ²³² Th activity	²³⁰ Th/ ²³⁸ U activity	Age (raw) Years BP	+	-	Age (corr) Years BP	+	-
N1_1	27.5	79.5		3.9	7.3E-05	481.2	1.9E-05	3.5	5.6E-02	4156	494	471	3218	694
N1_2	20.1	58.1		1.8	4.9E-05	487.8	2.7E-05	4.9	5.1E-02	3740	597	600	3129	675
N1_3	14.2	71.3		2.8	5.9E-05	479.4	2.1E-05	3.9	5.0E-02	3694	519	526	2931	677
N1_4	10.6	75.7		0.8	5.6E-05	479.0	7.0E-05	12.9	4.5E-02	3303	549	458	3097	551
N1_5	3.9	78.5		0.6	4.6E-05	488.6	7.2E-05	13.4	3.6E-02	2597	432	426	2440	435
N1_6	0.5	109.7		0.8	5.2E-05	467.7	6.8E-05	12.6	2.9E-02	2100	323	315	1964	326
														699
														697
														667
														474
														428
														319

Table 7.2: U and Th concentrations and isotopes ratios, and derived age data for subsamples N1_1 to N1_6. The age data was further corrected for the presence of detrital Th using bulk detrital value of (5.38E-06, +5.38E-06, -4.84E-06; *Hellstrom et al, 2006*). Ages are given in years BP i.e. relative to 1950.

The sample also shows couplets of alternating dark and light layers thought to represent one year's worth of calcite precipitation. As in the stalagmite from Akalagavi cave (see Chapter 5), it is thought that the white layer represents growth in the rainy season, while the darker layer represents the drier months.

Seven-hundred and three laminae were counted, which fits the U-Th age model, given the errors, but suggests a somewhat slower growth rate than indicated by U-Th chronology. It is likely that the lower apparent growth rate from laminae counting is due to the horizons where non-laminated texturally disturbed growth periods are observed in the sample (marked by green boxes in figure 7.7), or possibly by missing layers or subtle hiatuses.

In monsoon regions with a single rainfall season in a year, the lamina count can give a good assessment of sample growth period. If the age can be determined using U/Th dating, the relative ages provided by the lamina counting can be tied to absolute ages. In this study, that approach can only be attempted for the younger part of the sample during which growth is continuously laminated (figure 7.12).

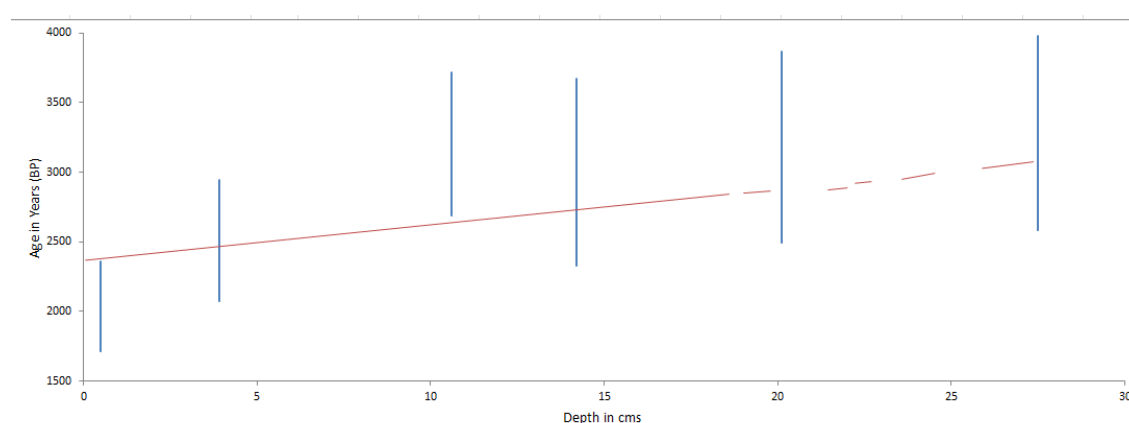


Figure 7.12: U-Th ages and lamina count relationship for the Kotumsar speleothem sample, the blue lines mark the 6 corrected U/Th ages against depth encompassing the error. The red line indicates the growth rate constrained by measurement of lamina thickness (lamina data table 19 of Appendix III). The red line can be moved up or down in an extremely limited way to include all U/Th ages. The gaps in the red line represent zones where the precipitation does not show any laminations and may demarcate periods of rapid growth.

It is encouraging that the growth rate suggested by lamina counting lies within error of that indicated by U-Th ages. This provides confidence that the U-Th ages are robust. These ages are therefore input to the software, StalAge (*Scholz and Hoffmann, 2011*) to provide an age model for the sample.

7.5.4 Stable isotope measurements and tests for equilibrium precipitation

$\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ are plotted versus age in figure 7.13 (data in table 20 of Appendix III). The $\delta^{18}\text{O}$ values vary between -6.5‰ and -2.4‰ with an average of -4.05‰. The $\delta^{13}\text{C}$ shows more variation than $\delta^{18}\text{O}$ with values ranging from -12.16‰ to -6.84‰ and an average value of -9.74‰.

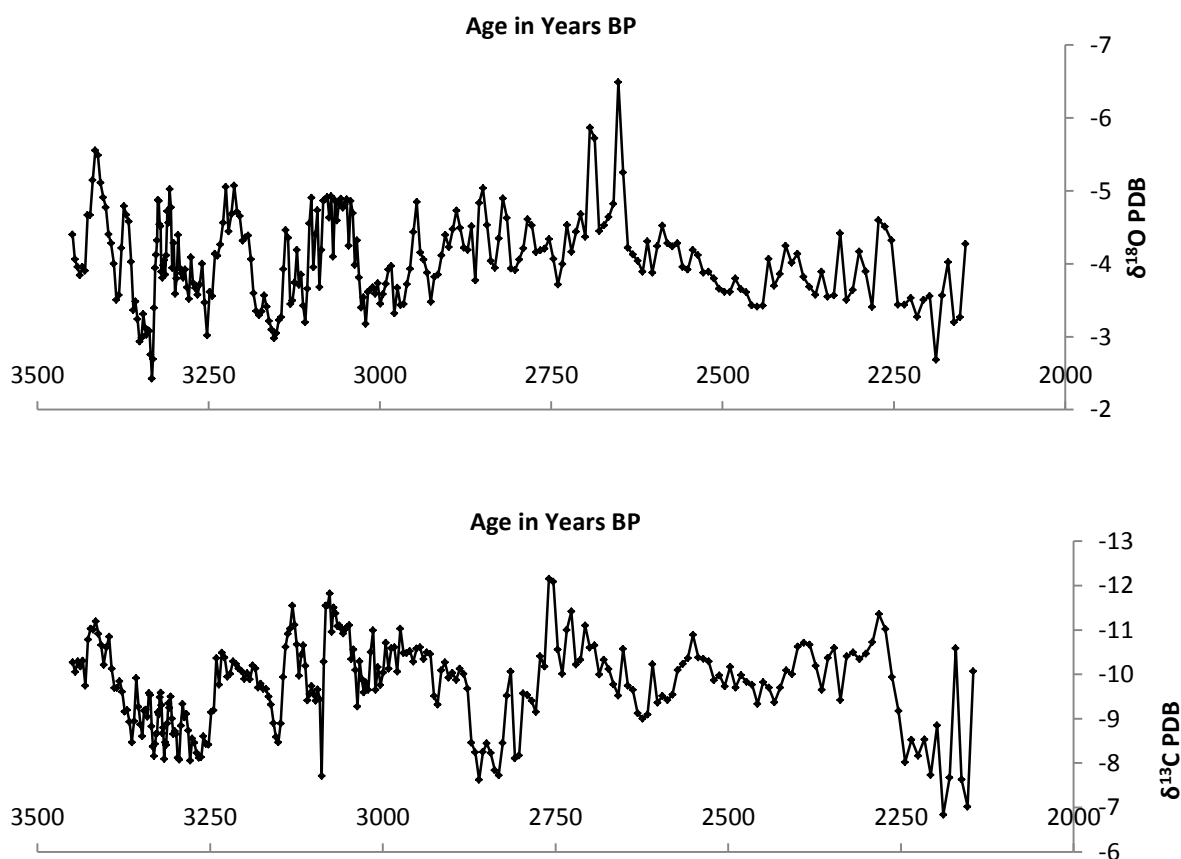


Figure 7.13: $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ (reversed axes) versus Age in years BP.

For the stalagmite sample to provide reliable information about rainfall $\delta^{18}\text{O}$, the stalagmite $\delta^{18}\text{O}$ must form without a kinetic overprint on the expected equilibrium fractionation

(Hendy, 1971). Deviations from equilibrium are caused by rapid depletion of the Dissolved Inorganic Carbon (DIC) pool in drip waters during stalagmite growth (for example, Hendy, 1971; Mickler et al, 2006; Day and Henderson, 2011; Hansen et al, 2013). Various tests can be used to evaluate whether this sample follows the expected equilibrium relationship and are employed below (see Chapter 4 for more information on equilibrium relationships).

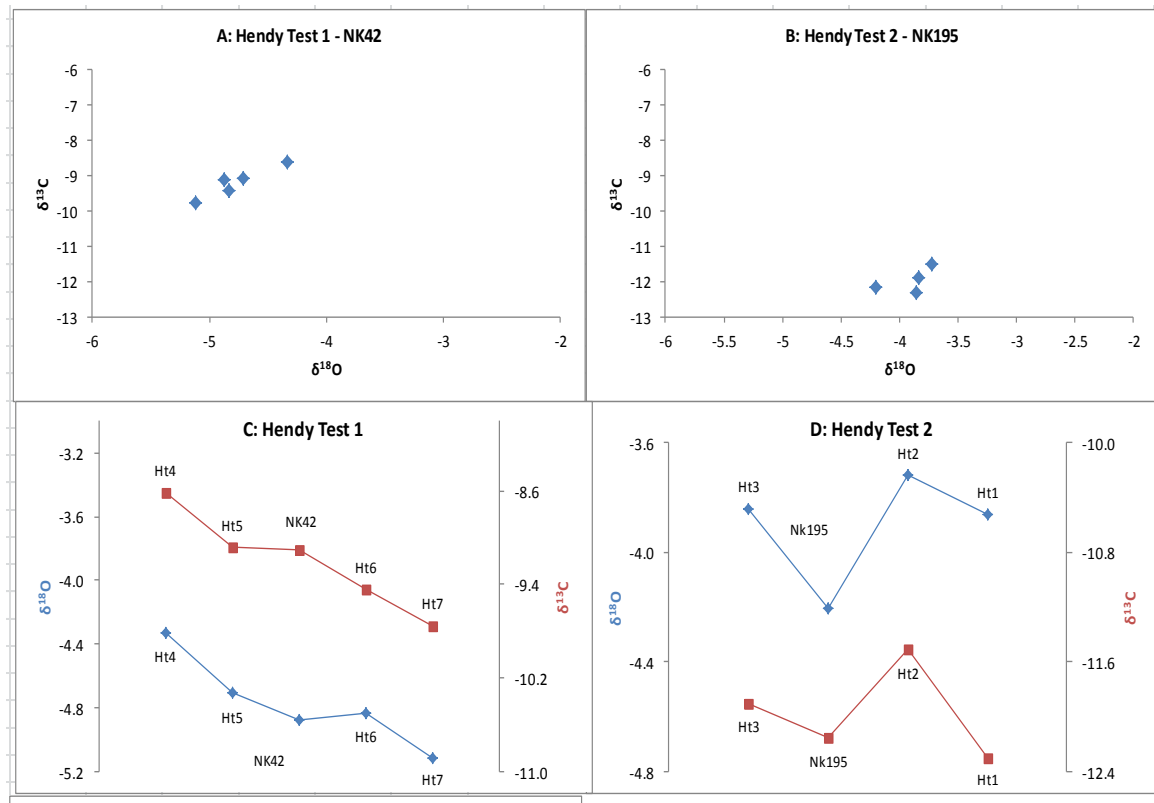


Figure 7.14: Results of two Hendy tests on the stalagmite, at locations shown on figure 7.6. (A and B): Along-growth-layer cross plots of $\delta^{18}\text{O}$ versus $\delta^{13}\text{C}$. (C and D): Along-growth-layer $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ plotted against distance from the growth axis (data in table 22 of Appendix III). Growth axis is represented by the subsamples Nk 42 and Nk195 respectively.

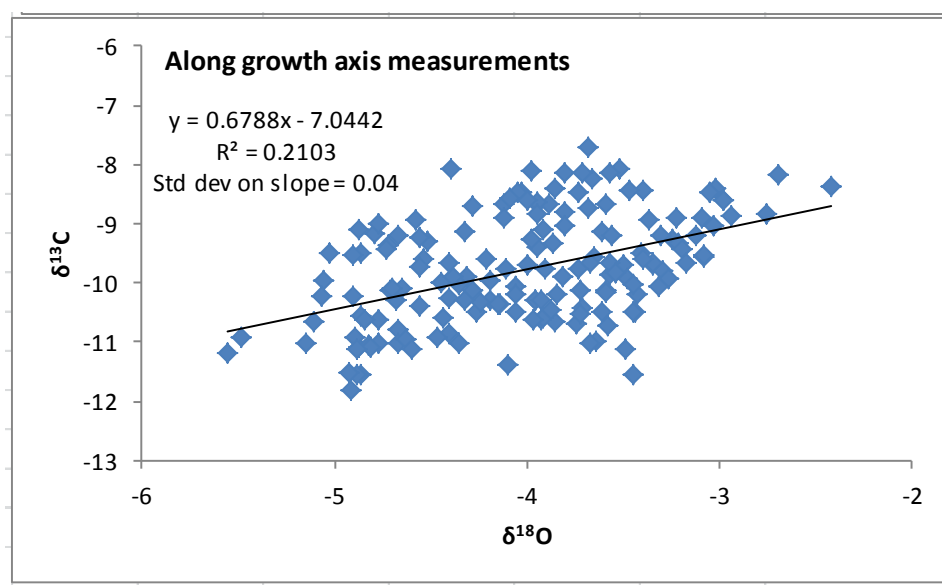


Figure 7.15: Along-growth-axis cross plot of $\delta^{18}\text{O}$ versus $\delta^{13}\text{C}$.

Measurement of $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values along specific laminae indicates that there is no progressive increase in $\delta^{18}\text{O}$ in panel D of figure 7.14 but there appears to be progressive increase in $\delta^{18}\text{O}$ in panel C (the growth axis is indicated by the subsample Nk42 in figure 7.14). Progressive increase in $\delta^{18}\text{O}$ is a sign of rapid Dissolved Inorganic Carbon (DIC) depletion and kinetic precipitation (*Mickler et al, 2006*). However, it is difficult to ensure that all sub-samples from the growth layer have been milled from the same growth lamina (*Dorale et al, 2002*). So this test indicates a kinetic overprint but is not conclusive.

A close positive correlation between $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ along the sample growth-axis can indicate incomplete oxygen isotope buffering and kinetic precipitation of $\delta^{18}\text{O}$ (*Mickler et al, 2006*). Such along-axis correlation can, however, also be caused by oxygen and carbon isotopes, both responding to the same climate or environmental forcing (for example, *Li et al, 2000*). In this study, no strong along-axis correlation between $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ is observed, suggesting a lack of strong kinetic overprint in the $\delta^{18}\text{O}$ data from this sample (figure 7.15).

An additional test for kinetic overprinting is comparing the measured $\delta^{18}\text{O}$ values of the stalagmite sample to that expected based on published equilibrium fractionation factors

between water and carbonate at the temperature of stalagmite growth. No measurements of drip water $\delta^{18}\text{O}$ nor of cave temperature were made. Previous measurements (Yadava, 2002) provide a drip water $\delta^{18}\text{O}$ range of -1.5 to -3.1‰ based on discrete measurements over two years for several caves in this area, including Kotumsar, Dandak and Jhumar (figure 7.16). Biswas, 2010 gives annual temperature averages of $26.3^{\circ}\text{C} \pm 1.0$ and $28.3^{\circ}\text{C} \pm 1.2$ for measurements made in Kotumsar cave during the 1990's. These drip water and temperature ranges have been used to calculate expected equilibrium values of $\delta^{18}\text{O}$ in calcite (figure 7.17). Expected equilibrium $\delta^{18}\text{O}$ are in the range from -6.68 to -3.05 ‰ vPDB (calculations in table 23 of Appendix III). The measured $\delta^{18}\text{O}$ values from the sample growth axis range between -5.56 to -2.43‰ vPDB. Only 12 subsamples of the measured 273 subsamples have a $\delta^{18}\text{O}$ value higher than -3.05‰ vPDB. Nearly all the $\delta^{18}\text{O}$ values of the stalagmite fall within the range of expected values for equilibrium based on the relationships of Kim and O'Neil, 1997 and Coplen, 2007. The comparison of the expected $\delta^{18}\text{O}$ values with measured $\delta^{18}\text{O}$ values suggests a lack of kinetic overprint over majority of the sample.

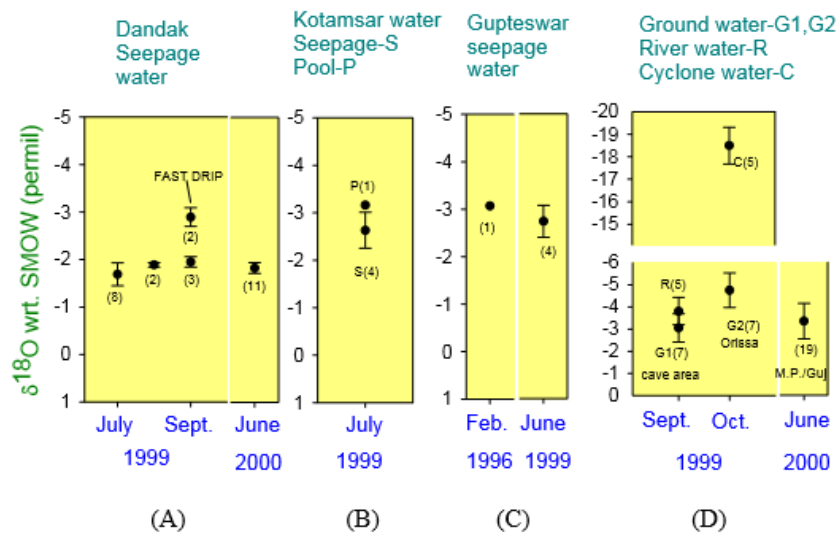


Figure 7.16: $\delta^{18}\text{O}$ plotted for water samples collected during different periods for (A) Dandak cave, (B) Kotumsar cave, (C) Gupteswar cave (Dandak and Gupteswar caves located ~20km away from Kotumsar cave) and (D) ground and river samples near the cave area. The figure and description are taken from MG Yadava, 2002.

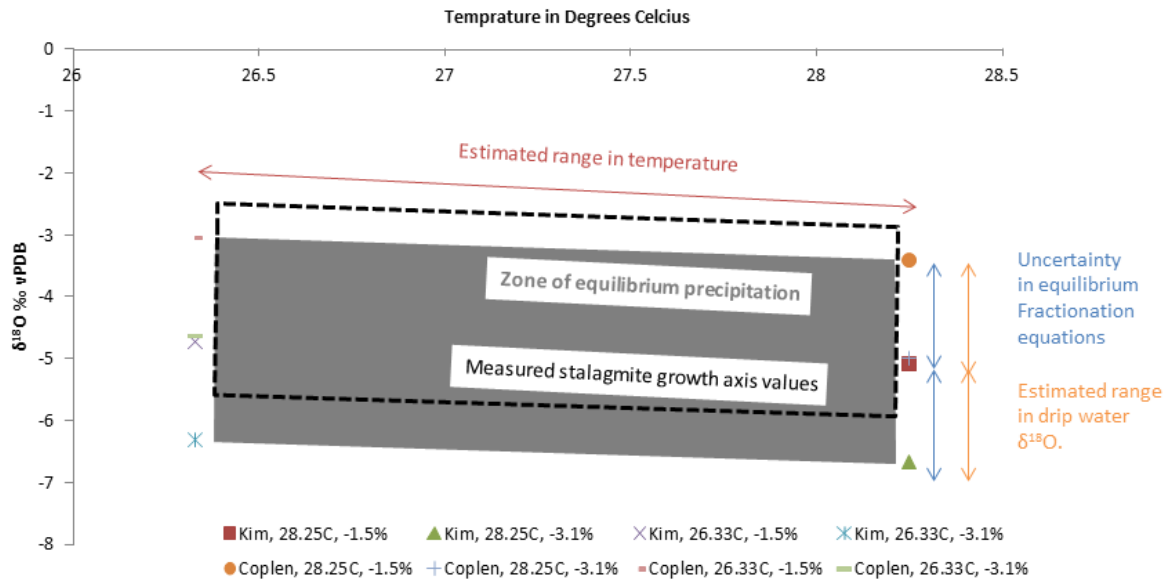


Figure 7.17: Zone of equilibrium precipitation (grey box) has been plotted using a temperature range of 26.33 to 28.25°C (Biswas, 2010), drip water $\delta^{18}\text{O}$ SMOW range of -1.5 to -3.1‰ (Yadava, 2002) and two published calcite fractionation equations of Kim and O’Neil, 1997 and Coplen, 2007. Note that the graph has $\delta^{18}\text{O}$ ‰ vPDB on the Y axis and is used to plot the expected and measured calcite $\delta^{18}\text{O}$ vPDB measurements. The black dashed box gives the range of along-growth-axis subsample measurements. The grey filled box gives the range of expected equilibrium $\delta^{18}\text{O}$ values. Calculations have been shown in table 23 of Appendix III.

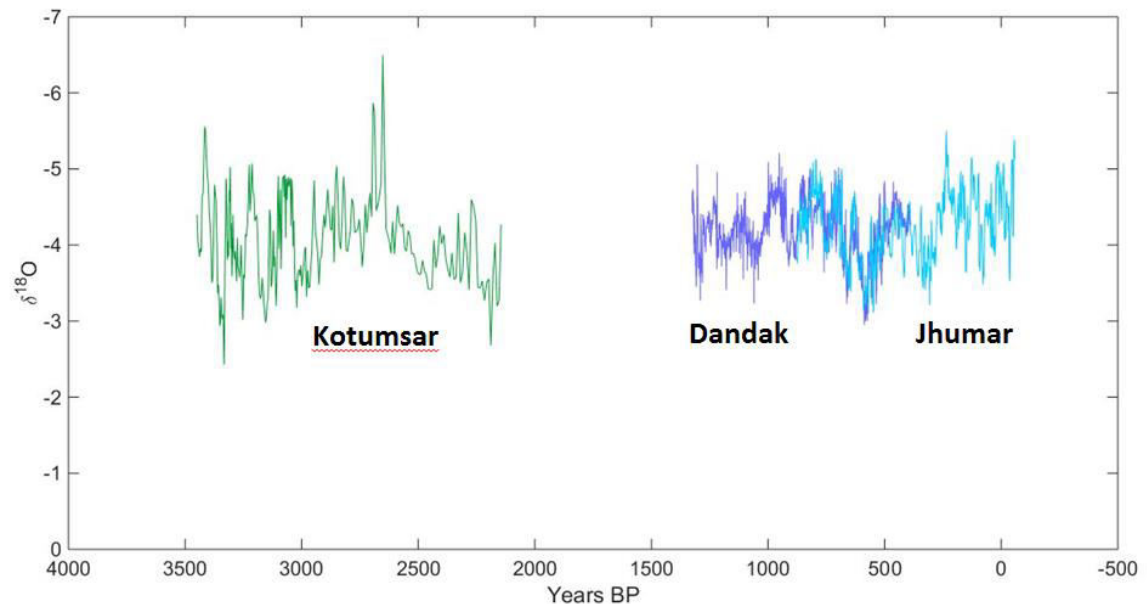


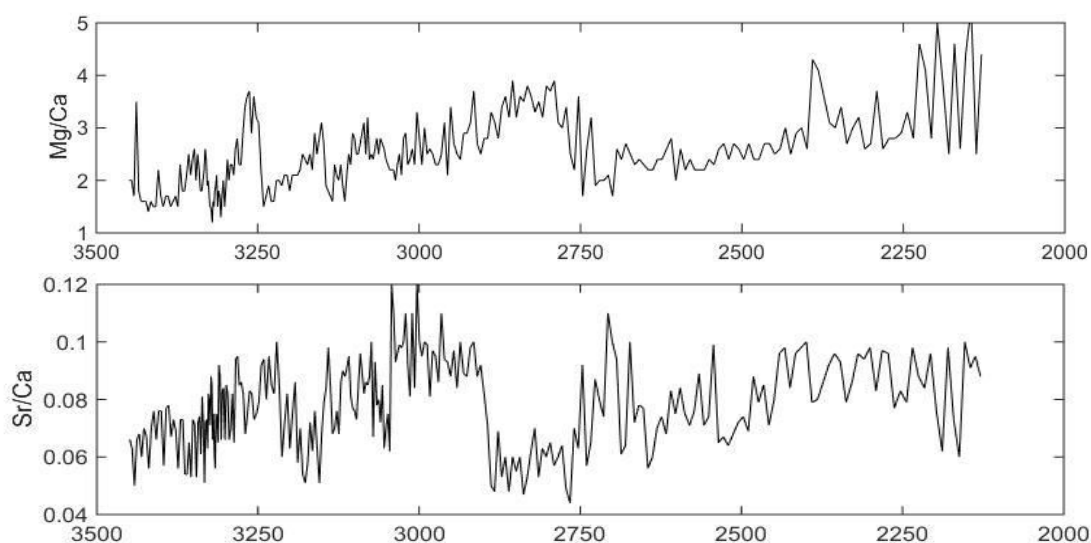
Figure 7.18: Kotumsar (measured as a part of this study), Dandak (Sinha et al, 2007) and Jhumar (Sinha et al, 2011) $\delta^{18}\text{O}$ time series. Dandak (noaa-cave-8639) and Jhumar (noaa-cave-11937) data sourced from NOAA paleoclimate database.

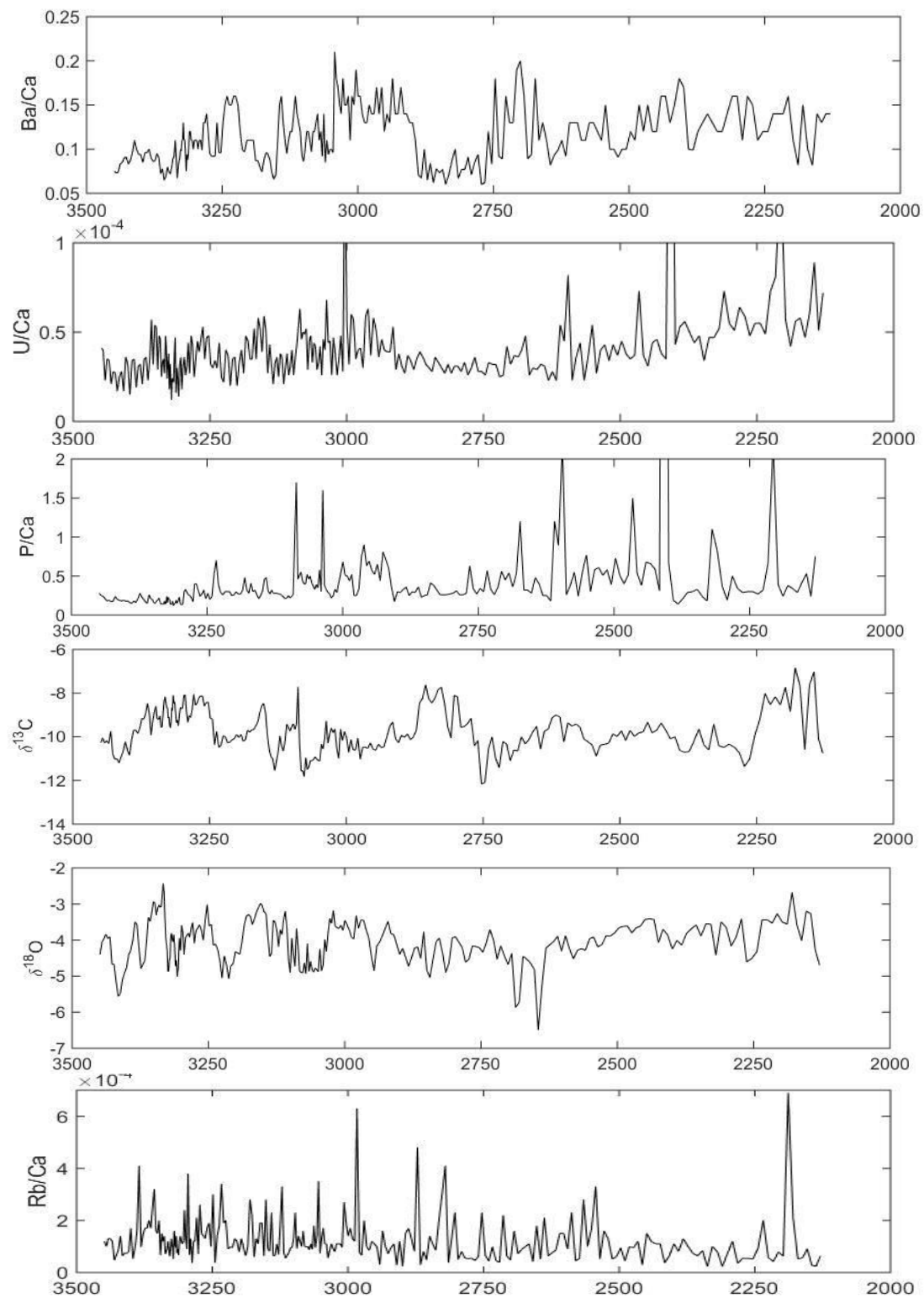
A final approach to assess the robustness of the measured $\delta^{18}\text{O}$ as a recorder of past rainfall is to compare measured $\delta^{18}\text{O}$ for this sample with that from other caves in the same region (for example, Dandak and Jhumar caves). Agreement between close-by caves indicates that there is a larger climate or environmental control on $\delta^{18}\text{O}$ rather than that of local sample kinetics alone. Figure 7.18 shows that all three samples so far studied from this region (Kotumsar, Dandak and Jhumar caves) show stalagmites with similar $\delta^{18}\text{O}$ ranges, again suggesting a lack of significant kinetic overprint in the $\delta^{18}\text{O}$ data.

In summary, the along-growth-layer relationships between oxygen and carbon isotopes may indicate some kinetic influence on calcite precipitation but is not conclusive. Along growth-axis $\delta^{13}\text{C}$ versus $\delta^{18}\text{O}$ data, comparison of measured oxygen isotope values with expected values for equilibrium, and the agreement between caves in the region all argue for equilibrium $\delta^{18}\text{O}$ during stalagmite growth.

7.5.5 Trace element measurements

Trace element measurements that were above detection limit are provided in table 20 of Appendix III and figure 7.19. Correlation analysis on trace element measurements has been shown in table 7.3. Sr/Ca and Ba/Ca show a strong correlation of $R^2 = 0.79$.





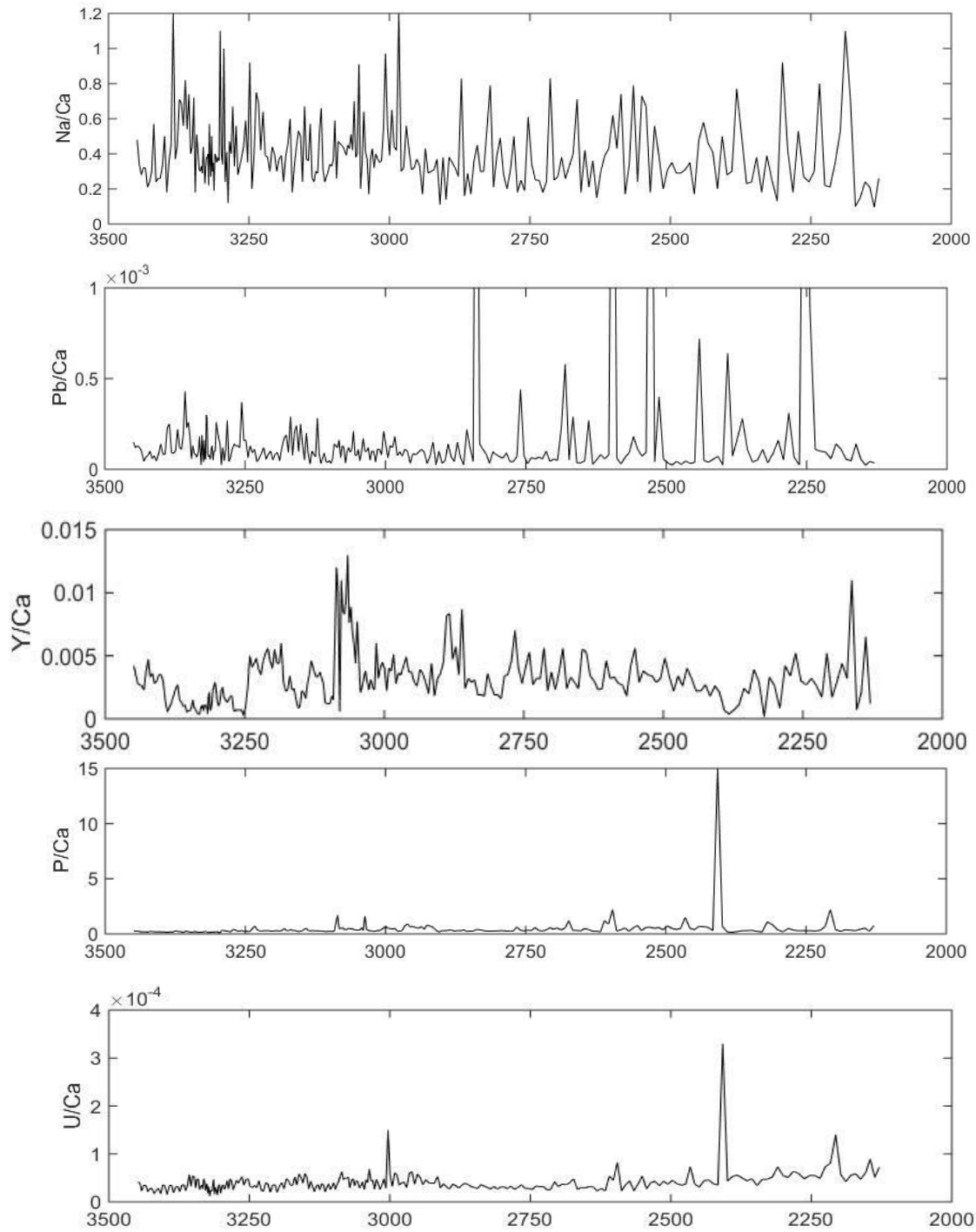


Figure 7.19: Kotumsar trace element (in mmol/mol) and stable isotope (in ‰vPDB) measurements plotted against time in years BP.

	Y/Ca	Ba/Ca	Pb/Ca	U/Ca	Na/Ca	Mg/Ca	P/Ca	Rb/Ca	Sr/Ca	$\delta^{18}O$	$\delta^{13}C$
Y/Ca	1.00										
Ba/Ca	0.00	1.00									
Pb/Ca	0.00	-0.01	1.00								
U/Ca	0.00	0.08	0.01	1.00							
Na/Ca	0.00	0.00	0.00	0.00	1.00						
Mg/Ca	0.00	0.00	0.01	0.13	0.00	1.00					
P/Ca	0.00	0.05	0.00	0.68	0.00	0.01	1.00				
Rb/Ca	0.00	-0.01	0.00	-0.01	0.68	0.00	0.00	1.00			
Sr/Ca	0.00	0.79	-0.01	0.12	0.00	0.00	0.03	-0.01	1.00		
$\delta^{18}O$	-0.13	0.00	0.00	0.04	0.01	0.04	0.00	0.00	0.02	1.00	
$\delta^{13}C$	-0.22	-0.07	0.00	0.00	0.00	0.08	0.00	0.01	-0.04	0.15	1.00

Table 7.3: Correlation analysis on trace element and stable isotope measurements. R^2 values above 0.7 have been highlighted in bold.

7.6 Discussion

I first discuss the trace element data, in terms of textural and possible climate controls, and then use the trace element data, to aid in interpretation of the stable isotopic data to derive information about past rainfall.

7.6.1 Textural control on trace element ratios

Textural control is distinct for Mg/Ca (figure 7.20), U/Ca, Y/Ca, Ba/Ca and $\delta^{18}O$ ratios. U/Ca, Mg/Ca and $\delta^{18}O$ increase in the texturally disturbed parts of the sample. Y/Ca and Ba/Ca decrease in the texturally disturbed part of the sample. While it is likely that there is a climatic reason for the disturbed texture, it is difficult to establish trace element relationships in such a texture so further interpretation has been restricted to the period between 3130 years (corresponding to subsample number Nk106) and 2100 years BP which shows dense calcite with distinct laminations.

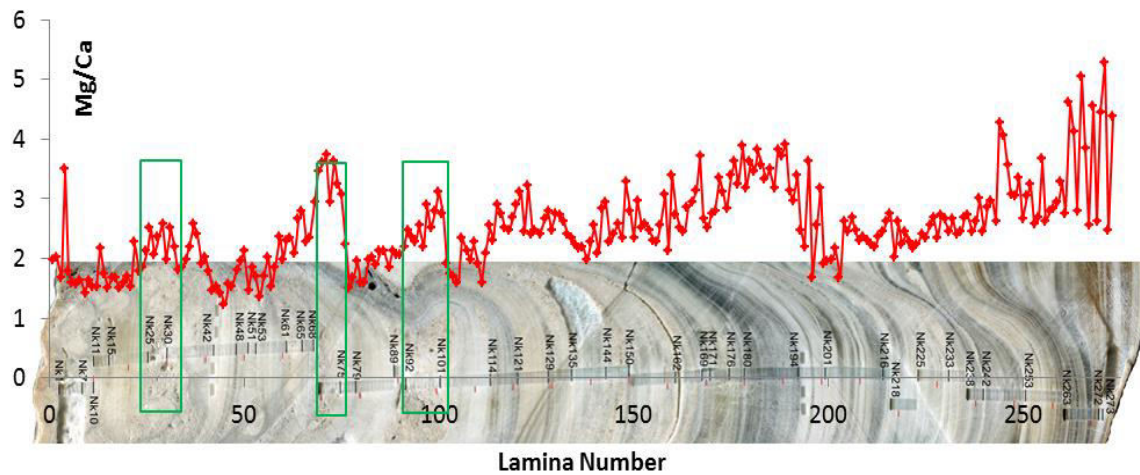


Figure 7.20: Mg/Ca in mmol/mol against subsample number.

7.6.2 Climate control on trace element relationships

	Y/Ca	Ba/Ca	Pb/Ca	U/Ca	Na/Ca	Mg/Ca	P/Ca	Rb/Ca	Sr/Ca	$\delta^{18}O$	$\delta^{13}C$
Y/Ca	1.00										
Ba/Ca	-0.06	1.00									
Pb/Ca	0.00	-0.01	1.00								
U/Ca	0.00	0.09	0.00	1.00							
Na/Ca	0.00	0.00	0.00	0.00	1.00						
Mg/Ca	-0.05	-0.12	0.00	0.05	0.00	1.00					
P/Ca	0.00	0.04	0.00	0.73	0.00	0.00	1.00				
Rb/Ca	0.00	-0.02	0.00	-0.01	0.65	0.00	0.00	1.00			
Sr/Ca	-0.04	0.83	-0.01	0.11	0.00	-0.04	0.02	-0.01			
$\delta^{18}O$	-0.08	0.12	0.00	0.03	0.01	0.02	0.00	0.00	0.14	1.00	
$\delta^{13}C$	-0.10	-0.04	0.01	0.01	0.00	0.27	0.00	0.00	-0.03	0.09	1.00

Table 7.4: Correlation analysis on trace element and stable isotope measurements for the time period between 3130 and 2100 years BP. R^2 values above 0.7 have been highlighted in bold.

Correlation analysis for trace element and stable isotope ratios for the time period between 3130 and 2100 years BP indicate that there may be a common dominant control on the trace element pairs of Sr/Ca-Ba/Ca and P/Ca-U/Ca respectively. The possible controls have been explored further below.

a) Controls on Sr/Ca and Ba/Ca

Different sources have been suggested for Sr including dust (*Goede et al, 1998; Frumkin and Stein, 2004*), sea salt aerosol (*Baker et al, 2000; Fairchild et al, 2000*) and the bedrock

(Fairchild *et al*, 2000). The calcite, dolomite and silicate bedrock and dust are all possible sources for Sr in this stalagmite (figures 2.20 and 2.21). The cave is located 250 km away from the sea and it is unlikely that sea salt aerosol will be a dominant source for Sr in this stalagmite. Less is known of the sources of Ba. In addition to the carbonate and silicate bedrocks, sulphates in the bedrock such as barite (BaSO_4) and celestine (SrSO_4) are possible sources for Ba and Sr (Fairchild *et al*, 2000). Pyrite oxidation may also be a source of S in drip waters (Fairchild *et al*, 2000). However, there is no information for the presence of sulphate minerals or pyrites in the bed rock (figures 2.20 and 2.21).

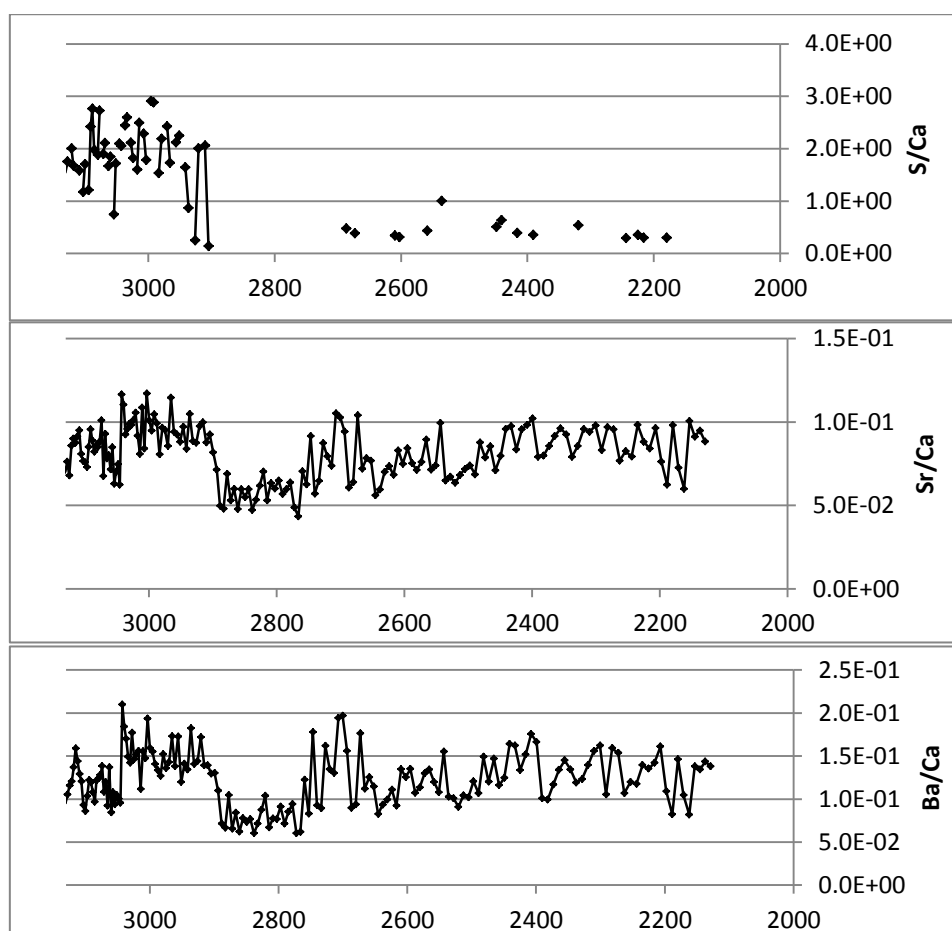


Figure 7.21: Kotumsar trace element (in mmol/mol) measurements plotted against time in years BP. Data from 3400 to 2000 years BP has been plotted. There is sharp decrease in S/Ca, Sr/Ca and Ba/Ca ratios at ~2900 years BP.

Figure 7.21 shows that S/Ca measurements decrease abruptly at 2926 years BP coinciding with the decrease in Sr/Ca and Ba/Ca ratios following which most S/Ca measurements are

below detection limit. However, there are very few S/Ca values above detection limit (table 21 of Appendix III). The S/Ca values do not return to pre-2900 years BP values even once the Sr and Ba have returned to pre-2900 values suggesting that the control is not straight forward. Further analysis of drip water S/Ca, Ba/Ca and Sr/Ca ratios are required to understand this control.

Sr/Ca is not significantly controlled by temperature (7-35°C) or growth rates (8 fold increase in growth rate) (*Day and Henderson, 2013*).

Johnson et al, 2006 find that Prior Calcite Precipitation (PCP) increase Sr and Ba concentrations in the remaining solution and the stalagmite precipitating from it. *Day and Henderson, 2013* similarly find that on shorter timescales the fraction of Ca remaining in solution is likely to be the dominant control on Mg and other trace element ratios. However, the process of PCP also results in the increase in Mg/Ca and $\delta^{13}\text{C}$ ratios (*Johnson et al, 2006, Griffiths et al, 2010*). The lack of strong correlation between Sr/Ca-Mg/Ca and Sr/Ca- $\delta^{13}\text{C}$ indicates that PCP is not the dominant common influence on the distribution of these trace elements in the stalagmite.

Where calcite and dolomite phases in bedrock are reasonably homogenous and are the main sources for Mg and Sr, their compositions can be used to understand ways in which chemical signals are generated and modified in the karst system (*Fairchild et al, 2000*). Dolomite has significantly higher concentrations of Mg than calcite and lower Sr and Ba concentrations than calcite (*Tucker and Wright, 1990*). Calcite and dolomite have different dissolution rates. Initially both calcite and dolomite dissolve congruently. After saturation for calcite is obtained, continued dissolution of dolomite increases Mg concentration in solution (*Plummer, 1977; Roberts et al, 1998*). Faster dissolution rate of calcite compared to dolomite allows for the possibility of increase in Mg/Ca ratios if water-rock interactions are increased during dry times (*Roberts et al, 1998; Fairchild et al, 2000*). Kotumsar cave is

located in a mixed limestone and dolomite region (figure 2.21). However, the lack of strong anti-correlation between Sr/Ca-Mg/Ca and Ba/Ca-Mg/Ca suggests that differential dissolution of calcite versus dolomite is also not a strong control on the Sr/Ca and Ba/Ca ratios in the stalagmite.

Day and Henderson, 2013 in cave-analogue laboratory measurements on calcite find that Sr/Ca and Ba/Ca in the precipitated calcite show strong correlation over a temperature range of 7-35°C and an 8 fold increase in growth rate and this is probably because they have similar partition coefficients in calcite. In this stalagmite, Sr/Ca and Ba/Ca ratios seem to indicate some changes in the water flow path to the drip site but the climatological control on them is not clear.

b) Controls on P/Ca and U/Ca

The sources of P/Ca and controls on P/Ca partitioning have been explored before in section 6.6.1. Soil is an important source of P (*Fairchild et al, 2001; Treble et al, 2003*) and is thought to be controlled in soil through seasonal vegetation uptake (*Heathwaite, 1997*) and decay (*Treble et al, 2003*). However, the fate of P is complicated because analysis reveals that even the dissolved form of P in drip waters can occur in various inorganic and organic forms (*Chapman et al, 1997*). P has previously been linked to ‘flushing’ of colloidal soil organic matter into the cave during high infiltration and the P concentration of the stalagmite reflects the P concentration in drip waters (*Huang et al, 2001*). It is known that P is strongly scavenged from ground waters during calcite precipitation (*Huang et al, 2001*) so that Prior Calcite Precipitation during dry periods will result in lower P concentrations in the stalagmite (*Johnson et al, 2006*). An additional control on P is microbial mediation which may colonise pores during reduced drip rates. The ‘flushing’ model, the PCP model and the microbial mediation model, all suggest higher P concentrations in the stalagmite during high rainfall periods.

Less is known about U partitioning into stalagmites. However, close association has been observed between U and P in ground waters (*Sanding and Bruno, 1992; Jerden and Sinha, 2003*). *Treble et al, 2003*, compare trace element and stable isotope measurements from a calcite stalagmite from Australia with instrumental records (1911-1992). They find the highest correlations of rainfall amount with P. They also find lower U concentrations during times of decreased rainfall. They suggest that complexes of U with phosphates and organics which increase during high rainfall periods is a likely climatological control on U concentrations in their calcite stalagmite.

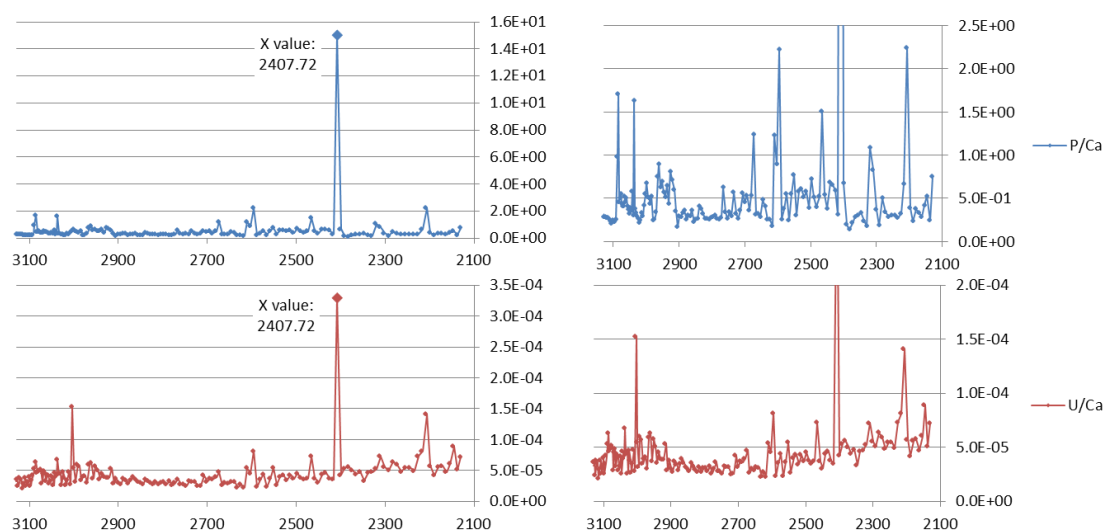


Figure 7.22: P/Ca and U/Ca in mmol/mol measurements against time in years AD have been shown. Plots to the left show the entire range of P/Ca (0 to 16 mmol/mol) and U/Ca (0 to 3.5E-04 mmol/mol) measured in the sample. The X value of the subsample with the highest U/Ca and P/Ca values has been shown. Plots to the right restrict the range of P/Ca (0 to 2.5) and U/Ca (0 to 2.0E-04) measured in the sample to look at the relationship between P/Ca and U/Ca of subsamples with lower P/Ca and U/Ca ratios.

Figure 7.22 shows the relationship between P/Ca and U/Ca measurements of the sample. The distinct peak seen in both P/Ca and U/Ca measurements is of the subsample Nk242 which is distinct white opaque layer in the stalagmite with increased precipitation along the flank. The layer also shows diffuse boundaries with adjoining layers along the left flank.

Figure 7.22 shows that there are discrete peaks in P/Ca ratios. Time periods between 3100 and 2900 years BP and between 2700 and 2400 years BP show longer period's higher infiltration. The time period between 2700 and 2400 years BP corresponds to subsample numbers Nk 217 and Nk242. Figure 7.23 shows that this part of the sample shows diffused growth surface boundaries which may be caused by increased water flow on the growth surface of the stalagmite.

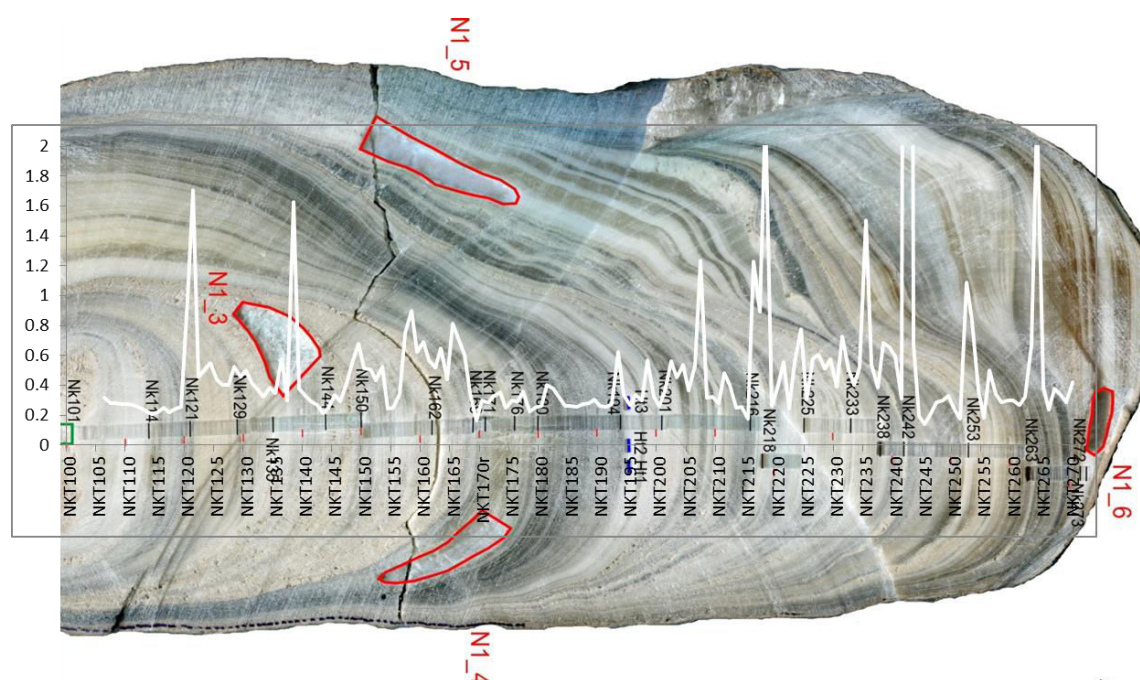


Figure 7.23: P/Ca in mmol/mol measurements against subsample number have been shown on a scanned image of the sample stalagmite.

The U/Ca ratios show similar trends to P/Ca ratios in terms of discrete peaks and the longer period of higher ratios between 3100 and 2900 years BP. However, U/Ca shows an increasing trend between 2500 and 2100 years BP which is not shown by P/Ca suggesting an additional long term control for U/Ca ratios.

7.6.3 Climate control on $\delta^{18}\text{O}$

As mentioned in the introduction, oxygen is sourced from rainfall whereas in Kotumsar cave, C, Mg, Ba, Sr, P, U, Na and S largely have local sources such as the bedrock and soil

(Fairchild and Treble, 2009). A change in oxygen isotopes in rainfall may result from a change in several local and non-local processes (see section 7.1).

Oxygen isotopes in speleothems pertaining to paleoclimate depend on drip water oxygen isotopes (i.e. rain water oxygen isotopes further modulated by karst hydrology) and the temperature of the cave (Duplessy et al, 1970; Schwarcz, 1986; Gascoyne, 1992).

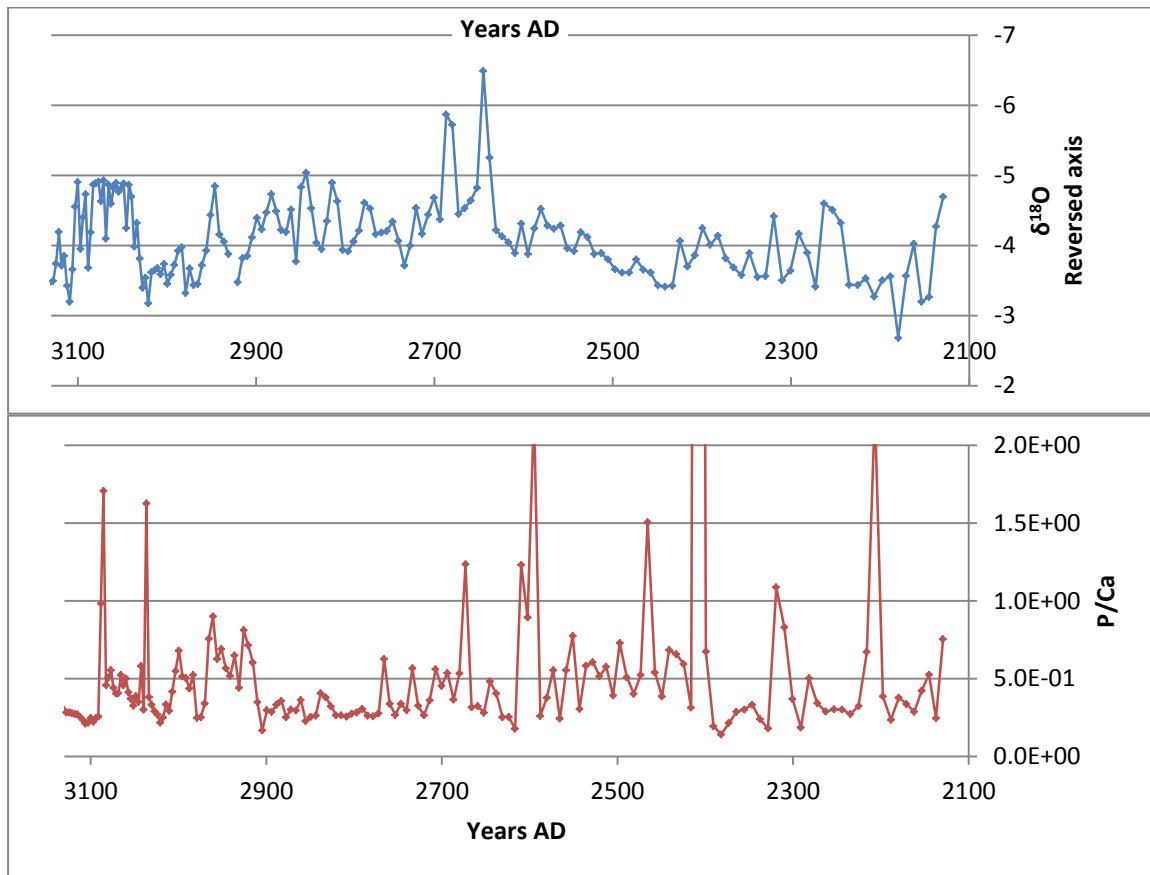


Figure 7.24: $\delta^{18}\text{O}$ in ‰V-PDB and P/Ca in mmol/mol measurements against time in years AD have been shown.

The $\delta^{18}\text{O}$ ratios decrease between 3130 years BP and ~2650 years BP following which the $\delta^{18}\text{O}$ ratios increase till 2100 years BP (figure 7.24). The $\delta^{18}\text{O}$ values are most negative between 2693 and 2631 years BP. Correlation analysis indicates that there is little correlation between $\delta^{18}\text{O}$ and P/Ca ($R^2 = 0.00$, table 7.4) suggesting that they don't have a common dominant control. Figure 7.24 shows that there is little correspondence between the discrete peaks in P/Ca and $\delta^{18}\text{O}$. Section 7.6.2b shows that higher P/Ca ratios most likely

result from episodes of higher rainfall. The lack of correlation between P/Ca and $\delta^{18}\text{O}$ suggests that rainfall amount may not be the dominant control on $\delta^{18}\text{O}$ ratios at this cave site.

7.6.4 Offset in mean $\delta^{18}\text{O}$ of records based on location

Figure 7.25 shows that the stalagmite $\delta^{18}\text{O}$ record of Qunf cave from Oman has a $\delta^{18}\text{O}$ range of 0 to -2‰ vPDB. The stalagmite records from peninsular India have a lower $\delta^{18}\text{O}$ range of -3 to -5‰ vPDB. The caves from east China i.e. Dongge, Heshang, Sanbao and Jiuxian show progressively lower $\delta^{18}\text{O}$ values ranging from -7 to -12‰ vPDB.

There is progressive increase in $\delta^{18}\text{O}$ ratios across the Holocene in stalagmites from Qunf cave in Oman and caves like Dongge in China. The $\delta^{18}\text{O}$ records are thought to reflect progressive drying across the Holocene based on the amount effect (*Yuan et al, 2004; Dykoski et al, 2005; Wang et al, 2005*). But the controls on $\delta^{18}\text{O}$ are complex. *Hu et al, 2008* use the difference in $\delta^{18}\text{O}$ records between Dongge and Heshang caves that lie along the same moisture path, thus removing the influence of controls other than the amount effect, to show that there is variation in rainfall amount of +/- 8% in the Holocene but there is no pattern of progressive drying during the Holocene. This suggests that the controls on $\delta^{18}\text{O}$ at Dongge and Heshang caves are not restricted to the amount effect alone. This can be resolved if the stalagmite $\delta^{18}\text{O}$ variations reflect rainfall source and air mass trajectories as well (*Maher, 2008*). The similar trends in long term Holocene trends of progressively increasing $\delta^{18}\text{O}$ records of stalagmites as far apart Qunf cave in Oman and Dongge and Heshang caves in China, support this idea. The $\delta^{18}\text{O}$ records from peninsular India do not cover the entire Holocene, but the available records which cover ~3000 years of the Holocene, give $\delta^{18}\text{O}$ values that are intermediate between Oman and Eastern China suggesting that progressive evolution of the $\delta^{18}\text{O}$ through progressive rainout support the idea of a common source and air mass trajectory control on $\delta^{18}\text{O}$ isotopes recorded in

stalagmites. *Maher, 2008* finds the $\delta^{18}\text{O}$ composition of modern rainfall from Oman to Eastern China show similar progressive decrease based on distance away from Oman. Similar results are found by *Pausata et al, 2011* who simulate a climate model with an embedded oxygen isotope model to assess what causes the shifts in $\delta^{18}\text{O}$ of precipitation during a climate perturbation designed to mimic a Heinrich event. The Heinrich event causes reduced precipitation over the Indian basin. The precipitation is isotopically heavier over India and the water vapour exported to China is isotopically enriched.

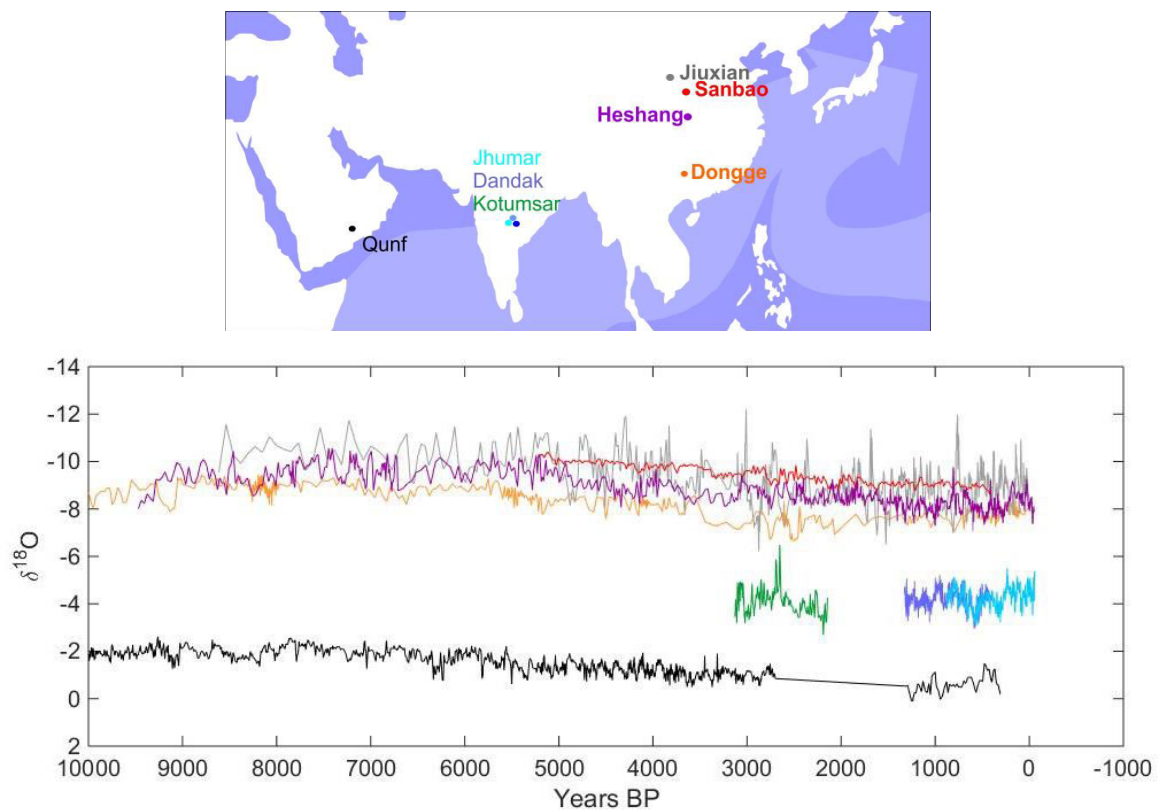


Figure 7.25: Cave locations across India and China with Holocene $\delta^{18}\text{O}$ records from calcite speleothems have been shown in the map. The light blue arrow on the map indicates the Indian Summer Monsoon and the East Asian Summer Monsoon paths respectively. The $\delta^{18}\text{O}$ records are shown in the plot against Years BP below. The colours of $\delta^{18}\text{O}$ records correspond to the colour of the caves on the map. Jiuxian (*Cai et al, 2010*; noaa-cave-9742), Sanbao (*Dong et al, 2010*; noaa-cave-10445), Heshang (*Hu et al, 2008*; noaa-cave-6095), Dongge (*Dykoski et al, 2005*; noaa-cave-5441), Jhumar (*Sinha et al, 2011*; noaa-cave-11937), Dandak (*Sinha et al, 2007*; noaa-cave-8639), Kotumsar (this study), Qunf (*Fleitmann et al, 2007*; noaa-cave-5541).

7.7 Conclusion

Trace elements concentrations in a stalagmite from peninsular India have been used to decouple local hydrological changes from the larger circulation pattern changes that are thought to be represented by oxygen isotopes.

High P/Ca ratios are interpreted to have resulted from flushing of P-rich colloidal material into the cave during high infiltration periods. Complexes of U with phosphates and organics may explain the strong correlation seen between U/Ca and P/Ca ratios in this stalagmite suggesting that there is climatological control on U/Ca ratios such that higher U/Ca ratios indicate increased infiltration. However, the increase in trend in U/Ca ratios seen over a 400 years period that is not shown by the P/Ca record suggest that there are other controls on U/Ca ratios. P/Ca and U/Ca ratios indicate discrete periods of increased infiltration and two sustained periods of increased infiltration between 3100 and 2900 years BP and between 2700 and 2400 years BP.

The stalagmite indicates that the process of PCP which is the dominant control on trace element ratios in stalagmites from monsoon regions is not the dominant control on trace element ratios in this stalagmite. This stalagmite also indicates that dissolution of sulphates in the epikarst maybe a control on Sr/Ca and Ba/Ca ratios. Further measurements of drip water U/Ca, P/Ca, Sr/Ca, Ba/Ca and S/Ca are required to understand the sources and controls on these trace element ratios.

The $\delta^{18}\text{O}$ values do not correlate with P/Ca and U/Ca records suggesting that rainfall amount is not the dominant control on $\delta^{18}\text{O}$ in this stalagmite. A systematic offset between the $\delta^{18}\text{O}$ values of stalagmites from this cave region compared to those from Oman and East China suggest that air parcel trajectory and rainout is the more likely dominant control on $\delta^{18}\text{O}$ values.

Chapter 8

U-Th, Stable Isotope and Trace Element Geochemistry in a Diagenetically Altered Stalagmite

Abstract

Diagenesis in a stalagmite from primary unstable aragonite to calcite can affect the stable isotope, trace element and U-Th systems giving erroneous ages and environmental proxy results. The effect of diagenesis on U-Th systematics of coral and marine carbonates have been extensively studied but there are few studies on speleothems. The triggers and processes of alteration are not well understood. Here, I look at a diagenetically altered stalagmite from peninsular India to assess the impact of diagenesis on stalagmite paleo-proxies and U-Th chronology.

Aragonite and calcite subsamples have distinct $\delta^{18}\text{O}$ compositions showing that the stable oxygen isotopic system is susceptible to alteration. The concentrations of U/Ca and Sr/Ca seen in calcite subsamples are higher than typically seen in calcite and are likely to be a remnant of the aragonite structure. But secondary calcite shows higher Mg/Ca ratios than primary aragonite indicating that diagenesis adds Mg relative to the original composition. Mg/Ca ratios can be used to differentiate between primary calcite, primary aragonite and secondary calcite. Although, it is not known if Mg/Ca partitions differently into primary versus secondary calcite or the fluid causing diagenesis was different from that which precipitated as primary calcite. The reaction front of diagenesis can further affect distribution of trace elements (including U and Th) in certain cases that is separate from a mineralogical control alone.

Both the aragonite and calcite ages are out of chronological order. The calcite ages are not necessarily older than the aragonite ages. The stalagmite shows loss in ^{232}Th during

alteration from aragonite to calcite indicating that Th is mobile. However, the ^{232}Th concentration of the subsamples is extremely low and cannot be responsible for the large age discrepancy seen between aragonite and calcite ages. There is differential loss/gain of U and Th isotopes during diagenesis giving rise to discrepancy in ages.

8.1 Introduction

The strength of speleothems as a source for paleoclimate proxies is based on the age control provided by U-Th dating methods and the multiple proxies of stable isotopes and trace elements that can be used to derive information of past climate and environmental conditions. The age and proxy information is reliable if the speleothem remains a closed system once precipitated. However, the opening of the speleothem system can occur when speleothems face environmental conditions sufficiently different from the ones in which they were initially precipitated. This can cause dissolution, dissolution-reprecipitation and recrystallization of speleothem material (*Borsato et al, 2005*). The opening of the system may alter the age of the speleothem through differential loss and gain of U and Th isotopes (*Borsato et al, 2005; Ortega et al, 2005; Lachniet et al, 2012*). Diagenetic alteration from aragonite to calcite, resulting from opening of the system when aragonite post-depositionally converts to calcite, has important implications for the stable isotope system because $\delta^{18}\text{O}$ of the two fluids (the first of initial precipitation and the second that causes diagenesis) may have differed and water- CaCO_3 fractionation factors are different for calcite and aragonite (*Lachniet, 2009*). Further, calcite and aragonite have different crystal structures and consequently different affinities for trace elements. For example, U and Sr are preferentially incorporated in aragonite (*Wassenberg et al, 2016*) while Co is preferentially incorporated in calcite (*Day and Henderson, 2013*). Thus opening of the speleothem system can result in erroneous ages and climatic interpretations.

Recrystallization cannot always be recognized by visibly examining the sample or through mineralogical tests like FTIR and XRD. Similarly, the recrystallization process may not

always result in opening of the U-Th system (*Spotl et al, 2002*). On the other hand, a first approach to identify corals with disturbed U-Th systematics relied on the use of mineral and minor element abundances (*Cross and Cross, 1983; Bar-Matthews et al, 1993; Stein et al, 1993*), but the fact that even apparently pristine samples show ^{234}U values higher than modern sea water and recent corals suggests that isotopic systems are more sensitive to diagenetic change than is any petrographic or general geochemical parameter (*Chen et al, 1991*). Thus it appears that diagenesis can have different effects on the U-Th, stable isotope and trace element geochemistry of aragonite and recrystallized calcite.

A sample that is undergoing diagenetic alteration may allow us to understand possible sources, pathways and movement of U-Th isotopes, stable isotopes and trace elements within the sample, as well as identifying which system would be the most susceptible to alteration, and which might be relatively robust.

8.2 Previous Work

8.2.1 Trace element geochemistry

Lachniet et al, 2012 found, in a partially altered sample from Mexico, that U/Ca and Mg/Ca closely match mineralogy revealing stark contrasts in elemental ratio between aragonite and calcite. *Ortega et al, 2005*, found, in stalactites from a French cave, a markedly higher U and Sr in aragonite than calcite forms. In calcite Sr is typically incorporated only in small quantities, so that a high Sr/Ca ratio in calcite, comparable to that typical of aragonite, could indicate an aragonitic precursor and diagenetic origin for the calcite. This logic relies on the suggestion that, during diagenesis, some of the Sr remains in the newly formed calcite, which was found to be the case in the study of *Ortega et al (2005)*. In the same study, *Ortega et al*, found loss of U during the transition to calcite, and explained this as due to migration of U towards aragonite in the aqueous solution that fills speleothem microporous

networks. This would lead to an enrichment in the calcite-aragonite boundary, though *Lachniet et al, (2012)* found no such enrichment in an altered sample.

8.2.2 U-Th systematics

Initial work on U-Th systematics to do with alteration was done on ocean corals and carbonates. Different models have been proposed to explain the alteration in age such as continuous gain of ^{230}Th and ^{234}U (*Bender et al, 1979; Gallup et al, 1994*), gain or loss of ^{230}Th and ^{238}U (*Chen et al, 1991; Hamelin et al, 1991; Henderson et al, 1993; Bar-Matthews et al, 1993*), gain or loss of ^{234}U and ^{238}U (*Ku et al, 1990; Scholz et al, 2004*) and the effects of α recoil (*Henderson et al, 2001; Villemant and Feuillet, 2003; Thompson et al, 2003*).

Corals and marine carbonates are immersed in a fluid environment that allows for dissolution and transport of U and Th whereas this condition would occur for speleothems only in case of cave flooding. This implies that there could be progressive or continuous loss or gain of nuclides in corals, whereas episodic loss/gain is more likely in speleothems.

Well mixed ocean water has a relatively constant $^{234}\text{U}/^{238}\text{U}$ ratio (*Turekan and Chan, 1971; Ku et al, 1977; Bloch, 1980; Cochran, 1982; Chen et al, 1986*). For sea water samples, this makes the calculation of gain/loss somewhat more straightforward due to the consistency of initial $^{234}\text{U}/^{238}\text{U}$ values so that all samples of the same age will have deviated from a specific $^{234}\text{U}/^{238}\text{U}$ value. For example, a common observation in old corals is the elevated initial $^{234}\text{U}/^{238}\text{U}$ ratios. The reason for this could be that older sea water had higher $^{234}\text{U}/^{238}\text{U}$ in the past or the higher ratio is a result of diagenetic alteration (*Henderson et al, 1993*). *Cheng et al, 1998* showed that a suite of coeval samples with different degrees of alteration can provide a series of points for a conchordia diagram. They modelled both continuous and episodic U gain or loss relative to ^{230}Th and continuous addition of ^{234}U and ^{230}Th . They showed that these processes would result in a continuous evolution of isotopes in a conchordia diagram and the intersection of this line/curve with the closed system curve

would represent the 'true' age of the sample. Speleothem U-Th systematics are different from ocean water in that the $^{234}\text{U}/^{238}\text{U}$ ratios of drip water can vary more than in the ocean. Isochrons for corals are often plotted to intersect with a known initial value of $^{234}\text{U}/^{238}\text{U}$ curve, but such an approach is not possible for stalagmites.

Open system uranium-thorium dynamics in a speleothem environment have not been as widely studied as for ocean samples (*Borsato et al, 2005; Ortega et al, 2005; Lachniet et al, 2012*). Since U is soluble in water but Th is not, it is expected that diagenesis mediated by a fluid would result in the loss of U during recrystallization from aragonite to calcite. For example, *Lachniet et al, 2012* find that replacement of aragonite with calcite is associated with U loss caused by recrystallization triggered by an aragonite under-saturated fluid. They find that all calcite shows ages that are older than primary aragonite ages i.e. older than true ages. However, *Ortega et al, 2005* found that ages in portions of their speleothems that had undergone recrystallization generally showed younger ages rather than older ages expected if U loss were dominant during recrystallization. *Borsato et al, 2005* published a critical review of 130 α -spectrometric U-Th analyses of speleothems from north-eastern Italy and found that about 33% of the measurements display activity ratios $[^{230}\text{Th}/^{238}\text{U}] > 1$ while maintaining $[^{234}\text{U}/^{238}\text{U}]$ close to unity, thus falling outside the closed system U series disequilibrium field. This suggests that the direction of alteration due to diagenesis i.e. whether samples will be older or younger is not consistent across speleothem systems and that there may be loss or gain or replacement of U and/or Th during diagenesis.

The mechanisms triggering diagenesis have also been explored. *Lachniet et al, 2012*, suggest a flushing model where heavy rainfall results in under-saturated drip water that drips onto a stalagmite causing recrystallization. *Borsato et al, 2005*, find that all the samples showing open system behaviour were found in cave zones clearly effected by flooding by glacial meltwater or re-dissolution due to under-saturated waters, and suggest a dramatic environmental change as a cause for opening of the U-Th system.

8.3 Climate, location and sample information

The sample was removed from Valmiki cave or Kuruvu Bali Guha (*Lone et al, 2014*) during field work conducted as a part of this thesis. The cave is located in Kurnool district of Andhra Pradesh state. Further information on the climate and location of the cave site has been given in section 2.5. The sample was retrieved from a ledge situated about 3 m above the observed water table in the sump of the cave (figure 8.2).

The sample is ~24 cm in length and ~12.5 cm in width (figure 8.1). The sample shows distinct signs of physical damage to the top right of the image. It doesn't show clear outer features of flowing water damage such as vugs or silty layers on the inside to indicate flooding (*Borsato et al, 2005*).

The sample has a variable growth axis. There are zones of the sample with distinct laminae while in other zones the laminae have been clearly disturbed or are completely absent. The laminated and non-laminated parts occur at the same stratigraphic height in the sample. In places the latter appears to replace the former. Cracks or shrinkage can be observed in the sample. The visible appearance of the cut sample indicates that the sample may have undergone diagenesis from primary aragonite to secondary calcite.

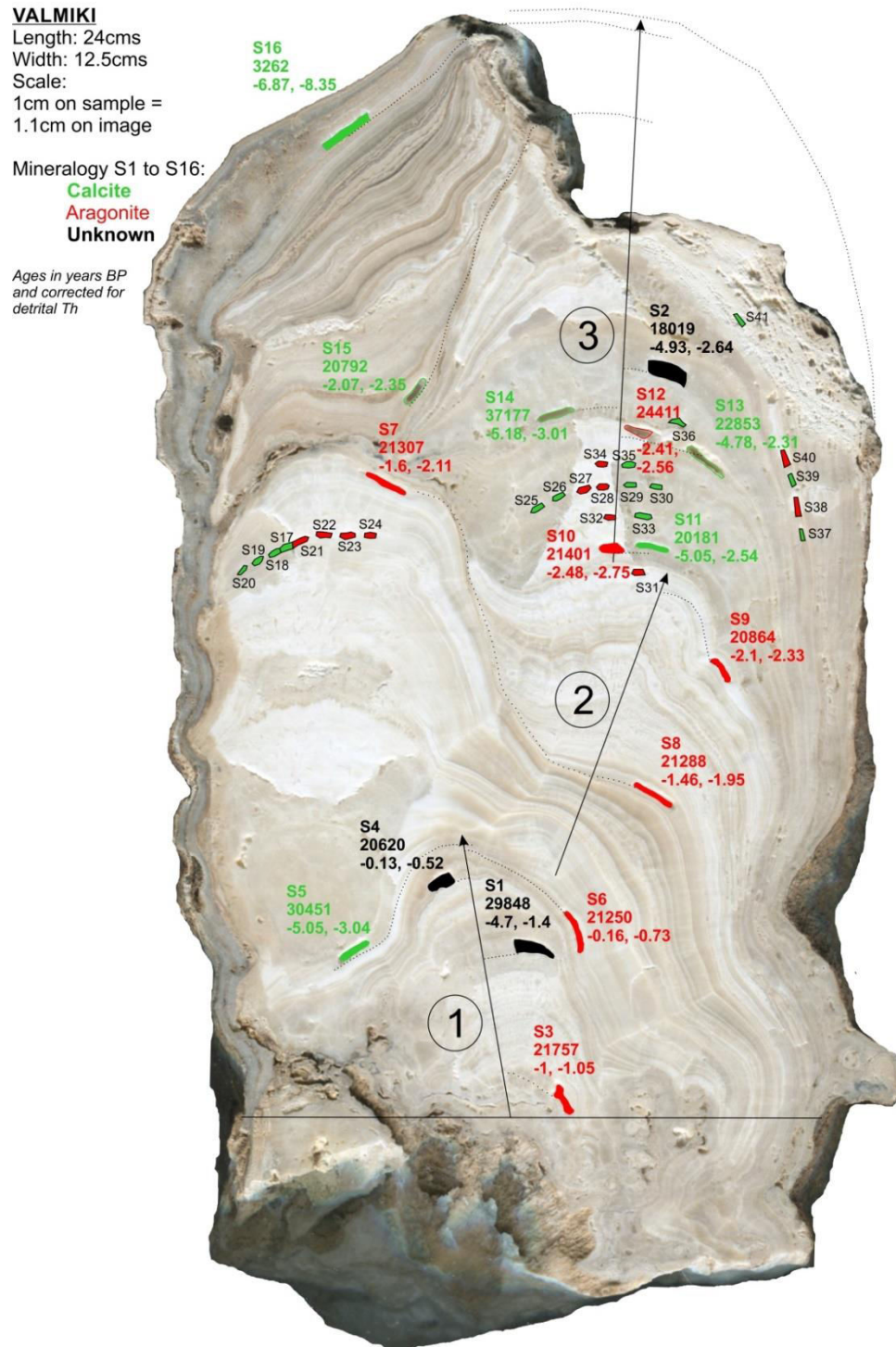


Figure 8.1: Sample and subsampling locations. Dimensions of the sample have been given to the top left. Growth axis directions have been marked by black arrows with adjoining numbers in circles.

S1 to S16 have been given in the format: subsample code followed by age in years BP followed by $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values in ‰. Red stands for dominantly aragonite subsamples, green for calcite and black for subsamples whose mineralogy was not determined.

S17 to S41 have been subsampled along diagenetic fronts and have a similar colour code.

8.4 Sampling and analytical methods

8.4.1 Field work

For this thesis research, the cave was visited in January, 2015. The sample stalagmite, one drip water sample and chips of modern carbonate were collected. No drip water was feeding the sample stalagmite at the time of collection. Modern carbonate chips were taken from the surface of a stalagmite but its drip waters could not be collected since the drip rate was too slow. Drip water with a reasonably fast drip rate was collected instead. The sample stalagmite, drip water and modern carbonate were all collected within a meter of each other. Spot temperature and humidity measurements were also made using a hand held device.

8.4.2 Sample and subsampling

The sample was cut in half longitudinally at PRL, India (see section 3.3.1 for sample cutting method). Half the section was shipped to Oxford and all further subsampling has been done on this half section.

Subsample names (for example N3VS5) indicate person handling subsamples and cave from which the stalagmite sample was removed (i.e. Nikita and Valmiki). However, for ease in this chapter, the subsample code names have been shortened and are often called as S4, S5 etc.

Subsampling was undertaken in 3 stages that have been summarised in table 8.1. Initial subsamples (S1 and S2) of ~50 mg were taken from the bottom and top of the stalagmite respectively to gauge the approximate age of the sample using U-Th dating. Stable isotopes of oxygen and carbon were also measured. In the second stage of subsampling, subsamples were measured to understand the control of mineralogy on stalagmite geochemistry variation. Subsamples (S3 to S16) of ~50 mg were milled in the second stage of

subsampling. FTIR (see section 3.3.6 for methodology) measurements of mineralogy, U-Th ages, trace elements and stable isotopes were measured. A third stage of subsampling (S17 to S41) was then carried out to map out variation in stalagmite geochemistry with respect to distance away from diagenetic fronts. XRD measurements of mineralogy (see section 3.3.6 for methodology), approximate U-Th, stable isotope and trace element measurements were made. The method used for approximate U-Th measurements of the third stage of subsamples is described in detail below.

<i>Subsampling stage and subsample numbers</i>	<i>U-Th ages</i>	<i>Mineralogy</i>	<i>Stable Isotopes</i>	<i>Trace Elements</i>
<i>First Stage: S1 and S2</i>	Yes	None	Yes	No
<i>Second Stage: S3 to S16</i>	Yes	FTIR	Yes	Yes
<i>Third Stage: S17 to S41</i>	Approximate U-Th measurements	XRD	Yes	Yes

Table 8.1: Summary of measurements made on subsamples.

8.4.3 U-Th systematics

a) First and second stage: Subsamples S1 to S16

S1 to S16 were dated using the method previously described in section 3.3.10.

b) Third stage: Subsamples S17 to S41

Age data from the second stage of subsampling demonstrated that the mineralogy of subsamples exerted control on $^{230}\text{Th}/^{238}\text{U}$. To further investigate the control of distance away from diagenetic front on $^{230}\text{Th}/^{238}\text{U}$ measurements, rapid, approximate measurements were made on the subsamples.

Approximately 1 mg of the subsample was dissolved in 3 ml of 10% distilled HNO_3 and spiked with ^{229}Th - ^{236}U in Poly-Propylene bottles before analysis on the Nu ICPMS used for the measurements described in section 3.3.10. No prior separation chemistry was conducted to isolate U and Th from the CaCO_3 matrix. The other significant differences in comparison to the procedure described above include; ^{234}U was not measured, bracketing standards were not used, no corrections were made for blank values or drift although both

were periodically checked for consistency, U and Th were run in a two step process with ^{235}U in common to both steps rather than being measured in two separate runs.

8.5 Results

This section is divided into six sub-sections:

- i. The cave location is first described to suggest possible triggers and pathways for diagenesis.
- ii. This is followed by (a) examination of the mineralogy of the sample (i.e. results from FTIR and XRD measurements of the subsamples) and (b) the variation in mineralogy based on distance away from diagenetic fronts.
- iii. This sub-section gives a description of visible mineralogical variation in the sample.
- iv. (a) Stable isotope measurements are given and (b) the variation in stable isotope compositions across diagenetic fronts is shown.
- v. Trace element measurements are then considered in terms of (a) trends between aragonite and calcite and (b) control of distance away from diagenetic fronts on trace element ratios.
- vi. Lastly, U-Th systematics in the sample have been explored based on (a) age data (b) cross plots of U-Th isotopes relevant for dating this sample (c) and trends along diagenetic fronts.

8.5.1 Cave setting and possible causes of diagenesis

The possible causes of diagenesis have been described below:

- (i) The cave intersects the water table at a depth thought not to change significantly during the year by those guiding me into the cave. The height of popcorn precipitation on the cave wall provides some indication of flood levels in the past (figure 8.1). The sample was taken from a ledge just above the maximum height of

observed pop-corn precipitation, though it remains feasible that flood waters reached sample level at some time in the past.

- (ii) The cave is in a generally arid region and the depth of the cave zone from which the sample was removed was significant. It is unlikely that the drip waters were unsaturated for calcite although it is possible that the drip waters were at times unsaturated for aragonite. This could be a second pathway for diagenesis.
- (iii) A third, though less likely possibility is that aragonite is an unstable form of calcium carbonate, perhaps a change in temperature or CO_2 of the cave, especially due to sudden influx of flood waters could cause diagenesis of aragonite in the absence of an external fluid medium but mediated by water from inclusions moving through the micro pores of the stalagmite.



Figure 8.2: Popcorn growth provides indication of past flood levels and the height of the sample with respect to past flood levels.

8.5.2 Mineralogy

a) Trends in aragonite and calcite subsamples

FTIR measurements indicate that S3, S6, S7, S8, S9, S10 and S12 are dominantly composed of aragonite (figure 8.3) while S5, S11, S13, S14, S15 and S16 are dominantly composed of calcite (figure 8.4). S4 was also measured but does not indicate a clear mineralogy. S1 and S2 were not measured. Raw measurements are given in table 24 of Appendix III.

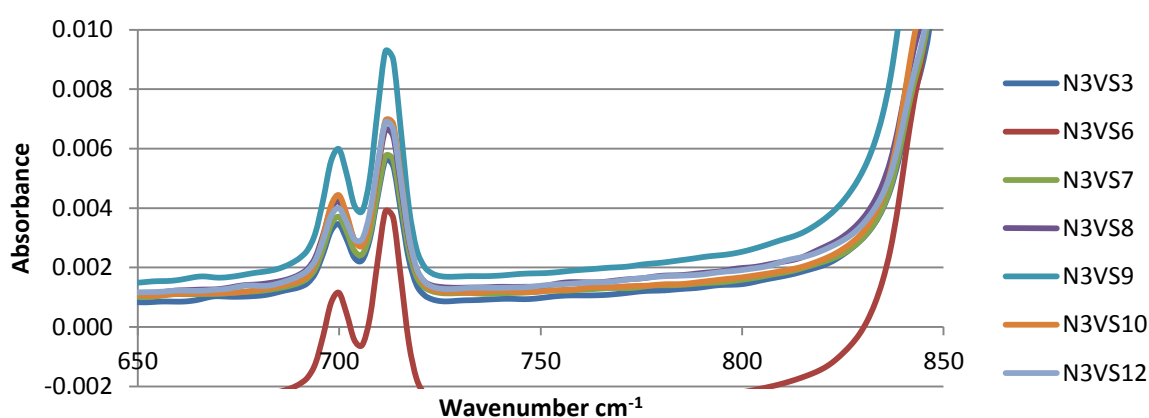


Figure 8.3: FTIR spectra of subsamples dominantly composed of aragonite.

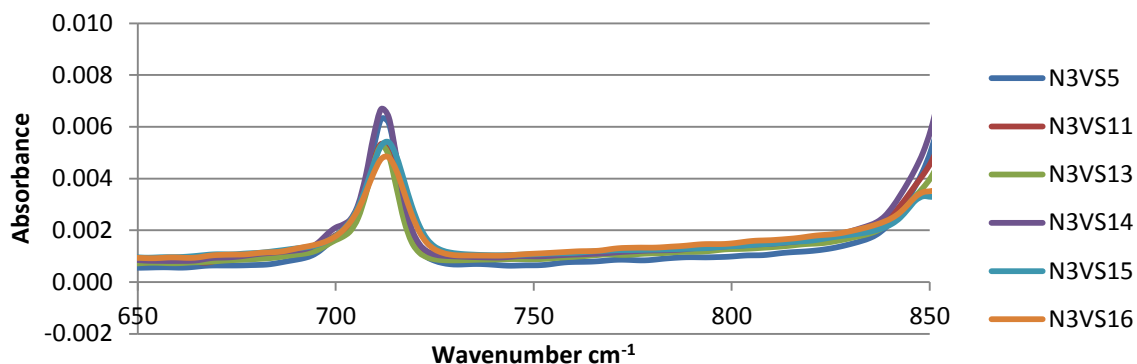


Figure 8.4 FTIR spectra of subsamples dominantly composed of calcite.

For the third stage of subsampling, more precise powder XRD measurements were performed and the results are given in figure 8.5. Subsamples consist of variable fractions of aragonite ranging from 100% to 10%, with the remaining material calcite, except in S41 which also includes 14% hydroxylapatite. Raw measurements are in table 25 of Appendix III.

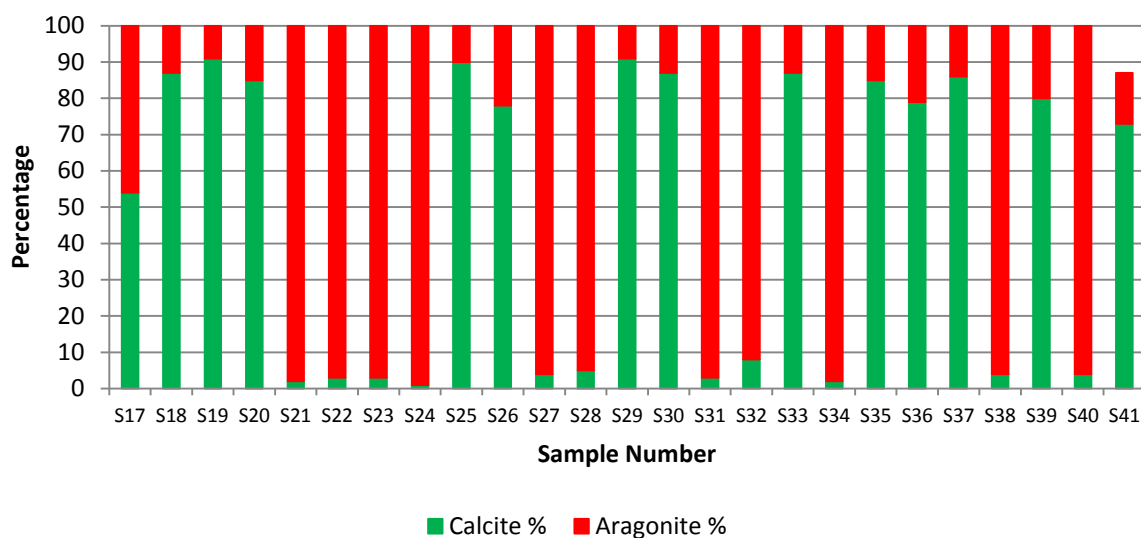


Figure 8.5: XRD results of mineralogy for subsamples S17 to S41. Dominantly aragonite subsamples are shown in red and dominantly calcite subsamples are shown in green.

b) Variation in mineralogy based on distance away from diagenetic fronts

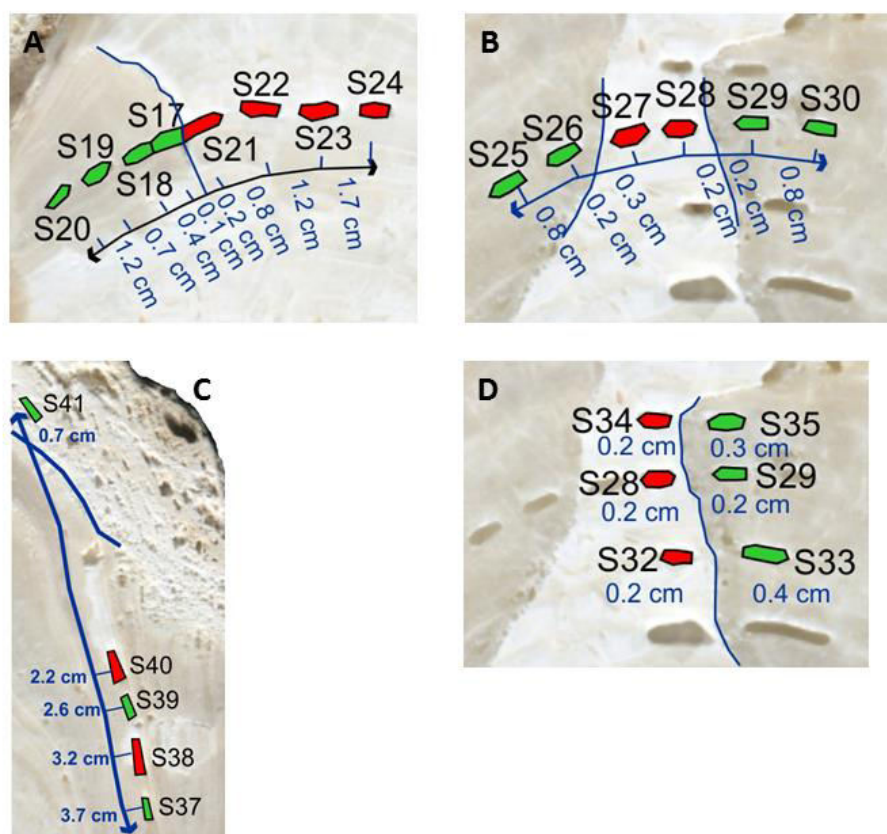


Figure 8.6: Distance of subsample measurements from the different diagenetic fronts have been shown in the figure. Location of subsamples on the sample can be seen in figure 8.1. Dominantly aragonite subsamples are in red, dominantly calcite subsamples are in green. Diagenetic fronts have been indicated by blue lines. Distances of subsamples away from diagenetic fronts are given in blue.

Figure 8.6 indicates that the four diagenetic fronts selected for study have distinct structures. Distinct boundaries between mineralogies have been considered to be diagenetic fronts. For subsamples S17 to S24 the diagenetic front is along a distinct crack in the stalagmite. For subsamples S25 to S35 (shown in panels B and D of the diagenetic front plots), there is primary aragonite on the growth axis with calcite on both flanks. Subsamples S37 to S41 are along a single lamina with patches of aragonite and calcite with one distinct diagenetic front between S41 and S40.

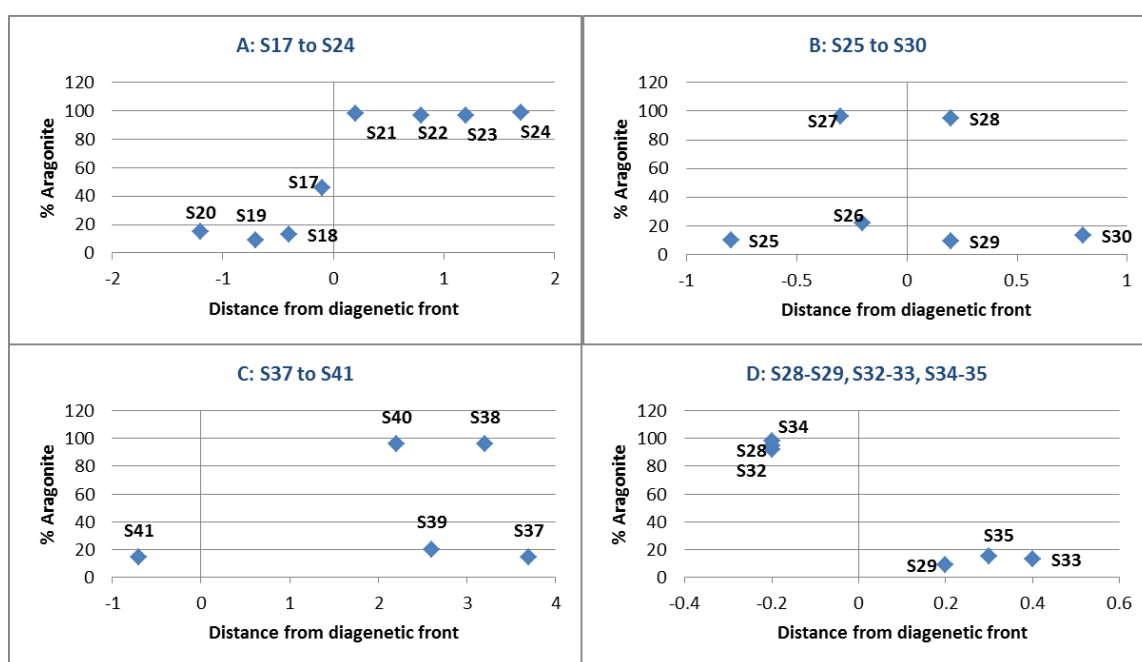


Figure 8.7: Percentage aragonite plotted against distance away from diagenetic front. The diagenetic fronts with respect to subsamples have been shown in figure 8.6. (A): Subsamples to the left of the diagenetic front have been represented by negative values. (B) There are two diagenetic fronts. S25, S26 and S27 have been represented with negative values. (C) S41 which is above the diagenetic axis has been shown with a negative value. (D) Subsamples to the left of the diagenetic axis have been represented with negative values.

Figure 8.7 shows that there is no clear relationship between the distance away from diagenetic front and percentage calcite.

8.5.3 Description of visible mineralogical variation

The visible mineralogical variation of the sample section has been made based on FTIR and XRD measurements. The measurements indicate that the milky coloured zones of the

sample are predominantly composed of aragonite while the translucent zones of the sample are predominantly composed of calcite.

This enables the subsamples to be divided into 5 zones (figure 8.8),

- (i) Subsamples S3, S1, S4, S6, S8, S9 and S31: Mixture of aragonite and calcite but dominantly composed of aragonite. Laminae have been largely preserved.
- (ii) Subsamples S5, S4, S20, S19, S18, S17, S21, S22, S23, S24 and S7: Distinct patches of calcite surrounded by aragonite. Laminae are not preserved.
- (iii) Subsamples S10, S11, S32, S33, S25, S26, S27, S28, S29, S30, S34, S35, S12 and S13: Growth axis composed of aragonite with calcite on either side. Laminae are not preserved.
- (iv) Subsamples S14, S36, S2, S37, S38, S39, S40 and S41: Largely calcite with patches of aragonite. Laminae are not preserved.
- (v) Subsamples S15 and S16: Dominantly composed of calcite. Well laminated with darker layers. Likely to be primary calcite since it shows few visible signs of diagenesis, such as effacing of layers and milky aragonite, when compared to the rest of the sample.

These observations are similar to those made in other diagenetically altered samples by *Lachniet et al, 2012* and *Spotl et al, 2002*. Also similar to *Lachniet et al, 2012* and *Railsback et al, 1994*, the upper boundaries of secondary calcite are usually defined by growth boundaries while the lower bounds of calcite show a botryoidal inter-fingering pattern with primary aragonite.

VALMIKI

Length: 24cms

Width: 12.5cms

Scale:

1cm on sample =

1.1cm on image

Mineralogy S1 to S16:

Calcite

Aragonite

Unknown

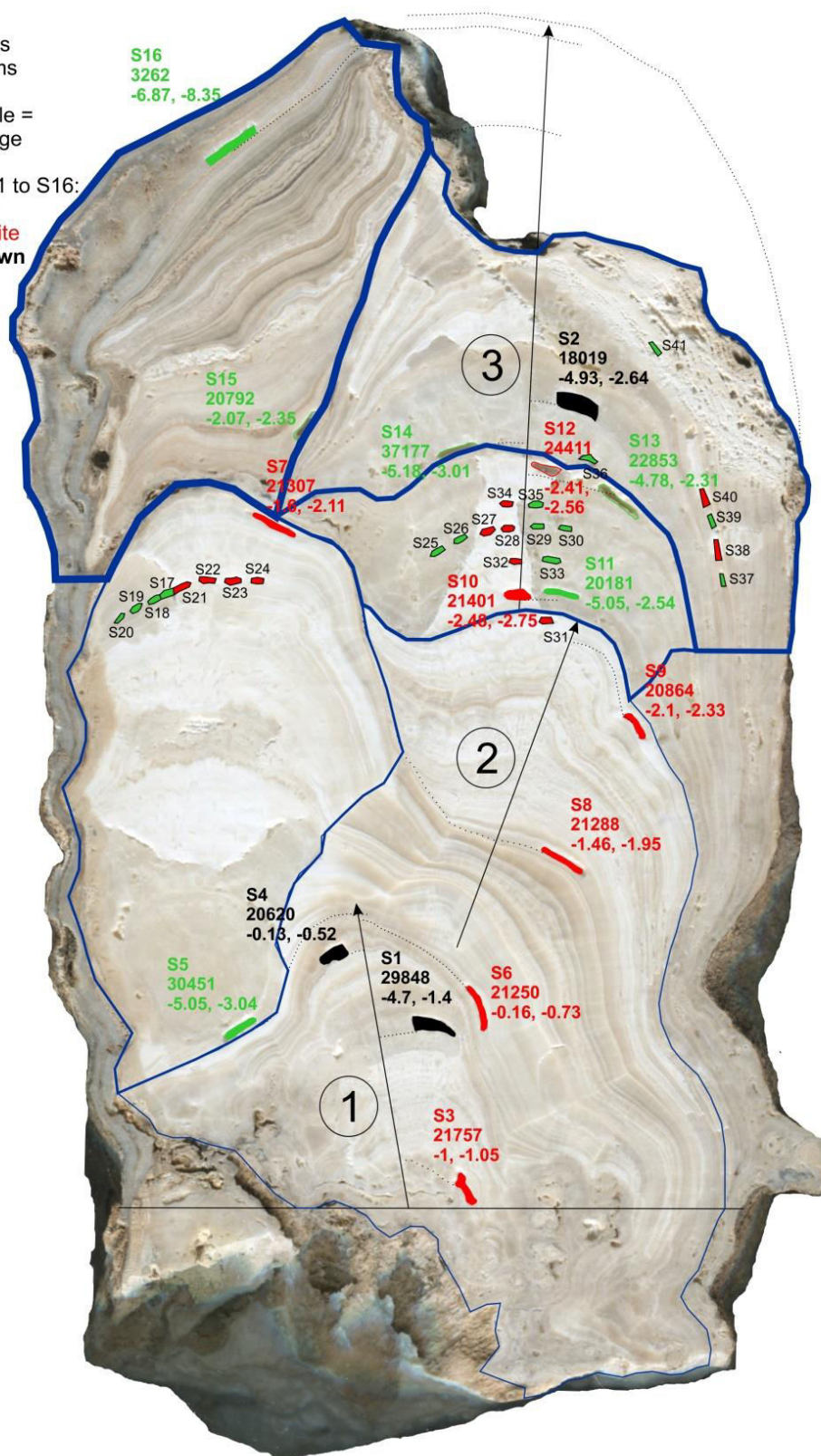
Ages in years BP
and corrected for
detrital Th

Figure 8.8: The sample has been divided into five zones based on the relationship between calcite and aragonite.

Sample	Mineralogy method	Mineralogy	$\delta^{18}\text{O}$ ‰VPDB	$\delta^{13}\text{C}$ ‰VPDB	V/Ca mmol/mol	Ba/Ca	U/Ca	Na/Ca	Mg/Ca	P/Ca	Mn/Ca	Co/Ca	Zn/Ca	Rb/Ca	Sr/Ca	K/Ca
S1	Not measured	Unknown	-4.70	-1.40												
S2	Not measured	Unknown	-4.93	-2.64												
S3	FTIR	>80% aragonite	-1.00	-1.05	4.6E-05	2.1E+00	5.8E-03	1.3E+00	1.6E+00	3.8E-01	6.9E-04	6.1E-05	4.4E-02	2.8E-05	3.4E+00	1.1E-01
S4	FTIR	Unknown	-0.13	-0.52	5.5E-05	2.3E+00	4.1E-03	1.2E+00	1.8E+00	5.2E-01	3.5E-03	1.6E-03	9.1E+00	1.4E-05	2.8E+00	3.7E-02
S5	FTIR	<20% aragonite	-5.05	-3.04	1.4E-05	4.7E-01	2.9E-03	5.5E-01	1.0E+01	6.0E-01	2.2E-03	1.4E-04	3.0E-02	2.5E-04	1.7E+00	6.8E-01
S6	FTIR	>80% aragonite	-0.16	-0.73	4.3E-05	2.0E+00	6.3E-03	1.5E+00	1.0E+00	2.8E-01	3.6E-04	5.5E-05	2.4E-02	1.8E-04	3.3E+00	4.6E-01
S7	FTIR	>80% aragonite	-1.60	-2.11	5.3E-05	2.2E+00	9.1E-03	1.5E+00	8.6E-01	1.1E+00	1.9E-03	1.1E-05	1.4E-02	1.5E-04	3.8E+00	4.0E-01
S8	FTIR	>80% aragonite	-1.46	-1.95	5.3E-05	2.7E+00	6.4E-03	1.6E+00	1.5E+00	3.5E-01	2.2E-03	1.4E-05	1.4E-02	3.5E-05	3.3E+00	1.1E-01
S9	FTIR	>80% aragonite	-2.10	-2.33	4.7E-05	2.8E+00	8.0E-03	1.2E+00	7.2E-01	4.2E-01	6.0E-04	2.4E-05	1.8E-02	1.2E-04	4.0E+00	3.3E-01
S10	FTIR	>80% aragonite	-2.48	-2.75	6.1E-05	3.2E+00	1.0E-02	2.0E+00	7.7E-01	4.6E-01	7.6E-04	1.8E-04	9.9E-02	5.0E-04	3.7E+00	1.5E+00
S11	FTIR	<20% aragonite	-5.05	-2.54	2.5E-05	9.2E-01	9.1E-03	3.5E-01	2.9E+00	3.3E-01	3.9E-04	1.1E-04	1.6E-02	1.1E-04	2.2E+00	2.9E-01
S12	FTIR	>80% aragonite	-2.41	-2.56	5.3E-05	2.4E+00	8.0E-03	1.8E+00	3.2E+00	6.2E-01	3.2E-03	1.2E-04	7.4E-02	4.2E-04	3.4E+00	1.3E+00
S13	FTIR	<20% aragonite	-4.78	-2.31	2.7E-05	1.1E+00	6.7E-03	2.8E-01	5.4E+00	4.8E-01	4.9E-03	1.1E-04	1.6E-02	1.1E-04	1.9E+00	3.0E-01
S14	FTIR	<20% aragonite	-5.18	-3.01	2.1E-05	7.6E-01	7.3E-03	1.9E+00	5.7E+00	6.0E-01	2.7E-03	2.9E-05	1.2E-01	8.4E-04	2.0E+00	2.5E+00
S15	FTIR	<20% aragonite	-2.07	-2.35	1.0E-05	2.6E-01	1.1E-03	1.3E+00		1.3E+00	8.9E-03	6.5E-05	1.9E-02	5.4E-04	1.2E+00	1.5E+00
S16	FTIR	<20% aragonite	-6.87	-8.35	7.8E-05	3.6E+00	4.4E-04	5.8E-01	4.0E+01	3.2E+00	2.3E-02	4.5E-05	3.1E-02	3.2E-04	1.5E-01	9.2E-01
S17	XRD	46% aragonite	-3.63	-2.70	3.5E-05	1.2E+00	7.5E-03	6.1E-01	4.7E+00	3.7E-01	5.1E-04	5.3E-05	3.6E-03	6.9E-06	3.0E+00	1.8E-02
S18	XRD	13% aragonite	-4.98	-2.77	2.3E-05	6.7E-01	4.9E-03	2.6E-01	5.6E+00	3.2E-01	5.9E-04	2.9E-05	7.8E-03	6.6E-05	2.4E+00	1.4E-01
S19	XRD	9% aragonite	-5.29	-3.33	2.0E-05	7.3E-01	2.8E-03	1.1E-01	1.0E+01	2.8E-01	3.2E-04	3.4E-05	1.1E-02	5.1E-06	1.8E+00	1.1E-02
S20	XRD	15% aragonite	-5.05	-3.52	1.7E-05	5.5E-01	2.4E-03	1.7E-01	1.5E+01	5.7E-01	7.9E-04	2.8E-05	1.0E-02	1.1E-05	1.6E+00	2.3E-02
S21	XRD	98% aragonite	-1.60	-2.63	5.7E-05	2.2E+00	9.6E-03	1.2E+00	9.1E-01	3.6E-01	4.1E-04	2.9E-05	3.6E-03	9.3E-06	4.3E+00	3.3E-02
S22	XRD	97% aragonite	-2.30	-3.60	6.1E-05	2.4E+00	1.3E-02	1.3E+00	9.0E-01	5.6E-01	4.4E-04	1.4E-05	2.2E-02	1.4E-05	4.4E+00	4.9E-02
S23	XRD	97% aragonite	-2.55	-3.49	8.3E-05	3.4E+00	1.3E-02	1.2E+00	1.2E+00	5.6E-01	6.4E-04	1.3E-05	8.2E-03	3.5E-05	4.5E+00	8.4E-02
S24	XRD	99% aragonite	-2.14	-3.18	6.2E-05	2.4E+00	1.1E-02	1.2E+00	1.0E+00	4.3E-01	5.3E-04	2.2E-05	1.1E-02	7.1E-06	4.3E+00	2.2E-02
S25	XRD	10% aragonite	-4.94	-2.77	1.3E-04	6.1E+00	6.6E-03	1.3E-01	5.3E+00	4.5E-01	1.6E-03	1.9E-05	1.3E-02	1.9E-05	1.8E+00	5.3E-02
S26	XRD	22% aragonite	-4.58	-3.01	2.2E-05	8.5E-01	1.0E-02	3.2E-01	5.3E+00	3.8E-01	2.4E-04	8.8E-06	4.0E-03	2.9E-05	2.1E+00	6.4E-02
S27	XRD	96% aragonite	-1.83	-2.59	6.1E-05	2.4E+00	9.7E-03	1.1E+00	9.4E-01	3.9E-01	8.9E-04	1.7E-05	7.1E-03	6.8E-06	3.1E+00	2.6E-02
S28	XRD	95% aragonite	-2.23	-3.23	4.9E-05	2.0E+00	9.1E-03	1.1E+00	1.5E+00	3.9E-01	1.8E-03	4.3E-05	8.3E-05	3.7E-05	3.2E+00	9.7E-02
S29	XRD	9% aragonite	-4.78	-2.86	1.8E-05	4.9E-01	8.0E-03	2.7E-01	6.0E+00	3.3E-01	4.6E-04	2.7E-05	2.7E-02	5.7E-05	1.7E+00	1.5E-01
S30	XRD	13% aragonite	-4.90	-2.39	1.4E-05	3.4E-01	8.7E-03	2.8E-01	3.3E+00	3.5E-01	6.0E-04	1.8E-05	1.5E-02	9.7E-05	1.8E+00	2.3E-01
S31	XRD	97% aragonite	-2.42	-2.75	8.0E-05	3.6E+00	9.4E-03	1.0E+00	8.0E-01	4.9E-01	1.2E-04	9.7E-06	8.2E-03	1.3E-05	3.9E+00	5.3E-02
S32	XRD	92% aragonite	-2.28	-3.12	6.4E-05	2.7E+00	7.2E-03	1.0E+00	2.4E+00	3.7E-01	1.4E-03	6.2E-05	2.2E-02	1.6E-05	2.7E+00	4.5E-02
S33	XRD	13% aragonite	-4.69	-2.77	3.6E-05	1.5E+00	7.4E-03	1.8E-01	6.9E+00	3.7E-01	1.9E-03	7.8E-05	6.9E-05	7.8E-06	1.7E+00	2.5E-02
S34	XRD	98% aragonite	-1.95	-2.84	5.8E-05	2.2E+00	1.1E-02	1.3E+00	1.0E+00	5.8E-01	3.8E-03	1.6E-05	6.8E-03	1.2E-05	3.3E+00	4.8E-02
S35	XRD	15% aragonite	-4.88	-2.61	1.3E-05	3.5E-01	8.7E-03	2.1E-01	4.7E+00	3.1E-01	3.5E-04	1.1E-05	5.1E-03	3.7E-05	1.9E+00	9.5E-02
S36	XRD	21% aragonite	-4.77	-2.27	2.1E-05	7.3E-01	6.2E-03	3.6E-01	3.8E+00	4.6E-01	1.8E-03	2.1E-05	4.0E-03	4.4E-05	2.0E+00	1.2E-01
S37	XRD	14% aragonite	-4.51	-2.64	1.1E-04	3.7E+00	8.4E-03	4.0E-01	6.7E+00	9.6E-01	2.1E-02	4.9E-05	5.2E-03	1.8E-05	2.4E+00	4.2E-02
S38	XRD	96% aragonite	-2.49	-2.47	7.9E-05	3.1E+00	1.0E-02	1.2E+00	1.6E+00	7.9E-01	1.3E-03	1.6E-05	1.7E-03	7.1E-06	4.5E+00	2.8E-02
S39	XRD	20% aragonite	-4.29	-2.36	4.7E-05	1.9E+00	8.8E-03	3.1E-01	6.0E+00	6.1E-01	6.8E-03	4.2E-05	1.3E-02	9.9E-06	2.2E+00	2.9E-02
S40	XRD	96% aragonite	-2.36	-2.18	6.8E-05	2.7E+00	9.8E-03	1.4E+00	1.4E+00	5.6E-01	2.1E-03	2.6E-05	7.3E-03	1.6E-04	4.5E+00	4.1E-01
S41	XRD	14% aragonite	-5.20	-3.53	1.1E-04	3.4E+00	7.9E-03	1.1E+00	1.1E+01	1.5E+02	5.0E-01	5.0E-04	1.4E-01	9.3E-05	1.2E+00	2.7E-01
ValMod	Not measured				1.3E-03	5.1E+00	6.4E-04	1.1E+00	9.3E+01	4.0E+01	2.3E-01	1.3E-03	5.1E-01	3.9E-04	2.1E-01	7.0E-01

Table 8.2: Mineralogy, stable isotope and trace element ratios of subsamples. ValMod stands for the modern aragonite that was collected from the same location but under a different drip site. Subsamples with dominantly aragonite mineralogy are in red while those with dominantly calcite mineralogy are in green and those which were not measured or had unsuccessful measurements are in black.

8.5.4 Stable isotope measurements

a) Stable isotope variation based on mineralogy of subsamples

Stable isotope measurements were made to understand the influence of diagenesis on $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ (figure 8.9). Data are given in table 8.2 along with mineralogy and trace element measurements. Aragonite and calcite subsamples have distinct $\delta^{18}\text{O}$ values, with an aragonite median of -2.2‰ vPDB and calcite median of -4.9‰ vPDB. There is less distinction in $\delta^{13}\text{C}$ values with aragonite median of -2.6‰ vPDB and calcite median of -2.8‰ vPDB (table 8.3).

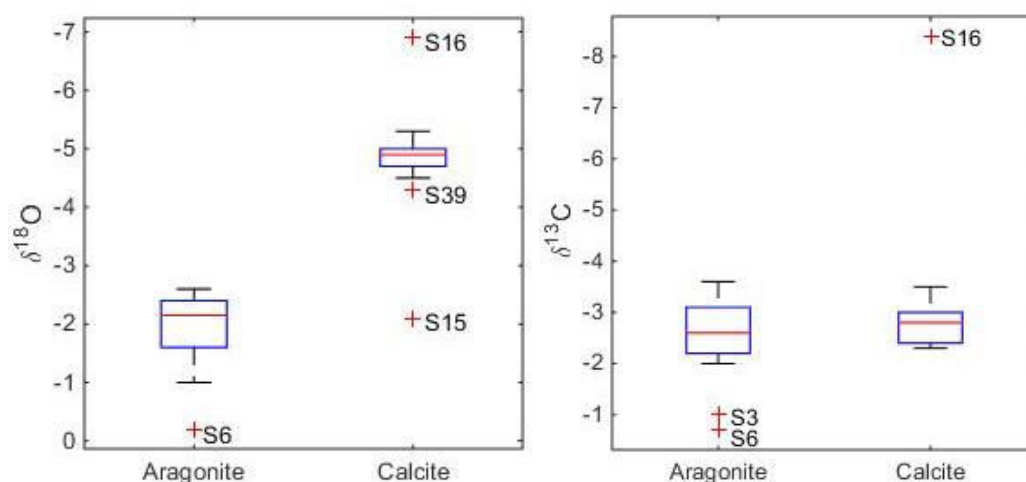


Figure 8.9: $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ measurements of subsamples from sample stalagmite. The maximum whisker length specified as 1.0 times the interquartile range. Data points beyond the whiskers are displayed using +.

The previously published Valmiki $\delta^{18}\text{O}$ range (*Lone et al, 2014*), for a stalagmite that is 100% aragonite, is between 0‰ and -3‰, matching the aragonite $\delta^{18}\text{O}$ values of this sample. Previously published $\delta^{18}\text{O}$ range for a calcite stalagmite from Belum cave (*Narayana et al, 2014*) which is from the same region but covers a time period from 109 to 100 ky BP, is between -4 to -6‰ similar to the calcite values in this study (apart from S15). Published $\delta^{13}\text{C}$ from Valmiki cave (*Lone et al, 2014*), is between -4 and -6‰, somewhat lower than for the sample of this study.

b) Variation in stable isotopic composition based on distance away from diagenetic fronts

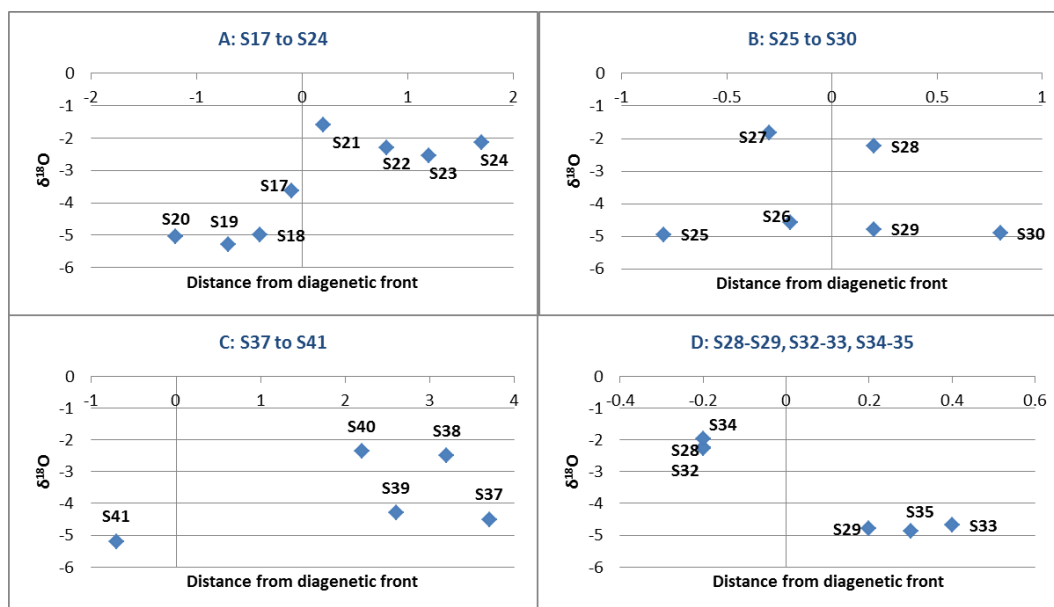


Figure 8.10: $\delta^{18}\text{O}$ ‰ vPDB plotted against distance away from diagenetic front. The diagenetic fronts with respect to subsamples have been shown in figure 8.6. (A): Subsamples to the left of the diagenetic front have been represented by negative values. (B) There are two diagenetic fronts. S25, S26 and S27 have been represented with negative values. (C) S41 which is above the diagenetic axis has been shown with a negative value. (D) Subsamples to the left of the diagenetic axis have been represented with negative values.

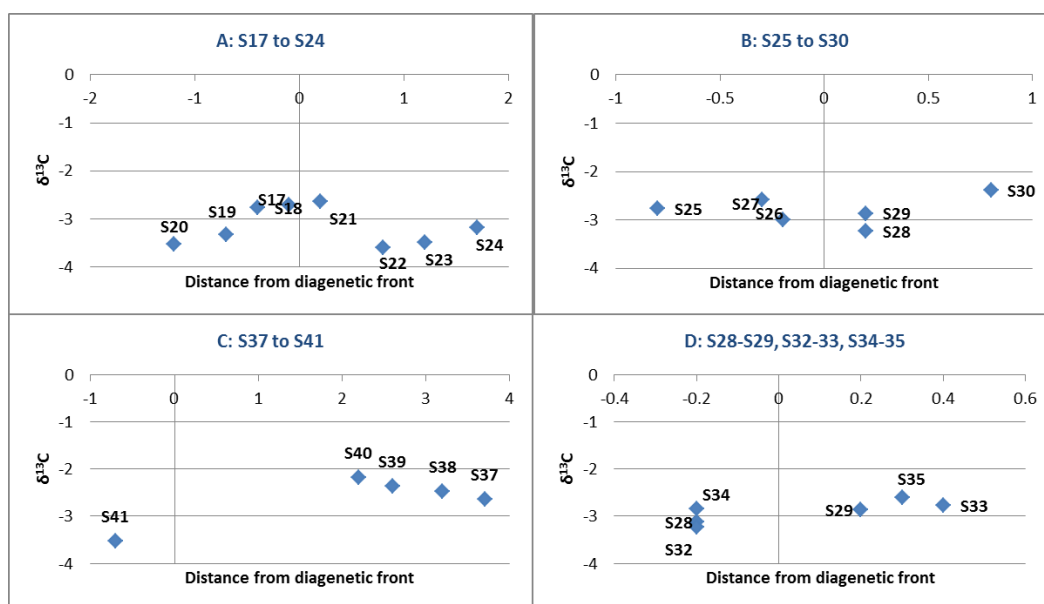


Figure 8.11: $\delta^{13}\text{C}$ ‰ vPDB plotted against distance away from the diagenetic front. The diagenetic fronts with respect to subsamples have been shown in figure 8.6. (A): Subsamples to the left of the diagenetic front have been represented by negative values. (B) There are two diagenetic fronts. S25, S26 and S27 have been represented with negative values. (C) S41 which is above the diagenetic axis has been shown with a negative value. (D) Subsamples to the left of the diagenetic axis have been represented with negative values.

Figure 8.10 shows that there is no clear relationship between the distance away from diagenetic front and $\delta^{18}\text{O}$ composition. Figure 8.11 shows that panels A, C and D show some relationship between distance away from diagenetic front and $\delta^{13}\text{C}$ composition but the relationship is not consistent across all panels.

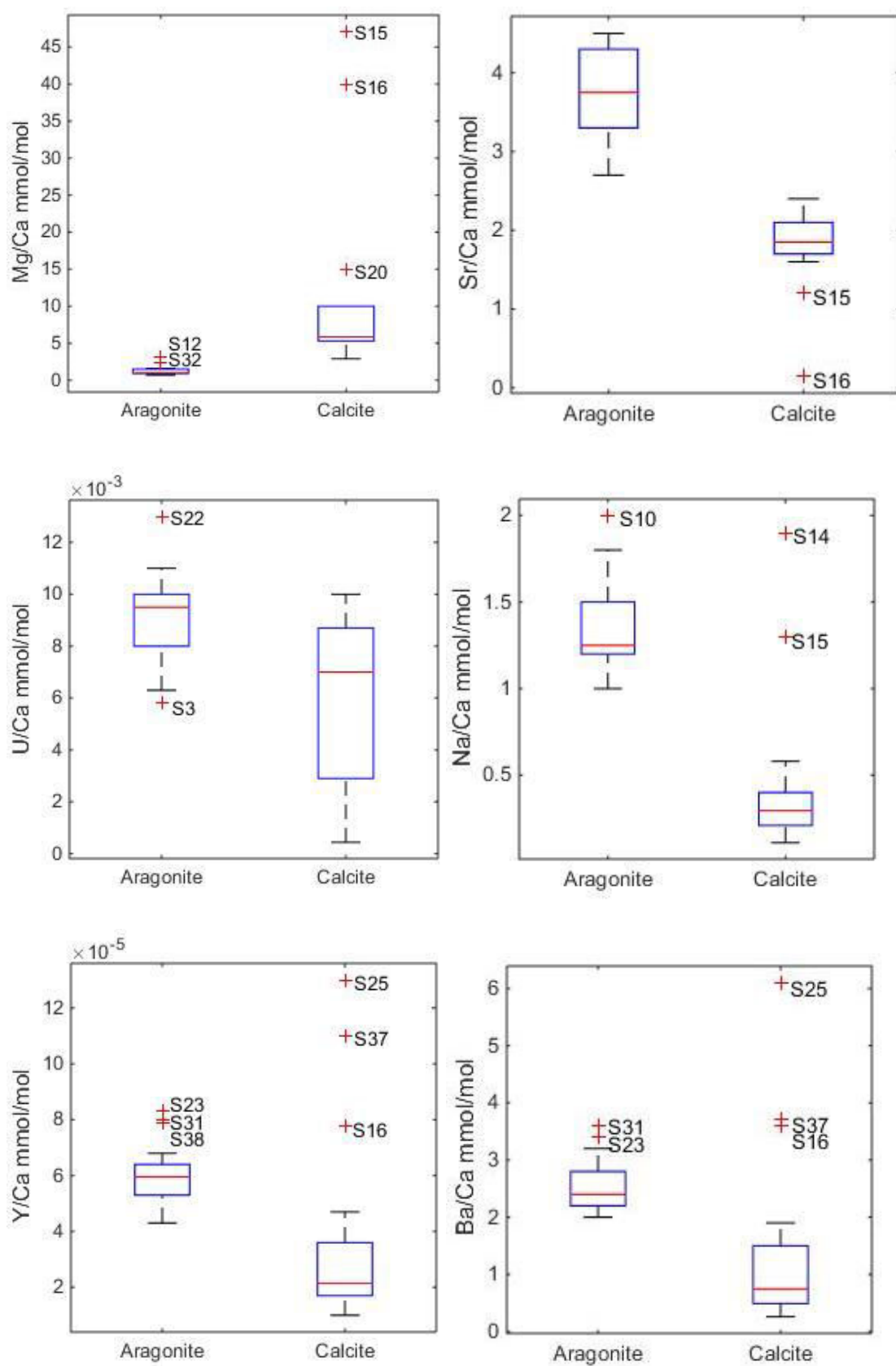
8.5.5 Trace element measurements

a) Trace element variation based on mineralogy of subsamples

Ratios of Y/Ca, Ba/Ca, U/Ca, Na/Ca, Mg/Ca, P/Ca, Mn/Ca, Zn/Ca and Sr/Ca were measured for subsamples S3 to S41 to understand the trace element distribution differences between calcite and aragonite (table 8.3 and figure 8.12).

<i>Parameter</i>	<i>Aragonite</i>		<i>Calcite</i>	
	<i>Median</i>	<i>Median Absolute Deviation</i>	<i>Median</i>	<i>Median Absolute Deviation</i>
$\delta^{18}\text{O}$	-2.2	0.5	-4.9	0.4
$\delta^{13}\text{C}$	-2.6	0.5	-2.8	0.7
Y/Ca	6.0E-05	8.9E-06	2.2E-05	2.5E-05
Ba/Ca	2.4E+00	3.9E-01	7.5E-01	1.1E+00
U/Ca	9.5E-03	1.5E-03	7.0E-03	2.5E-03
Na/Ca	1.3E+00	2.0E-01	3.0E-01	2.8E-01
Mg/Ca	1.00E+00	4.60E-01	5.9E+00	7.8E+00
P/Ca	4.45E-01	1.37E-01	4.6E-01	3.9E-01
Mn/Ca	8.25E-04	8.24E-04	1.7E-03	4.8E-03
Sr/Ca	3.75E+00	4.89E-01	1.9E+00	3.1E-01
Zn/Ca	1.25E-02	1.70E-02	1.3E-02	1.4E-02

Table 8.3: Stable isotope and trace element ratios (in mmol/mol) for calcite and aragonite subsamples. The median trace element ratio values and mean absolute deviation on ratio values are given.



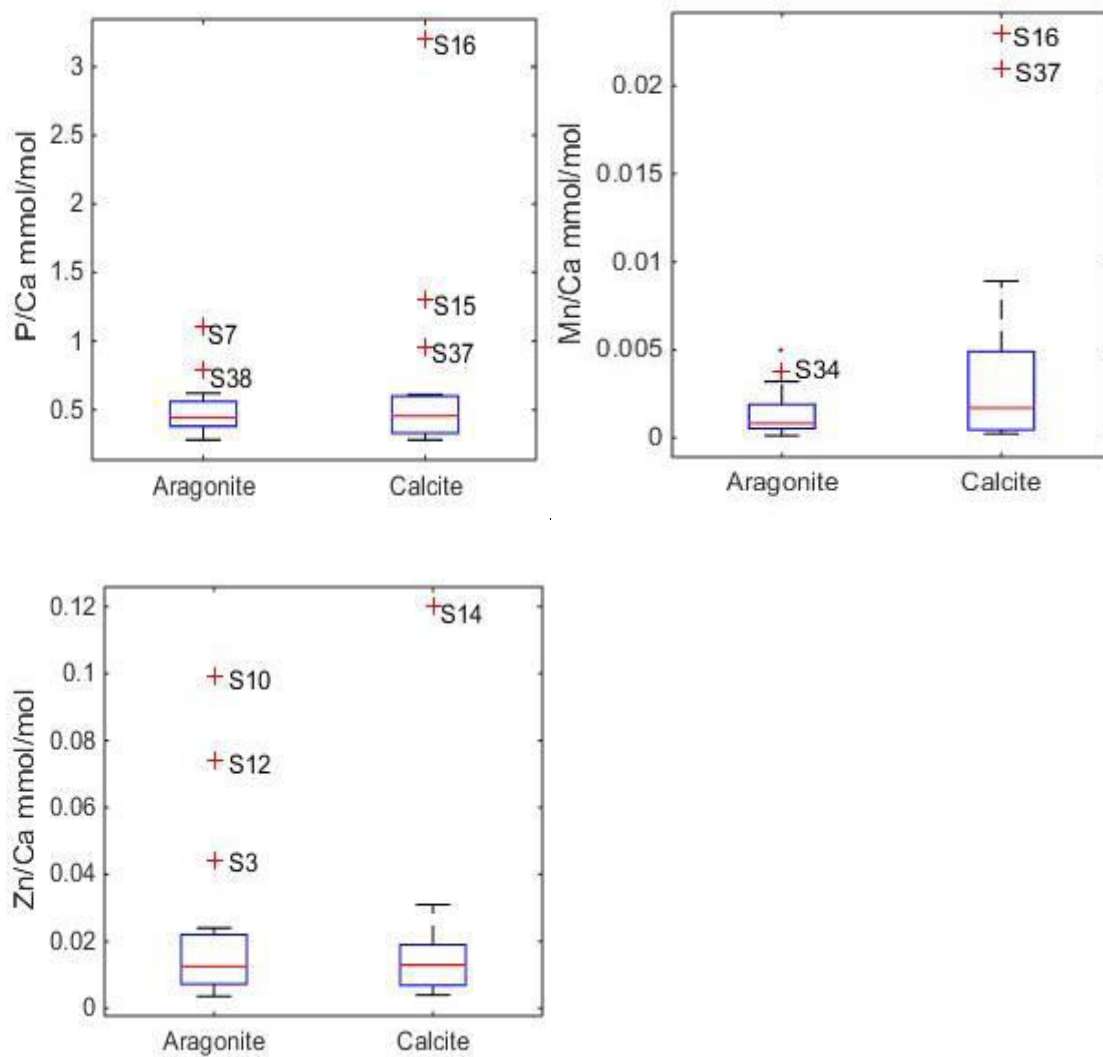


Figure 8.12: Trace element measurements of subsamples from sample stalagmite. The maximum whisker length specified as 1.0 times the interquartile range. Data points beyond the whiskers are displayed using +.

5 specific trends are seen (figure 8.12 and table 8.3):

- i. Mg/Ca is higher in calcite subsamples than in aragonite subsamples.
- ii. Sr/Ca is higher in aragonite subsamples than in calcite subsamples.
- iii. U/Ca and Na/Ca are generally higher in aragonite subsamples but not necessarily so.
- iv. Y/Ca and Ba/Ca show a scattered distribution in calcite subsamples but are restricted to a narrow zone for aragonite subsamples.
- v. P/Ca, Mn/Ca and Zn/Ca show random distribution in aragonite and calcite subsamples.

b) Control of distance away from diagenetic fronts on trace element ratios

Analysis of control of distance from diagenetic front on trace element ratios have been shown in figures 8.13 to 8.20.

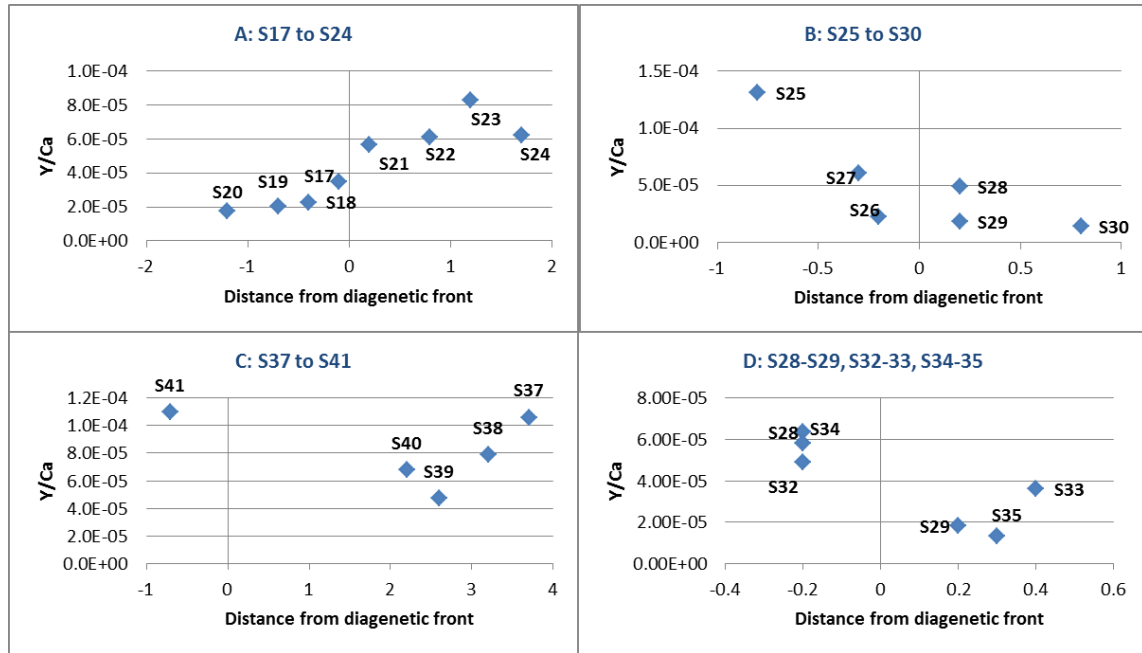


Figure 8.13: Y/Ca mmol/mol plotted against distance away from the diagenetic front. The diagenetic fronts with respect to subsamples have been shown in figure 8.6. (A): Subsamples to the left of the diagenetic front have been represented by negative values. (B) There are two diagenetic fronts. S25, S26 and S27 have been represented with negative values. (C) S41 which is above the diagenetic front has been shown with a negative value. (D) Subsamples to the left of the diagenetic front have been represented with negative values.

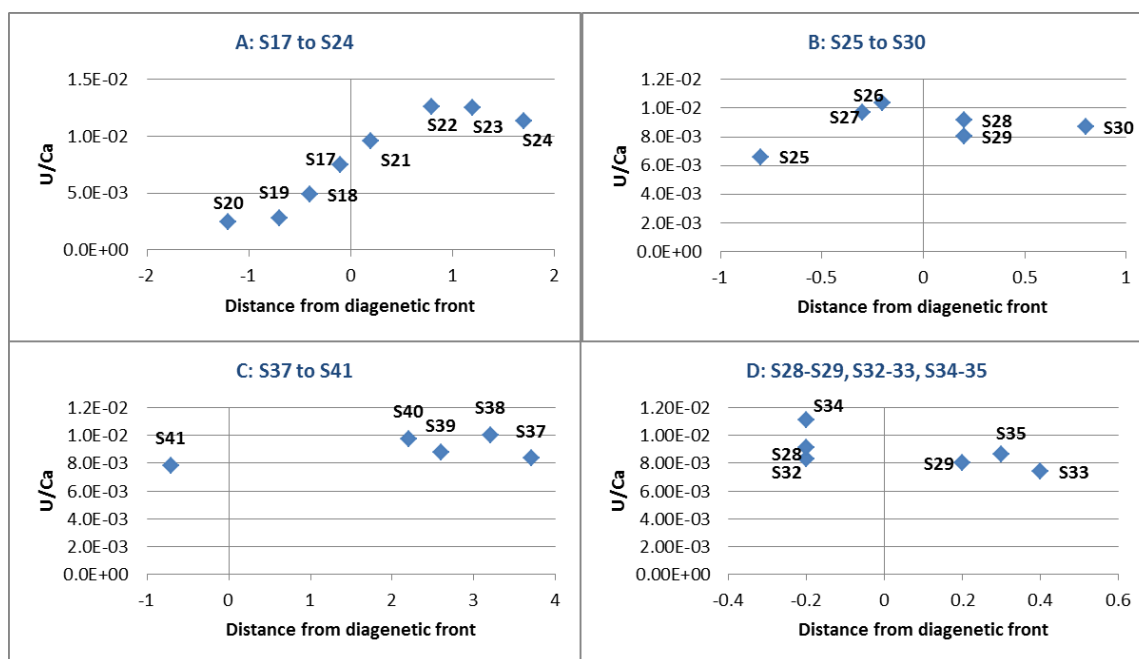


Figure 8.14: U/Ca mmol/mol plotted against distance away from the diagenetic front. The diagenetic fronts with respect to subsamples have been shown in figure 8.6. (A): Subsamples to the left of the diagenetic front have been represented by negative values. (B) There are two diagenetic fronts. S25, S26 and S27 have been represented with negative values. (C) S41 which is above the diagenetic front has been shown with a negative value. (D) Subsamples to the left of the diagenetic front have been represented with negative values.

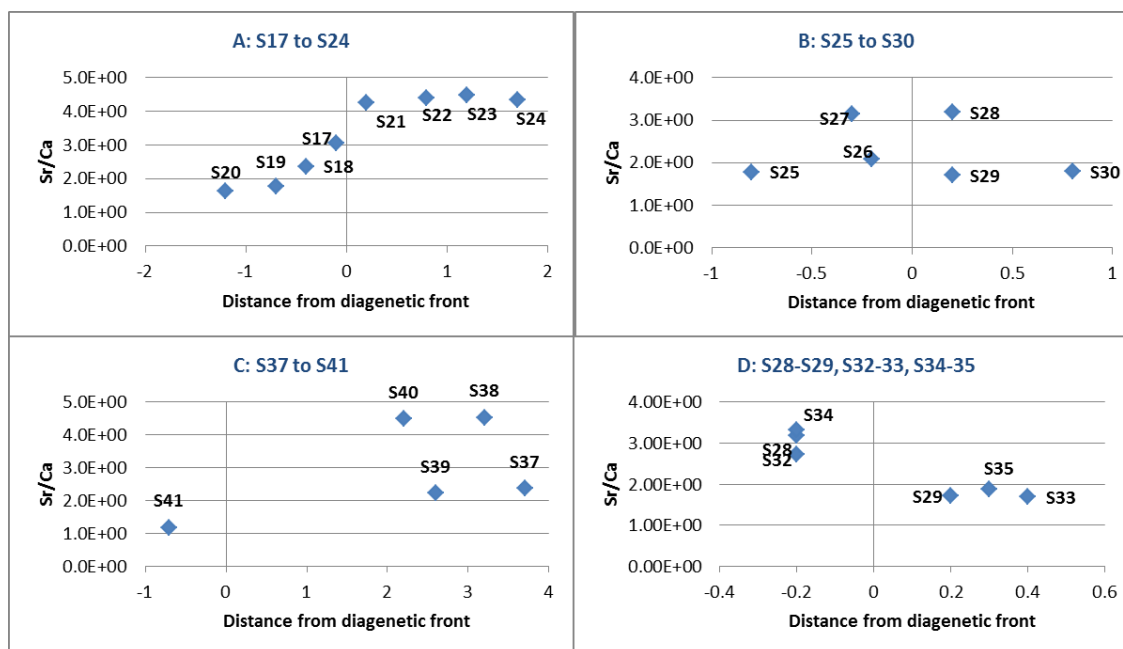


Figure 8.15: Sr/Ca mmol/mol plotted against distance away from the diagenetic front. The diagenetic fronts with respect to subsamples have been shown in figure 8.6. (A): Subsamples to the left of the diagenetic front have been represented by negative values. (B) There are two diagenetic fronts. S25, S26 and S27 have been represented with negative values. (C) S41 which is above the diagenetic front has been shown with a negative value. (D) Subsamples to the left of the diagenetic front have been represented with negative values.

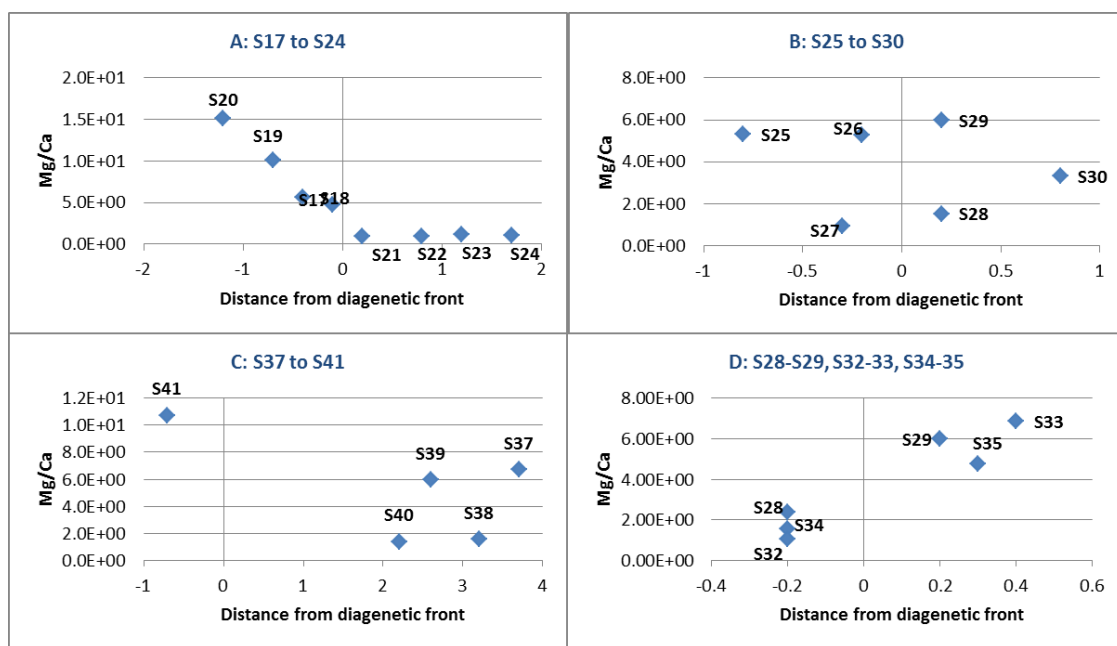


Figure 8.16: Mg/Ca mmol/mol plotted against distance away from the diagenetic front. The diagenetic fronts with respect to subsamples have been shown in figure 8.6. (A): Subsamples to the left of the diagenetic front have been represented by negative values. (B) There are two diagenetic fronts. S25, S26 and S27 have been represented with negative values. (C) S41 which is above the diagenetic front has been shown with a negative value. (D) Subsamples to the left of the diagenetic front have been represented with negative values.

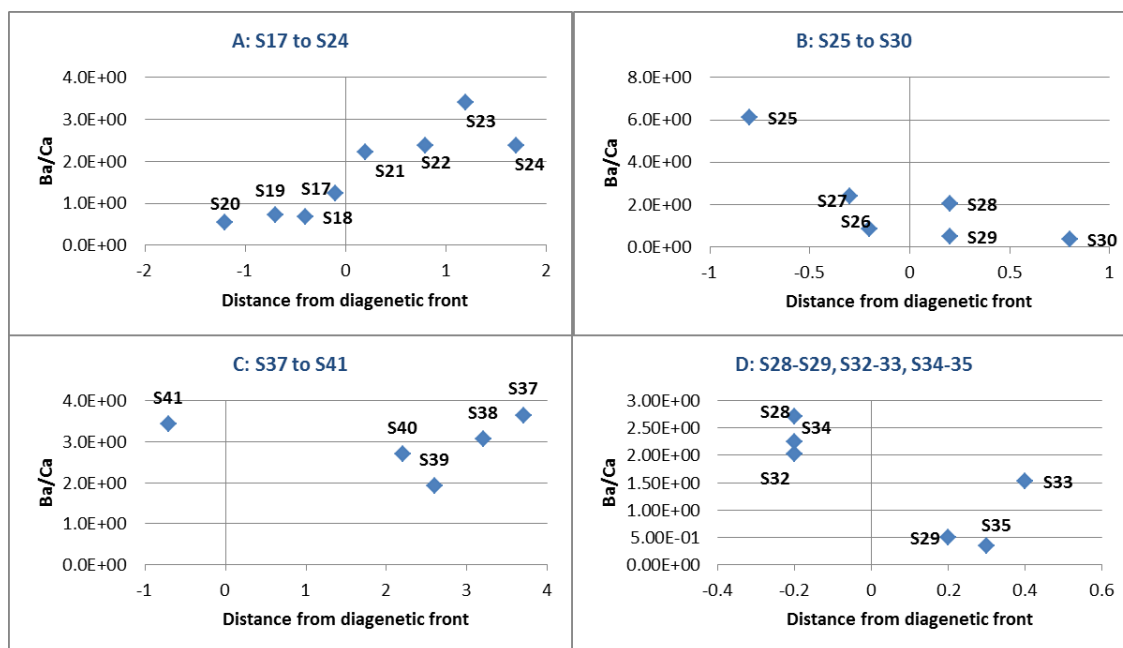


Figure 8.17: Ba/Ca mmol/mol plotted against distance away from the diagenetic front. The diagenetic fronts with respect to subsamples have been shown in figure 8.6. (A): Subsamples to the left of the diagenetic front have been represented by negative values. (B) There are two diagenetic fronts. S25, S26 and S27 have been represented with negative values. (C) S41 which is above the diagenetic front has been shown with a negative value. (D) Subsamples to the left of the diagenetic front have been represented with negative values.

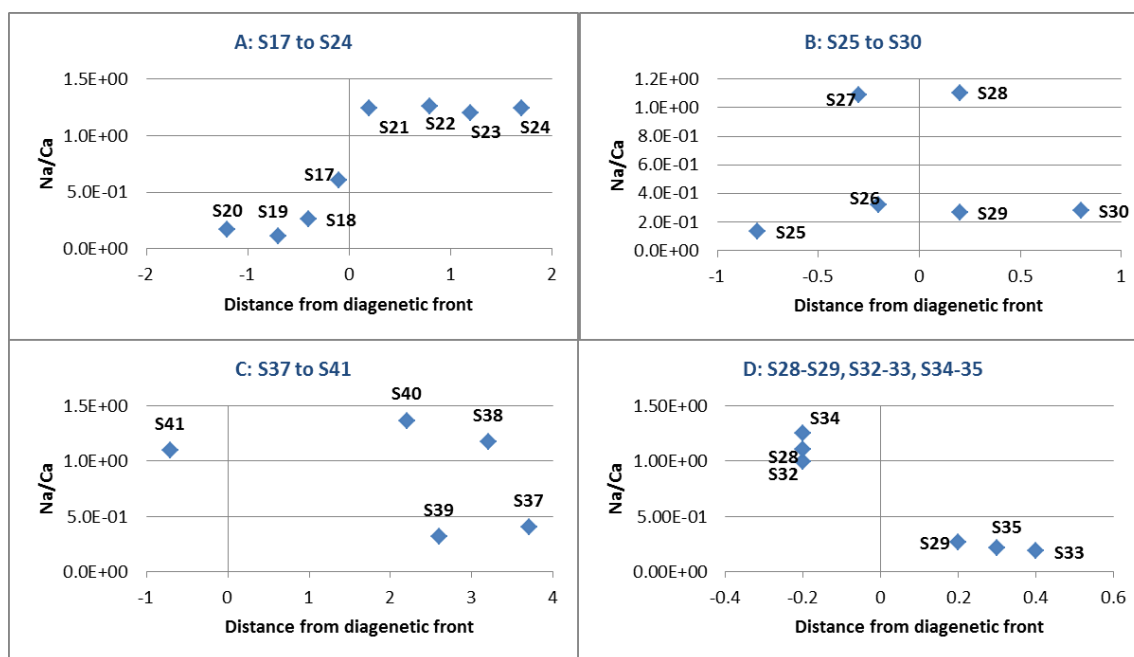


Figure 8.18: Na/Ca mmol/mol plotted against distance away from the diagenetic front. The diagenetic fronts with respect to subsamples have been shown in figure 8.6. (A): Subsamples to the left of the diagenetic front have been represented by negative values. (B) There are two diagenetic fronts. S25, S26 and S27 have been represented with negative values. (C) S41 which is above the diagenetic front has been shown with a negative value. (D) Subsamples to the left of the diagenetic front have been represented with negative values.

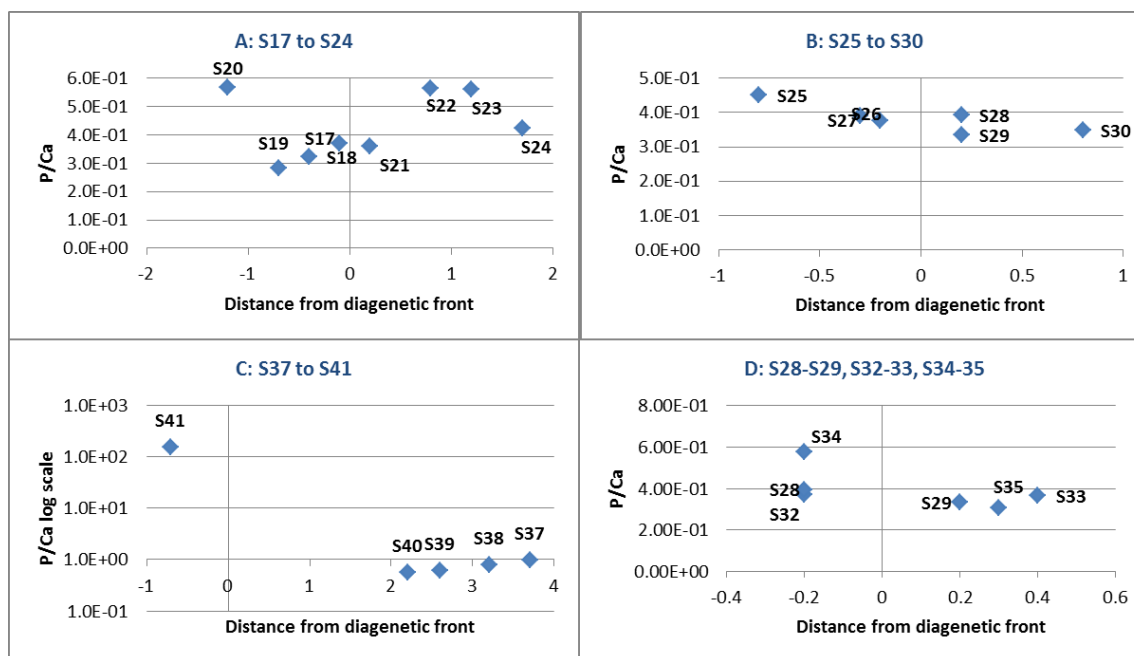


Figure 8.19: P/Ca mmol/mol plotted against distance away from the diagenetic front. Panel C has X axis on log scale. The diagenetic fronts with respect to subsamples have been shown in figure 8.6. (A): Subsamples to the left of the diagenetic front have been represented by negative values. (B) There are two diagenetic fronts. S25, S26 and S27 have been represented with negative values. (C) S41 which is above the diagenetic front has been shown with a negative value. (D) Subsamples to the left of the diagenetic front have been represented with negative values.

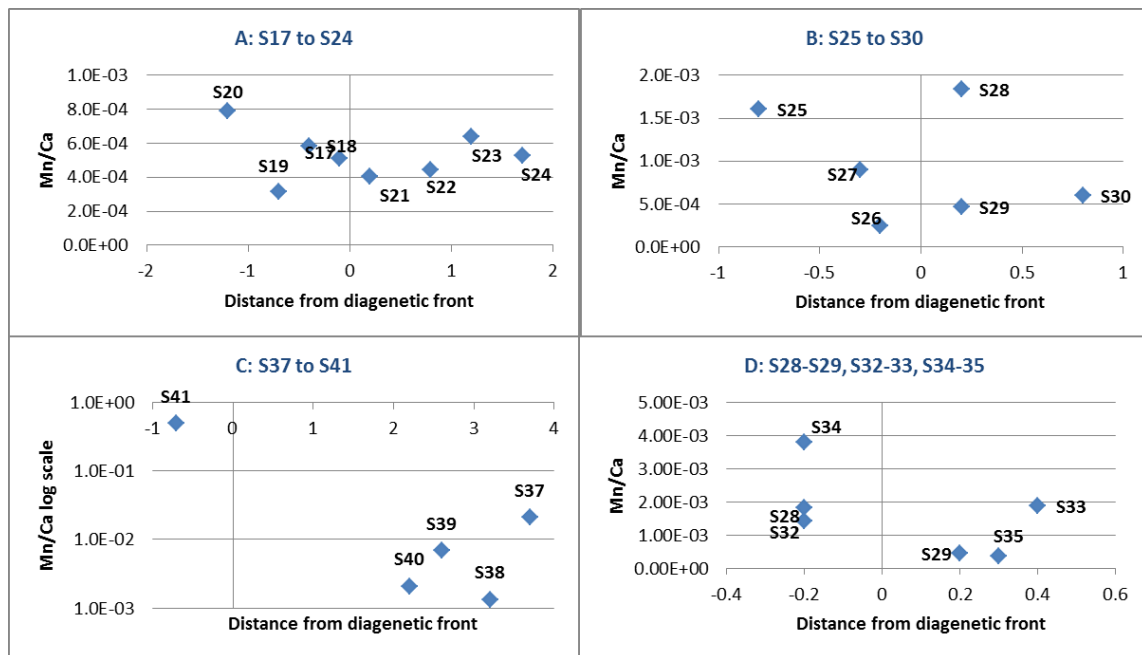


Figure 8.20: Mn/Ca mmol/mol plotted against distance away from the diagenetic front. Panel C has X axis on log scale. The diagenetic fronts with respect to subsamples have been shown in figure 8.6. (A): Subsamples to the left of the diagenetic front have been represented by negative values. (B) There are two diagenetic fronts. S25, S26 and S27 have been represented with negative values. (C) S41 which is above the diagenetic front has been shown with a negative value. (D) Subsamples to the left of the diagenetic front have been represented with negative values.

The following trends are seen:

- i) S17 to S24: Distance away from diagenetic front shows some control on ratios of Y/Ca, U/Ca, Sr/Ca and Mg/Ca.
- ii) S25 to S30: Distance away from diagenetic front shows some control on ratios of Y/Ca, U/Ca, Ba/Ca, P/Ca and Mn/Ca.
- iii) S37 to S41: Distance away from diagenetic front shows some control on P/Ca ratios.
- iv) S28-S29, S32-S33, S34-S35: Distance away from diagenetic front shows some control on Na/Ca ratios.

8.5.6 U-Th systematics

a) Age data

The age data is given in figure 8.21 and table 8.4.

Examination of visual mineralogy, measurements of stable isotope, trace elements and U-Th indicate that subsamples S15 and S16 may be primary calcite rather than secondary calcite. The age data has been summarised in table 8.5 and subsamples S15 and S16 have been considered separately to the other calcite subsamples.

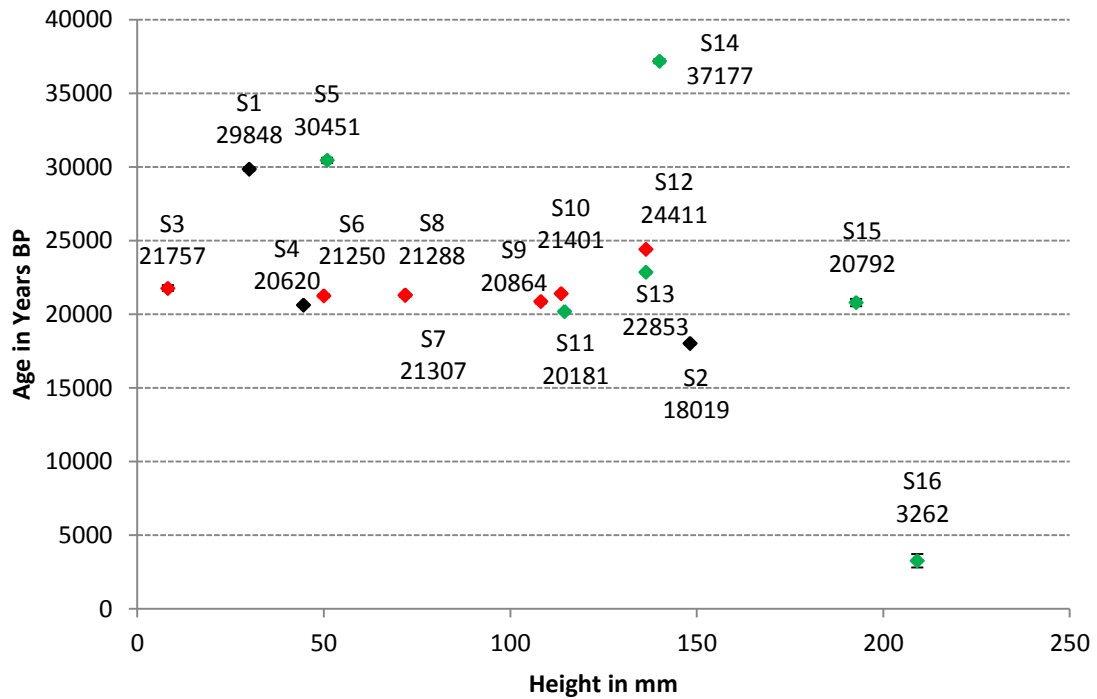


Figure 8.21: U-Th ages against height above based of sample. Data labels give the sample names and ages. Error bars on sample measurements have also been shown but errors are smaller than the marker point sizes. Subsamples of dominant aragonite mineralogy are in red. Subsamples of dominant calcite mineralogy are in green. Subsamples without mineralogical measurements are in black.

Sample	Height sample mm	^{238}U conc ppb	^{232}Th conc ppb	^{230}Th conc ppb	$\delta^{234}\text{U}$	$\delta^{234}\text{U}$	$\delta^{234}\text{U}$	$^{230}\text{Th}/^{232}\text{Th}$ atomic	$^{230}\text{Th}/^{232}\text{Th}$ activity	$^{230}\text{Th}/^{232}\text{Th}$ activity	$^{230}\text{Th}/^{238}\text{U}$ activity	Age (raw) Years	Age (corr) Years	-	+	-	+
N3VS3	8.2	1.4E+04	5.3E-01	8.0E-02	855.4	906.5	1.5E-01	2.8E+04	3.4E-01	21824	223	166	21757	224	166		
N2VS1	30.0	9.6E+03	3.0E-01	7.1E-01	854.6	926.7	2.4E-01	4.5E+04	4.5E-01	29914	136	110	29848	135	109		
N3VS4	44.5	1.0E+04	7.1E-01	5.3E-02	847.1	895.2	7.5E-02	1.4E+04	3.2E-01	20688	78	83	20620	78	84		
N3VS6	50.0	1.8E+04	8.5E-01	9.9E-02	842.8	892.0	1.2E-01	2.2E+04	3.3E-01	21317	91	97	21250	91	97		
N3VS5	50.9	5.9E+03	1.1E-01	4.4E-02	838.9	911.3	4.1E-01	7.6E+04	4.6E-01	30518	180	186	30451	180	186		
N3VS7	71.8	2.3E+04	1.2E+00	1.3E-01	841.5	890.6	1.1E-01	2.0E+04	3.3E-01	21374	77	112	21307	77	112		
N3VS8	71.8	1.6E+04	2.5E-01	8.6E-02	841.9	891.3	3.5E-01	6.4E+04	3.3E-01	21354	81	107	21288	81	107		
N3VS9	108.2	2.4E+04	3.1E-01	1.3E-01	841.4	889.7	4.2E-01	7.7E+04	3.3E-01	20930	90	128	20864	90	128		
N3VS10	113.6	2.2E+04	7.7E-01	1.2E-01	840.9	890.3	1.6E-01	2.9E+04	3.3E-01	21467	104	94	21401	103	94		
N3VS11	114.5	2.2E+04	3.1E-05	1.1E-01	839.6	886.0	7.4E+02	1.4E+08	3.1E-01	20247	73	68	20181	73	68		
N3VS12	136.4	1.9E+04	3.3E-01	1.2E-01	839.9	897.0	3.7E-01	6.8E+04	3.7E-01	24477	91	88	24411	91	88		
N3VS13	136.4	1.8E+04	1.2E-01	1.0E-01	840.8	893.9	8.9E-01	1.6E+05	3.5E-01	22919	81	86	22853	81	86		
N3VS14	140.0	1.6E+04	1.0E-01	1.5E-01	843.4	933.5	1.4E+00	2.7E+05	5.4E-01	37243	143	147	37177	143	147		
N2VS2	148.2	1.7E+04	2.3E-01	7.7E-02	841.8	882.8	3.4E-01	6.4E+04	2.8E-01	18086	70	81	18019	70	81		
N3VS15	192.7	2.4E+03	3.1E-01	1.3E-02	838.0	885.9	4.1E-02	7.6E+03	3.2E-01	20861	244	254	20792	243	253		
N3VS16	209.1	9.9E+02	1.4E+00	8.9E-04	824.7	829.9	6.4E-04	1.2E+02	5.5E-02	3356	463	461	3262	455	450		

Table 8.4: Age data for samples S1 to S16 in stratigraphic order. Subsamples of dominant aragonite mineralogy are in red. Subsamples of dominant calcite mineralogy are in green. Subsamples without mineralogical measurements are in black.

	Range in primary aragonite	Range in secondary calcite	Range in primary calcite (?)
^{238}U concentration (ppm)	14.3 to 24.1	5.9 to 21.7	0.9 to 2.4
^{232}Th concentration (ppt)	251 to 1182	0.03 to 117	314 to 1193
$\delta^{234}\text{U}_{\text{initial}}$	890 to 906	886 to 934	830 to 886
Age in ky BP	24.4 to 20.9	20.2 to 37.2	3.3 to 20.7

Table 8.5: Summary of age data. Primary aragonite subsamples are S3, S6, S7, S8, S9, S10, S12. Secondary calcite subsamples are S5, S11, S13 and S14. Primary calcite subsamples are S15 and S16. Subsamples S1, S2 and S4 have not been considered in this summary table since they lack measurements to identify mineralogy.

The 7 aragonite ages are not in chronological order (figure 8.21) but have a narrow range of ages between 24.4 and 20.9 ky BP. In fact only one subsample has an older age of 24.4 ky BP, with the other 6 subsamples all ~21 ky BP, suggesting that the growth of much of this sample was rapid. This growth rate is similar to that observed in the published study on an unaltered aragonite stalagmite from this cave (15 cm within 1000 years, *Lone et al, 2014*).

Secondary calcite subsamples are typically of some similar age to aragonite samples or are older, with ages falling between 20.2 and 37.2 ky BP. One primary calcite subsample (S16) has an age of 3262 +455/-450 ky BP, consistent with this being a period of later growth around the existing earlier stalagmite.

b) Cross plots of U-Th data

Apart from subsample S16 which is likely to be primary calcite, the remaining calcite subsamples are roughly of the same age as the aragonite subsamples.

There are a few models that have been suggested to understand sources of discrepancies in age during diagenesis, the ones applicable to this sample have been explored further below:

- i) The old ages seen in some secondary calcites could be because of detrital contamination with high initial $^{230}\text{Th}/^{232}\text{Th}$ ratios (*Ivanovich and Alexander, 1987; Lachniet et al, 2012*).
- ii) Movement of U (*Boudron et al, 2003; Borsato et al, 2005*)

iii) Differential mobility of U and Th (*Henderson et al, 1993; Lachniet et al, 2012*).

Figure 8.22 indicates that there is no systematic change in secondary calcite subsample ages with ^{232}Th concentrations. Figure 8.23 indicates that there is no systematic change in secondary calcite subsample ages with ^{238}U concentrations. Figures 8.24 and 8.25 indicate that the alteration in secondary calcite ages are likely to be due to a change in the $^{230}\text{Th}/^{238}\text{U}$ ratio.

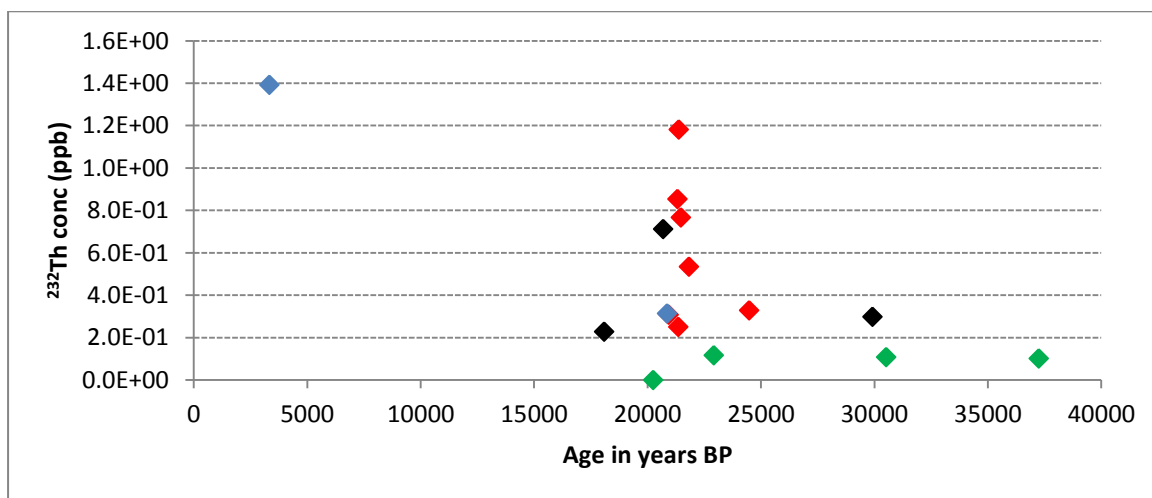


Figure 8.22: U-Th ages against ^{232}Th concentration (ppb). Aragonite subsamples are plotted in red, secondary calcite subsamples are plotted in green, primary calcite subsamples are plotted in blue, subsamples without mineralogical measurements are plotted in black.

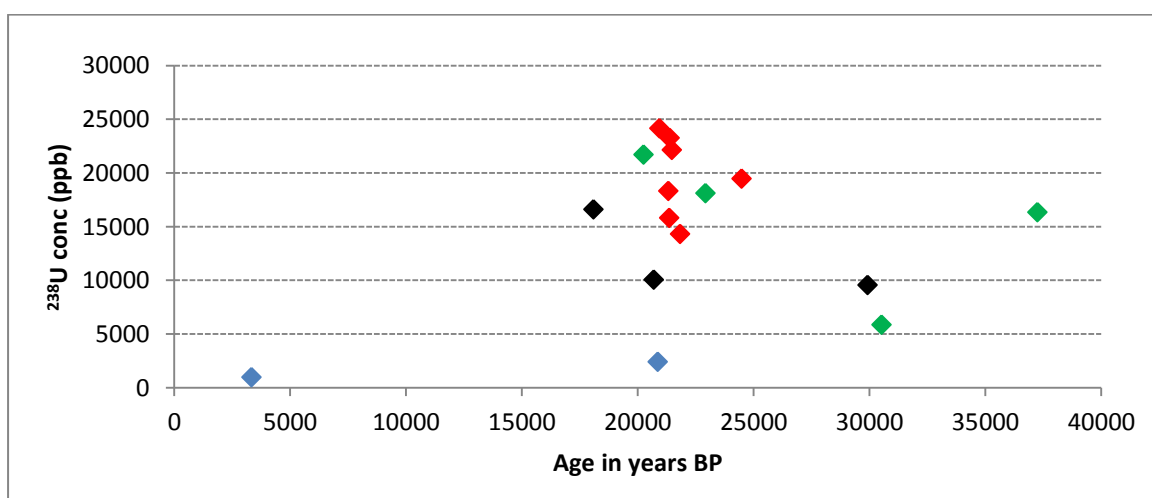


Figure 8.23: U-Th ages against ^{238}U concentration (ppb). Aragonite subsamples are plotted in red, secondary calcite subsamples are plotted in green, primary calcite subsamples are plotted in blue, subsamples without mineralogical measurements are plotted in black.

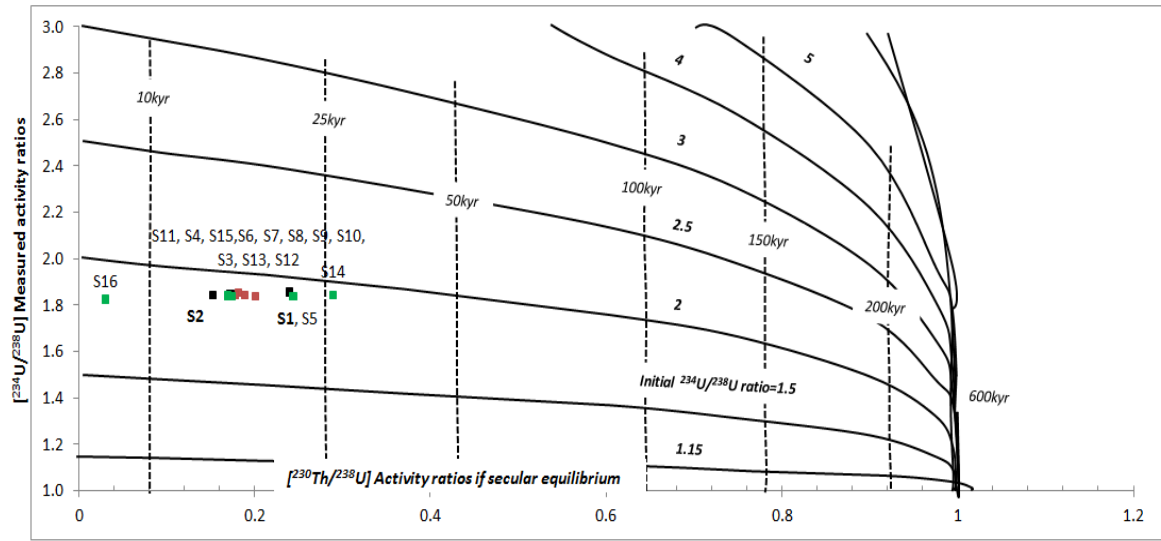


Figure 8.24: $^{230}\text{Th}/^{238}\text{U}$ activity ratios calculated using formula $^{230}\text{Th}/^{238}\text{U} = 1 - e^{(-\lambda^{230}\text{Th}t)}$ i.e. assuming that the $^{234}\text{U}/^{238}\text{U}$ is in secular equilibrium have been plotted against $^{234}\text{U}/^{238}\text{U}$ measured activity ratios for the different subsamples. Aragonite subsamples are in red, calcite subsamples in green. Subsamples without FTIR measurements are plotted in black. The expected ages and initial $^{234}\text{U}/^{238}\text{U}$ lines have also been plotted.

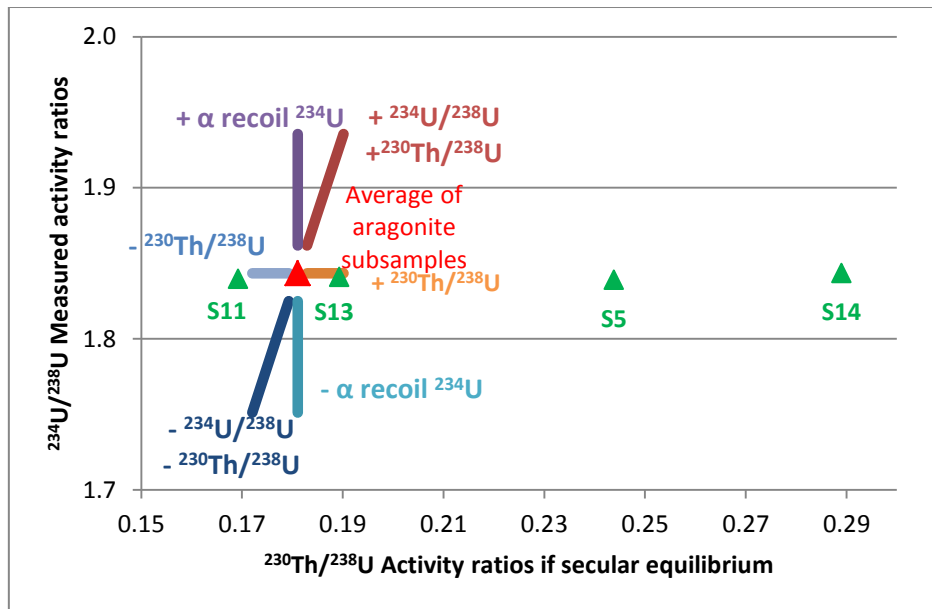


Figure 8.25: $^{230}\text{Th}/^{238}\text{U}$ activity ratios calculated using formula $^{230}\text{Th}/^{238}\text{U} = 1 - e^{(-\lambda^{230}\text{Th}t)}$ i.e. assuming that the $^{234}\text{U}/^{238}\text{U}$ is in secular equilibrium have been plotted against $^{234}\text{U}/^{238}\text{U}$ measured activity ratios for the different subsamples. An average of aragonite subsamples is plotted in red. All secondary calcite subsamples are plotted in green. The respective codes for calcite subsamples have been indicated on the graph. The trend lines indicate the directions of change expected with a 1-5% increase or decrease respectively in ^{230}Th , ^{234}U and ^{238}U activity ratios.

c) U-Th changes across diagenetic reaction fronts

Panels A and B of figure 8.26 indicate some control of reaction front on $^{230}\text{Th}/^{238}\text{U}$ but this is not distinct in the other panels. Raw data in table 29 of Appendix III.

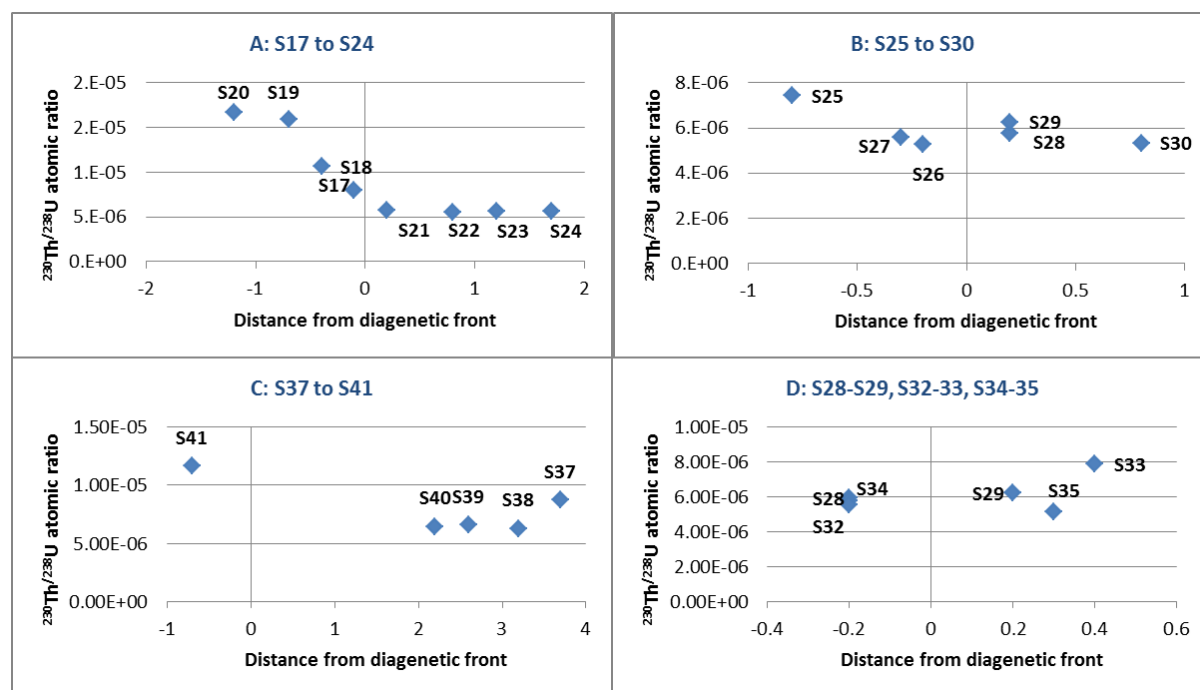


Figure 8.26: $^{230}\text{Th}/^{238}\text{U}$ atomic ratios plotted against distance away from the diagenetic front. The diagenetic fronts with respect to subsamples have been shown in figure 8.6. (A): Subsamples to the left of the diagenetic front have been represented by negative values. (B) There are two diagenetic fronts. S25, S26 and S27 have been represented with negative values. (C) S41 which is above the diagenetic front has been shown with a negative value. (D) Subsamples to the left of the diagenetic front have been represented with negative values.

8.6 Discussion

8.6.1 Aragonite, primary calcite and secondary calcite

Examination of the visible mineralogy of the sample indicates that the section between subsamples S15 and S16 is largely translucent and well layered, giving some indication that it may be composed of primary calcite. Primary and diagenetic calcite subsamples have higher Mg/Ca ratios than the aragonite subsamples, but the Mg/Ca ratios of S15 and S16 are particularly high (figure 8.12). Their U concentrations are nearly an order of magnitude lower than that of aragonite or diagenetic calcite subsamples. Their Sr/Ca values are lower

than that seen in secondary calcite. These lines of evidence strongly suggest that the sample section between S15 and S16 is composed of primary calcite.

If the youngest layers i.e. the sample between subsamples S15 and S16 are primary calcite then it indicates that there are certainly times at which one or more of the drips feeding the sample have been saturated for calcite. This section covers a time period of nearly 17000 years, it is more likely that water routing is affecting this part of the stalagmite rather than changing saturation states due to prior carbonate precipitation or water-rock interaction times.

8.6.2 Mineralogical control on stable isotopes, trace elements and U/Th systematics

	$\delta^{18}\text{O}$	$\delta^{13}\text{C}$	^{238}U	^{230}Th	$^{230}\text{Th}/^{238}\text{U}$	Y/Ca	Ba/Ca	U/Ca	Na/Ca	Mg/Ca	P/Ca	Mn/Ca	Zn/Ca	Sr/Ca
Calcite%	0.96	0.01	0.23	0.05	0.22	0.11	0.14	0.47	0.88	0.58	0.02	0.02	0.02	0.80
Aragonite%	0.97	0.01	0.22	0.04	0.24	0.10	0.12	0.46	0.84	0.61	0.04	0.04	0.04	0.82

Table 8.6: R^2 values for calcite/aragonite mineralogy and stable isotopes, trace elements and U-Th systematics measurements for subsamples S17 to S41.

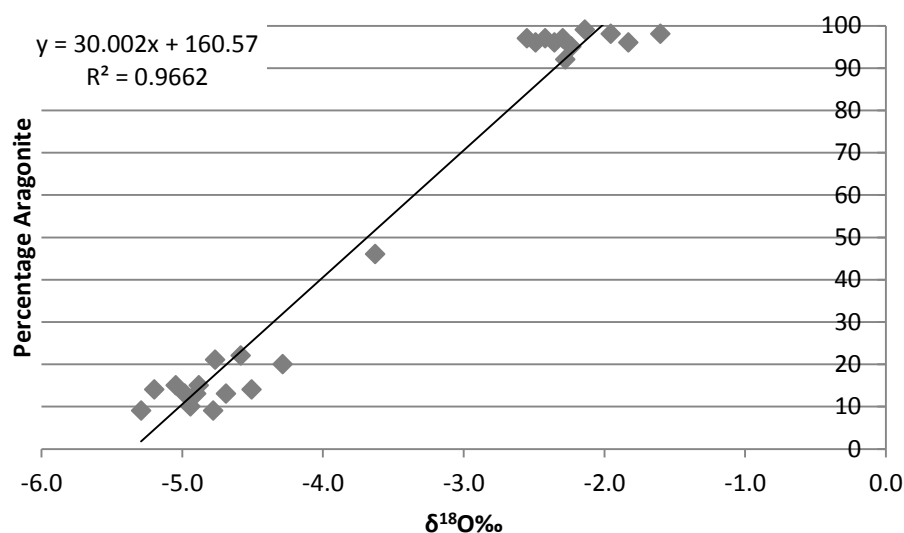


Figure 8.27: $\delta^{18}\text{O}$ ‰vPDB plotted against percentage aragonite. The line equation and R^2 values have been given on the figure.

The hierarchy of mineralogical control is $\delta^{18}\text{O} > \text{Na/Ca} > \text{Sr/Ca} > \text{Mg/Ca} > \text{U/Ca}$ (table 8.6 and figure 8.27). It appears that diagenesis will reflect most on $\delta^{18}\text{O}$ measurements. U/Ca is not the trace element to be most affected by mineralogy, similarly, the distribution of isotopes of U-Th systematics are not dominantly controlled by mineralogy. This table looks exclusively at percentages of aragonite and calcite and does not reflect changes across diagenetic boundaries.

The fact that $\delta^{18}\text{O}$ is so sensitive to percentage calcite and aragonite is interesting since it indicates the alteration in a major element of the precipitated CaCO_3 .

Aragonite is typically precipitated at high Mg/Ca ratios, recrystallization to calcite would have resulted from a fluid with low Mg/Ca ratios (*Lachniet et al, 2012*). Since aragonite incorporates less Mg/Ca at the time of formation, the higher Mg/Ca ratios of calcite subsamples indicates that the increase in Mg must have been contributed by a fluid mediated diagenesis. Primary calcite subsamples also have higher Mg/Ca and P/Ca than secondary calcite. *Hopley et al, 2009* find similar results for Mg/Ca and suggest that this is because the primary and secondary calcites are essentially precipitating from different fluids.

Calcite and aragonite can incorporate a variety of metal ions. Co^{2+} , Fe^{2+} , Mn^{2+} , Cu^{2+} , Zn^{2+} and Cd^{2+} which have ionic radii less than that of Ca^{2+} , co-precipitate preferentially in the rhombohedral carbonate calcite. In contrast Sr^{2+} , Ba^{2+} and UO_2^{2+} which are larger than Ca^{2+} are expected to be concentrated in orthorhombic carbonate of aragonite. The k_{Sr} value for diagenetic calcite subsamples is much higher than that expected in calcite and it is expected that some of Sr from the aragonite is retained in the new calcite structure. U shows similar behaviour. k_{Ba} for the diagenetic subsamples, on the other hand, is much closer to the k values typically obtained for calcite than for aragonite.

8.6.3 Diagenetic front control on stable isotopes, trace elements and U/Th systematics

Figure 8.7 shows that mineralogy is not controlled by distance away from diagenetic front in any of the four panels.

The subsamples of S17 to S20 from the secondary calcite portion and moving progressively away from the diagenetic front perhaps shows the most distinct relationship with the diagenetic front. $\delta^{13}\text{C}$, Y/Ca, U/Ca and Sr/Ca decrease progressively away from the diagenetic front while Mg/Ca and $^{230}\text{Th}/^{238}\text{U}$ atomic ratios increase away from the diagenetic front. Analysis shows that different structures of diagenesis respond differently and further mapping of these diagenetic zones is required to understand this control.

8.6.4 Comparison of $\delta^{18}\text{O}$ with expected equilibrium relationships and implications for diagenesis

To test for equilibrium precipitation of calcite and aragonite subsamples, the measured $\delta^{18}\text{O}$ values were plotted against expected $\delta^{18}\text{O}$ values for the measured cave temperature and drip water $\delta^{18}\text{O}$ based on published equilibrium fractionation equations for aragonite and calcite (figure 8.28, calculations in table 26 of Appendix III). The sample grew ~20 ky BP and modern temperature and drip water measurements are for comparison with expected equilibrium relationships. This may not be correct in detail but is a reasonable starting point.

Measurements during field work of January, 2015 gives the temperature of the cave as 32.8°C and high humidity. The depth of the cave and lack of ventilation suggests that the temperature is unlikely to vary during the year. $\delta^{18}\text{O}$ composition of drip water collected in January, 2015 was -1.59‰ vSMOW. Hyderabad GNIP station is located 150 km to the North of the cave site and has similar climatic characteristics (section 1.4) as the cave site. The $\delta^{18}\text{O}$ of precipitation for measurements made in Hyderabad have been discussed before in

section 7.3. 65% of the rainfall is during the monsoon rainfall months of June, July, August and September (JJAS) with an average $\delta^{18}\text{O}$ of -3.23‰ vSMOW. The depth of the cave indicates that the $\delta^{18}\text{O}$ composition has probably been averaged for a few years and is not a seasonal signal. The heavier $\delta^{18}\text{O}$ value obtained for January, 2015 could be an actual annual average value taking into account evaporation effects on $\delta^{18}\text{O}$ composition. These two values then give the two extremes of $\delta^{18}\text{O}$ values of drip water possible for the cave.

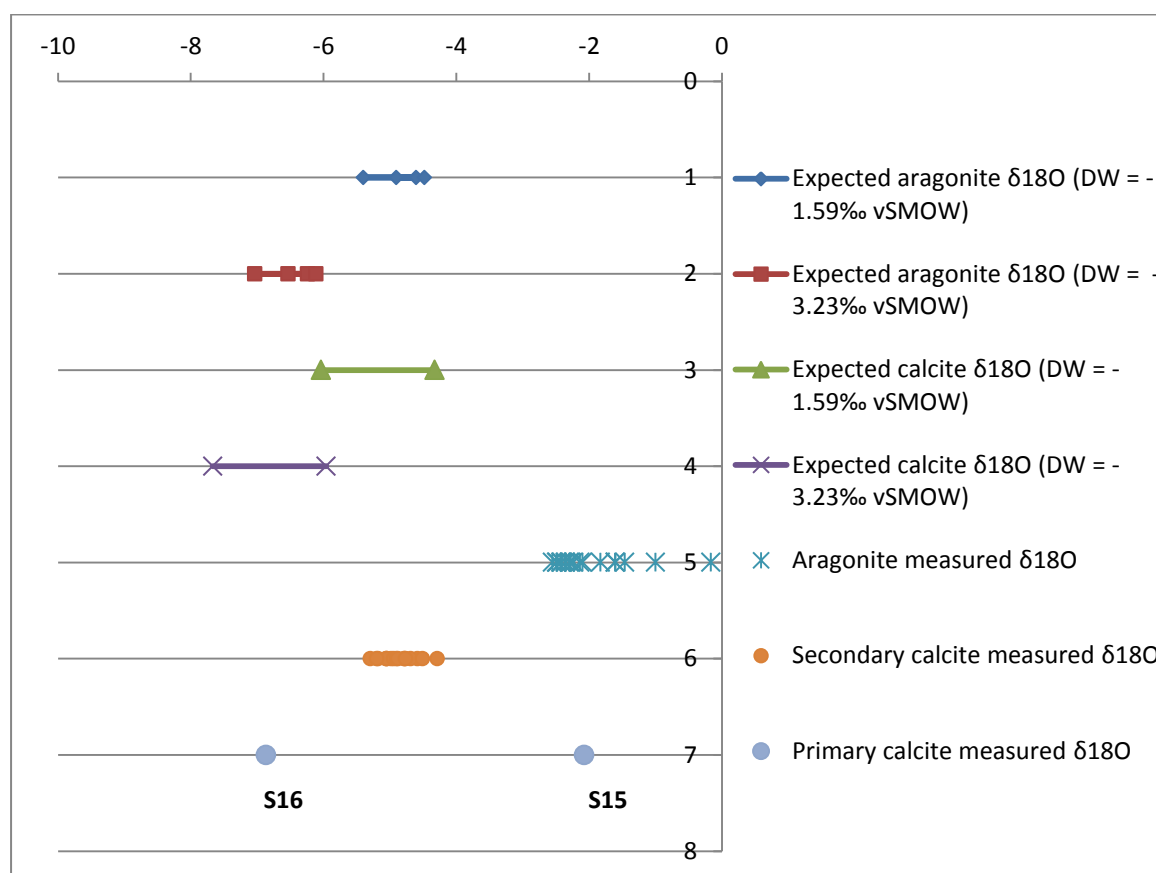


Figure 8.28: Expected equilibrium $\delta^{18}\text{O}\text{‰}$ vPDB values of precipitated aragonite and calcite based on a temperature of 32.8°C measured in the cave and drip water $\delta^{18}\text{O}$ range of -1.59 to -3.25‰ vSMOW have been shown in the graph. Published fractionation equations for the water-aragonite system given by *Grossman and Ku, 1986; Patterson et al, 1993; Thorrold et al, 1997* and *Kim et al, 2007* have been used for calculation of expected values. And published fractionation equations for the water-calcite system given by *Kim and O'Neil, 1997* and *Coplen, 2007* have been used for calculation of expected values. Measured $\delta^{18}\text{O}\text{‰}$ vPDB of aragonite and calcite subsamples have also been plotted. Fractionation equations and calculations have been given in table 26 of Appendix III.

Figure 8.28 shows that the $\delta^{18}\text{O}$ of aragonite subsamples is heavier by $\sim 1.5\text{‰}$ than expected from equilibrium values. The $\delta^{18}\text{O}$ of calcite subsamples fit well with the *Coplen, 2007*

equation for the water-calcite system with the heavier drip water value of -1.59‰ VSMOW or with fractionation equations given for the water-aragonite system, again with the heavier drip water value of -1.59‰ vSMOW.

S16, which precipitated in the Holocene (3262 ± 450 years BP) has a value of -6.87‰ vPDB which is plausible for equilibrium given a more negative drip water value of -3.23‰ vSMOW. The stalagmite sample from Kotumsar cave, which grew during a similar time period (3130 to 2100 years BP) has a $\delta^{18}\text{O}$ range of -6.5‰ and -2.4‰ with an average of -4.05‰ vPDB (Chapter 7).

The primary aragonite is from the Last Glacial Maxima (LGM $\sim 24,000$ to $17,000$ years BP in the Northern Hemisphere) and has a value about 5‰ vPDB heavier than S16. The hydrological cycle is heavier at the LGM, but only by about 1‰ vPDB in comparison to the modern (for example, see figure 2.4). It is unlikely that there is 4‰ vSMOW difference in rain water $\delta^{18}\text{O}$ composition between the LGM and 3262 years BP. If the $\delta^{18}\text{O}$ of rainwater is interpreted in terms of the amount of rainout between source and cave (see section 7.6.4), it is hard to believe there is so much less rainfall from source to cave that we can get 4‰ vSMOW difference in rainfall $\delta^{18}\text{O}$. It is more likely that the primary aragonite has precipitated out of isotopic equilibrium.

The secondary calcite has a value around -5‰ vPDB which can be explained by equilibrium with modern waters and looks similar to values obtained for the stalagmite sample from Kotumsar cave. It seems likely that the secondary calcite has precipitated in isotopic equilibrium with the water causing diagenesis. As the aragonite recrystallized to calcite, it took on an equilibrium value with the water it was flooded by. Since C is not a major element in water, it is likely that $\delta^{13}\text{C}$ of secondary calcite was not as altered by the water causing diagenesis.

8.6.5 U-Th systematics

The different models of changes to U-Th system during diagenesis suggested in section 8.5.6b have been explored in detail below.

i) Th addition due to scavenging from waters

Figure 8.22 indicates that there is little control of detrital Th on the age variation seen in the subsamples. Further, the concentration of ^{232}Th in the calcite subsamples is extremely low, and certainly lower in the calcite subsamples compared to the aragonite subsamples (table 8.4). There is no mechanism which would explain the retention of ^{230}Th associated with detrital material with movement of ^{232}Th during diagenesis. It is unlikely that the older calcite ages in this sample are due to ^{230}Th associated with detrital material.

ii) U loss

Figures 8.23 and 8.25 indicate that the age of the subsamples are not controlled by loss and gain in U concentration alone.

iii) Differential mobility of U and Th

Figures 8.24 and 8.25 indicate that the coupled addition/loss of U and ^{230}Th is the most likely cause for the alteration of ages of subsamples due to diagenesis. Since there is little to no variation along the Y axis in figure 8.25, this also suggests that loss of ^{238}U is coupled to the loss of ^{234}U rather than α recoil generated ^{234}U alone.

The analysis of U-Th systematics suggests that

- i) U and Th are both lost/gained during diagenesis.
- ii) ^{232}Th is lost during diagenesis indicating that Th is mobile.
- iii) There is differential loss/gain in U and Th which is generating the difference in ages.

8.7 Conclusion

Mineralogy in terms of percentage of aragonite versus calcite in subsamples is not controlled by distance away from diagenetic front. This indicates that there may be two possible controls of diagenesis on stable isotope, trace element and U-Th systems: firstly mineralogy i.e. the precise composition of each subsample in terms of percentage aragonite to calcite and secondly, the control on their distribution based on distance away from the diagenetic front.

Diagenetic fronts can have different structures such that the geochemical systems behave differently in the different structures. Analysis in this chapter suggests that mineralogy plays a more dominant role on the geochemical systems than distance away from diagenetic fronts. But further mapping of the sample is required to understand the diagenetic front control.

The hierarchy of mineralogical control is $\delta^{18}\text{O} > \text{Na/Ca} > \text{Sr/Ca} > \text{Mg/Ca} > \text{U/Ca}$ showing that oxygen is extremely susceptible to mineralogical changes produced as a result of diagenesis. This is interesting, since oxygen is a major element of CaCO_3 . Analysis of expected equilibrium relationships using published fractionation equations for calcite and modern drip water $\delta^{18}\text{O}$ and temperature ranges indicates that the secondary calcite may have precipitated in equilibrium with the diagenetic fluid. On the other hand, since C is not a major component of water, the C shows no distinguishable variation between primary aragonite and secondary calcite.

The concentrations of U/Ca and Sr/Ca seen in calcite subsamples are higher than typically seen in calcite (including the primary calcite subsamples of this stalagmite) and are likely to be a remnant of the aragonite structure. But secondary calcite shows higher Mg/Ca ratios than primary aragonite indicating that diagenesis adds Mg relative to the original composition. Mg/Ca ratios can be used to differentiate between primary calcite, primary

aragonite and secondary calcite. Although, it is not known if Mg/Ca partitions differently into primary versus secondary calcite or the fluid causing diagenesis was different from that which precipitated as primary calcite.

Both the aragonite and calcite ages are out of chronological order. The calcite ages are not necessarily older than the aragonite ages. The stalagmite shows loss in ^{232}Th during alteration from aragonite to calcite indicating that Th is mobile. However, the ^{232}Th concentration of the subsamples is extremely low and cannot be responsible for the large age discrepancy seen between aragonite and calcite ages. Similarly, the age discrepancy between coeval primary aragonite and secondary calcite cannot be accounted for by loss of ^{234}U from α recoil alone. Instead, there is differential loss/gain of U and Th isotopes during diagenesis giving rise to discrepancy in ages.

Appendix I

^{230}Th Blanks in U-Th Dating Chemistry

a) Overview

During the process of dating Kotumsar speleothem sample (Chapter 7) it was observed that the main source of blank error was from blank ^{230}Th , more specifically the curiously low $^{230}\text{Th}/^{232}\text{Th}$ atomic ratio. An effort was made to isolate the source of low $^{230}\text{Th}/^{232}\text{Th}$ atomic ratio and has been detailed below.

b) Isolating the Source of ^{230}Th Blank

The error bars of age measurement indicate complications associated with the young age of the sample, low uranium content and a significant proportion of detrital thorium (see section 7.5.3). An effort was made to narrow down the sources of error to check if the ages could be improved.

A significant proportion of the error was found to be due to blank correction of ^{230}Th (~20% of subsample ^{230}Th measurements) (table 1). A database of blank concentrations is maintained in the Oxford dating laboratory. In comparison to the database, the blank values for this run of U/Th measurements on the ICPMS seem well within range (table 2).

Sample	Th230 blank proportion	Th232 blank proportion	U238 blank proportion
	%	%	%
N1_1	15.58	0.23	0.71
N1_2	20.58	0.44	0.90
N1_3	18.38	0.30	0.77
N1_4	18.88	1.03	0.72
N1_5	21.19	1.23	0.66
N1_6	19.69	1.05	0.48

Table 1: Blank proportion of Th and U in the sample measurements.

	<i>Th230 grams</i>	<i>Th232 grams</i>	<i>U238 grams</i>
<i>N1 set blank</i>	4.10E-15	2.62E-12	1.66E-10
<i>Oxford average blank</i>	4.00E-15	4.56E-11	1.39E-10

Table 2: Blank values for N1 set of chemistry versus an average of Oxford blank values (n=76).

The $^{232}\text{Th}/^{230}\text{Th}$ atomic ratio of the blank is 639 which is unusual since contamination by normal crustal material gives a $^{232}\text{Th}/^{230}\text{Th}$ ratio in the range of tens of thousands. Contamination from this stalagmite would give an atomic ratio similar to the other subsamples. The $^{232}\text{Th}/^{230}\text{Th}$ ratios of the subsamples range from 13,839 to 52,283. This suggests that the blank has not been contaminated by the other subsamples.

Data from the mass spectrometer was checked for instrument run related errors associated with memory effects and contaminated washes but the blank error seems to be real: i.e. not an instrumental error but the actual low level contamination of blank (table 3). This could be contamination of samples in the laboratory or contamination of the ion counter, perhaps with organics.

	<i>Th229 cps</i>	<i>Th230 cps</i>	<i>Th232 cps</i>	<i>Th232/Th230</i>
Blank 1	1953.2	6.8	3759.3	555.6
Blank 2	2.9	0.3	132.8	465.4
Blank 3	617.7	7.8	3723.7	474.7
Memory measurement	0.7	0.1	-479.5	-4176.1
Sample	1369.0	65.0	803911.7	12372.9
<i>*Blanks are without memory correction</i>				

Table 3: Three blanks were run in the same set in the instrument although only Blank 3 represents the chemistry blank (same set of column chemistry). The memory measurement given above was measured between Blank 2 and Blank 3. The sample measurement has been given for comparison. cps = counts per second

It seems clear that while the blank is well within the range of blanks obtained by other researchers in the department working on speleothem U-Th dating, the low ^{230}Th content in the Kotumsar speleothem requires a still lower ^{230}Th blank value.

This could be a one off contamination (perhaps from samples of very clean stalagmites/corals processed previously in the laboratory) or the blank may, instead, be derived from reagents or laboratory equipment used.

The Oxford blank database was plotted against researcher and against time but no trend was observed, although a similar ratio of $^{232}\text{Th}/^{230}\text{Th}$ between 500-2000 was frequently seen. There was also no trend seen of $^{232}\text{Th}/^{230}\text{Th}$ against ^{230}Th or ^{232}Th concentrations.

c) Results and Conclusion

Multiple blanks should be processed during each set of chemistry. This will help differentiate between consistent blank sources and incidental blanks especially when running similar samples of young age, low U and high ^{232}Th concentrations.

Appendix II

U-Th Dating of Belum Sample

A sample from Belum cave (figure 1) that has previously been collected by Physical Research Laboratory has been dated using U-Th dating. The 'top' and 'bottom' ages for the stalagmite sample have previously been measured and calculated by Asmerom's group at the U-Th laboratory in the University of New Mexico. These ages have been replicated and more subsamples have been measured to develop an age model for this sample using the methods described in section 3.3.10.

16 age measurements for the sample were made at Oxford (figure 2 and table 1). The sample grew between 190,420 and 61,634 years BP. The larger errors associated with subsamples S13 and S8 are from the stalagmite zone that has significant detrital material (figure 1) combined with low uranium concentrations. The powders from this zone also required a combination of acids to breakdown organic material consequently generating higher chemistry blank values though the blank proportion is still at a part per mille level with the highest being that for ^{230}Th at $\sim 30\text{‰}$. Together these age measurements provide the best possible age model for this sample.

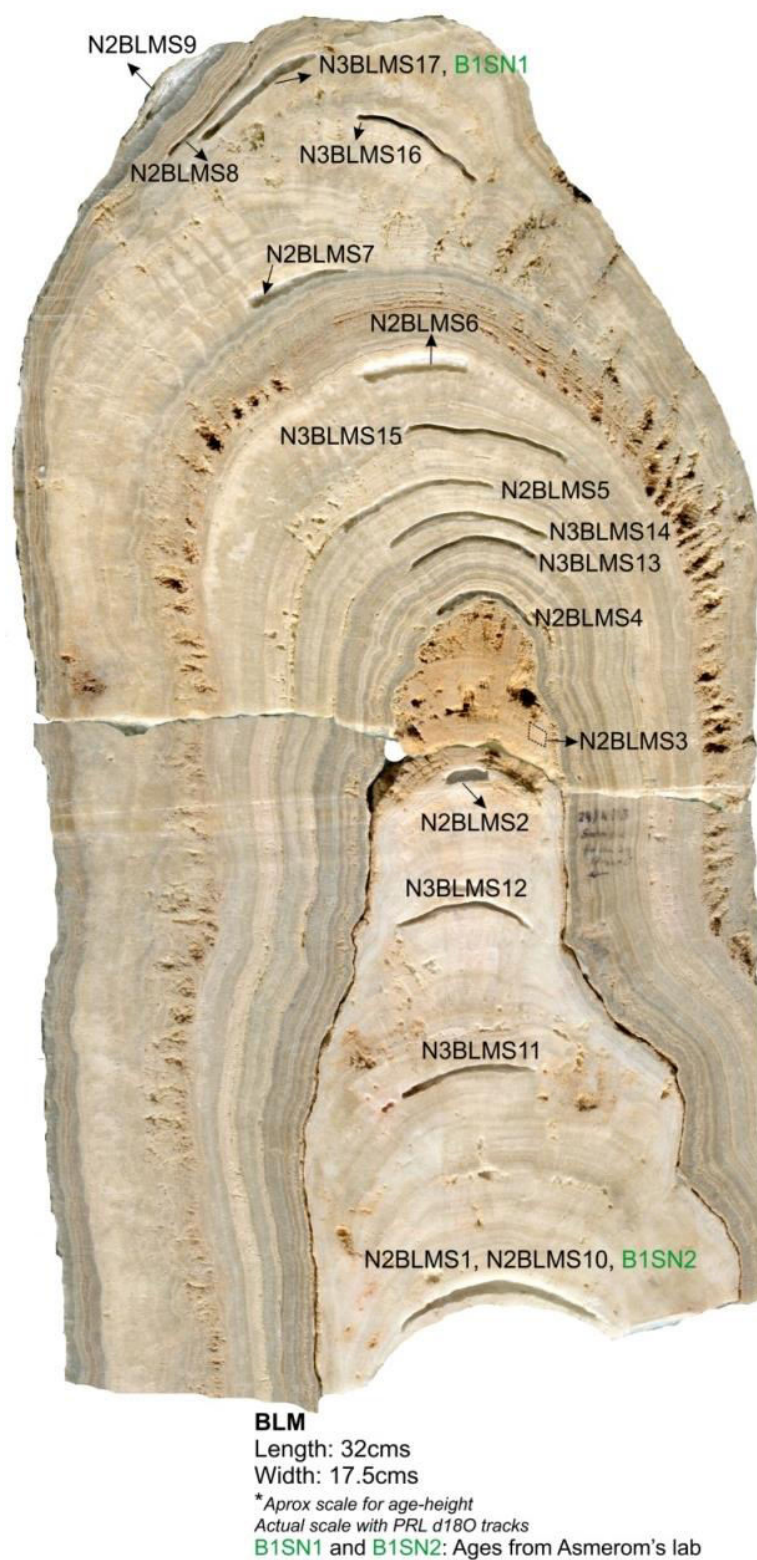


Figure 1: BLM sample. Subsample locations for U-Th dating have been shown in the figure. Subsamples analysed by Asmerom's laboratory (University of New Mexico) are in green. The Oxford laboratory measurements made by me are in black.

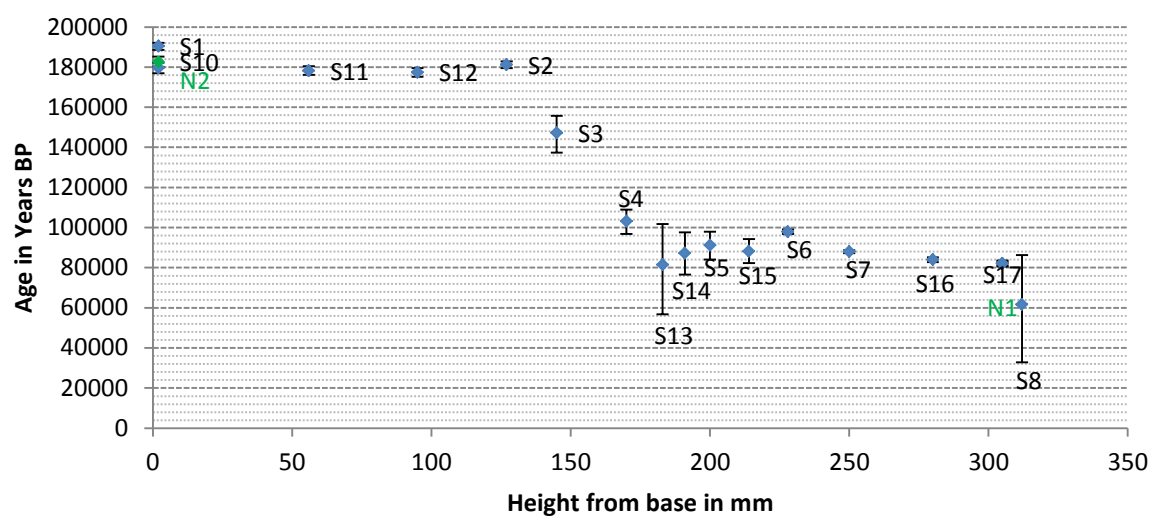


Figure 2: Age versus height model for the Belum stalagmite. Ages produced by Asmerom's laboratory (University of New Mexico) are in green. The Oxford laboratory measurements made by me are in black.

Sample	Height from base mm	^{238}U conc ppb	^{232}Th conc ppb	^{230}Th conc ppb	$\delta^{234}\text{U}$ initial	$^{230}\text{Th}/^{232}\text{Th}$ atomic	$^{230}\text{Th}/^{232}\text{Th}$ activity	$^{230}\text{Th}/^{238}\text{U}$ activity	Age (raw) Years BP	-	Age (corr) +	-			
N2BLMS1		2	271.51	8.85	4.56E-03	198.24	335.81	5.19E-04	96.12	1.03	191293	1668	190354	1776	1685
N3BLMS10		2	306.99	9.75	5.09E-03	203.46	337.66	5.27E-04	97.48	1.01	183547	2627	182679	2587	2560
B1SN2		2	271.8	9.47	198	331		6.66E-04	88.44	1.01	183081	1998	179557	2615	2615
N3BLMS11		56	421.38	10.15	6.70E-03	172.04	281.60	6.66E-04	123.26	0.97	178864	2087	178156	2277	2076
N3BLMS12		95	424.79	10.61	6.83E-03	184.30	301.11	6.49E-04	120.14	0.98	178084	2070	177354	2124	2129
N2BLMS2		127	163.62	8.34	2.78E-03	231.64	383.05	3.36E-04	62.27	1.04	182596	1336	181228	1645	1780
N2BLMS3		145	500.02	166.68	7.74E-03	203.26	305.16	4.68E-05	8.67	0.95	157018	1044	147135	8559	9734
N2BLMS4		170	396.17	90.37	5.03E-03	197.50	261.67	5.62E-05	10.39	0.78	109867	622	103184	5821	6390
N3BLMS13		183	82.76	59.15	1.04E-03	220.96	276.02	1.77E-05	3.28	0.77	104247	2765	81375	20375	24614
N3BLMS14		191	63.60	22.54	7.78E-04	230.73	293.36	3.48E-05	6.45	0.75	98373	3013	87238	10446	10660
N2BLMS5		200	97.39	25.68	1.22E-03	253.99	326.06	4.79E-05	8.87	0.77	99033	893	91223	6795	7138
N3BLMS15		214	63.91	12.21	7.67E-04	243.33	310.31	6.34E-05	11.73	0.73	93813	3206	88172	6057	5790
N2BLMS6		228	174.28	6.76	2.25E-03	286.53	374.84	3.35E-04	62.05	0.79	98962	521	97941	1112	1185
N2BLMS7		250	278.18	5.53	3.28E-03	269.09	342.61	6.00E-04	110.99	0.72	88599	442	88023	683	767
N3BLMS16		280	464.44	16.63	5.35E-03	274.28	344.97	3.25E-04	60.10	0.70	84925	671	83957	1216	1241
N3BLMS17		305	272.01	13.62	3.09E-03	270.23	338.11	2.29E-04	42.35	0.69	83468	820	82052	1563	1478
B1SN1		305	256.80	7.14	270.00	341.00		75.78	676	0.68	82615	676	82009	737	737
N2BLMS8		312	478.55	383.38	5.52E-03	232.76	275.03	1.45E-05	2.69	0.70	89568	640	61568	24809	28693

Table 1: U-Th measurements, ages and errors. Ages produced by Asmerom's laboratory (University of New Mexico) are in green. The Oxford laboratory measurements made by me are in black.

Appendix III

Searching for station nr 43198 in ghcnm.tavg.v3.qca v3.3.0.20170102

BELGAUM/SAMBR (INDIA)

coordinates: 15.85N, 74.62E, 747.0m (prob: 743m)

WMO station code: 43198 BELGAUM/SAMBR

tavg [Celsius] daily mean temperature (adjusted) from GHCN-M

v3.3.0.20170102

Year	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	Annual Av
1976	21.5	22.7	26.6	27.3	27.3	24.1	23.2	23	23.2	24.8	24.3	22.4	24.2
1977	21.5	24.3	26.9	27.3	27	24.7	22.9	23.3	23.5	24.1	23.9	20.7	24.2
1978	22	22.9	25.7	28.1	27.3	23.6	22.9	22.6	23	24.1	23.3	22.2	24.0
1979	22.3	22.7	26.5	28.7	27.7	25.3	23.4	22.5	23.9	24.5	23.7	22.1	24.4
1980	21.9	24.5	26.8	28.5	28.7	24.1	23.1	22.8	23.8	24.9	23.5	21.1	24.5
1981	21.1	24.2	26.5	28.3	27.7	24.3	23.1	22.7	23.9	23.9	22.1	21.7	24.1
1982	21.9	24.3	26.6	27.8	27.7	25.1	23.4	22.9	23.5	24.9	22.9	22.1	24.4
1983	21.7	22.7	26.4	28.2	28.5	25.7	23.9	23.5	23.5	23.9	21.3	22.4	24.3
1984	22.5	24.7	26.6	27.7	29.1	24.5	22.9	22.5	23.3	23.9	22.1	21.9	24.3
1985	23.3	23.8	27.5	27.9	27.9	23.9	22.9	22.6	23.7	23	22.7	22.9	24.3
1986	21.9	23.1	27.4	28.9	27.9	25.1	23.2	22.5	24.1	24.9	23.3	22.3	24.6
1987	22.3	22.9	25.5	28.3	27.7	24.7	23.7	23.9	24.7	24.5	23.4	22	24.5
1988	22.1	24.3	26.7	28.3	28.7	24.9	23.2	23.2	23.8	24.5	22.3	21.3	24.4
1989	22	23.9	25.5	28	27.3	24.4	23.3	22.7	23.8	24.5	23.5	22.1	24.3
1990	22.5	23.3	25.1	28.3	27.3	24.4	22.7	22.7	24	24.5	22.8	22	24.1
1991	22.7	24.1	27.1	27.9	28.2	25.2	22.9	22.7	24	24.5	23.1	21.4	24.5
1992	21	22.8	26.9	28.9	28.6	25.5	23.8	22.9	23.7	23.7	22.9	20.6	24.3
1993	21.9	22.8	25.4	28.1	28.6	25.2	23.1	22.9	23.3	24.4	23.1	20.8	24.1
1994	22.3	23.3	27.3	27.1	28.5	24.1	22.7	22.7	22.9	24.1	22.1	21.7	24.1
1995	20.4	23.7	26.5	28.3	27.1	24.1	24.1	23.9	23.7	24.1	21.7	21.7	24.1
1996	22.2	24.3	27.1	28.3	28.7	25.3	23.6	23.1	24	23.2	22.6	21.2	24.5
1997	21.1	22.4	26.5	26.8	28.2	25.3	23.8	23.1	24.3	25.3	24.1	22.9	24.5
1998	22.5	23	26.7	29.7	29	25.9	24.1	24.1	24.1	24	22.5	21.1	24.7
1999	20.7	24.6	26.1	28.4	26.8	24.1	23.2	23.3	23.6	24.3	22.7	21.3	24.1
2000	22.7	22.7	26.1	28.5	26.5	24.7	22.5	23.3	24.4	24.3	22.9	21.3	24.2
2001	22.3	24.1	25.7	28.5	27.7	25	23.3	23.1	24.2	23.9	23.3	21.7	24.4
2002	21.6	24.5	27.3	28.8	28.5	25.1	23.9	23.1	24.1	25	23.3	22.1	24.8
2003	22.9	25.1	27.4	28.4	28.6	26.1	24	23.7	23.7	24.5	24.1	22	25.0
2004	21.9	24.3	26.6	27.9	26.8	24.1	23.7	22.6	23.7	24	23.7	21.5	24.2
2005	22.7	24.5	26.6	27.9	28.5	25.5	23.5	22.9	23.3	23.8	22.1	21.1	24.4
2006	21.9	23.7	25.7	28.3	27.9	24.6	22.9	22.4	23.9	24.2	23.7	21.5	24.2
2007	21.9	23	26.7	28.3	27.7	25.3	23.8	23.4	23.7	24.6	22.4	22	24.4
2008	21.9	23.5	25.4	26.6	27.2	24.3	23.7	23	23.4	24.3	22.9	22	24.0
2009	22.1	24.6	26.6	28.3	28	25.2	22.9	23.9	24.3	23.7	23.2	22.1	24.6
2010	21.8	24.4	27.2	29.2	29	25.6	23.5	23.8	23.7	24.2	23.5	22.1	24.8
2011	21	23.5	25.6	27.6	27.8	25.4	23.4	23.3	23.4	23.8	22.5	22.4	24.1
2012	21	23.5	25.6	27.6	27.8	25.4	23.4	23.3	23.4	23.8	22.5	22.4	24.1
2013	22.2	23.7	26.3	28	28.1	23.9	22.3	23	23.8	24.1	22.2	20.7	24.0
2014	22	23.1	25.9	28.3	27.3	25.7	23.7	23.7	24.1	24.3	22.2	21.5	24.3
2015	20.8	23.3	26	27.5	28.1	25	24.5	24.2	25.1	25.3	24.3	24	24.8
2016	22.4	25.5	28.1	29.6	28.7	25	23.1	23.2	23.5	23.6	22.6	24	24.9
Mean	21.9	23.7	26.5	28.2	27.9	24.9	23.3	23.1	23.8	24.2	23.0	21.9	24.4

Table 1: Monthly mean temperature data from the GHCNM database for Belgaum sourced from KNMI Explorer. The red data points mark times for which no data is available; they have been replaced with temperature data from the same month of the year immediately before or after. Calculated monthly mean values have been given in the last row. Annual averages are in the last column.

Searching for station nr 43063 in ghcnm.tavg.v3.qca v3.3.0.20160103

POONA (INDIA)

coordinates: 18.53N, 73.85E, 559.0m (prob: 576m)

WMO station code: 43063 POONA

tavg [Celsius] daily mean temperature (adjusted) from GHCN-M

v3.3.0.20160103

Year	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	Annual Av
1876	22.3	23.8	27	29.9	28.8	26.1	23.2	22.9	23.2	25.5	23.4	21.8	24.8
1877	21.4	22.7	26.1	28.3	28.7	26.2	25	24.2	25.1	24.1	23.6	20.7	24.7
1878	22.4	22.7	28.1	29.1	28.8	27.4	24.5	23.6	24.5	24.9	20.9	20.7	24.8
1879	21.6	21.8	27.8	29.8	28.7	24.9	24.5	22.7	23.4	24	20.9	18.5	24.1
1880	19.6	21.8	27.8	29	28.6	25.7	23.4	23.8	23.6	25	22.8	20.8	24.3
1881	20.6	22.6	25.6	28.9	29.5	26.8	23.4	23.5	23.9	24.7	21.1	20.1	24.2
1882	21.9	22.3	26.9	28.6	28.4	24.8	23	23.6	23.9	24	21.8	20.4	24.1
1883	20	22.9	25.4	27.6	29.5	25.5	23.5	23.4	22.6	23.5	20.2	17	23.4
1884	18.1	21.9	26.3	28.1	28.7	27	23.8	23.9	22.8	24.1	20.6	19.1	23.7
1885	21.2	21.1	26.2	28.4	28.7	27.2	24.4	23.8	24.5	24.6	21.8	19.8	24.3
1886	19.5	22.8	25.7	28.7	29.5	26.6	24.2	24.1	24.7	24.6	22.4	19.7	24.4
1887	20.2	21.9	25.5	29.1	27.7	25.3	23	23	23.6	24.2	21.7	19	23.7
1888	19.8	22.8	26.8	29.3	28.6	27.4	23.9	23.5	24.7	24.9	23.1	20.1	24.6
1889	21.4	23	26.6	30	30.4	26.4	24.8	23.9	25.5	23.5	20.5	19.4	24.6
1890	19.8	23.7	26.2	29.4	29.4	25.7	23.6	22.9	23.6	24.6	22.4	21.1	24.4
1891	19.9	22.4	25.4	29.1	29.6	28.7	24.6	23.5	24	24.4	21.9	19.5	24.4
1892	21.7	23.5	27.1	30.9	28.9	26.4	24.5	23.6	23.6	24.7	20.1	19.8	24.6
1893	19.7	21.1	24.9	28.5	28.4	25	24.2	23	23.6	24.1	23.1	19.7	23.8
1894	21	23.4	26.6	28.8	28.9	26.5	23.9	24.1	24	24.3	21.2	21.1	24.5
1895	21.3	22.5	26.9	29	29.6	26.7	24.5	23.4	23.9	24.4	22.2	19.4	24.5
1896	20.5	22.7	27	30.2	29.6	26.4	24.1	22.8	24.6	24.6	24.6	22.7	25.0
1897	22.5	24.1	26.1	30	30.1	27.7	25.2	23.9	24.9	24.6	20.7	18.6	24.9
1898	19.4	21.7	27	30.2	30.1	26.7	24	23.1	24	25.4	22.8	22	24.7
1899	18.9	22.6	27	27.4	28.6	26.2	24.4	24.7	25	27.1	23.4	20.8	24.7
1900	21.6	23.6	26.7	29.5	29.7	28.3	25.1	23.5	23.7	24.6	23.1	22.3	25.1
1901	20.9	21	26.9	29.4	28.7	26.7	24.2	23.3	24.5	25.5	22.2	20.7	24.5
1902	21.7	23.4	27.3	29.2	30	27.4	25.1	24.4	24.2	26.1	21.7	20.5	25.1
1903	20.7	21.6	25	29	29.2	27.7	24.5	23.8	24.6	24.2	21.8	19.8	24.3
1904	20.9	22.7	25.5	28.8	29.7	27	24.6	24.5	24.4	25.3	21.1	20	24.5
1905	19.9	20.1	24.4	27	30.5	27.9	24.5	23.7	24.2	25.8	22.2	19.1	24.1
1906	19.7	20.6	24.7	28.9	29.6	26.1	24	23.7	23.1	24.1	22.6	20.6	24.0
1907	20.5	22.1	24.9	26.5	28.2	26.6	24.2	22.4	23.7	25.4	22.8	18.9	23.9
1908	19.9	21.3	25	28.8	28.7	27.2	23.4	22.9	24.4	25	21	17.9	23.8
1909	21	22	26.9	27	29.6	25.9	23.4	23.7	23.5	24.3	21.9	21	24.2
1910	20.2	21.5	25.5	28.7	29	26.7	24.5	23.4	23.6	23.6	19.7	18.7	23.8
1911	21	21.3	24.4	28.2	30	26	25	23.1	24	26.5	24	21.3	24.6
1912	20.9	22.8	25.7	29.6	29.7	28.5	24.9	23.7	24.9	25.1	21.7	19.7	24.8
1913	19.3	23.1	24.9	29.5	29	25.2	24.1	23.4	24.2	24.9	22.1	21.4	24.3
1914	20.4	22.7	24.7	27.7	29.9	26.9	23.8	23.4	24.1	24.9	22.8	20.7	24.3
1915	20.7	21.9	25.1	28.6	29.1	28	24.7	23.6	24.1	24.1	23.5	19.2	24.4
1916	20.4	21.5	26.6	29	30	25.8	25.5	23.8	24.4	24.6	22.6	19.2	24.5
1917	20.1	21.6	24.5	26.8	27.8	25.7	24.7	24.1	24	23.4	20.9	19.1	23.6
1918	19.2	22.4	24.7	27	27.8	26.2	25.4	24.4	24.6	26.4	24.3	21.6	24.5
1919	21.2	22.9	25.7	28	29	26	24.2	23.7	24.2	24.6	23.5	19.7	24.4
1920	21.5	21.5	25.5	28	28.4	26.2	23.4	23.3	24.6	25.1	22	20	24.1
1921	21	21.7	26.5	29.5	29.2	27	24.7	23	23.6	24.7	21.3	20	24.4
1922	21.1	22.9	25.7	29.1	29.1	26.6	23.4	23.1	23.7	24.7	21.5	18.4	24.1
1923	20.1	20.6	25.5	27.5	28.2	27.9	24	23.4	23.6	24.2	21.9	21	24.0
1924	21.6	22.7	27.2	29.2	29.6	27.2	25	24.2	24	23.1	20.4	20.1	24.5
1925	19	21.3	25.9	29.5	28.9	25.6	23.7	23.8	24.5	25.1	23.6	20.2	24.3
1926	21.6	23.9	25.5	26.2	29	28.2	24.7	23.5	24	25.4	22	20.1	24.5
1927	21	22	25.8	28.1	28.9	25.9	23.4	23	24.4	24.7	20.6	20.1	24.0
1928	20.9	22.1	25.7	28.7	28.9	27.2	24.3	23.4	23	24.6	22.5	20.4	24.3
1929	20.1	22.4	27	27.9	29.5	26.2	23.9	23.4	24.8	24.5	22.4	20.6	24.4
1930	21.1	20.2	26	27.8	29.3	26.6	23.2	23.2	24.2	25.2	20.9	20.9	24.1

Year	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	Annual Av
1931	20.6	22.7	25	29.9	29.4	28.3	24.2	24	23.9	23.6	21.8	19.1	24.4
1932	19.6	20.7	25.4	27.9	29.1	26.4	24	24.5	24.4	25.4	22.2	19.7	24.1
1933	20	22.1	25.2	28.1	27.7	25.4	24.4	23.5	23.9	24.3	22.5	19.5	23.9
1934	19.4	22	24.7	28.6	28.5	26.2	23.9	23.2	23.6	24.9	21	19	23.8
1935	19.1	21.7	24.2	26.8	29	26.9	24	23.9	23.4	25.4	21	20.4	23.8
1936	20.1	21	25.4	27.9	30	25.5	24.1	23.9	25	25	23.2	19.9	24.3
1937	19.7	22.1	25	27.6	29	26.5	23.6	23.8	24.2	24.4	21.7	20.1	24.0
1938	21.8	20.8	26.4	28.9	28.4	24.6	23.8	24	23.7	23.2	21.2	19.4	23.9
1939	20.9	23	24.7	28.1	28.5	26.7	23.8	23.9	24	25.2	20.9	18.8	24.0
1940	19.5	22.4	23	28.4	29.1	26.7	23.9	23.4	24.5	24.6	23.1	19.9	24.0
1941	20.1	23.4	26.9	29.4	29.6	27.2	24.5	24.7	25.2	25.9	22.7	22.1	25.1
1942	20.9	22.8	27.1	30	29.5	27.2	23.6	23.7	24	25.8	21.8	20.1	24.7
1943	21.1	21.2	26.2	27.9	29.1	25.8	23.6	23.4	23.9	24.1	23.2	18.9	24.0
1944	20.7	21.4	24.7	28	30.2	27.1	24.1	23.7	24.7	24.8	22.6	21.4	24.5
1945	19.6	21.8	26	27.5	29	27	24.2	24.2	23.9	24.9	21.1	18.9	24.0
1946	19.9	22.7	26.1	28.5	28.2	26.2	23.9	23.4	24.2	25.9	23	22.4	24.5
1947	21	22.9	26.2	27.4	29.4	27.9	24.7	25.1	23.9	21.6	22.7	20.6	24.5
1948	21.7	22.5	26	29.4	29.7	27.2	24.7	24.2	24.1	25.6	24.1	19.2	24.9
1949	21.5	22.1	26.8	28.9	29	26.6	25	24.4	24.1	25.1	21.8	20.2	24.6
1950	20.8	21.5	25.3	28.7	28.7	27.1	24.1	24.7	24.6	23.9	21.5	20.5	24.3
1951	20.5	22.5	25.9	27.6	29.7	27	25.2	24	24.5	25.6	23.2	19.6	24.6
1952	20.9	23.1	24.7	29.1	29.5	26.7	24.5	23.5	24.5	25.5	21.6	22.4	24.7
1953	20.8	24.2	28	29	29	27.2	24.9	23.9	24.9	25.4	22.6	20	25.0
1954	20.2	23.7	26	29	29.7	26.1	24.1	23.9	23.2	24.1	21.4	21	24.4
1955	21.7	23.5	26.6	28	29.4	27	24.9	23.7	24.8	24.5	20.9	20	24.6
1956	21.3	22.2	26.8	29.4	28	26.4	23.1	23.5	23.9	24.4	22.4	20.2	24.3
1957	21.4	21.6	25.2	28.9	29.6	27.8	24.4	24	24.6	25.9	23	22	24.9
1958	21.4	22.4	25.9	29.4	29.9	28	24.3	24.4	24.5	25.4	23.7	21.4	25.1
1959	22.1	23.3	26.9	29.5	30.1	27.3	23.6	23.8	23.9	24.2	22.4	21.4	24.9
1960	21.4	23.5	25.6	29.4	29.4	26.6	24.8	23.2	24.4	24.4	22.4	21.6	24.7
1961	21.4	21	26.9	29.2	29.4	26.6	24.8	23.2	24.4	24.4	22.4	21.6	24.6
1962	21.4	22.1	25.6	27.5	29.7	27.1	24.9	23.7	24.4	25	22.4	20.8	24.6
1963	19.7	22.1	25.6	27.5	29.7	27.1	24.9	23.7	24.4	25	22.4	20.8	24.4
1964	19.7	21.7	26.4	30.2	29.4	27.1	24.8	23.7	24.1	24.7	21.4	19.4	24.4
1965	20.7	22	25.1	28.7	29.3	27.1	24.9	24.9	25.4	25.7	22.8	21.3	24.8
1966	20.5	22.8	25.7	29	29	28.3	26	25	25.2	25.9	23.5	20.7	25.1
1967	20.3	22.7	26	29.2	30.4	27.7	25.2	24.3	24.7	24.8	22	22	24.9
1968	19.2	21.6	25.4	28.8	29.6	28.2	25.4	24.4	25.7	23.9	21.1	20.1	24.5
1969	20.1	22.9	27	30.3	31	28	25.3	24.6	24.6	25.2	24	21.2	25.4
1970	20.6	23.3	25.9	30	30.5	27	25	24.3	24.6	25	20.3	17.8	24.5
1971	19.5	22.1	25.5	29.7	29.5	26.2	25.3	24.7	25.3	23.8	20	18.4	24.2
1972	19.7	21	27	28.5	29.8	28.9	25.4	25.1	26	26.6	21.8	22	25.2
1973	21	23.4	26.3	30.6	30.6	27.9	25	24.3	24	24.8	20.9	20.8	25.0
1974	20.1	22.2	26.2	29.3	29.3	28	25.7	24.3	25.3	24.7	19.9	18.9	24.5
1975	19.2	21.8	25.1	29.8	29.3	26.7	25.2	24.4	24.8	25	20.3	18.1	24.1
1976	19	22.3	25.8	28.4	28.9	26.6	25.1	24.5	24.9	26	24.5	21.3	24.8
1977	20	22.7	27.5	28.7	29.4	27.5	25.1	24.5	24.6	24.8	24.5	19.5	24.9
1978	20.2	21.8	24.4	28.8	29.8	26.2	25.1	24.3	24.8	25.1	24.2	20.7	24.6
1979	22	21.2	24.9	28.9	29.8	28.3	25.7	24.3	25.3	25.9	24.4	21.2	25.2
1980	20.9	22.8	25.6	29.9	30.1	26.8	25	24.4	25.1	25.7	23.6	19.7	25.0
1981	19.6	22.2	24.9	28.7	29.9	28.2	24.9	24.3	25.7	25.4	21.4	20.6	24.7
1982	21.1	22.5	25	27.8	29.6	27.9	26.2	25.1	25.3	25.9	23.2	20.6	25.0
1983	20	20.7	25.2	27.7	30.3	28.4	26.8	25	25	24.3	20.4	20.1	24.5
1984	20.3	22	26.4	28.9	30.3	27.1	24.6	23.7	24.4	24.8	20.5	20.6	24.5
1985	21.1	21.6	26.5	27.8	30	26.9	25.1	24.4	25.5	23.6	21.3	20.9	24.6
1986	20.5	22.4	25.8	28.5	29.8	26.7	24.9	24	25.5	25.6	23.4	20.4	24.8
1987	21.6	21.9	25.6	29	29.3	28.1	26.1	25.9	26.1	24.6	23.4	20.4	25.2
1988	21.1	22.9	25	28.7	29.4	28	25.5	25	25.6	23.8	21.3	19.8	24.7
1989	20.5	21.2	25.3	28.2	29.5	26.2	25.4	24.1	25	24.9	22.9	19.8	24.4
1990	20.9	21.8	24.2	28.2	29.3	26.5	24.5	24.1	24.4	24.6	23.2	20.9	24.4

Year	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	Annual Av
1991	20.2	22.4	25.9	28.3	30.2	27	24.6	24	25.4	25	23	19.3	24.6
1992	19.8	20.7	25.7	28.2	30.1	28.3	26.1	24.4	24.7	24.7	22.9	19.3	24.6
1993	20.6	20.8	24.6	28	30	28	25.1	24.6	24.7	25.3	22.4	18.8	24.4
1994	20.4	21.2	26.6	27.5	29.5	26.1	24.2	24.4	24.2	25.3	22.1	19	24.2
1995	18.4	22.4	25.2	28.4	29.4	29	25.9	25.6	25	25.1	22.1	20.8	24.8
1996	21.5	22.8	26.6	28.3	29.4	27.9	25.6	24.4	24.9	23.9	21.4	19.9	24.7
1997	19.1	20.4	25.5	27.1	28.9	27	25.7	24.5	25	25.5	24.8	21.9	24.6
1998	21	21.5	25.3	29.5	31.3	28.4	25.8	25.5	25.4	25.1	22.7	19	25.0
1999	19	23.3	26.3	29.3	28.9	26.5	25.1	24.4	24.8	24.6	21.9	19.6	24.5
2000	20.7	21.4	24.3	29.7	28.9	26.9	24.8	25.1	25.3	25.9	22.3	19.1	24.5
2001	21	22.6	24.8	29.1	29.5	26.9	24.5	24.3	25.5	24.8	22.3	20.5	24.7
2002	18.9	23.4	25.8	29.9	30.5	27.2	25.7	24.3	25.2	26.1	22.6	21.5	25.1
2003	20.9	23.7	27.2	29.7	30.4	27.6	25.7	24.7	25.3	25.6	23.7	20.8	25.4
2004	20.9	22.9	27.2	28.7	29.4	26.9	25.5	24.1	25.3	24.4	23	20.1	24.9
2005	20.6	22	25.3	28.7	29.9	28	25.3	24.3	24.8	24.5	21.1	19.7	24.5
2006	19.9	23.2	25.3	28.5	30.2	27.2	24.6	24.2	25.7	25.5	23	21.9	24.9
2007	20.7	22	27	29.2	29.9	28.5	25.7	25.3	25.7	25.5	23	21.9	25.4
2008	20.7	22	27	29.2	29.9	27	25.5	24.8	25.3	24.6	23.5	22.2	25.1
2009	21.8	23.6	26.6	30.2	30.4	28.7	25.5	25.8	26.2	24.9	23.5	21.7	25.7
2010	21.1	23.6	27.2	30.2	31.3	27.9	25.9	25.6	25	25.9	24.9	20.4	25.8
2011	20	22	25.6	28.7	30.1	26.6	25.5	25	25	25.5	23	21.3	24.9
2012	20	22.4	25	29.3	29.7	28.2	26.1	24.9	24.8	25.1	22.7	21.7	25.0
2013	21.2	23.4	25.4	28.5	30.7	26.3	24.3	24.5	25.3	25.7	22.6	20.1	24.8
2014	21.1	21.7	25.4	29.3	30.3	29.1	26	25.4	25.3	25.7	23.6	20.3	25.3
2015	20.1	22.6	25	28.1	30.1	27.1	25.9	25.5	25.9	26.5	24.3	20.3	25.1

Table 2: Monthly mean temperature data from the GHCNM database for Poona sourced from KNMI Explorer. The red data points mark times for which no data is available; they have been replaced with temperature data from the same month of the year immediately before or after. Calculated annual average values have been given in the last column.

using minimal fraction of valid points 30.00

temperature_anomaly [Celsius] from CRUTEM4 temperature

anomalies

cutting out region lon= 70.000 75.000, lat= 15.000 20.000

Year	Jan	Feb	Year	Mar	Apr	Year	May	Jun	Year	Jul	Aug	Year	Annual Av
1876	2.0E+00	1.4E+00	8.0E-01	7.0E-01	-7.0E-01	-8.0E-01	-1.5E+00	-1.0E+00	-1.4E+00	7.0E-01	1.2E+00	1.7E+00	0.3
1877	1.1E+00	3.0E-01	-1.0E-01	-9.0E-01	-8.0E-01	-7.0E-01	3.0E-01	3.0E-01	5.0E-01	-7.0E-01	1.4E+00	3.1E+00	0.3
1878	2.1E+00	3.1E+00	1.9E+00	-1.0E-01	-7.0E-01	5.0E-01	-2.0E-01	-3.0E-01	-1.0E-01	1.0E-01	3.0E-01	6.0E-01	0.6
1879	1.3E+00	1.5E+00	7.0E-01	6.0E-01	-8.0E-01	-2.0E+00	-2.0E-01	-1.2E+00	-1.2E+00	-8.0E-01	-1.3E+00	-1.6E+00	-0.4
1880	-7.0E-01	-6.0E-01	1.6E+00	-2.0E-01	-9.0E-01	-1.2E+00	-1.3E+00	-1.0E-01	-1.0E+00	2.0E-01	6.0E-01	7.0E-01	-0.2
1881	3.0E-01	2.0E-01	-6.0E-01	-3.0E-01	0.0E+00	-1.0E-01	-1.3E+00	-4.0E-01	-7.0E-01	-1.0E-01	-1.1E+00	0.0E+00	-0.3
1882	1.6E+00	-1.0E-01	7.0E-01	-6.0E-01	-1.1E+00	-2.1E+00	-1.7E+00	-3.0E-01	-7.0E-01	-8.0E-01	-4.0E-01	3.0E-01	-0.4
1883	-3.0E-01	5.0E-01	-8.0E-01	-1.6E+00	0.0E+00	-1.4E+00	-1.2E+00	-5.0E-01	-2.0E+00	-1.3E+00	-2.0E+00	-3.1E+00	-1.1
1884	-2.2E+00	-5.0E-01	1.0E-01	-1.1E+00	-8.0E-01	1.0E-01	-9.0E-01	0.0E+00	-1.8E+00	-7.0E-01	-1.6E+00	-1.0E+00	-0.9
1885	9.0E-01	-1.3E+00	0.0E+00	-8.0E-01	-8.0E-01	3.0E-01	-3.0E-01	-1.0E-01	-1.0E-01	-2.0E-01	-4.0E-01	-3.0E-01	-0.3
1886	-8.0E-01	4.0E-01	-5.0E-01	-5.0E-01	0.0E+00	-3.0E-01	-5.0E-01	2.0E-01	1.0E-01	-2.0E-01	2.0E-01	-4.0E-01	-0.2
1887	-1.0E-01	-5.0E-01	-7.0E-01	-1.0E-01	-1.8E+00	-1.6E+00	-1.7E+00	-9.0E-01	-1.0E+00	-6.0E-01	-5.0E-01	-1.1E+00	-0.9
1888	-5.0E-01	4.0E-01	6.0E-01	1.0E-01	-9.0E-01	5.0E-01	-8.0E-01	-4.0E-01	1.0E-01	1.0E-01	9.0E-01	0.0E+00	0.0
1889	1.1E+00	6.0E-01	4.0E-01	8.0E-01	9.0E-01	-5.0E-01	1.0E-01	0.0E+00	9.0E-01	-1.3E+00	-1.7E+00	-7.0E-01	0.1
1890	-5.0E-01	1.3E+00	0.0E+00	2.0E-01	-1.0E-01	-1.2E+00	-1.1E+00	-1.0E+00	-1.0E+00	-2.0E-01	2.0E-01	1.0E+00	-0.2
1891	-4.0E-01	0.0E+00	-8.0E-01	-1.0E-01	1.0E-01	1.8E+00	-1.0E-01	-4.0E-01	-6.0E-01	-4.0E-01	-3.0E-01	-6.0E-01	-0.1
1892	1.4E+00	1.1E+00	9.0E-01	1.7E+00	-6.0E-01	-5.0E-01	-2.0E-01	-3.0E-01	-1.0E+00	-1.0E-01	-2.1E+00	-3.0E-01	0.0
1893	-1.0E+00	-1.9E+00	-1.3E+00	-3.0E-01	-9.0E-01	-1.7E+00	-4.5E-01	-6.5E-01	-9.0E-01	-1.1E+00	-5.0E-02	-5.5E-01	-0.9
1894	3.0E-01	7.0E-01	2.0E-01	-2.0E-01	-3.5E-01	-4.0E-01	-6.5E-01	1.0E-01	-9.5E-01	-1.0E+00	-1.5E+00	-3.0E-01	-0.3
1895	-1.5E-01	-3.0E-01	2.5E-01	-3.0E-01	-1.5E-01	-2.0E-01	-2.0E-01	-5.0E-01	-9.0E-01	-6.0E-01	-2.0E-01	-8.5E-01	-0.3
1896	3.5E-01	-1.5E-01	4.0E-01	9.0E-01	2.0E-01	-4.0E-01	-4.5E-01	-8.5E-01	5.0E-02	1.4E+00	1.0E+00	1.3E+00	0.3
1897	6.0E-01	3.0E-01	-7.5E-01	3.0E-01	1.5E-01	6.5E-01	2.0E-01	1.5E-01	1.0E-01	-5.5E-01	-1.6E+00	-1.5E+00	-0.2
1898	-3.5E-01	-5.5E-01	3.5E-01	6.0E-01	3.5E-01	-2.5E-01	-5.5E-01	-4.5E-01	-6.5E-01	4.0E-01	2.0E-01	9.0E-01	0.0
1899	-1.6E+00	-1.5E-01	3.5E-01	-9.5E-01	-5.5E-01	-7.5E-01	-5.0E-02	6.0E-01	1.5E-01	1.1E+00	-5.0E-02	1.5E-01	-0.1
1900	1.5E-01	5.0E-02	5.0E-02	0.0E+00	0.0E+00	1.2E+00	6.0E-01	-3.0E-01	-6.0E-01	-5.0E-01	5.0E-02	1.1E+00	0.1
1901	-4.0E-01	-1.8E+00	-6.0E-02	-2.6E-01	-6.6E-01	-3.2E-01	-3.0E-01	-4.6E-01	-2.0E-02	-3.8E-01	-2.2E-01	-1.0E-01	-0.4
1902	4.2E-01	2.0E-02	3.8E-01	-6.0E-02	3.2E-01	2.2E-01	4.0E-02	5.8E-01	-6.6E-01	1.2E-01	-1.1E+00	-6.8E-01	0.0
1903	-5.8E-01	-1.5E+00	-1.6E+00	-7.8E-01	-9.2E-01	1.4E-01	-4.8E-01	-3.4E-01	-3.6E-01	-1.3E+00	-1.6E+00	-1.4E+00	-0.9
1904	-6.0E-02	-5.8E-01	-1.0E+00	-6.0E-01	-2.4E-01	-6.4E-01	-3.0E-01	-4.0E-02	-5.0E-01	-3.0E-01	-1.9E+00	-1.3E+00	-0.6
1905	-1.3E+00	-2.7E+00	-2.2E+00	-2.1E+00	1.0E-01	7.4E-01	-1.0E-01	6.0E-02	-3.0E-01	2.0E-01	-1.0E-01	-1.1E+00	-0.7
1906	-7.8E-01	-1.9E+00	-1.2E+00	-2.6E-01	2.2E-01	-3.6E-01	-4.2E-01	2.0E-02	-9.0E-01	-5.4E-01	-2.0E-02	-1.4E-01	-0.5
1907	-4.0E-02	-3.4E-01	-5.8E-01	-1.3E+00	-9.8E-01	-1.0E-01	-1.4E-01	-1.2E+00	-6.0E-01	1.2E-01	2.2E-01	-1.0E+00	-0.5
1908	-6.2E-01	-7.2E-01	-9.4E-01	-2.2E-01	-6.6E-01	1.4E-01	-7.6E-01	-6.4E-01	4.2E-01	-2.0E-01	-1.3E+00	-1.9E+00	-0.7
1909	-1.8E-01	-7.8E-01	2.2E-01	-1.4E+00	-6.0E-02	-7.4E-01	-1.0E+00	-6.0E-02	-1.0E+00	-9.6E-01	-8.8E-01	-4.4E-01	-0.6
1910	-4.2E-01	-4.2E-01	-3.6E-01	-1.8E-01	-5.2E-01	-6.0E-01	-1.0E-01	-5.0E-01	-1.3E+00	-1.4E+00	-2.0E+00	-1.9E+00	-0.8
1911	-1.0E-01	-1.4E+00	-1.4E+00	-8.6E-01	1.0E-01	-5.8E-01	-6.0E-02	-8.8E-01	-5.6E-01	1.8E-01	4.6E-01	4.6E-01	-0.4
1912	1.0E-01	-1.6E-01	-5.6E-01	3.0E-01	1.4E-01	9.0E-01	-4.0E-02	-3.2E-01	1.2E-01	-1.4E-01	-1.0E+00	-9.4E-01	-0.1
1913	-9.2E-01	-6.0E-02	-1.1E+00	-8.0E-02	-3.6E-01	-9.6E-01	-4.6E-01	-5.2E-01	-4.0E-01	-4.4E-01	-8.2E-01	-4.4E-01	-0.5
1914	-2.0E-01	-3.6E-01	-1.3E+00	-1.4E+00	2.4E-01	-2.0E-02	-5.4E-01	-5.0E-01	-4.6E-01	2.4E-01	1.2E-01	-1.6E-01	-0.4
1915	0.0E+00	-9.4E-01	-8.4E-01	-3.6E-01	-1.2E-01	9.2E-01	6.0E-02	-1.4E-01	-4.4E-01	-1.1E+00	2.8E-01	-1.4E+00	-0.3
1916	-3.2E-01	-1.3E+00	1.6E-01	-1.8E-01	-1.4E-01	-1.2E+00	1.8E-01	-2.8E-01	-5.8E-01	-1.1E+00	-8.0E-01	-1.7E+00	-0.6
1917	-4.6E-01	-8.8E-01	-1.3E+00	-1.5E+00	-2.0E+00	-1.1E+00	-8.0E-02	-1.8E-01	-9.2E-01	-2.0E+00	-1.8E+00	-1.7E+00	-1.1
1918	-7.6E-01	-3.8E-01	-7.2E-01	-1.4E+00	-1.6E+00	-7.6E-01	5.4E-01	1.4E-01	-2.4E-01	4.2E-01	8.0E-01	-6.0E-02	-0.3
1919	2.0E-01	-2.2E-01	-6.8E-01	-7.2E-01	-3.2E-01	-5.6E-01	-2.6E-01	-2.6E-01	-1.8E-01	-3.8E-01	3.0E-01	-8.0E-01	-0.3
1920	7.6E-01	-4.0E-01	-2.2E-01	-4.4E-01	-6.4E-01	-1.2E-01	-4.8E-01	-2.0E-01	1.4E-01	4.8E-01	-2.0E-01	-4.4E-01	-0.1
1921	5.6E-01	-4.4E-01	3.4E-01	3.6E-01	2.0E-02	-1.2E-01	-2.6E-01	-4.6E-01	-1.1E+00	-2.8E-01	-1.4E+00	-6.8E-01	-0.3
1922	1.6E-01	2.8E-01	-1.6E-01	6.0E-02	-1.2E-01	-4.2E-01	-9.0E-01	-5.2E-01	-7.8E-01	-4.0E-02	-6.8E-01	-1.7E+00	-0.4
1923	1.2E-01	-1.6E+00	-3.8E-01	-8.2E-01	-7.4E-01	1.1E+00	-9.2E-01	-4.2E-01	-6.8E-01	-3.8E-01	-1.0E+00	1.4E-01	-0.5
1924	3.0E-01	-1.4E-01	9.4E-01	3.4E-01	1.4E-01	3.6E-01	6.0E-02	2.6E-01	-5.8E-01	-1.5E+00	-1.6E+00	-5.8E-01	-0.2
1925	-1.5E+00	-1.5E+00	-5.4E-01	3.4E-01	-6.2E-01	-1.1E+00	-5.4E-01	-2.2E-01	-2.6E-01	2.0E-01	5.4E-01	-5.4E-01	-0.5
1926	5.0E-01	7.4E-01	-4.6E-01	-2.0E+00	-3.6E-01	8.4E-01	2.2E-01	-2.8E-01	-3.0E-01	-4.0E-02	-7.0E-01	-7.6E-01	-0.2
1927	0.0E+00	-5.6E-01	-3.4E-01	-6.6E-01	-6.6E-01	-5.2E-01	-7.4E-01	-3.8E-01	-1.6E-01	-7.2E-01	-2.0E+00	-6.2E-01	-0.6
1928	1.8E-01	-7.0E-01	-3.6E-01	-8.0E-02	-3.6E-01	-3.4E-01	-4.0E-01	-5.6E-01	-1.3E+00	-8.6E-01	-3.4E-01	-5.2E-01	-0.5
1929	-6.0E-01	-6.4E-01	5.8E-01	-4.8E-01	1.2E-01	-9.6E-01	-4.8E-01	-3.8E-01	-1.0E-01	-1.2E+00	-1.2E-01	-5.0E-01	-0.4
1930	-6.0E-02	-1.5E+00	-1.4E-01	-8.2E-01	-2.4E-01	-3.8E-01	-7.2E-01	-4.6E-01	-3.4E-01	1.2E-01	-1.3E+00	2.6E-01	-0.5

Year	Jan	Feb	Year	Mar	Apr	Year	May	Jun	Year	Jul	Aug	Year	Annual Av
1931	6.8E-01	3.0E-01	-5.8E-01	6.2E-01	8.0E-02	9.6E-01	-5.4E-01	-2.0E-02	-4.6E-01	-1.4E+00	-3.4E-01	-9.4E-01	-0.1
1932	0.0E+00	-1.1E+00	-1.2E-01	-5.2E-01	-2.6E-01	-3.2E-01	-5.0E-01	4.0E-01	-3.0E-01	2.2E-01	-3.2E-01	-5.2E-01	-0.3
1933	-1.2E-01	-3.4E-01	-1.8E-01	-2.4E-01	-9.6E-01	-8.4E-01	2.0E-01	-2.4E-01	-5.4E-01	-7.0E-01	-2.2E-01	-1.2E+00	-0.4
1934	-1.0E+00	-6.0E-02	-9.4E-01	-1.0E-01	-4.8E-01	-3.4E-01	-4.8E-01	-6.8E-01	-9.0E-01	-8.0E-02	-2.2E+00	-9.8E-01	-0.7
1935	-9.2E-01	-1.2E+00	-6.2E-01	-1.4E+00	-2.4E-01	0.0E+00	-4.2E-01	-1.8E-01	-1.3E+00	-4.0E-02	-1.1E+00	-2.2E-01	-0.6
1936	-6.4E-01	-1.2E+00	-2.0E-01	-5.6E-01	1.6E-01	-1.1E+00	-1.2E-01	-1.6E-01	2.2E-01	1.0E-01	2.8E-01	-6.0E-01	-0.3
1937	-5.2E-01	-5.0E-01	-8.4E-01	-1.3E+00	-4.2E-01	-2.0E-02	-7.8E-01	-8.0E-02	-4.0E-01	-8.4E-01	-2.2E-01	-9.8E-01	-0.6
1938	5.8E-01	-1.0E+00	4.0E-01	1.0E-01	-6.4E-01	-1.8E+00	-7.4E-01	4.0E-02	-6.8E-01	-1.8E+00	-1.5E+00	-7.2E-01	-0.7
1939	5.4E-01	1.6E-01	-1.2E+00	-8.4E-01	-7.2E-01	-3.8E-01	-7.8E-01	-2.2E-01	-5.6E-01	-1.8E-01	-1.1E+00	-9.8E-01	-0.5
1940	-5.4E-01	-2.0E-02	-2.4E+00	-5.8E-01	-2.4E-01	-1.2E-01	-3.0E-01	-4.0E-01	-1.4E-01	-2.0E-01	6.8E-01	-4.6E-01	-0.4
1941	-4.6E-01	7.6E-01	7.0E-01	7.4E-01	3.6E-01	8.2E-01	2.2E-01	7.8E-01	4.2E-01	8.0E-01	7.6E-01	8.8E-01	0.6
1942	2.0E-02	4.8E-01	8.6E-01	7.2E-01	4.8E-01	-2.0E-02	-6.8E-01	-4.4E-01	-7.0E-01	2.2E-01	-7.6E-01	-4.4E-01	0.0
1943	1.6E-01	-3.0E-01	1.4E-01	-6.8E-01	-5.4E-01	-1.1E+00	-8.4E-01	-3.2E-01	-1.0E+00	-9.2E-01	1.6E-01	-8.8E-01	-0.5
1944	-1.4E-01	-1.3E+00	-1.1E+00	-9.8E-01	4.4E-01	5.0E-01	-4.6E-01	-2.8E-01	0.0E+00	-3.8E-01	2.0E-02	2.8E-01	-0.3
1945	-1.2E+00	-4.2E-01	1.8E-01	-9.6E-01	-3.2E-01	0.0E+00	-1.0E-01	1.0E-01	-6.6E-01	-5.6E-01	-8.8E-01	-1.6E+00	-0.5
1946	-4.2E-01	5.2E-01	2.2E-01	-1.4E-01	-5.6E-01	-8.6E-01	-3.2E-01	-3.2E-01	-5.0E-01	4.4E-01	-6.0E-02	7.0E-01	-0.1
1947	1.4E-01	1.8E-01	8.0E-02	-8.8E-01	-2.0E-02	8.0E-01	1.2E-01	6.8E-01	-4.4E-01	-1.1E+00	-5.6E-01	0.0E+00	-0.1
1948	6.6E-01	1.0E-01	6.2E-01	3.8E-01	4.0E-01	2.8E-01	-4.0E-02	2.0E-02	-7.8E-01	-4.0E-02	7.4E-01	-1.1E+00	0.1
1949	6.4E-01	-3.2E-01	5.8E-01	1.0E-01	-4.8E-01	-4.2E-01	4.6E-01	4.6E-01	-6.6E-01	-5.0E-01	-1.1E+00	-9.3E-01	-0.2
1950	-3.0E-01	-1.5E+00	-8.8E-01	-4.2E-01	-2.7E-01	3.5E-01	-3.8E-01	3.3E-01	-6.0E-01	-1.1E+00	-1.2E+00	-1.2E+00	-0.6
1951	-3.7E-01	-4.2E-01	-1.0E-01	-1.2E+00	-2.7E-01	-3.2E-01	-1.0E-01	-3.3E-02	7.7E-01	2.0E-01	8.0E-01	-8.3E-01	-0.2
1952	2.7E-01	2.7E-01	-1.0E+00	5.0E-02	-3.0E-01	-3.0E-01	1.7E-02	-3.5E-01	-2.3E-01	-3.2E-01	-1.7E+00	5.3E-01	-0.3
1953	-3.0E-01	8.3E-01	1.0E+00	5.0E-02	-3.2E-01	1.8E-01	-3.3E-01	-3.7E-01	-3.0E-01	-1.0E-01	-6.0E-01	-8.2E-01	-0.1
1954	-4.7E-01	5.7E-01	3.0E-01	-1.7E-01	3.3E-02	-4.5E-01	-7.8E-01	-2.5E-01	-1.3E+00	-1.2E+00	-1.3E+00	-4.3E-01	-0.5
1955	7.0E-01	4.8E-01	1.3E-01	-7.8E-01	-6.7E-02	-3.7E-01	-3.3E-02	-7.2E-01	-1.0E-01	-7.8E-01	-1.9E+00	-9.3E-01	-0.4
1956	-2.0E-01	-4.8E-01	5.3E-01	3.7E-01	-1.4E+00	-9.8E-01	-1.2E+00	-6.7E-01	-9.3E-01	-8.7E-01	-5.3E-01	-8.2E-01	-0.6
1957	1.7E-01	-1.1E+00	-1.7E+00	-3.8E-01	-2.3E-01	8.0E-01	-2.3E-01	-4.2E-01	-2.2E-01	2.3E-01	1.5E-01	5.8E-01	-0.2
1958	8.7E-01	-1.7E-01	0.0E+00	2.0E-01	4.3E-01	8.5E-01	-2.8E-01	-1.7E-01	-3.0E-01	-2.3E-01	5.2E-01	5.2E-01	0.2
1959	6.2E-01	1.7E-01	4.2E-01	4.7E-01	9.2E-01	1.0E-01	-5.8E-01	-1.0E-01	-2.8E-01	-8.3E-01	6.7E-02	9.8E-01	0.2
1960	5.0E-01	1.3E+00	-1.5E-01	2.5E-01	1.8E-01	-3.7E-01	4.5E-01	-2.5E-01	3.3E-02	-4.2E-01	3.3E-02	5.8E-01	0.2
1961	7.4E-01	-1.0E+00	4.4E-01	1.1E-01	-8.7E-01	-7.4E-01	-9.1E-01	7.1E-02	-4.1E-01	-9.6E-01	1.4E-01	-1.4E-02	-0.3
1962	-9.9E-01	7.0E-01	-3.0E-01	-3.1E-01	-1.9E-01	2.1E-01	-1.9E-01	-1.3E-01	-4.4E-01	-2.9E-02	-3.9E-01	-3.0E-01	-0.2
1963	6.3E-01	2.6E-01	1.4E-01	-7.9E-01	-1.9E-01	-5.3E-01	-1.1E-01	-5.9E-01	-1.7E-01	-2.6E-01	2.1E-01	4.6E-01	-0.1
1964	-1.0E+00	-5.6E-01	4.3E-02	3.9E-01	-4.3E-02	-2.1E-01	-3.1E-01	-6.4E-01	-8.0E-01	-8.1E-01	-8.0E-01	-1.1E+00	-0.5
1965	3.1E-01	-2.6E-01	-9.1E-01	-5.1E-01	-5.4E-01	-8.6E-02	-4.6E-01	2.1E-01	1.7E-01	4.9E-01	6.0E-01	4.9E-01	0.0
1966	2.3E-01	7.7E-01	-1.7E-01	-3.9E-01	-7.4E-01	5.1E-01	3.9E-01	5.6E-01	2.3E-01	8.7E-01	6.1E-01	0.0E+00	0.2
1967	-1.7E-01	5.7E-01	5.7E-02	2.7E-01	4.4E-01	2.9E-01	-1.1E-01	1.0E-01	-4.3E-02	-1.9E-01	-2.0E-01	5.0E-01	0.1
1968	-4.7E-01	-7.0E-01	1.7E-01	-5.0E-01	-4.1E-01	5.0E-01	1.1E-01	3.3E-01	3.0E-01	-3.3E-01	-1.4E-02	-2.9E-02	-0.1
1969	-1.3E-01	3.4E-01	6.4E-01	7.9E-01	8.6E-01	3.9E-01	1.4E-02	4.0E-01	-5.7E-01	2.7E-01	1.0E+00	9.0E-01	0.4
1970	7.1E-02	1.1E-01	-4.6E-01	2.7E-01	4.3E-02	-6.1E-01	1.1E-01	-1.9E-01	-3.7E-01	-1.6E-01	-7.9E-01	-1.6E+00	-0.3
1971	-7.1E-01	-4.0E-01	1.4E-01	5.9E-01	-1.7E-01	-9.6E-01	5.7E-02	-1.6E-01	8.6E-02	-1.2E+00	-1.2E+00	-8.1E-01	-0.4
1972	-2.3E-01	-1.2E+00	1.7E-01	-3.1E-01	-2.0E-01	1.2E+00	3.0E-01	5.0E-01	8.3E-01	1.2E+00	-2.4E-01	9.4E-01	0.2
1973	-3.9E-01	7.9E-01	3.0E-01	1.3E+00	7.7E-01	4.7E-01	-1.6E-01	-4.1E-01	-5.6E-01	-2.9E-01	-4.1E-01	-8.6E-02	0.1
1974	7.1E-02	1.1E-01	6.7E-01	6.0E-01	-5.4E-01	1.9E-01	2.9E-02	-1.3E-01	3.6E-01	-7.9E-01	-1.7E+00	-1.2E+00	-0.2
1975	-6.1E-01	-2.6E-01	-6.4E-01	2.0E-01	-2.0E-01	-5.9E-01	-1.4E-01	-1.9E-01	-3.0E-01	-6.0E-01	-1.5E+00	-1.4E+00	-0.5
1976	-6.0E-01	-2.4E-01	4.9E-01	-8.6E-01	-7.7E-01	-6.9E-01	-5.7E-02	1.4E-02	-7.1E-02	8.6E-01	1.2E+00	7.3E-01	0.0
1977	1.4E-01	4.6E-01	1.4E+00	1.3E-01	5.0E-01	2.4E-01	-7.1E-02	4.1E-01	5.7E-02	6.1E-01	1.4E+00	-2.7E-01	0.4
1978	-1.0E-01	-3.6E-01	-1.2E+00	-2.4E-01	2.0E-01	-1.0E+00	-2.4E-01	-8.6E-02	-1.9E-01	2.7E-01	9.1E-01	8.3E-01	-0.1
1979	8.1E-01	-8.9E-01	-5.0E-01	-1.9E-01	-3.1E-01	8.1E-01	4.1E-01	-3.4E-01	2.9E-01	5.9E-01	9.4E-01	5.7E-01	0.2
1980	3.3E-01	7.7E-01	7.1E-02	7.4E-01	5.4E-01	-7.0E-01	1.1E-01	-2.0E-01	1.4E-01	7.1E-01	9.9E-01	-3.9E-01	0.3
1981	2.9E-02	5.6E-01	1.7E-01	-2.3E-01	3.1E-01	5.0E-01	-7.1E-02	-4.3E-02	3.0E-01	4.3E-01	-4.3E-01	1.3E-01	0.1
1982	2.7E-01	3.3E-01	-7.3E-01	-7.9E-01	1.3E-01	6.0E-01	5.0E-01	3.9E-01	1.4E-02	7.3E-01	2.3E-01	3.3E-01	0.2
1983	-3.0E-01	-1.1E+00	-9.0E-01	-1.2E+00	3.2E-01	1.2E+00	6.0E-01	2.0E-01	-1.2E-01	-5.6E-01	-1.2E+00	-8.0E-02	-0.3
1984	-4.2E-01	5.6E-01	1.1E+00	5.6E-01	6.4E-01	-1.6E-01	-4.4E-01	-3.0E-01	-3.0E-01	-2.6E-01	-2.0E-01	8.0E-02	0.1
1985	3.6E-01	-2.0E-02	9.6E-01	-1.2E-01	1.6E-01	-5.4E-01	-1.2E-01	-2.0E-02	4.0E-01	-9.2E-01	-5.6E-01	5.2E-01	0.0
1986	4.6E-01	-1.4E-01	4.0E-01	1.8E-01	2.4E-01	1.0E-01	3.0E-01	-2.6E-01	4.8E-01	4.4E-01	3.2E-01	-2.8E-01	0.2
1987	8.4E-01	3.2E-01	8.0E-02	4.0E-01	1.6E-01	2.8E-01	7.0E-01	7.2E-01	1.2E+00	4.0E-01	8.8E-01	7.0E-01	0.6
1988	9.8E-01	8.0E-01	-5.6E-01	3.2E-01	6.0E-01	4.8E-01	0.0E+00	4.8E-01	2.8E-01	-4.5E-01	-4.4E-01	-2.5E-02	0.2
1989	2.2E-01	4.0E-02	-2.4E-01	-2.2E-01	1.2E-01	-4.6E-01	3.2E-01	-2.4E-01	-1.2E-01	-1.4E-01	5.0E-01	-1.8E-01	0.0
1990	9.2E-01	4.0E-01	-9.4E-01	-5.2E-01	-2.0E-01	-3.8E-01	-1.4E-01	-5.2E-01	-3.0E-01	6.0E-02	3.0E-01	6.4E-01	-0.1

Year	Jan	Feb	Year	Mar	Apr	Year	May	Jun	Year	Jul	Aug	Year	Annual Av
1991	-4.3E-01	-1.0E-01	-3.3E-01	3.0E-01	6.0E-01	4.3E-01	-3.0E-01	-2.5E-02	5.5E-01	1.3E-01	5.7E-01	-8.0E-01	0.0
1992	7.5E-02	-8.5E-01	-2.3E-01	-8.3E-01	1.3E-01	8.8E-01	7.5E-01	-2.5E-02	5.3E-01	-2.0E-01	7.3E-01	1.8E-01	0.1
1993	2.8E-01	3.3E-01	-3.3E-01	-6.8E-01	2.3E-01	6.3E-01	1.3E-01	4.5E-01	-4.0E-01	1.3E-01	5.7E-01	-1.8E-01	0.1
1994	6.3E-01	-3.3E-01	8.3E-01	-3.3E-01	7.5E-02	-4.3E-01	-5.3E-01	1.5E-01	-4.8E-01	3.5E-01	4.0E-01	-1.0E+00	-0.1
1995	-9.0E-01	4.5E-01	-2.5E-01	-7.5E-02	2.3E-01	1.6E+00	3.2E-01	1.1E+00	7.5E-01	3.3E-01	-4.0E-01	1.0E-01	0.3
1996	3.8E-01	9.5E-01	1.1E+00	-5.0E-02	7.5E-02	7.5E-01	2.0E-01	1.0E-01	2.3E-01	-6.0E-01	-4.8E-01	1.3E-01	0.2
1997	-5.3E-01	-9.5E-01	6.5E-01	-8.0E-01	-1.0E-01	1.0E-01	7.5E-01	3.8E-01	4.3E-01	5.8E-01	1.5E+00	-1.0E-01	0.2
1998	8.0E-01	2.3E-01	-2.0E-01	7.3E-01	1.5E+00	9.0E-01	7.5E-01	1.1E+00	3.8E-01	0.0E+00	2.3E-01	-7.5E-02	0.5
1999	-4.0E-01	1.5E+00	6.0E-01	1.3E-01	-7.5E-01	-6.5E-01	1.0E-01	5.3E-01	-1.3E-01	1.3E-01	5.0E-02	-2.5E-02	0.1
2000	1.0E+00	-6.3E-01	-7.3E-01	5.3E-01	-6.0E-01	-2.5E-01	-1.8E-01	3.3E-01	6.5E-01	6.5E-01	4.3E-01	-2.3E-01	0.1
2001	6.3E-01	1.7E-01	-5.3E-01	3.0E-01	-3.3E-02	3.3E-02	-2.7E-01	1.7E-01	7.0E-01	1.7E-01	6.7E-01	5.0E-01	0.2
2002	-3.3E-01	1.2E+00	6.7E-01	9.3E-01	1.1E+00	2.0E-01	1.2E+00	-6.7E-02	2.7E-01	1.1E+00	5.3E-01	5.0E-01	0.6
2003	1.2E+00	1.2E+00	5.5E-01	6.3E-01	5.7E-01	3.7E-01	3.7E-01	6.7E-01	1.0E-01	7.0E-01	1.3E+00	6.7E-02	0.6
2004	2.7E-01	7.7E-01	1.4E+00	2.3E-01	1.3E-01	-3.3E-02	2.0E-01	-3.3E-02	2.0E-01	-2.3E-01	8.3E-01	6.7E-02	0.3
2005	-2.0E-01	-6.7E-02	-5.0E-01	2.0E-01	1.7E-01	5.7E-01	1.7E-01	1.7E-01	-2.3E-01	-2.0E-01	-4.7E-01	-4.7E-01	-0.1
2006	4.0E-01	1.5E+00	3.3E-02	-2.7E-01	1.7E-01	3.3E-02	1.7E-01	-3.3E-02	5.0E-01	6.3E-01	1.1E+00	6.3E-01	0.4
2007	1.1E+00	8.7E-01	7.0E-01	8.3E-01	6.3E-01	8.5E-01	5.7E-01	4.7E-01	1.3E-01	3.0E-01	2.3E-01	7.0E-01	0.6
2008	-3.3E-02	-8.0E-01	5.0E-01	1.7E-01	3.0E-01	-2.3E-01	2.3E-01	-3.3E-02	-3.3E-02	3.7E-01	6.7E-01	1.3E+00	0.2
2009	1.3E+00	1.0E+00	9.7E-01	1.0E+00	6.3E-01	1.1E+00	2.0E-01	1.0E+00	8.0E-01	0.0E+00	6.3E-01	1.0E+00	0.8
2010	1.6E+00	1.2E+00	1.2E+00	1.4E+00	1.6E+00	6.0E-01	1.7E-01	6.0E-01	1.7E-01	4.3E-01	1.4E+00	-3.3E-01	0.8
2011	6.7E-02	5.7E-01	7.7E-01	1.0E-01	5.3E-01	-1.3E-01	-6.7E-02	4.0E-01	2.0E-01	7.0E-01	1.0E+00	7.3E-01	0.4
2012	-4.3E-01	3.3E-01	-4.0E-01	6.7E-01	1.3E-01	3.7E-01	7.7E-01	5.3E-01	3.0E-01	5.3E-01	1.3E-01	9.7E-01	0.3
2013	4.0E-01	1.2E+00	4.7E-01	-1.0E-01	8.3E-01	-6.7E-01	-8.7E-01	2.7E-01	2.0E-01	3.3E-01	4.0E-01	-2.0E-01	0.2
2014	5.7E-01	0.0E+00	1.7E-01	2.7E-01	-3.3E-02	1.6E+00	1.7E-01	6.3E-01	5.0E-01	8.0E-01	9.0E-01	1.0E-01	0.5

Table 3: Monthly mean temperature anomaly data from the CRUTEM4 database for lon= 70.000 75.000, lat= 15.000 20.000 grid sourced from KNMI Explorer. Calculated annual average values have been given in the last column.

using minimal fraction of valid points 30.00

pre [mm/month] from CRU TS 3.23 Precipitation

cutting out region lon= 74.000 75.000, lat= 15.000

16.000

Year	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	JJAS total	FMAM total	ONDJ total	Annual total
1901	0.5	0.4	7.7	119.9	74.9	627.6	423.7	320.1	177.4	114.4	9.6	3.8	1548.8	202.8	128.3	1879.9
1902	0.0	0.0	2.0	9.7	59.7	431.3	643.9	140.5	222.7	184.0	64.3	49.7	1438.4	71.3	297.9	1807.6
1903	0.0	0.0	0.0	6.5	131.4	314.5	736.2	246.5	112.5	73.2	21.5	10.0	1409.7	137.9	104.8	1652.4
1904	0.0	0.1	3.3	55.7	96.8	736.5	441.5	234.9	95.4	81.8	0.4	0.0	1508.3	155.8	82.2	1746.4
1905	0.0	0.0	2.1	10.0	68.6	305.4	310.2	186.9	54.9	128.9	13.8	0.0	857.4	80.7	142.7	1080.8
1906	0.7	0.0	0.0	6.7	55.2	330.6	576.3	311.4	169.6	126.6	16.8	30.4	1387.9	61.9	174.6	1624.4
1907	0.0	0.0	0.4	117.2	5.7	338.8	450.6	649.5	290.1	20.4	28.5	2.9	1729.1	123.4	51.7	1904.2
1908	0.0	0.1	4.4	39.2	61.7	353.1	919.9	404.5	90.3	28.1	5.0	0.0	1767.9	105.4	33.1	1906.4
1909	0.2	0.0	5.3	2.3	72.7	410.3	749.9	162.8	147.0	54.0	30.2	0.4	1470.0	80.3	84.8	1635.1
1910	0.0	0.0	13.2	6.8	36.5	493.7	303.3	374.0	169.3	94.9	31.8	0.0	1340.3	56.4	126.7	1523.5
1911	0.0	0.0	0.0	19.3	81.4	344.4	515.8	379.0	105.0	115.9	28.9	12.2	1344.3	100.7	157.0	1602.0
1912	0.0	0.0	2.4	12.2	60.3	297.5	888.8	358.2	111.9	111.0	38.2	2.5	1656.3	74.9	151.7	1882.9
1913	0.0	0.0	0.0	21.1	55.4	438.9	439.9	270.6	130.7	120.4	13.5	0.0	1280.1	76.5	134.0	1490.6
1914	0.0	0.0	0.0	24.9	34.7	305.8	1107.9	803.0	191.8	59.3	33.8	51.2	2408.5	59.6	144.3	2612.4
1915	0.7	0.0	4.6	35.3	59.1	492.8	454.8	238.1	286.6	79.6	28.6	13.5	1472.4	98.9	122.3	1693.6
1916	0.0	0.0	0.1	24.8	111.9	429.5	377.9	345.8	287.0	119.4	173.9	0.0	1440.1	136.8	293.3	1870.2
1917	0.0	4.5	9.5	5.6	10.9	496.4	302.2	310.5	297.9	232.0	110.3	0.0	1407.0	30.5	342.3	1779.8
1918	0.6	0.0	0.1	20.2	311.9	189.4	194.1	271.6	139.8	17.5	113.2	0.4	794.9	332.1	131.7	1258.7
1919	0.1	0.4	0.0	8.2	89.8	469.4	435.1	304.5	162.0	131.4	61.6	12.3	1370.9	98.3	205.4	1674.6
1920	2.8	0.0	0.5	125.0	49.0	338.3	509.0	173.9	156.8	126.5	1.3	0.0	1178.0	174.5	130.6	1483.2
1921	0.1	0.0	5.3	70.7	2.8	387.8	496.4	310.9	111.0	133.8	88.5	0.0	1306.1	78.8	222.4	1607.3
1922	0.0	1.4	0.0	59.8	47.4	408.6	654.3	224.5	78.4	68.0	105.3	0.0	1365.8	108.6	173.3	1647.7
1923	0.0	0.4	10.9	19.9	96.8	131.9	941.1	447.0	164.7	8.9	0.2	1.5	1684.7	128.0	10.6	1823.3
1924	0.0	0.0	7.6	33.4	21.6	386.5	827.7	267.5	135.5	47.9	11.3	2.0	1617.1	62.7	61.2	1741.0
1925	0.0	0.0	2.4	75.8	122.3	500.1	605.5	235.8	98.0	97.4	26.8	16.9	1439.4	200.5	141.1	1780.9
1926	1.3	0.0	0.0	0.3	54.5	242.4	534.6	576.9	156.8	37.9	0.4	0.0	1510.6	54.8	39.6	1605.0
1927	0.0	0.0	0.0	23.3	61.4	352.6	645.6	214.2	222.1	42.5	70.7	0.0	1434.5	84.7	113.2	1632.5
1928	0.0	2.9	3.4	40.0	39.8	415.4	630.9	366.2	73.3	219.0	0.3	14.2	1485.9	86.1	233.5	1805.5
1929	0.0	0.0	8.7	112.4	70.6	534.0	476.5	211.1	237.2	163.1	43.8	0.3	1458.8	191.6	207.2	1857.6
1930	0.1	0.0	3.1	3.2	70.6	548.6	345.7	210.3	140.5	204.7	6.4	7.3	1245.1	76.9	218.5	1540.5
1931	0.0	0.0	9.4	37.8	29.7	299.9	692.4	482.1	140.3	143.4	88.5	35.7	1614.6	77.0	267.5	1959.1
1932	0.0	0.0	0.0	77.3	76.9	221.9	786.9	382.5	237.1	254.7	83.7	3.5	1628.3	154.3	341.9	2124.5
1933	0.0	0.0	15.3	44.4	219.6	537.7	571.7	427.7	233.7	223.8	52.1	13.0	1770.8	279.2	288.9	2338.9
1934	0.2	0.0	0.0	24.6	12.8	546.6	572.3	352.0	93.5	86.8	50.9	0.0	1564.4	37.4	137.9	1739.7
1935	0.0	1.9	0.0	10.7	41.4	257.3	451.7	281.1	102.5	182.8	11.0	1.9	1092.7	54.0	195.7	1342.3
1936	0.0	1.1	1.3	57.8	76.0	638.6	307.8	200.6	153.6	92.3	81.4	1.5	1300.6	136.1	175.3	1612.0
1937	0.0	0.0	11.8	83.2	20.2	302.9	628.3	121.6	218.2	245.7	0.0	3.9	1271.0	115.2	249.6	1635.8
1938	0.0	0.0	18.7	30.4	48.5	358.7	414.1	246.5	229.6	113.2	16.4	11.3	1249.0	97.6	140.8	1487.4
1939	0.0	0.0	7.9	11.0	5.9	546.5	546.5	564.5	78.9	98.0	26.1	0.0	1736.5	24.9	124.1	1885.5
1940	0.0	0.0	0.1	13.7	59.7	386.3	583.6	498.7	76.1	114.8	37.8	19.7	1544.7	73.5	172.3	1790.5
1941	0.3	0.2	2.8	36.8	31.3	382.5	543.4	157.5	105.0	112.3	0.0	18.8	1188.5	71.0	131.4	1390.9
1942	0.0	1.8	0.7	84.6	69.5	534.6	766.6	292.4	94.1	67.4	11.0	17.7	1687.6	156.6	96.1	1940.3
1943	0.0	0.0	0.1	33.3	288.6	317.5	686.8	127.2	159.1	180.4	62.1	0.0	1290.5	321.9	242.5	1855.0
1944	0.0	0.4	16.7	5.3	72.8	415.1	760.6	207.0	77.8	210.7	39.9	0.0	1460.6	95.3	250.6	1806.4
1945	0.0	0.0	0.0	11.7	25.9	411.6	747.1	323.6	137.9	46.9	17.8	0.0	1620.2	37.6	64.8	1722.6
1946	0.0	0.0	0.8	108.5	70.2	468.1	640.1	524.3	163.7	108.4	147.4	12.9	1796.3	179.6	268.7	2244.5
1947	0.1	0.2	12.1	27.2	67.7	305.6	533.3	472.7	165.9	47.3	9.7	52.2	1477.6	107.2	109.4	1694.2
1948	1.7	0.0	0.0	47.8	30.1	496.6	495.1	372.5	221.8	85.1	147.7	2.2	1586.1	77.9	236.8	1900.8
1949	0.0	0.0	13.6	28.4	240.8	232.8	476.1	253.8	185.1	105.5	21.5	0.0	1147.8	282.8	127.0	1557.5
1950	0.0	0.0	0.0	16.5	97.8	272.6	907.5	371.2	299.2	139.2	20.9	0.3	1850.5	114.3	160.4	2125.2
1951	0.0	0.0	0.1	66.9	111.2	575.4	572.3	241.6	139.8	169.3	39.1	0.0	1529.1	178.1	208.4	1915.6
1952	0.0	1.4	0.0	63.8	71.4	430.9	616.4	353.7	46.7	198.9	0.0	7.1	1447.7	136.6	206.0	1790.3
1953	0.0	0.0	4.2	63.7	14.1	738.9	842.7	510.6	141.4	204.4	0.0	0.0	2233.6	82.0	204.4	2520.1
1954	0.0	0.0	8.2	105.3	47.0	212.5	698.2	645.8	183.3	145.3	2.8	9.4	1739.8	160.4	157.5	2057.7
1955	0.0	0.0	0.9	74.1	202.9	549.3	365.9	305.2	289.3	260.1	22.2	0.0	1509.7	277.9	282.3	2069.8
1956	0.0	4.3	8.6	86.6	155.9	501.5	750.4	421.1	149.9	179.4	93.3	0.0	1823.0	255.4	272.6	2351.0
1957	0.0	0.0	3.0	15.5	104.2	417.1	472.8	478.9	73.4	228.4	77.9	0.0	1442.2	122.6	306.4	1871.1
1958	0.0	0.0	0.2	40.7	190.7	399.0	850.0	334.8	135.1	93.1	42.5	0.0	1719.0	231.6	135.6	2086.2
1959	0.0	0.0	0.0	42.1	86.0	670.9	939.2	241.3	251.1	32.9	44.7	2.3	2102.5	128.1	79.9	2310.5
1960	0.0	0.0	14.3	38.0	261.0	307.3	504.3	284.9	220.1	35.2	23.3	0.0	1316.7	313.3	58.5	1688.4

Year	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	JJAS total	FMAM total	ONDJ total	Annual total
1961	0.0	0.0	0.1	32.0	383.6	375.0	1054.5	357.3	216.3	132.1	13.7	0.0	2003.1	415.7	145.8	2564.7
1962	0.0	1.3	4.1	34.6	181.8	133.6	692.9	383.6	160.3	146.1	30.6	88.0	1370.3	221.8	264.7	1856.7
1963	1.1	1.8	18.3	71.9	153.0	275.4	436.9	531.7	66.6	221.5	3.5	0.1	1310.6	245.0	226.2	1781.8
1964	0.0	0.0	14.1	28.3	39.2	355.4	437.2	664.6	270.6	192.6	25.0	5.1	1727.9	81.6	222.6	2032.1
1965	0.1	0.0	1.1	42.5	62.6	382.1	777.2	200.0	143.9	32.7	10.1	79.8	1503.3	106.2	122.6	1732.0
1966	1.3	2.4	4.0	5.0	278.4	250.1	665.8	111.0	240.9	121.1	205.9	18.6	1267.8	289.8	346.9	1904.6
1967	0.2	0.0	0.1	29.8	51.8	410.2	781.4	320.0	161.1	121.7	3.5	29.5	1672.7	81.7	154.8	1909.2
1968	0.0	2.0	1.0	51.7	63.5	420.5	553.0	175.0	100.1	168.6	22.8	0.1	1248.6	118.1	191.5	1558.3
1969	0.0	0.0	17.2	44.0	29.7	228.9	603.0	578.6	167.9	82.5	47.9	2.7	1578.3	90.9	133.1	1802.3
1970	0.0	0.0	0.0	35.2	211.5	401.3	559.5	474.1	179.1	173.0	0.2	0.0	1614.1	246.8	173.2	2034.0
1971	0.0	0.0	0.1	40.0	114.5	521.4	359.1	232.3	158.1	52.8	2.0	0.0	1270.9	154.7	54.8	1480.4
1972	0.0	1.2	3.6	28.5	72.2	331.6	429.1	146.5	125.9	59.0	33.0	0.0	1033.2	105.5	92.0	1230.7
1973	0.0	0.0	0.0	22.6	39.0	414.4	359.7	344.9	92.5	128.0	11.6	0.1	1211.5	61.6	139.7	1412.9
1974	0.0	0.0	21.2	41.5	206.7	249.9	507.2	242.0	296.7	180.5	0.0	0.0	1295.8	269.3	180.5	1745.6
1975	0.0	1.6	0.4	15.4	73.4	595.5	552.2	247.5	285.3	162.1	53.7	0.0	1680.5	90.9	215.8	1987.3
1976	0.0	0.0	4.3	38.1	6.2	319.3	495.3	235.6	139.7	24.6	115.3	0.0	1189.9	48.5	139.9	1378.4
1977	0.0	0.1	15.6	39.7	84.7	471.8	530.8	200.1	124.5	149.1	130.8	0.1	1327.2	140.1	279.9	1747.2
1978	0.0	2.0	0.0	32.8	182.5	453.0	427.7	361.7	178.9	59.9	52.4	4.1	1421.3	217.2	116.5	1754.9
1979	0.0	2.1	0.4	6.0	70.5	471.5	285.5	367.4	202.6	67.8	110.3	0.0	1327.1	79.1	178.1	1584.3
1980	0.0	0.0	0.3	90.0	24.1	500.9	490.9	395.1	97.2	35.3	46.7	13.6	1484.1	114.4	95.5	1694.1
1981	0.0	0.0	3.7	40.3	73.4	443.6	433.1	348.4	272.0	46.5	13.6	0.0	1497.1	117.4	60.2	1674.7
1982	0.0	0.0	0.2	26.0	132.1	331.6	479.2	330.4	101.7	105.1	52.5	0.0	1243.0	158.3	157.6	1558.9
1983	0.0	0.0	0.0	0.0	37.7	702.3	465.2	522.9	284.6	62.8	29.3	23.1	1974.9	37.7	115.2	2127.8
1984	0.0	4.4	15.0	96.5	14.3	342.0	566.2	189.7	163.9	165.9	3.9	26.1	1261.8	130.3	195.9	1588.0
1985	0.0	0.1	1.1	26.7	70.7	383.1	262.9	286.3	74.0	159.4	3.6	0.5	1006.3	98.5	163.5	1268.4
1986	1.2	0.0	5.2	19.4	33.0	478.2	199.4	219.4	69.1	89.3	95.1	0.1	966.0	57.6	185.6	1209.3
1987	0.0	0.2	3.4	5.4	76.2	309.5	275.9	196.4	177.0	117.5	21.3	48.5	958.7	85.3	187.2	1231.3
1988	0.0	0.0	0.2	59.6	16.0	356.1	556.9	379.5	308.4	41.6	1.5	10.0	1600.9	75.8	53.0	1729.7
1989	0.0	0.0	15.1	55.2	38.6	410.9	398.9	208.1	221.2	30.0	3.2	1.3	1239.2	108.9	34.4	1382.5
1990	0.0	0.0	0.0	23.0	155.6	268.3	282.1	251.4	85.9	110.0	44.9	0.0	887.6	178.6	154.9	1221.1
1991	0.0	0.0	0.1	81.8	74.4	300.2	587.2	270.5	152.2	29.4	22.1	0.0	1310.0	156.3	51.5	1517.9
1992	0.0	0.0	0.0	18.7	58.4	514.3	365.8	327.4	260.4	129.4	112.8	0.0	1467.9	77.1	242.2	1787.3
1993	0.0	0.0	16.4	17.8	68.3	290.2	632.8	240.0	79.1	203.8	11.4	31.4	1242.1	102.5	246.5	1591.1
1994	0.0	0.0	0.5	77.0	34.5	459.7	715.4	328.6	114.1	230.1	2.0	0.3	1617.8	112.0	232.4	1962.2
1995	0.7	0.0	0.2	21.9	43.8	366.5	573.4	258.3	162.6	189.8	8.6	0.0	1360.8	65.8	199.1	1625.8
1996	0.0	0.1	0.5	15.2	15.8	504.2	420.4	162.6	175.3	146.0	2.5	2.7	1262.5	31.7	151.2	1445.4
1997	1.2	0.0	8.8	17.8	10.8	510.6	516.4	488.6	37.5	101.6	55.0	61.0	1553.1	37.4	218.7	1809.2
1998	0.0	0.1	0.1	1.1	62.1	504.6	381.0	279.4	203.8	99.6	51.3	5.1	1368.8	63.5	156.0	1588.3
1999	0.0	0.1	0.3	2.1	154.7	470.9	553.0	115.6	71.3	173.4	4.9	0.6	1210.8	157.2	178.9	1546.8
2000	0.0	0.1	0.0	31.7	137.6	363.8	528.7	228.5	222.6	96.8	12.6	2.5	1343.6	169.3	111.9	1624.8
2001	0.0	0.1	0.0	23.1	72.6	220.3	375.2	203.7	102.1	93.4	40.8	2.2	901.4	95.8	136.4	1133.6
2002	0.0	0.3	0.1	13.5	51.7	452.0	134.4	320.2	42.9	169.7	3.3	0.0	949.6	65.7	173.1	1188.3
2003	0.0	0.1	10.8	38.9	27.8	326.6	326.1	143.5	76.2	128.2	5.4	0.0	872.4	77.6	133.6	1083.6
2004	0.0	0.0	0.4	15.5	195.0	394.7	202.8	329.9	105.2	61.1	29.4	0.0	1032.6	210.9	90.5	1334.1
2005	0.0	0.0	0.2	59.2	28.1	582.0	564.9	308.3	422.2	125.8	6.1	0.5	1877.4	87.5	132.4	2097.3
2006	0.0	0.0	25.8	3.2	276.3	467.1	380.4	362.0	245.5	136.3	39.5	0.0	1455.0	305.4	175.8	1936.1
2007	0.0	0.0	0.1	39.3	85.3	812.1	431.1	415.5	357.3	53.2	82.7	0.3	2016.1	124.6	136.2	2276.9
2008	0.0	4.7	13.2	63.3	32.6	348.4	257.3	411.5	255.3	80.0	16.1	14.2	1272.5	113.9	110.3	1496.7
2009	0.0	0.0	5.9	13.7	67.6	297.6	705.2	186.4	296.0	208.0	108.5	2.4	1485.3	87.2	318.9	1891.5
2010	0.4	0.0	0.0	33.7	28.7	472.7	538.1	299.9	356.9	145.3	112.7	2.3	1667.6	62.5	260.7	1990.8
2011	0.0	0.4	0.0	59.3	65.1	356.7	421.0	369.3	261.0	148.7	16.4	0.0	1408.0	124.9	165.0	1697.9
2012	0.0	0.1	0.0	61.6	25.9	335.2	279.6	264.8	167.4	59.3	28.6	0.1	1047.0	87.5	88.0	1222.6
2013	0.0	1.3	1.9	23.2	84.4	342.2	602.3	194.5	265.9	81.0	5.4	0.3	1404.9	110.8	86.7	1602.4
2014	0.0	0.1	7.5	20.8	155.0	249.3	562.5	375.7	146.1	195.0	55.1	24.2	1333.6	183.4	274.3	1791.4

Table 4: Monthly rainfall amount data (in mm) from the CRU TS3.23 database for lon= 74.000 75.000, lat= 15.000 16.000 grid sourced from KNMI Explorer. Calculated JJAS (monsoon), FMAM (summer), ONDJ (winter) and annual total rainfall amounts have been given in the last 4 columns.

Number	SampleDate	PeriodFrom	PeriodTo	SampleType	H3	H3_ERR	H3 LabName	H2	H2 LabName	O18	O18 LabName	Precipitation	AirTemp
1	1960-01-15	1960-01-01	1960-01-31	28								0	24.7
2	1960-02-15	1960-02-01	1960-02-29	28								0	26.9
3	1960-03-15	1960-03-01	1960-03-31	28								0	27.1
4	1960-04-15	1960-04-01	1960-04-30	28								0	28.8
5	1960-05-15	1960-05-01	1960-05-31	28								40	30.7
6	1960-06-15	1960-06-01	1960-06-30	1								999	29.1
7	1960-07-15	1960-07-01	1960-07-31	28								500	28
8	1960-08-15	1960-08-01	1960-08-31	28								230	27.2
9	1960-09-15	1960-09-01	1960-09-30	28								100	27.7
10	1960-10-15	1960-10-01	1960-10-31	28								240	28.4
11	1960-11-15	1960-11-01	1960-11-30	28								0	28.1
12	1960-12-15	1960-12-01	1960-12-31	28								0	26.9
13	1961-01-15	1961-01-01	1961-01-31	28								0	25.3
14	1961-02-15	1961-02-01	1961-02-28	28								20	24
15	1961-03-15	1961-03-01	1961-03-31	28								0	27
16	1961-04-15	1961-04-01	1961-04-30	28								1	28.5
17	1961-05-15	1961-05-01	1961-05-31	28								12	30.1
18	1961-06-15	1961-06-01	1961-06-30	1	44	10	TIFR	-10	UC	-1.5	UC	393	29.4
19	1961-07-15	1961-07-01	1961-07-31	28	19	8	TIFR	-11.8	UC	-2.1	UC	1110	26.9
20	1961-08-15	1961-08-01	1961-08-31	28	14	8	TIFR	3.7	UC	-0.2	UC	299	27.5
21	1961-09-15	1961-09-01	1961-09-30	28	1	10	TIFR	-3.1	UC	-1.2	UC	270	27.6
22	1961-10-15	1961-10-01	1961-10-31	28	18	8	TIFR	-11.8	UC	-2.4	UC	101	27.9
23	1961-11-15	1961-11-01	1961-11-30	28								0	28.3
24	1961-12-15	1961-12-01	1961-12-31	28								1	26.1
25	1962-01-15	1962-01-01	1962-01-31	28								6	23.7
26	1962-02-15	1962-02-01	1962-02-28	28								0	26.1
27	1962-03-15	1962-03-01	1962-03-31	28								0	26.7
28	1962-04-15	1962-04-01	1962-04-30	28								1	28.5
29	1962-05-15	1962-05-01	1962-05-31	28								27	30.3
30	1962-06-15	1962-06-01	1962-06-30	28	90	18	TIFR	11.2	UC	0.2	UC	433	29.7
31	1962-07-15	1962-07-01	1962-07-31	28	65	18	TIFR	-6.9	UC	-1.2	UC	751	27.3
32	1962-08-15	1962-08-01	1962-08-31	28	40	18	TIFR	4.4	UC	-0.7	UC	397	27.5
33	1962-09-15	1962-09-01	1962-09-30	28	45	18	TIFR	-8.1	UC	-2.2	UC	341	27.7
34	1962-10-15	1962-10-01	1962-10-31	28								21	29
35	1962-11-15	1962-11-01	1962-11-30	28								1	28.5
36	1962-12-15	1962-12-01	1962-12-31	28	70	16	TIFR	6.2	UC	-0.2	UC	51	26.6
37	1963-01-15	1963-01-01	1963-01-31	28								6	26.1
38	1963-02-15	1963-02-01	1963-02-28	28								0	26.6
39	1963-03-15	1963-03-01	1963-03-31	28								0	27.9
40	1963-04-15	1963-04-01	1963-04-30	28								0	28.7
41	1963-05-15	1963-05-01	1963-05-31	28								0	30.4
42	1963-06-15	1963-06-01	1963-06-30	28	545	23	TIFR	1.8	UC	-0.3	UC	370	29.1
43	1963-07-15	1963-07-01	1963-07-31	28	525	18	TIFR	1.2	UC	-0.9	UC	797	27.7
44	1963-08-15	1963-08-01	1963-08-31	28	345	18	TIFR	1.8	UC	-1	UC	1004	26.7
45	1963-09-15	1963-09-01	1963-09-30	28	170	17	TIFR	1.8	UC	-0.2	UC	330	27.6
46	1963-10-15	1963-10-01	1963-10-31	28	300	19	TIFR	-63.2	UC	-7.8	UC	18	28.9
47	1963-11-15	1963-11-01	1963-11-30	28								5	28.5
48	1963-12-15	1963-12-01	1963-12-31	28								0	26.9
49	1964-01-15	1964-01-01	1964-01-31	28								0	22.9
50	1964-02-15	1964-02-01	1964-02-29	28								0	24
51	1964-03-15	1964-03-01	1964-03-31	28								0	26.7
52	1964-04-15	1964-04-01	1964-04-30	28								0	28.9
53	1964-05-15	1964-05-01	1964-05-31	28								0	30.3
54	1964-06-15	1964-06-01	1964-06-30	28	160	22	TIFR	-6.2	UC	-2	UC	655	28.9
55	1964-07-15	1964-07-01	1964-07-31	28	230	16	TIFR	1.8	UC	-1.1	UC	471	27.7
56	1964-08-15	1964-08-01	1964-08-31	28	130	16	TIFR	-6.9	UC	-2	UC	464	27.1
57	1964-09-15	1964-09-01	1964-09-30	28	110	16	TIFR	-11.2	UC	-2.5	UC	258	27.1
58	1964-10-15	1964-10-01	1964-10-31	28								115	27.9
59	1964-11-15	1964-11-01	1964-11-30	28								1	27.7
60	1964-12-15	1964-12-01	1964-12-31	28								0	25.5
61	1965-01-15	1965-01-01	1965-01-31	28								1	25.7
62	1965-02-15	1965-02-01	1965-02-28	28								0	25.6
63	1965-03-15	1965-03-01	1965-03-31	28								0	26
64	1965-04-15	1965-04-01	1965-04-30	28								3	28.3
65	1965-05-15	1965-05-01	1965-05-31	28								0	29.5
66	1965-06-15	1965-06-01	1965-06-30	28	110	6	TIFR	8	UC	-0.5	UC	654	29
67	1965-07-15	1965-07-01	1965-07-31	28	162.9	9.3	IAEA	-3.2	UC	-3.4	UC	918	27
68	1965-08-15	1965-08-01	1965-08-31	28	105	5	TIFR	-9.1	UC	-2.9	UC	361	27.4
69	1965-09-15	1965-09-01	1965-09-30	28	110	7	TIFR					78	28.1
70	1965-10-15	1965-10-01	1965-10-31	28								0	28.5

Number	SampleDate	PeriodFrom	PeriodTo	SampleType	H3	H3_ERR	H3 LabName	H2	H2 LabName	O18	O18 LabName	Precipitation	AirTemp
71	1965-11-15	1965-11-01	1965-11-30	28								4	28.2
72	1965-12-15	1965-12-01	1965-12-31	28								3	26.5
73	1966-01-15	1966-01-01	1966-01-31	28								0	25.2
74	1966-02-15	1966-02-01	1966-02-28	28								0	26.3
75	1966-03-15	1966-03-01	1966-03-31	28								0	26.8
76	1966-04-15	1966-04-01	1966-04-30	28								0	27.8
77	1966-05-15	1966-05-01	1966-05-31	28								2	29.9
78	1966-06-15	1966-06-01	1966-06-30	28	60	6	TIFR	7.3	UC	0.3	UC	342	29.2
79	1966-07-15	1966-07-01	1966-07-31	28	67	6	TIFR	-9.2	UC	-2.1	UC	884	27.8
80	1966-08-15	1966-08-01	1966-08-31	28	67	6	TIFR	8.6	UC	0	UC	131	27.5
81	1966-09-15	1966-09-01	1966-09-30	28	70.5	6.3	IAEA	2.7	UC	-1	UC	183	28.1
82	1966-10-15	1966-10-01	1966-10-31	28	103.2	5.6	IAEA	17.3	UC	0.8	UC	18	29.9
83	1966-11-15	1966-11-01	1966-11-30	28								0	28.7
84	1966-12-15	1966-12-01	1966-12-31	28								0	26.2
85	1967-01-15	1967-01-01	1967-01-31	28								0	23.8
86	1967-02-15	1967-02-01	1967-02-28	28								0	25.5
87	1967-03-15	1967-03-01	1967-03-31	28								0	27.3
88	1967-04-15	1967-04-01	1967-04-30	28								0	28.9
89	1967-05-15	1967-05-01	1967-05-31	28								0	30.2
90	1967-06-15	1967-06-01	1967-06-30	1	43	4	TIFR					795	28.7
91	1967-07-15	1967-07-01	1967-07-31	1	62	4	TIFR					975	27.3
92	1967-08-15	1967-08-01	1967-08-31	1	34	4	TIFR					299	27.3
93	1967-09-15	1967-09-01	1967-09-30	1	45	4	TIFR					205	27.7
94	1967-10-15	1967-10-01	1967-10-31	1								72	28.5
95	1967-11-15	1967-11-01	1967-11-30	28								0	27.6
96	1967-12-15	1967-12-01	1967-12-31	1								28	25.8
97	1968-01-15	1968-01-01	1968-01-31	28								0	23.7
98	1968-02-15	1968-02-01	1968-02-29	28								0	22.9
99	1968-03-15	1968-03-01	1968-03-31	28								0	27.1
100	1968-04-15	1968-04-01	1968-04-30	28								0	27.5
101	1968-05-15	1968-05-01	1968-05-31	28								0	28.8
102	1968-06-15	1968-06-01	1968-06-30	1	32	5	TIFR					178	29.6
103	1968-07-15	1968-07-01	1968-07-31	1								468	27.7
104	1968-08-15	1968-08-01	1968-08-31	1	19	4	TIFR					125	27.7
105	1968-09-15	1968-09-01	1968-09-30	1	20	4	TIFR					152	27.9
106	1968-10-15	1968-10-01	1968-10-31	1								33	28.8
107	1968-11-15	1968-11-01	1968-11-30	1								2	28.3
108	1968-12-15	1968-12-01	1968-12-31	28								0	26.1
109	1969-01-15	1969-01-01	1969-01-31	28								0	24.1
110	1969-02-15	1969-02-01	1969-02-28	28								0	24.7
111	1969-03-15	1969-03-01	1969-03-31	28								0	26.8
112	1969-04-15	1969-04-01	1969-04-30	28								0	29.1
113	1969-05-15	1969-05-01	1969-05-31	28								0	30.5
114	1969-06-15	1969-06-01	1969-06-30	1	25	5	TIFR					457	29.3
115	1969-07-15	1969-07-01	1969-07-31	1	16	4	TIFR					540	27.8
116	1969-08-15	1969-08-01	1969-08-31	1	13	3	TIFR					219	27.3
117	1969-09-15	1969-09-01	1969-09-30	1	11	3	TIFR					366	26.9
118	1969-10-15	1969-10-01	1969-10-31	28								0	28.7
119	1969-11-15	1969-11-01	1969-11-30	1								1	28.8
120	1969-12-15	1969-12-01	1969-12-31	28								0	27.7
121	1970-01-15	1970-01-01	1970-01-31	1								1	24.3
122	1970-02-15	1970-02-01	1970-02-28	28								0	24.4
123	1970-03-15	1970-03-01	1970-03-31	28								0	26.2
124	1970-04-15	1970-04-01	1970-04-30	28								0	28.5
125	1970-05-15	1970-05-01	1970-05-31	1								29	30.1
126	1970-06-15	1970-06-01	1970-06-30	1								943	28.4
127	1970-07-15	1970-07-01	1970-07-31	1	31	5	NGRI					549	27.9
128	1970-08-15	1970-08-01	1970-08-31	1	52	6	NGRI					730	26.9
129	1970-09-15	1970-09-01	1970-09-30	1	44	4	NGRI					311	27.1
130	1970-10-15	1970-10-01	1970-10-31	1	54	5	NGRI					63	28.5
131	1970-11-15	1970-11-01	1970-11-30	28								0	27.4
132	1970-12-15	1970-12-01	1970-12-31	28								0	25
133	1971-01-15	1971-01-01	1971-01-31	28								0	23.5
134	1971-02-15	1971-02-01	1971-02-28	1								1	24.1
135	1971-03-15	1971-03-01	1971-03-31	28								0	27.1
136	1971-04-15	1971-04-01	1971-04-30	28								0	29.2
137	1971-05-15	1971-05-01	1971-05-31	1								60	30.2
138	1971-06-15	1971-06-01	1971-06-30	1	39	4	NGRI					1094	28.3
139	1971-07-15	1971-07-01	1971-07-31	1	45	3	NGRI					315	27.3
140	1971-08-15	1971-08-01	1971-08-31	1	28	3	NGRI					604	27

Number	SampleDate	PeriodFrom	PeriodTo	SampleType	H3	H3_ERR	H3 LabName	H2	H2 LabName	O18	O18 LabName	Precipitation	AirTemp
141	1971-09-15	1971-09-01	1971-09-30	1	49	4	NGRI					347	27.5
142	1971-10-15	1971-10-01	1971-10-31	1								23	27.3
143	1971-11-15	1971-11-01	1971-11-30	28								0	26.9
144	1971-12-15	1971-12-01	1971-12-31	28								0	25.3
145	1972-01-15	1972-01-01	1972-01-31	28								0	24.1
146	1972-02-15	1972-02-01	1972-02-29	1								2	23.5
147	1972-03-15	1972-03-01	1972-03-31	28								0	26.1
148	1972-04-15	1972-04-01	1972-04-30	1								1	28
149	1972-05-15	1972-05-01	1972-05-31	1								1	29.9
150	1972-06-15	1972-06-01	1972-06-30	1								732	29.5
151	1972-07-15	1972-07-01	1972-07-31	1								555	28.5
152	1972-08-15	1972-08-01	1972-08-31	1								122	27.7
153	1972-09-15	1972-09-01	1972-09-30	1								68	28.1
154	1972-10-15	1972-10-01	1972-10-31	28								0	29.5
155	1972-11-15	1972-11-01	1972-11-30	1								32	27.5
156	1972-12-15	1972-12-01	1972-12-31	28								0	25.9
157	1973-01-15	1973-01-01	1973-01-31	28								0	22.7
158	1973-02-15	1973-02-01	1973-02-28	28								0	25
159	1973-03-15	1973-03-01	1973-03-31	28								0	26.7
160	1973-04-15	1973-04-01	1973-04-30	1								1	29.3
161	1973-05-15	1973-05-01	1973-05-31	28								0	30.5
162	1973-06-15	1973-06-01	1973-06-30	1	15.7	3.2	NGRI	-10.8	IAEA	-2.73	IAEA	366	29.5
163	1973-07-15	1973-07-01	1973-07-31	1	35.1	3.2	NGRI			-0.36	IAEA	594	27.5
164	1973-08-15	1973-08-01	1973-08-31	1	46.3	3.4	NGRI	5.4	IAEA	-0.46	IAEA	474	27.1
165	1973-09-15	1973-09-01	1973-09-30	1	34.4	3.3	NGRI	4.3	IAEA	-0.41	IAEA	351	26.7
166	1973-10-15	1973-10-01	1973-10-31	1	16.7	3.5	NGRI	-52.6	IAEA	-7.74	IAEA	65	28.4
167	1973-11-15	1973-11-01	1973-11-30	28								0	27.7
168	1973-12-15	1973-12-01	1973-12-31	28								0	25.8
169	1974-01-15	1974-01-01	1974-01-31	28								0	24.3
170	1974-02-15	1974-02-01	1974-02-28	28								0	24.3
171	1974-03-15	1974-03-01	1974-03-31	28								0	27.3
172	1974-04-15	1974-04-01	1974-04-30	1								28	29.3
173	1974-05-15	1974-05-01	1974-05-31	1								27	29.7
174	1974-06-15	1974-06-01	1974-06-30	1	18	3.7	NGRI	1.8	IAEA	-0.98	IAEA	85	29.6
175	1974-07-15	1974-07-01	1974-07-31	1	25.7	3.8	NGRI	-13.2	IAEA	-2.55	IAEA	1441	27.5
176	1974-08-15	1974-08-01	1974-08-31	1	11.2	3.7	NGRI	8	IAEA	0.06	IAEA	533	27.3
177	1974-09-15	1974-09-01	1974-09-30	1	34.2	4.2	NGRI	-8.5	IAEA	-1.89	IAEA	148	28.1
178	1974-10-15	1974-10-01	1974-10-31	1	29.3	3.9	NGRI					108	27.9
179	1974-11-15	1974-11-01	1974-11-30	28								0	26.7
180	1974-12-15	1974-12-01	1974-12-31	28								0	25.1
181	1975-01-15	1975-01-01	1975-01-31	28								0	23.9
182	1975-02-15	1975-02-01	1975-02-28	28								0	24.3
183	1975-03-15	1975-03-01	1975-03-31	28								0	25.8
184	1975-04-15	1975-04-01	1975-04-30	28								0	28.1
185	1975-05-15	1975-05-01	1975-05-31	1								1	30.1
186	1975-06-15	1975-06-01	1975-06-30	1				-6.2	IAEA	-1.62	IAEA	539	28.7
187	1975-07-15	1975-07-01	1975-07-31	1				1.7	IAEA	-1.24	IAEA	910	27.7
188	1975-08-15	1975-08-01	1975-08-31	1	19.7	3.6	NGRI	-13.7	IAEA	-2.66	IAEA	715	27
189	1975-09-15	1975-09-01	1975-09-30	28				-40.6	IAEA	-5.52	IAEA	453	27.3
190	1975-10-15	1975-10-01	1975-10-31	1				-31.5	IAEA	-5.39	IAEA	174	27.9
191	1975-11-15	1975-11-01	1975-11-30	28									
192	1975-12-15	1975-12-01	1975-12-31	28									
193	1976-01-15	1976-01-01	1976-01-31	28								0	24.5
194	1976-02-15	1976-02-01	1976-02-29	28								0	25.4
195	1976-03-15	1976-03-01	1976-03-31	28								0	27.5
196	1976-04-15	1976-04-01	1976-04-30	28								0	27.7
197	1976-05-15	1976-05-01	1976-05-31	28								0	29.4
198	1976-06-15	1976-06-01	1976-06-30	1	23.4	3.1	NGRI	-18.5	IAEA	-3.58	IAEA	2	28.7
199	1976-07-15	1976-07-01	1976-07-31	1	13.4	3.1	NGRI	5.2	IAEA	-0.49	IAEA	696	27.8
200	1976-08-15	1976-08-01	1976-08-31	1	23.9	3.1	NGRI	3.9	IAEA	-0.23	IAEA	332	27.6
201	1976-09-15	1976-09-01	1976-09-30	1				6.5	IAEA	-0.32	IAEA	399	27.3
202	1976-10-15	1976-10-01	1976-10-31	28								0	29.5
203	1976-11-15	1976-11-01	1976-11-30	1				-29.6	IAEA	-5.43	IAEA	34	28.9
204	1976-12-15	1976-12-01	1976-12-31	28								0	26.1
205	1977-01-15	1977-01-01	1977-01-31	28								0	24.8
206	1977-02-15	1977-02-01	1977-02-28	28								0	24.9
207	1977-03-15	1977-03-01	1977-03-31	28								0	27.5
208	1977-04-15	1977-04-01	1977-04-30	1								1	29.3
209	1977-05-15	1977-05-01	1977-05-31	28								0	30.5
210	1977-06-15	1977-06-01	1977-06-30	1	28.9	3.1	NGRI	-1.2	IAEA	-1.37	IAEA	463	29.3

Number	SampleDate	PeriodFrom	PeriodTo	SampleType	H3	H3_ERR	H3 LabName	H2	H2 LabName	O18	O18 LabName	Precipitation	AirTemp
211	1977-07-15	1977-07-01	1977-07-31	1	23.3	3.6	NGRI	3.7	IAEA	-0.88	IAEA	647	27.7
212	1977-08-15	1977-08-01	1977-08-31	1	27.2	3.6	NGRI			-0.06	IAEA	272	29
213	1977-09-15	1977-09-01	1977-09-30	1	23.9	3.6	NGRI	-5.4	IAEA	-1.81	IAEA	93	24.5
214	1977-10-15	1977-10-01	1977-10-31	1								237	21.7
215	1977-11-15	1977-11-01	1977-11-30	1								45	18.1
216	1977-12-15	1977-12-01	1977-12-31	1								11	25.4
217	1978-01-15	1978-01-01	1978-01-31	28								0	24.3
218	1978-02-15	1978-02-01	1978-02-28	1								1	24.9
219	1978-03-15	1978-03-01	1978-03-31	28								0	25.7
220	1978-04-15	1978-04-01	1978-04-30	28								0	28.5
221	1978-05-15	1978-05-01	1978-05-31	1								7	30.7
222	1978-06-15	1978-06-01	1978-06-30	1	26.7	3.1	NGRI					833	28.2
223	1978-07-15	1978-07-01	1978-07-31	1	15.2	3.1	NGRI					150	27.7
224	1978-08-15	1978-08-01	1978-08-31	1	12	3.6	NGRI					200	27.3
225	1978-09-15	1978-09-01	1978-09-30	1	13.2	3.6	NGRI					256	27.5
226	1978-10-15	1978-10-01	1978-10-31	1								63	28.9
227	1978-11-15	1978-11-01	1978-11-30	1								24	28.7
228	1978-12-15	1978-12-01	1978-12-31	28								0	27.5

Table 5: GNIP data for Mumbai sourced from the WISER database. 28: Precipitation-unknown origin, 1: Precipitation-rain, TIFR- Tata Institute of Fundamental Research (Colaba## Bombay## India), IAEA- International Atomic Energy Agency (Vienna## Austria), NGRI- National Geophysical Research Institute (Hyderabad## India), UC- University of Copenhagen (Copenhagen## Denmark).

Sample	Lamina width	Depth	Year	$\delta^{18}\text{O}$	$\delta^{13}\text{C}$	Sample	Lamina width	Depth	Year	$\delta^{18}\text{O}$	$\delta^{13}\text{C}$
1	0.00	0	1996	-1.012	-11.462	71	0.15	8.95	1923.784	-1.473	-12.529
2	0.20	0.2	1994.295	-1.125	-12.784	72	0.15	9.1	1922.405	-2.185	-12.57
3	0.05	0.25	1993.869	-1.242	-11.907	73	0.20	9.3	1920.568	-1.067	-11.316
4	0.15	0.4	1992.59	-1.696	-12.938	74	0.15	9.45	1919.189	-0.168	-9.936
5	0.05	0.45	1992.164	-1.489	-13.014	75	0.10	9.55	1918.27	-0.889	-11.288
6	0.05	0.5	1991.738	-1.594	-12.996	76	-	-	-	-	-
7	0.05	0.55	1991.311	-1.607	-13.073	77	0.10	9.65	1917.351	-0.641	-11.139
8	0.05	0.6	1990.885	-1.322	-12.911	78	0.15	9.8	1915.973	-0.019	-9.664
9	0.10	0.7	1990.033	-1.397	-12.599	79	0.20	10	1914.135	-0.397	-10.924
10	0.10	0.8	1989.18	-1.412	-12.802	80	0.10	10.1	1913.216	-0.843	-11.594
11	0.10	0.9	1988.328	-1.186	-12.507	81	0.15	10.25	1911.838	-1.397	-12.979
12	0.15	1.05	1987.049	-1.879	-12.356	82	0.20	10.45	1910	-1.269	-11.526
13	0.05	1.1	1986.623	-1.279	-12.586	83	0.10	10.55	1909.081	-0.707	-11.365
14	0.10	1.2	1985.77	-1.256	-12.417	84	0.15	10.7	1907.703	-0.796	-11.643
15	0.10	1.3	1984.918	-1.251	-11.624	85	0.20	10.9	1905.865	-0.49	-11.304
16	0.10	1.4	1984.066	-1.205	-11.739	86	0.15	11.05	1904.486	-0.848	-11.222
17	0.15	1.55	1982.787	-0.764	-10.545	87	0.15	11.2	1903.108	0.054	-9.871
18	0.10	1.65	1981.934	-0.408	-11.096	88					
19	0.05	1.7	1981.508	-0.659	-11.441	89					
20	0.15	1.85	1980.23	-1.012	-11.649	90	0.20	11.4	1901.27	-0.07	-9.424
21	0.15	2	1978.951	-1.154	-12.281	91	0.10	11.5	1900.351	-0.249	-10.194
22	0.20	2.2	1977.246	-1.742	-12.426	92	-	-	-	-	-
23	-	-	-	-	-	93	0.10	11.6	1899.432	0.949	-12.04
24	-	-	-	-	-	94	0.15	11.75	1898.054	-0.303	-10.235
25	0.15	2.35	1975.967	-1.233	-12.29	95	0.20	11.95	1896.216	0.135	-8.241
26	0.20	2.55	1974.262	-1.482	-12.753	96	0.20	12.15	1894.378	-0.012	-8.402
27	0.15	2.7	1972.984	-1.577	-12.169	97	0.15	12.3	1893	-0.267	-8.024
28	0.20	2.9	1971.279	-1.193	-12.17	98	0.10	12.4	1892.081	0.846	-8.118
29	0.05	2.95	1970.852	-1.362	-12.349	99	-	-	-	-	-
30	0.10	3.05	1970	-1.425	-12.52	100	0.15	12.7	1889.324	-0.566	-10.167
31	0.20	3.25	1968.295	-1.228	-12.561	101	-	-	-	-	-
32	0.15	3.4	1967.016	-2.1	-12.967	102	0.15	12.85	1887.946	-0.705	-9.098
33	0.15	3.55	1965.738	-1.622	-12.758	103	0.10	12.95	1887.027	-0.529	-9.651
34	0.15	3.7	1964.459	-1.426	-12.539	104	0.20	13.15	1885.189	-0.896	-11.314
35	0.15	3.85	1963.18	-1.32	-12.35	105	0.15	13.3	1883.811	-0.621	-10.57
36	0.20	4.05	1961.475	-1.59	-13.051	106	0.15	13.45	1882.432	0.164	-9.242
37	0.25	4.3	1959.344	-1.398	-12.982	107	0.10	13.55	1881.514	0.475	-8.602
38	0.15	4.45	1958.066	-1.345	-12.128	108	0.15	13.7	1880.135	0.46	-8.457
39	0.15	4.6	1956.787	-1.801	-13.26	109	0.15	13.85	1878.757	0.091	-9.997
40	0.10	4.7	1955.934	-2.001	-12.991	110	0.15	14	1877.378	0.504	-8.158
41	0.10	4.8	1955.082	-1.452	-12.81	111	0.10	14.1	1876.459	1.595	-8.001
42	0.15	4.95	1953.803	-2.026	-12.452	112	0.20	14.3	1874.622	0.002	-9.068
43	-	-	-	-	-	113	0.25	14.55	1872.324	0.028	-10.457
44	0.05	5	1953.377	-1.879	-13.08	114	0.15	14.7	1870.946	-0.214	-10.6
45	0.10	5.1	1952.525	-1.321	-11.939	115	0.20	14.9	1869.108	0.085	-9.551
46	0.15	5.25	1951.246	-1.541	-12.252	116	0.20	15.1	1867.27	-0.156	-10.519
47	0.30	5.55	1948.689	-1.714	-12.723	117	0.20	15.3	1865.432	-0.553	-11.318
48	0.15	5.7	1947.41	-1.411	-11.834	118	0.15	15.45	1864.054	-0.733	-11.154
49	0.20	5.9	1945.705	-1.105	-11.522	119	0.15	15.6	1862.676	-0.82	-11.241
50	0.15	6.05	1944.426	-1.167	-11.669	120	0.15	15.75	1861.297	-0.949	-10.825
51	0.05	6.1	1944	-1.145	-10.87	121	0.15	15.9	1859.919	0.529	-8.605
52	0.15	6.25	1942.98	-1.343	-10.751	122	0.10	16	1859	-0.974	-11.202
53	-	-	-	-	-	123	0.15	16.15	1858.185	0.745	-9.199
54	0.15	6.4	1941.96	-0.953	-11.299	124	0.10	16.25	1857.641	0.058	-9.967
55	0.20	6.6	1940.6	-1.398	-12.132	125	0.10	16.35	1857.098	-0.407	-11.285
56	0.15	6.75	1939.58	-1.334	-12.394	126	0.15	16.5	1856.283	0.263	-10.657
57	0.15	6.9	1938.56	-1.175	-11.703	127	0.15	16.65	1855.467	0.192	-10.623
58	0.15	7.05	1937.54	-1.573	-12.756	128	0.10	16.75	1854.924	-0.566	-10.797
59	0.15	7.2	1936.52	-1.467	-12.652	129	0.15	16.9	1854.109	-0.153	-10.903
60	0.15	7.35	1935.5	-1.049	-11.464	130	0.15	17.05	1853.293	-0.154	-11.148
61	0.20	7.55	1934.14	-1.461	-12.4005	131	0.15	17.2	1852.478	-0.744	-11.649
62	0.15	7.7	1933.12	-1.562	-10.64	132	0.10	17.3	1851.935	-0.483	-11.528
63	0.25	7.95	1931.42	-1.083	-11.906	133	0.15	17.45	1851.12	-0.568	-12.019
64	0.10	8.05	1930.74	-1.032	-11.837	134	0.15	17.6	1850.304	-0.979	-12.751
65	0.20	8.25	1929.38	-1.355	-12.224	135	0.20	17.8	1849.217	-0.441	-11.822
66	0.15	8.4	1928.36	-1.565	-12.689	136	0.15	17.95	1848.402	-0.652	-11.643
67	0.10	8.5	1927.68	-1.26	-12.724	137	0.15	18.1	1847.587	-0.723	-11.865
68	0.05	8.55	1927.34	-1.027	-12.209	138	0.15	18.25	1846.772	-1.173	-11.868
69	0.05	8.6	1927	-0.65	-9.853	139	0.20	18.45	1845.685	-0.806	-12.049
70	0.20	8.8	1925.162	-1.65	-12.171	140	0.15	18.6	1844.87	-0.675	-12.081

Sample	Lamina width	Depth	Year	$\delta^{18}\text{O}$	$\delta^{13}\text{C}$	Sample	Lamina width	Depth	Year	$\delta^{18}\text{O}$	$\delta^{13}\text{C}$
141	0.20	18.8	1843.783	-1.077	-12.444	211	0.15	29.5	1775.916	-0.71	-12.176
142	0.15	18.95	1842.967	-0.67	-11.802	212	0.15	29.65	1774.937	-1.066	-11.891
143	0.10	19.05	1842.424	-1.072	-11.673	213	0.25	29.9	1773.305	-0.89	-12.897
144	0.20	19.25	1841.337	-0.856	-12.338	214	0.20	30.1	1772	-1.101	-12.388
145	0.20	19.45	1840.25	-0.361	-11.445	215	0.05	30.15	1771.649	-1.023	-12.382
146	0.20	19.65	1839.163	-0.435	-12.319	216	0.10	30.25	1770.947	-1.236	-12.2
147	0.25	19.9	1837.804	-0.187	-11.019	217	0.15	30.4	1769.894	-1.092	-12.326
148	0.25	20.15	1836.446	-0.273	-11.45	218	0.30	30.7	1767.788	-1.766	-13.064
149	0.15	20.3	1835.63	-0.743	-10.799	219	0.15	30.85	1766.735	-1.539	-13.108
150	0.15	20.45	1834.815	-0.213	-8.686	220	0.15	31	1765.682	-1.436	-13.335
151	0.15	20.6	1834	-0.941	-11.361	221	0.10	31.1	1764.98	-1.463	-13.559
152	0.15	20.75	1833.021	-0.475	-10.707	222	0.05	31.15	1764.629	-1.139	-11.648
153	0.10	20.85	1832.368	-0.485	-10.375	223	0.15	31.3	1763.576	-1.257	-11.708
154	0.20	21.05	1831.063	-1.111	-12.728	224	0.10	31.4	1762.874	-1.283	-10.633
155	0.25	21.3	1829.432	-0.523	-11.677	225	0.15	31.55	1761.821	-1.086	-11.621
156	0.25	21.55	1827.8	-0.894	-12.355	226	0.15	31.7	1760.768	-1.293	-11.869
157	0.20	21.75	1826.495	-0.698	-12.547	227	0.10	31.8	1760.066	-1.485	-11.438
158	0.15	21.9	1825.516	-0.455	-12.417	228	0.10	31.9	1759.364	-1.031	-10.443
159	0.25	22.15	1823.884	-0.73	-12.343	229	0.10	32	1758.662	-1.092	-10.512
160	0.15	22.3	1822.905	-0.561	-12.118	230	0.10	32.1	1757.96	-1.33	-10.763
161	0.20	22.5	1821.6	-0.43	-12.101	231	0.15	32.25	1756.907	-1.293	-11.473
162	0.15	22.65	1820.621	-0.674	-11.574	232	0.05	32.3	1756.556	-0.402	-10.398
163	0.25	22.9	1818.989	0.09	-11.034	233	0.10	32.4	1755.854	-0.54	-9.633
164	0.20	23.1	1817.684	-0.265	-11.499	234	0.15	32.55	1754.801	-0.718	-10.474
165	0.15	23.25	1816.705	-0.632	-11.455	235	0.10	32.65	1754.099	-0.63	-10.161
166	0.15	23.4	1815.726	-0.146	-10.597	236	0.15	32.8	1753.046	-0.32	-9.736
167	0.15	23.55	1814.747	-0.587	-11.115	237	0.10	32.9	1752.344	-0.433	-10.173
168	0.15	23.7	1813.768	-0.473	-11.146	238	0.20	33.1	1750.94	-1.333	-10.763
169	0.15	23.85	1812.789	-1.391	-11.804	239	0.15	33.25	1749.887	-1.429	-10.833
170	0.15	24	1811.811	-0.778	-11.466	240	0.15	33.4	1748.834	-1.01	-11.168
171	0.15	24.15	1810.832	-1.237	-11.907	241	0.15	33.55	1747.781	-0.774	-9.189
172	0.15	24.3	1809.853	-1.007	-11.716	242	0.15	33.7	1746.728	-0.578	-9.213
173	0.15	24.45	1808.874	-0.465	-11.108	243	0.15	33.85	1745.675	-0.807	-9.543
174	0.10	24.55	1808.221	-1.039	-11.749	244	0.15	34	1744.623	-0.428	-9.649
175	0.10	24.65	1807.568	-0.474	-11.273	245	0.20	34.2	1743.219	-0.781	-10.12
176	0.10	24.75	1806.916	-0.578	-11.071	246	0.15	34.35	1742.166	-0.789	-9.677
177	0.25	25	1805.284	-0.662	-11.301	247	0.10	34.45	1741.464	-1.576	-9.968
178	0.20	25.2	1803.979	-0.602	-11.218	248	0.10	34.55	1740.762	-0.311	-9.449
179	0.10	25.3	1803.326	-1.121	-11.427	249	0.10	34.65	1740.06	-0.167	-9.254
180	0.20	25.5	1802.021	-0.491	-11.088	250	0.15	34.8	1739.007	-0.629	-9.458
181	0.20	25.7	1800.716	-0.56	-10.768	251	0.10	34.9	1738.305	-0.444	-9.463
182	0.15	25.85	1799.737	-0.612	-10.791	252	0.15	35.05	1737.252	-0.841	-9.291
183	0.10	25.95	1799.084	-0.543	-11.037	253	0.10	35.15	1736.55	-0.608	-9.344
184	0.05	26	1798.758	-0.472	-11.324	254	0.15	35.3	1735.497	-0.642	-10.189
185	0.10	26.1	1798.105	-0.802	-11.282	255	0.15	35.45	1734.444	-0.606	-10.522
186	0.10	26.2	1797.453	-0.825	-11.123	256	0.15	35.6	1733.391	-0.146	-9.848
187	0.15	26.35	1796.474	-0.949	-12.035	257	0.25	35.85	1731.636	-0.213	-10.277
188	0.15	26.5	1795.495	-0.701	-11.099	258	0.15	36	1730.583	-0.493	-10.477
189	0.20	26.7	1794.189	-0.589	-11.646	259	0.10	36.1	1729.881	-0.444	-10.228
190	0.10	26.8	1793.537	-0.518	-11.402	260	0.15	36.25	1728.828	-0.171	-9.982
191	0.20	27	1792.232	-0.201	-11.127	261	0.15	36.4	1727.775	-0.826	-10.403
192	0.20	27.2	1790.926	-0.123	-10.885	262	0.15	36.55	1726.722	-0.384	-10.453
193	0.15	27.35	1789.947	-0.252	-10.508	263	0.15	36.7	1725.669	-0.967	-10.763
194	-	-	-	-	-	264	0.20	36.9	1724.265	-0.346	-10.259
195	0.20	27.55	1788.642	-1.015	-12.882	265	0.15	37.05	1723.212	-0.595	-10.698
196	0.15	27.7	1787.663	-0.987	-13.075	266	0.10	37.15	1722.51	-0.704	-10.383
197	0.10	27.8	1787.011	-0.816	-11.543	267	0.15	37.3	1721.457	-1.088	-10.58
198	0.15	27.95	1786.032	-1.125	-12.488	268	0.25	37.55	1719.702	-0.753	-11.193
199	0.10	28.05	1785.379	-0.734	-11.668	269	0.10	37.65	1719	-0.805	-11.089
200	0.15	28.2	1784.4	-1.158	-12.715	270	0.15	37.8	1717.795	-1.007	-10.943
201	0.20	28.4	1783.095	-1.002	-12.87	271	0.25	38.05	1715.788	-0.893	-10.495
202	0.10	28.5	1782.442	-1.862	-13.415	272	0.15	38.2	1714.583	-0.844	-10.866
203	0.15	28.65	1781.463	-1.235	-12.376	273	0.15	38.35	1713.379	-2.022	-11.227
204	0.10	28.75	1780.811	-0.962	-12.267	274	0.15	38.5	1712.174	-0.523	-10.376
205	0.15	28.9	1779.832	-0.056	-10.409	275	-	-	-	-	-
206	0.15	29.05	1778.853	-0.228	-11.618	276	0.15	38.65	1710.97	-0.205	-10.199
207	0.10	29.15	1778.2	-0.465	-11.678	277	0.10	38.75	1710.167	-0.569	-9.999
208	-	-	-	-	-	278	-	-	-	-	-
209	0.10	29.25	1777.547	-1.023	-12.825	279	0.10	38.85	1709.364	-0.585	-9.953
210	0.10	29.35	1776.895	-0.578	-11.803	280	0.15	39	1708.159	-0.458	-9.348

Sample	Lamina width	Depth	Year	$\delta^{18}\text{O}$	$\delta^{13}\text{C}$	Sample	Lamina width	Depth	Year	$\delta^{18}\text{O}$	$\delta^{13}\text{C}$
281	0.15	39.15	1706.955	-0.417	-9.471	301	0.20	41.75	1686.076	-1.388	-9.333
282	0.10	39.25	1706.152	-0.682	-9.177	302	0.20	41.95	1684.47	-0.649	-9.236
283	0.15	39.4	1704.947	-0.991	-9.163	303	0.20	42.15	1682.864	-0.918	-8.378
284	0.10	39.5	1704.144	-0.404	-8.835	304	0.15	42.3	1681.659	-1.238	-9.324
285	0.10	39.6	1703.341	-1.227	-10.225	305	0.15	42.45	1680.455	-0.537	-9.464
286	0.15	39.75	1702.136	-0.687	-8.639	306	0.10	42.55	1679.652	-0.87	-10.42
287	0.20	39.95	1700.53	-0.756	-9.17	307	0.20	42.75	1678.045	-0.317	-9.471
288	0.20	40.15	1698.924	-0.315	-7.947	308	0.15	42.9	1676.841	-2.137	-11.001
289	0.15	40.3	1697.72	-0.453	-8.31	309	0.15	43.05	1675.636	-0.941	-10.731
290	0.15	40.45	1696.515	-0.525	-8.723	310	0.10	43.15	1674.833	-1.195	-11.224
291	0.15	40.6	1695.311	-0.923	-9.548	311	0.15	43.3	1673.629	-1.072	-11.483
292	-	-	-	-	-	312	0.10	43.4	1672.826	-1.415	-11.968
293	-	-	-	-	-	313	0.10	43.5	1672.023	-0.92	-10.602
294	0.15	40.75	1694.106	-0.405	-8.438	314	0.10	43.6	1671.22	-0.855	-9.591
295	0.15	40.9	1692.902	-1.024	-8.968	315	0.15	43.75	1670.015	-1.542	-10.734
296	0.10	41	1692.098	-0.544	-8.966	316	0.15	43.9	1668.811	-2.685	-11.067
297	-	-	-	-	-	317	0.20	44.1	1667.205	-2.267	-10.949
298	0.20	41.2	1690.492	-0.987	-9.782	318	0.15	44.25	1666	-2.07	-11.692
299	0.20	41.4	1688.886	-0.889	-9.785						
300	0.15	41.55	1687.682	-1.163	-9.561						

Table 6: Along growth axis oxygen and carbon isotopic data for sample stalagmite from Akalagavi cave by *Yadava et al, 2004*.

Number	Identifier 1	PRL $\delta^{18}O$	PRL $\delta^{13}C$	Oxford $\delta^{18}O$	Oxford $\delta^{13}C$	$\delta^{18}O$	$\delta^{13}C$
						difference	
1	NKS-104	-4.46	-10.91	-4.49	-10.81	-0.03	0.10
2	NKS-139	-4.32	-10.29	-4.37	-10.40	-0.05	-0.10
3	NKS-141	-3.40	-9.59	-3.44	-9.64	-0.03	-0.05
4	NKS-189	-4.06	-9.57	-3.71	-9.55	0.35	0.02
5	NKS-200	-4.53	-11.42	-4.51	-11.45	0.03	-0.03
6	NKS-233	-3.61	-9.71	-3.61	-9.63	0.01	0.08
7	NKS-238	-3.41	-9.82	-3.48	-9.70	-0.07	0.12
8	NKHTS-7	-5.12	-9.75	-5.33	-9.73	-0.22	0.02

Table 7: Oxygen and carbon stable isotopic data for aliquots of the same subsamples measured at PRL and Oxford stable isotopic laboratories.

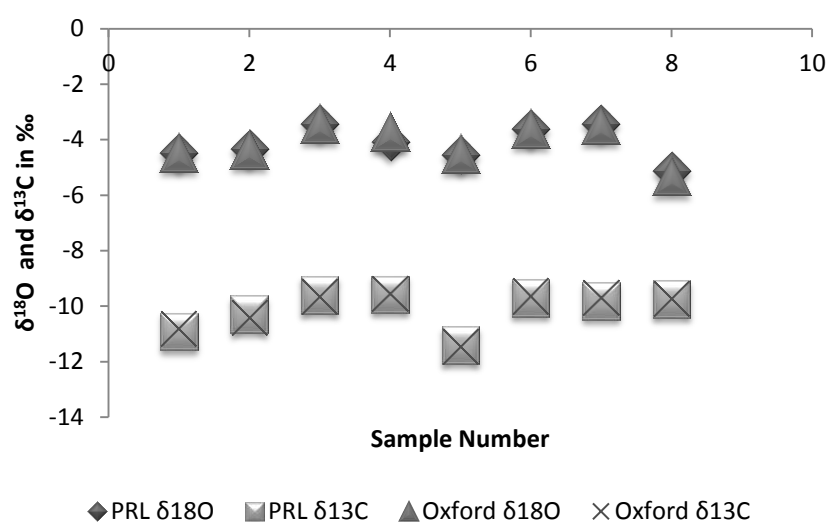


Figure 1: Inter-laboratory replication of carbon and oxygen stable isotope measurements.

<i>Number</i>	<i>Sample code</i>	$\delta^{18}O$	$\delta^{13}C$
1	NA189	-2.9	-14.8
2	NA190	-2.7	-13.5
3	NA191	-2.6	-13.0
4	NA192	-2.4	-12.8
5	NA193	-2.5	-12.5
6	NA194	-2.2	-12.5
7	NA195	-2.1	-12.8
8	NA196	-2.1	-12.8
9	NA197	-2.4	-12.5
10	NA198	-2.6	-12.6
11	NA199	-2.5	-12.6
12	NA200	-2.5	-12.5
13	NA201	-2.3	-12.6

Table 8: Oxygen and carbon stable isotopic data for subsamples milled from a chip of modern carbonate.

Number	Sample code	$\delta^{18}O$	$\delta^{13}C$	White or dark layer?
1	NA43	-1.26	-11.59	top end of dark layer
2	NA44	-1.37	-11.99	mixture: top end of dark layer + white layer
3	NA45	-1.25	-11.35	mixture: top end of white layer + very little dark layer
4	NA46	-1.27	-12.14	top end of dark layer
5	NA47	-1.69	-12.49	beginning of white layer
6	NA48	-1.27	-11.56	beginning of thick dark layer
7	NA49	-1.27	-11.39	dark layer
8	NA50	-1.18	-11.74	dark layer
9	NA51	-1.28	-11.52	dark layer
10	NA52	-1.34	-11.49	dark layer
11	NA53	-1.59	-11.99	beginning of white layer
12	NA54	-1.34	-11.86	mixture: end of white + beginning of dark layer
13	NA55	-1.33	-11.37	mixture: end of dark + beginning of white layer
14	NA56	-1.32	-11.68	white layer
15	NA57	-1.37	-11.86	white layer
16	NA58	-1.94	-12.47	white layer
17	NA59	-1.82	-12.62	dark layer
18	NA60	-1.81	-12.33	white layer
19	NA61	-1.84	-12.79	white layer
20	NA62	-1.89	-12.56	mixture: white + dark layers
21	NA63	-1.65	-12.07	dark layer
22	NA64	-1.50	-11.82	beginning of white layer
23	NA65	-1.39	-11.62	white layer
24	NA66	-1.45	-11.70	beginning of dark layer
25	NA67	-1.93	-12.56	mixture: porous white and dark layers
26	NA68	-1.61	-12.08	top end of dark porous layer
27	NA69	-1.54	-11.83	mixture: dark + white layers
28	NA70	-1.56	-11.90	white layer
29	NA71	-1.41	-11.83	Pale dark layer. Beware of pen marking contamination
30	NA72	-1.30	-11.05	Pale dark layer. Beware of pen marking contamination
31	NA73	-1.12	-11.04	Pale dark layer
32	NA74	-1.82	-12.15	dark porous layer
33	NA75	-1.95	-12.69	white layer between two porous layers
34	NA76	-1.53	-11.50	mixture: top of dark porous layer + white layer
35	NA77	-1.56	-11.65	white layer
36	NA78	-1.22	-11.59	white layer
37	NA79	-1.18	-10.70	edge pale dark layer
38	NA80	-1.07	-10.46	edge pale dark layer

Table 9: Oxygen and carbon stable isotopic data for subsamples milled at a seasonal resolution from a section of the sample stalagmite. White or dark layer as observed during milling has also been reported. The data in red are to be treated with caution.

<i>Seperation (mm)</i>	$\delta^{18}O$	$\delta^{13}C$
0.25	-0.38	-11.73
16.4	0.18	-11.05
25.4	0.07	-10.14
43.3	-1.06	-9.91
68.5	-1.29	-7.87
129.2	-0.72	-8.21
159.6	-1.29	-7.65
193.5	-1.06	-8.21

Table 10: Distance from growth axis, oxygen and carbon stable isotopic measurements for Hendy Test Layer B. Data obtained using GetData graph digitizer.

Number	Equation reference	T (C)	T (K)	$1000 \ln a$	$1000/T(K)$	a	Drip water $\delta^{18}O$	Rwater $\delta^{18}O$	Rarag $\delta^{18}O$	$\delta_{arag} VSMOW$	Calculated aragonite $\delta^{18}O$
Increasing temperature, decreasing drip water $\delta^{18}O$											
1	Grossman and Ku, 1986	24.4	298.55	29.476	3.350	1.0295	-0.39	0.002004	0.002064	29.075	-1.780
2	Grossman and Ku, 1986	25.6	299.75	29.230	3.336	1.0292	-2.45	0.002000	0.002059	26.709	-4.075
3	Patterson et al, 1993	24.4	298.55	28.677	3.350	1.0287	-0.39	0.002004	0.002062	28.276	-2.555
4	Patterson et al, 1993	25.6	299.75	28.428	3.336	1.0284	-2.45	0.002000	0.002057	25.909	-4.851
5	Tharrolld et al, 1997	24.4	298.55	29.627	3.350	1.0296	-0.39	0.002004	0.002064	29.226	-1.634
6	Tharrolld et al, 1997	25.6	299.75	29.378	3.336	1.0294	-2.45	0.002000	0.002059	26.856	-3.932
7	Kim et al, 2007	24.4	298.55	29.129	3.350	1.0291	-0.39	0.002004	0.002063	28.728	-2.116
8	Kim et al, 2007	25.6	299.75	28.890	3.336	1.0289	-2.45	0.002000	0.002058	26.369	-4.405
Decreasing temperature, increasing drip water $\delta^{18}O$											
9	Grossman and Ku, 1986	25.6	299.75	29.230	3.336	1.0292	-0.39	0.002004	0.002063	28.829	-2.019
10	Grossman and Ku, 1986	24.4	298.55	29.476	3.350	1.0295	-2.45	0.002000	0.002059	26.954	-3.837
11	Patterson et al, 1993	25.6	299.75	28.428	3.336	1.0284	-0.39	0.002004	0.002061	28.027	-2.796
12	Patterson et al, 1993	24.4	298.55	28.677	3.350	1.0287	-2.45	0.002000	0.002058	26.157	-4.611
13	Tharrolld et al, 1997	25.6	299.75	29.378	3.336	1.0294	-0.39	0.002004	0.002063	28.977	-1.875
14	Tharrolld et al, 1997	24.4	298.55	29.627	3.350	1.0296	-2.45	0.002000	0.002060	27.105	-3.691
15	Kim et al, 2007	25.6	299.75	28.890	3.336	1.0289	-0.39	0.002004	0.002062	28.488	-2.349
16	Kim et al, 2007	24.4	298.55	29.129	3.350	1.0291	-2.45	0.002000	0.002059	26.608	-4.173
Formulas											
$T(K) = T(C) + 274.15$											
$1000 \ln a = \text{Respective equilibrium fractionation equation, see table 4.5}$											
$a = \text{fractionation factor} = (1000 \ln a/1000) + 1 = R_{water}/R_{arag}$											
$R_{water} = \text{conversion of drip water } \delta \text{ value to } R_{water} = (((\text{drip water } \delta^{18}O_{VSMOW}/1000)+1)) * (2005.2 * (10^{-6})) \text{ where } (2005.2 * (10^{-6})) \text{ is } R_{standard} VSMOW$											
$R_{arag} = a \times R_{water}$											
$\delta_{arag} VSMOW = \text{conversion of arag from } R_{arag} \text{ back to } \delta \text{ value}$											
$\text{Calculated aragonite } \delta^{18}O = \text{conversion of } VSMOW \text{ value to } VPDB \text{ value} = (\delta_{arag} VSMOW - 30.91 \text{‰})/1.03091$											

Table 11: Calculations of expected equilibrium aragonite values based on measured temperature and drip water $\delta^{18}O$ ranges.

Number	Sample code	Mg/Ca	FD k_{Mg}	SD k_{Mg}	Sr/Ca	FD k_{Sr}	SD k_{Sr}	Mn/Ca	FD k_{Mn}	SD k_{Mn}
1	NA43	4.5E-01	3.4E-04	3.3E-04	4.9E-01	2.7E+00	2.6E+00	5.8E-03	1.6E-01	
2	NA44	3.6E-01	2.7E-04	2.7E-04	4.8E-01	2.6E+00	2.6E+00	1.4E-03	4.0E-02	
3	NA45	4.4E-01	3.3E-04	3.2E-04	4.9E-01	2.7E+00	2.6E+00	7.4E-03	2.1E-01	
4	NA46	5.3E-01	4.0E-04	3.9E-04	4.6E-01	2.6E+00	2.5E+00	1.1E-02	3.1E-01	
5	NA47	3.7E-01	2.8E-04	2.7E-04	4.7E-01	2.6E+00	2.5E+00	2.3E-03	6.4E-02	
6	NA48	4.3E-01	3.2E-04	3.1E-04	5.1E-01	2.8E+00	2.7E+00	1.2E-02	3.2E-01	
7	NA49	4.2E-01	3.2E-04	3.1E-04	5.0E-01	2.8E+00	2.7E+00	1.5E-02	4.1E-01	
8	NA50	3.6E-01	2.7E-04	2.6E-04	5.1E-01	2.8E+00	2.7E+00	8.9E-03	2.5E-01	
9	NA51	4.2E-01	3.1E-04	3.1E-04	5.2E-01	2.8E+00	2.8E+00	1.6E-02	4.3E-01	
10	NA52	3.5E-01	2.6E-04	2.5E-04	5.0E-01	2.8E+00	2.7E+00	6.4E-03	1.8E-01	
11	NA53	4.4E-01	3.2E-04	3.2E-04	4.9E-01	2.7E+00	2.7E+00	2.7E-03	7.5E-02	
12	NA54	5.7E-01	4.3E-04	4.2E-04	5.1E-01	2.8E+00	2.7E+00	2.8E-03	7.9E-02	
13	NA55	3.5E-01	2.6E-04	2.6E-04	5.2E-01	2.9E+00	2.8E+00	2.5E-03	6.9E-02	
14	NA56	3.6E-01	2.7E-04	2.6E-04	5.0E-01	2.8E+00	2.7E+00	1.8E-03	4.9E-02	
15	NA57	4.7E-01	3.5E-04	3.4E-04	5.2E-01	2.9E+00	2.8E+00	3.7E-03	1.0E-01	
16	NA58	6.7E-01	5.0E-04	4.9E-04	5.4E-01	3.0E+00	2.9E+00	1.8E-02	5.0E-01	
17	NA59	9.1E-01	6.8E-04	6.6E-04	5.4E-01	3.0E+00	2.9E+00	2.6E-02	7.4E-01	
18	NA60	5.1E-01	3.8E-04	3.7E-04	5.7E-01	3.1E+00	3.1E+00	1.9E-02	5.3E-01	
19	NA61	6.3E-01	4.7E-04	4.6E-04	5.6E-01	3.1E+00	3.0E+00	2.1E-02	5.9E-01	
20	NA62	3.4E+00	2.5E-03	2.5E-03	4.8E-01	2.7E+00	2.6E+00	3.0E-02	8.3E-01	
21	NA63	1.0E+00	7.8E-04	7.6E-04	5.4E-01	3.0E+00	2.9E+00	1.8E-02	4.9E-01	
22	NA64	5.8E-01	4.3E-04	4.2E-04	5.3E-01	2.9E+00	2.8E+00	5.1E-03	1.4E-01	
23	NA65	5.0E-01	3.7E-04	3.7E-04	5.3E-01	2.9E+00	2.8E+00	4.2E-03	1.2E-01	
24	NA66	4.3E-01	3.2E-04	3.1E-04	5.3E-01	2.9E+00	2.9E+00	4.6E-03	1.3E-01	
25	NA67	8.8E-01	6.5E-04	6.4E-04	5.2E-01	2.9E+00	2.8E+00	1.4E-02	4.0E-01	
26	NA68	7.1E-01	5.3E-04	5.2E-04	5.2E-01	2.9E+00	2.8E+00	2.0E-02	5.6E-01	
27	NA69	3.8E-01	2.8E-04	2.8E-04	5.1E-01	2.8E+00	2.8E+00	7.5E-03	2.1E-01	
28	NA70	3.4E-01	2.5E-04	2.5E-04	5.1E-01	2.8E+00	2.8E+00	1.1E-03	3.2E-02	
29	NA71	7.0E-01	5.2E-04	5.1E-04	5.2E-01	2.9E+00	2.8E+00	1.8E-03	5.1E-02	
30	NA72	4.7E-01	3.5E-04	3.4E-04	5.1E-01	2.8E+00	2.8E+00	3.7E-03	1.0E-01	
31	NA73	8.8E-01	6.5E-04	6.4E-04	5.3E-01	2.9E+00	2.9E+00	1.3E-02	3.7E-01	
32	NA74	7.6E-01	5.7E-04	5.6E-04	5.3E-01	2.9E+00	2.8E+00	1.5E-02	4.3E-01	
33	NA75	1.3E+00	9.4E-04	9.2E-04	5.0E-01	2.8E+00	2.7E+00	2.4E-02	6.7E-01	
34	NA76	1.0E+00	7.8E-04	7.7E-04	5.1E-01	2.8E+00	2.7E+00	1.7E-02	4.6E-01	
35	NA77	5.6E-01	4.2E-04	4.1E-04	5.2E-01	2.9E+00	2.8E+00	2.7E-03	7.5E-02	
36	NA78	1.2E+00	9.3E-04	9.1E-04	5.2E-01	2.9E+00	2.8E+00	1.0E-02	2.9E-01	
37	NA79	1.6E+00	1.2E-03	1.1E-03	5.0E-01	2.7E+00	2.7E+00	2.0E-02	5.6E-01	
38	NA80	1.4E+00	1.0E-03	1.0E-03	5.1E-01	2.8E+00	2.7E+00	1.2E-02	3.4E-01	
Average/drip			5.3E-04	5.2E-04		2.8E+00	2.8E+00		3.0E-01	
1 Std Dev/drip			4.1E-04	4.0E-04		1.2E-01	1.2E-01		2.2E-01	
Average both drips			5.3E-04			2.8E+00			3.0E-01	
1 Std Dev both drips			4.1E-04			1.2E-01			2.2E-01	

Number	Sample code	Na/Ca	FD k_{Na}	SD k_{Na}	U/Ca	FD k_U	SD k_U	P/Ca	FD k_P	SD k_P
1	NA43	1.6E+00	7.4E-03	7.3E-03	9.6E-04	9.2E+00	9.4E+00	4.0E-01	1.9E+00	1.6E+00
2	NA44	1.3E+00	5.8E-03	5.7E-03	1.3E-03	1.3E+01	1.3E+01	4.7E-01	2.3E+00	1.9E+00
3	NA45	1.4E+00	6.2E-03	6.1E-03	1.0E-03	1.0E+01	1.0E+01	4.2E-01	2.0E+00	1.7E+00
4	NA46	1.5E+00	7.1E-03	6.9E-03	8.5E-04	8.2E+00	8.4E+00	4.6E-01	2.2E+00	1.9E+00
5	NA47	1.3E+00	6.1E-03	6.0E-03	1.8E-03	1.8E+01	1.8E+01	4.2E-01	2.0E+00	1.7E+00
6	NA48	1.5E+00	7.2E-03	7.0E-03	1.0E-03	9.8E+00	1.0E+01	3.0E-01	1.4E+00	1.2E+00
7	NA49	1.2E+00	5.7E-03	5.6E-03	8.2E-04	7.9E+00	8.0E+00	3.3E-01	1.6E+00	1.4E+00
8	NA50	1.2E+00	5.3E-03	5.2E-03	1.1E-03	1.1E+01	1.1E+01	4.8E-01	2.3E+00	2.0E+00
9	NA51	1.4E+00	6.3E-03	6.1E-03	9.9E-04	9.6E+00	9.8E+00	5.3E-01	2.6E+00	2.2E+00
10	NA52	1.5E+00	7.0E-03	6.9E-03	7.4E-04	7.2E+00	7.3E+00	4.5E-01	2.2E+00	1.9E+00
11	NA53	1.6E+00	7.6E-03	7.5E-03	1.2E-03	1.2E+01	1.2E+01	5.7E-01	2.8E+00	2.4E+00
12	NA54	2.0E+00	9.1E-03	8.9E-03	1.3E-03	1.3E+01	1.3E+01	5.4E-01	2.6E+00	2.2E+00
13	NA55	1.3E+00	6.0E-03	5.8E-03	9.1E-04	8.8E+00	9.0E+00	4.7E-01	2.3E+00	1.9E+00
14	NA56	1.6E+00	7.4E-03	7.3E-03	9.5E-04	9.2E+00	9.3E+00	5.1E-01	2.5E+00	2.1E+00
15	NA57	1.7E+00	8.1E-03	7.9E-03	1.3E-03	1.2E+01	1.3E+01	6.6E-01	3.2E+00	2.7E+00
16	NA58	1.6E+00	7.4E-03	7.2E-03	2.3E-03	2.3E+01	2.3E+01	6.6E-01	3.2E+00	2.7E+00
17	NA59	2.9E+00	1.4E-02	1.3E-02	3.2E-03	3.1E+01	3.2E+01	5.6E-01	2.7E+00	2.3E+00
18	NA60	2.0E+00	9.3E-03	9.1E-03	2.0E-03	1.9E+01	2.0E+01	4.6E-01	2.2E+00	1.9E+00
19	NA61	2.0E+00	9.0E-03	8.8E-03	2.1E-03	2.0E+01	2.1E+01	4.8E-01	2.3E+00	2.0E+00
20	NA62	1.9E+00	8.8E-03	8.6E-03	2.9E-03	2.8E+01	2.9E+01	5.0E-01	2.4E+00	2.0E+00
21	NA63	2.3E+00	1.1E-02	1.0E-02	1.7E-03	1.7E+01	1.7E+01	5.3E-01	2.6E+00	2.2E+00
22	NA64	1.7E+00	7.9E-03	7.7E-03	1.1E-03	1.1E+01	1.1E+01	4.5E-01	2.2E+00	1.8E+00
23	NA65	3.0E+00	1.4E-02	1.4E-02	1.3E-03	1.2E+01	1.3E+01	5.1E-01	2.4E+00	2.1E+00
24	NA66	1.6E+00	7.3E-03	7.1E-03	1.3E-03	1.2E+01	1.2E+01	5.4E-01	2.6E+00	2.2E+00
25	NA67	1.8E+00	8.5E-03	8.4E-03	2.5E-03	2.5E+01	2.5E+01	6.2E-01	3.0E+00	2.5E+00
26	NA68	1.9E+00	8.9E-03	8.7E-03	1.9E-03	1.8E+01	1.8E+01	4.0E-01	1.9E+00	1.6E+00
27	NA69	1.9E+00	8.8E-03	8.6E-03	1.1E-03	1.0E+01	1.1E+01	3.5E-01	1.7E+00	1.4E+00
28	NA70	2.1E+00	9.5E-03	9.3E-03	1.3E-03	1.3E+01	1.3E+01	4.4E-01	2.1E+00	1.8E+00
29	NA71	1.7E+00	7.7E-03	7.6E-03	1.5E-03	1.4E+01	1.5E+01	5.7E-01	2.8E+00	2.4E+00
30	NA72	1.5E+00	6.9E-03	6.8E-03	7.2E-04	7.0E+00	7.1E+00	4.2E-01	2.1E+00	1.7E+00
31	NA73	1.7E+00	7.8E-03	7.7E-03	1.1E-03	1.0E+01	1.0E+01	5.7E-01	2.7E+00	2.3E+00
32	NA74	2.0E+00	9.1E-03	9.0E-03	1.6E-03	1.6E+01	1.6E+01	7.4E-01	3.6E+00	3.0E+00
33	NA75	1.9E+00	8.6E-03	8.4E-03	2.8E-03	2.7E+01	2.8E+01	5.8E-01	2.8E+00	2.4E+00
34	NA76	3.7E+00	1.7E-02	1.7E-02	1.5E-03	1.4E+01	1.4E+01	4.2E-01	2.0E+00	1.7E+00
35	NA77	1.6E+00	7.4E-03	7.3E-03	1.3E-03	1.2E+01	1.2E+01	4.6E-01	2.2E+00	1.9E+00
36	NA78	2.0E+00	9.2E-03	9.0E-03	2.7E-03	2.6E+01	2.6E+01	7.4E-01	3.6E+00	3.0E+00
37	NA79	3.0E+00	1.4E-02	1.4E-02	1.0E-03	1.0E+01	1.0E+01	5.0E-01	2.4E+00	2.0E+00
38	NA80	2.1E+00	9.8E-03	9.6E-03	7.9E-04	7.6E+00	7.8E+00	5.6E-01	2.7E+00	2.3E+00
Average/drip			8.5E-03	8.3E-03		1.4E+01	1.5E+01		2.4E+00	2.1E+00
1 Std Dev/drip			2.5E-03	2.5E-03		6.4E+00	6.5E+00		4.8E-01	4.0E-01
Average both drips			8.4E-03			1.4E+01			2.2E+00	
1 Std Dev both drips			2.5E-03			6.4E+00			4.4E-01	

Number	Sample code	Rb/Ca	FD k_{Rb}	SD k_{Rb}	K/Ca	FD k_K	SD k_K
1	NA43	1.3E-04	1.4E-01	9.5E-02	2.7E-01	1.2E-01	8.0E-02
2	NA44	8.5E-05	9.2E-02	6.4E-02	2.0E-01	8.6E-02	5.7E-02
3	NA45	1.1E-04	1.2E-01	8.2E-02	2.8E-01	1.2E-01	8.1E-02
4	NA46	2.1E-04	2.3E-01	1.6E-01	3.3E-01	1.5E-01	9.7E-02
5	NA47	7.5E-05	8.1E-02	5.7E-02	3.9E-01	1.7E-01	1.1E-01
6	NA48	1.6E-04	1.8E-01	1.2E-01	3.2E-01	1.4E-01	9.2E-02
7	NA49	1.9E-04	2.1E-01	1.4E-01	2.8E-01	1.2E-01	8.3E-02
8	NA50	9.0E-05	9.7E-02	6.7E-02	9.5E-02	4.2E-02	2.8E-02
9	NA51	1.2E-04	1.3E-01	8.9E-02	2.5E-01	1.1E-01	7.3E-02
10	NA52	1.6E-04	1.8E-01	1.2E-01	4.7E-01	2.1E-01	1.4E-01
11	NA53	2.8E-04	3.1E-01	2.1E-01	8.4E-01	3.7E-01	2.5E-01
12	NA54	1.4E-04	1.5E-01	1.0E-01	5.9E-01	2.6E-01	1.7E-01
13	NA55	1.3E-04	1.4E-01	9.8E-02	3.1E-01	1.4E-01	9.2E-02
14	NA56	2.9E-04	3.2E-01	2.2E-01	9.2E-01	4.1E-01	2.7E-01
15	NA57	2.3E-04	2.5E-01	1.8E-01	6.9E-01	3.0E-01	2.0E-01
16	NA58	1.0E-04	1.1E-01	7.8E-02	2.3E-01	1.0E-01	6.8E-02
17	NA59	5.0E-04	5.5E-01	3.8E-01	1.3E+00	5.7E-01	3.8E-01
18	NA60	2.3E-04	2.5E-01	1.8E-01	5.2E-01	2.3E-01	1.5E-01
19	NA61	2.5E-04	2.8E-01	1.9E-01	5.5E-01	2.4E-01	1.6E-01
20	NA62	2.8E-04	3.0E-01	2.1E-01	4.1E-01	1.8E-01	1.2E-01
21	NA63	4.9E-04	5.3E-01	3.7E-01	1.2E+00	5.2E-01	3.4E-01
22	NA64	1.5E-04	1.6E-01	1.1E-01	3.5E-01	1.5E-01	1.0E-01
23	NA65	9.9E-04	1.1E+00	7.5E-01	2.6E+00	1.1E+00	7.6E-01
24	NA66	1.3E-04	1.4E-01	9.6E-02	3.0E-01	1.3E-01	8.9E-02
25	NA67	3.1E-04	3.3E-01	2.3E-01	6.7E-01	2.9E-01	1.9E-01
26	NA68	2.4E-04	2.6E-01	1.8E-01	3.4E-01	1.5E-01	9.9E-02
27	NA69	3.5E-04	3.8E-01	2.6E-01	7.7E-01	3.4E-01	2.3E-01
28	NA70	4.6E-04	5.0E-01	3.5E-01	1.1E+00	5.0E-01	3.3E-01
29	NA71	8.8E-05	9.5E-02	6.6E-02	2.4E-01	1.0E-01	7.0E-02
30	NA72	9.9E-05	1.1E-01	7.4E-02	2.3E-01	1.0E-01	6.9E-02
31	NA73	1.9E-04	2.1E-01	1.4E-01	4.5E-01	2.0E-01	1.3E-01
32	NA74	3.0E-04	3.2E-01	2.3E-01	6.5E-01	2.9E-01	1.9E-01
33	NA75	2.3E-04	2.5E-01	1.7E-01	3.6E-01	1.6E-01	1.0E-01
34	NA76	1.6E-03	1.8E+00	1.2E+00	2.6E+00	1.2E+00	7.7E-01
35	NA77	1.7E-04	1.8E-01	1.3E-01	4.4E-01	1.9E-01	1.3E-01
36	NA78	2.4E-04	2.6E-01	1.8E-01	5.0E-01	2.2E-01	1.5E-01
37	NA79	3.8E-04	4.1E-01	2.9E-01	1.2E+00	5.3E-01	3.5E-01
38	NA80	3.9E-04	4.2E-01	2.9E-01	9.5E-01	4.2E-01	2.8E-01
Average/drip			3.0E-01	2.1E-01		2.8E-01	1.9E-01
1 Std Dev/drip			3.0E-01	2.1E-01		2.5E-01	1.7E-01
Average both drips			2.6E-01			2.3E-01	
1 Std Dev both drips			2.6E-01			2.1E-01	

Table 12: Calculation of empirical partition coefficients using subsample measurements from sample stalagmite seasonally milled section and trace-element ratio measurements of drip waters feeding the sample collected in January, 2015. FD stands for fast drip and SD for slow drip. Drip water trace-element ratio values have been given in table 5.1.

using minimal fraction of valid points 30.00

SST [C] from Hadley Centre SST data set HadISST1

cutting out region lon= 73.000 74.000, lat= 15.000

16.000

Year	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	Annual mean
1870	27.22	27.15	28.16	29.09	29.46	28.58	27.73	27.29	27.35	28.34	28.16	27.53	28.01
1871	26.88	27.01	27.56	28.73	29.46	28.54	27.74	27.11	27.3	28.21	28.41	27.53	27.87
1872	27.16	27.18	28.01	28.8	29.52	28.74	27.78	27.23	27.5	28.2	28.3	27.28	27.98
1873	27.08	26.88	27.54	28.77	29.48	28.72	27.66	26.99	27.24	28	27.86	27.21	27.79
1874	27.02	26.87	27.69	28.44	29.39	28.52	27.62	26.83	26.84	27.6	27.54	26.91	27.61
1875	26.66	26.99	27.8	28.7	29.5	28.45	27.24	26.73	27.35	28.39	28.6	27.46	27.82
1876	26.98	27	27.86	28.62	29.43	28.59	27.68	27.17	27.33	28.41	28.25	27.72	27.92
1877	27.3	27.5	28.04	28.83	29.59	29.02	28.03	27.43	28.14	28.98	28.86	28.07	28.32
1878	27.68	27.87	28.39	29.39	30.11	29.54	28.34	27.56	27.69	28.51	28.29	27.82	28.43
1879	27.43	27.46	28.03	28.79	29.42	28.58	27.54	26.77	27.3	28.13	28.04	27.29	27.90
1880	26.58	26.96	27.93	28.89	29.59	28.4	27.62	26.79	27.11	28.09	28.24	27.59	27.82
1881	26.94	27.03	28.2	29.12	29.94	29.03	27.99	27.23	27.55	28.11	27.89	27.32	28.03
1882	26.94	27.21	27.9	28.83	29.52	28.68	27.6	26.92	27.15	28.17	28.24	27.63	27.90
1883	27.23	27.3	28.05	28.97	29.68	28.98	27.72	27.14	27.52	28.16	28.16	27.38	28.02
1884	26.71	26.73	27.31	28.57	29.64	28.64	27.87	27.18	27.46	28.14	28.07	27.4	27.81
1885	26.78	26.7	27.65	28.74	29.63	28.58	27.64	27.23	27.74	28.6	28.47	27.68	27.95
1886	27.04	27.04	28.05	28.79	29.42	28.61	27.62	26.95	27.3	28.12	28.07	27.3	27.86
1887	26.9	26.83	27.55	28.31	29.11	28.41	27.7	26.8	27.22	28.07	27.97	27.43	27.69
1888	27.03	27.04	27.64	28.52	29.39	28.8	28.16	27.17	27.29	28.73	28.54	27.71	28.00
1889	27.39	27.63	28.09	28.8	29.64	28.45	27.66	26.89	27.19	27.91	27.97	27.36	27.92
1890	27.04	27.02	27.79	28.82	29.44	28.19	27.03	26.23	26.77	27.79	27.75	27.27	27.60
1891	26.74	27	27.83	28.96	29.56	28.65	27.77	27.22	27.6	28.36	28.16	27.39	27.94
1892	26.78	27.14	27.73	28.53	29.28	28.48	27.37	26.6	27.03	27.66	27.97	27.32	27.66
1893	26.9	26.78	27.42	28.12	28.92	28.16	27.29	26.59	26.89	27.73	27.69	27.01	27.46
1894	26.63	26.65	27.4	28.31	29.15	28.24	27.4	26.67	26.95	27.74	27.61	27	27.48
1895	26.67	27.05	27.7	28.39	29	28.29	27.44	27.22	27.41	28.25	28.32	27.44	27.77
1896	26.73	27.01	27.86	28.77	29.57	28.6	27.6	27.03	27.62	28.62	28.53	27.84	27.98
1897	27.4	27.46	28.07	28.91	29.61	28.76	27.85	27.25	27.49	28.23	28.09	27.61	28.06
1898	27.26	27.24	27.74	28.67	29.37	28.84	27.71	26.89	27.1	28.07	27.99	27.31	27.85
1899	26.83	26.98	27.7	28.59	29.54	28.39	27.28	27.02	27.17	28.12	28.05	27.53	27.77
1900	27.02	27.09	27.76	28.87	29.7	28.83	27.87	27.09	27.47	28.28	28.27	27.64	27.99
1901	27.44	27.16	27.92	28.94	29.6	28.41	27.47	26.86	27.08	28.07	27.93	27.33	27.85
1902	27.02	27.05	27.64	28.87	29.35	28.78	27.71	27.46	27.5	28.41	28.27	27.81	27.99
1903	27.08	27.17	27.59	28.35	29.42	28.61	27.89	27.28	27.4	28.02	28.03	27.27	27.84
1904	26.75	26.95	27.57	28.43	29.3	28.51	27.52	26.97	27.19	28.08	27.92	27.31	27.71
1905	26.9	26.91	27.56	28.18	29.42	28.5	27.89	27.36	27.64	28.18	28.29	27.51	27.86
1906	27.06	27.03	27.64	28.32	28.97	28.64	27.54	27.03	27.22	28.04	27.86	27.26	27.72
1907	26.82	26.71	27.56	28.5	29.2	28.55	27.66	26.8	27.25	28.34	28.39	27.56	27.78
1908	27.22	26.74	27.48	28.26	29.21	28.41	27.57	26.74	27.28	27.98	28.11	27.34	27.70
1909	26.74	26.82	27.68	28.72	29.32	28.28	27.12	26.42	26.69	27.57	27.85	27.11	27.53
1910	26.84	26.69	27.49	28.07	28.94	28.17	27.37	26.88	26.63	27.56	27.72	27.07	27.45

Year	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	Annual mean
1911	26.73	26.91	27.63	27.95	28.8	28.26	27.39	26.9	27.15	28.29	28.09	27.73	27.65
1912	27.24	27.12	27.9	28.98	30.09	28.92	27.87	27.1	27.45	28.45	28.11	27.48	28.06
1913	27.01	27.02	27.5	28.51	29.61	28.5	27.49	26.93	27.26	28.41	27.96	27.28	27.79
1914	27.07	26.95	27.45	28.23	29.29	28.54	27.42	26.98	27.7	28.68	28.51	27.51	27.86
1915	26.94	26.97	27.75	28.79	29.82	29.27	28.21	27.63	27.78	28.51	28.24	27.54	28.12
1916	27	27.24	27.89	28.92	29.5	28.65	27.57	27.03	27.24	28.14	27.9	27.29	27.86
1917	26.8	26.92	27.47	28.51	29.32	28.59	27.6	27.02	27.31	28.06	27.77	27.17	27.71
1918	26.67	27.16	28.01	28.33	28.8	28.19	27.85	27.27	27.8	28.77	28.7	27.36	27.91
1919	27.24	27.35	27.88	28.95	29.65	28.76	27.67	27.09	27.63	28.68	28.45	27.69	28.09
1920	27.22	27.22	27.95	28.83	29.65	28.65	27.56	27.03	27.27	28.12	28.18	27.39	27.92
1921	26.75	26.95	27.73	28.64	29.55	28.56	27.87	26.98	27.34	28.42	28.39	27.65	27.90
1922	27.27	27.28	27.78	28.65	29.37	28.68	27.59	26.85	27.15	28.35	27.98	27.28	27.85
1923	26.73	27	27.8	28.87	29.32	28.68	27.65	27.03	27.43	28.41	28.32	27.2	27.87
1924	26.91	27.11	27.97	29.12	29.87	28.82	28.04	27.05	27.5	27.89	28.1	27.3	27.97
1925	26.59	26.34	27.53	28.56	29.38	28.87	27.64	27.03	27.62	28.53	28.62	27.65	27.86
1926	27.18	27.18	28.27	28.9	29.85	29.32	28.35	27.8	28.02	28.72	28.47	27.8	28.32
1927	27.04	27.46	27.75	28.72	29.36	28.51	27.37	26.91	27.54	28.26	28.13	27.59	27.89
1928	27.24	27.29	28.21	28.88	29.77	29.14	28.04	27.27	27.5	28.26	28.39	27.6	28.13
1929	27.25	27.28	28.04	29.12	29.91	28.99	27.91	27.05	27.61	28.53	28.57	27.96	28.19
1930	27.36	27.2	27.72	28.95	29.73	29.01	27.92	27.07	27.7	28.82	28.56	27.9	28.16
1931	27.54	27.37	28.25	29.18	30.32	29.33	28.12	27.42	27.48	28.35	28.44	27.65	28.29
1932	27.19	27.05	27.93	28.71	29.7	29.14	28	27.19	27.41	28.25	28.05	27.42	28.00
1933	27.3	27.19	28.25	28.95	29.99	28.86	27.75	27.22	27.32	27.96	28.28	27.56	28.05
1934	26.79	26.87	27.67	28.77	29.63	29.28	27.81	27.22	27.39	28.48	28.08	27.65	27.97
1935	27.12	27.22	28.12	28.82	29.64	29.22	28.01	27.18	27.66	28.85	28.45	27.95	28.19
1936	27.06	27.32	27.86	28.84	30.2	28.71	27.96	27.2	27.79	28.57	28.62	27.97	28.18
1937	27.26	27.41	27.89	28.79	29.97	28.64	27.91	27.12	27.76	28.6	28.77	27.6	28.14
1938	27.37	27.29	28.13	28.64	29.72	28.75	27.54	27.03	27.47	28.28	28.04	27.6	27.99
1939	26.96	27.21	27.87	28.6	29.45	28.62	27.64	26.72	27.53	28.62	28.61	27.76	27.97
1940	27.27	27.12	27.74	28.91	30.13	29.13	27.86	27.26	27.67	28.58	28.7	27.97	28.20
1941	27.82	27.53	28.09	29.35	30.11	29.5	28.44	27.95	28.08	29.3	29.29	28.41	28.66
1942	27.62	27.69	28.36	29.11	30.01	28.92	27.67	27.32	27.61	28.42	28.3	27.68	28.23
1943	27.22	27.37	27.95	28.82	29.85	28.87	27.85	27.3	27.44	28.31	28.62	28.12	28.14
1944	27.48	27.64	28.5	29.01	30.18	29.05	27.98	27.37	27.85	28.38	28.55	28.15	28.35
1945	27.4	27.72	28.14	29.02	29.83	29.03	28.3	27.41	27.73	28.56	28.66	27.83	28.30
1946	27.38	27.42	28.15	29.39	29.46	28.83	28.2	27.2	27.49	28.18	28.47	27.55	28.14
1947	27.22	27.41	28.09	28.63	29.99	29	27.9	27.03	27.3	28.01	28.18	27.48	28.02
1948	27.14	27.01	27.77	28.68	29.45	28.92	27.65	26.93	27.03	28.26	28.16	27.3	27.86
1949	27.16	27.33	27.97	29	29.93	28.82	28.15	27.26	27.37	28.17	28.08	27.33	28.05
1950	27.28	27.16	27.89	28.65	29.59	28.77	27.76	26.75	27.49	28.37	28.17	27.35	27.94
1951	27.04	27.04	28.02	28.48	29.5	28.85	27.88	27.03	27.84	28.71	28.52	27.79	28.06
1952	27.32	27.75	28.44	29.46	29.86	29.13	27.82	27.08	27.27	28.07	28.13	27.75	28.17
1953	27.28	27.33	28.53	28.88	29.87	29.08	28.03	27.54	27.63	28.34	28.54	27.91	28.25
1954	27.11	27.27	27.99	29.13	29.7	28.84	27.75	27.18	27.3	28.21	28.22	27.36	28.01
1955	26.98	27.17	28.09	28.75	29.27	28.25	27.47	26.6	27.26	28.11	28.19	27.26	27.78
1956	27.07	27.04	27.88	28.76	29.2	28.3	27.57	26.79	26.94	27.79	27.81	27.45	27.72
1957	27.08	27.19	27.92	29.1	30.05	29.02	28.05	27.36	27.7	28.22	28.51	27.8	28.17
1958	27.24	27.13	27.9	28.92	30.01	28.92	28.2	27.53	27.59	28.29	28.01	27.47	28.10
1959	27.23	27.15	27.9	29.52	29.92	29.04	27.83	27.31	27.52	28.33	28.36	28.06	28.18
1960	27.45	27.54	28.46	29.29	29.79	29.21	28.27	27.33	27.57	28.37	28.56	27.85	28.31

Year	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	Annual mean
1961	27.16	27.2	27.99	28.88	29.36	29.09	27.74	27.6	27.74	28.39	28.42	27.61	28.10
1962	27.01	27.34	27.97	28.92	29.58	29.07	28.29	27.4	27.99	28.88	28.19	27.8	28.20
1963	27.4	27.63	28.4	29.29	30.12	29.24	28.16	27.76	28.04	28.7	28.78	28.06	28.47
1964	27.43	27.32	28.13	29.46	29.98	29.27	28	27.43	27.86	28.4	28.32	27.52	28.26
1965	27.21	27.12	28.1	28.66	29.34	28.98	28.01	27.43	27.91	29.26	29.12	28.14	28.27
1966	27.59	27.62	27.75	29	29.94	29.42	28.71	27.98	28.2	29.22	28.56	27.93	28.49
1967	27.35	27.49	28.5	29.48	30.22	29.42	28.39	27.19	27.75	29.03	28.73	28.02	28.46
1968	27.26	27.23	27.98	28.84	29.5	29.09	27.91	27.49	27.85	28.9	28.68	27.93	28.22
1969	27.47	27.5	27.75	29.54	30.33	29.4	28.41	27.51	27.92	28.93	28.85	28.04	28.47
1970	27.69	27.62	28.33	29.35	30.09	29.16	28.25	27.71	27.76	28.51	28.44	27.68	28.38
1971	27.28	27.07	27.89	29	29.62	28.72	27.71	27.13	27.47	28.22	28.24	27.47	27.99
1972	27.17	26.79	27.76	28.78	29.78	29.09	28.22	27.54	28.17	29.21	29.41	28.44	28.36
1973	27.32	27.17	28.34	28.97	30.16	28.88	27.98	27.16	27.67	28.59	28.42	27.52	28.18
1974	27.19	27.41	28.19	28.8	29.62	28.74	27.76	27.15	27.29	28.01	28.03	27.53	27.98
1975	26.94	26.95	27.62	27.93	29.83	28.63	27.7	27.16	26.83	27.99	27.75	26.71	27.67
1976	26.77	27	27.85	28.79	29.86	28.84	28.19	27.46	27.77	29.25	28.94	27.75	28.21
1977	27.22	27.15	28.35	29.68	29.65	28.96	28.15	27.42	27.76	29.04	28.69	28.03	28.34
1978	27.09	27.19	27.44	29.34	29.97	28.56	27.51	26.94	27.31	28.78	28.12	27.61	27.99
1979	27.44	27.4	27.91	29.19	29.76	29.34	28.37	27.68	28.06	29.04	28.88	28.12	28.43
1980	27.57	27.41	28.35	29.24	30.45	29.5	28.05	27.54	27.99	28.97	28.9	27.95	28.49
1981	27.34	27.49	28.52	29.51	29.99	28.76	28.04	27.57	27.93	28.88	28.45	27.8	28.36
1982	27.52	27.6	28.1	28.95	29.78	29.04	28.03	27.3	27.82	29.34	28.83	27.89	28.35
1983	27.26	27.19	27.81	28.9	29.87	29.16	28.38	27.58	27.81	28.56	28.61	28.04	28.26
1984	27.42	27.38	28.23	29.27	30.09	28.53	27.54	26.83	27.26	28.25	28.62	27.89	28.11
1985	27.45	27.51	28.6	29.24	30.3	28.73	27.29	27.28	27.93	28.5	28.15	27.9	28.24
1986	27.7	27.76	28.28	29.12	29.87	29.17	27.99	27.21	27.59	28.84	28.79	28.07	28.37
1987	27.61	27.71	28.1	29.24	30.19	29.25	28.43	27.95	28.42	29.28	29.27	28.42	28.66
1988	28.2	28.11	28.97	29.61	30.29	29.25	28.51	27.73	28.18	28.84	28.99	28.27	28.75
1989	27.78	27.65	28.37	28.98	29.59	28.71	27.65	26.91	27.51	28.74	28.9	28.21	28.25
1990	27.76	28.1	28.18	29.16	29.93	28.7	27.84	27.18	27.55	28.77	28.63	27.97	28.31
1991	27.58	27.65	28.3	29.35	30.1	29.24	28.44	27.51	27.89	28.69	28.52	27.97	28.44
1992	27.32	27.35	28.1	28.77	29.46	28.69	28.02	27.3	27.74	28.53	28.56	27.66	28.13
1993	27.31	27.44	28.22	29.01	29.94	28.9	28.17	27.29	28.12	28.6	28.65	27.96	28.30
1994	27.75	27.64	28.34	29.24	29.96	28.87	27.83	27.05	27.54	28.78	28.61	28.03	28.30
1995	27.46	27.65	28.29	29.07	29.73	29.06	28.01	27.24	27.74	28.65	28.54	28.16	28.30

Table 13: SST data for the region between 73°E and 74°E longitudes and 15° and 16°N has been plotted using the HadISST1 dataset sourced from KNMI Explorer.

Sample Code	Y/Ca	Ca/Ca	Ba/Ca	Th/Ca	U/Ca	Na/Ca	Mg/Ca	P/Ca	S/Ca	Mn/Ca	Fe/Ca	Co/Ca	Zn/Ca	Rb/Ca	Sr/Ca	Pb/Ca	K/Ca
Mmol/mol																	
Detection limit	2.8E-05	6.6E-04	1.4E-02	5.1E-05	1.6E-06	5.6E-02	6.6E-03	2.6E-02	6.7E-01	1.3E-03	8.4E-03	2.0E-04	8.2E-03	1.4E-05	2.6E-03	3.1E-05	1.8E-02
Precision%	0.10	0.20	0.07	0.10	0.06	0.02	0.01	0.01	0.04	0.12	7.95	0.02	0.44	0.01	0.02	0.03	0.02
NAT81	2.2E-05	2.1E-05	2.7E-04	2.2E-05	1.0E-03	1.4E+00	3.2E+00	9.8E-01	1.3E-01	3.5E-02	9.7E-02	2.1E-04	-5.4E-02	3.9E-05	5.1E-01	3.3E-04	-7.0E-02
NAT82	1.3E-05	1.2E-05	1.6E-04	1.4E-05	9.5E-04	1.3E+00	2.5E+00	1.3E+00	9.4E-01	5.9E-03	3.3E-02	2.4E-04	-5.8E-02	2.5E-05	5.2E-01	1.8E-04	-9.6E-02
NAT83	5.9E-05	2.9E-05	3.3E-04	9.3E-06	1.3E-03	2.3E+00	3.0E+00	1.1E+00	1.8E-01	9.0E-03	2.2E-01	5.9E-05	-1.2E-02	1.1E-04	5.3E-01	3.6E-04	8.4E-02
NAT84	2.6E-04	2.6E-05	5.7E-04	1.3E-05	1.5E-03	1.9E+00	3.4E+00	1.0E+00	1.6E-01	2.9E-02	1.2E+00	7.6E-04	-3.1E-02	2.3E-04	5.4E-01	3.9E-04	6.0E-02
NAT85	7.6E-05	1.6E-05	4.4E-04	8.4E-06	1.5E-03	1.4E+00	2.7E+00	9.4E-01	1.2E-01	1.9E-02	7.8E-01	2.2E-04	-4.2E-02	1.3E-04	5.4E-01	1.9E-04	-3.6E-02
NAT86	5.9E-05	4.6E-05	4.3E-04	5.2E-06	1.2E-03	1.9E+00	3.2E+00	8.9E-01	1.3E-01	1.3E-02	5.3E-01	1.3E-04	2.6E-02	1.2E-04	5.3E-01	4.4E-04	1.9E-03
NAT87	5.9E-05	5.1E-04	5.6E-04	6.0E-06	1.1E-03	1.9E+00	2.2E+00	9.0E-01	1.6E-01	1.6E-02	6.5E-01	4.5E-04	-1.7E-02	1.4E-04	5.2E-01	8.5E-03	4.2E-02
NAT88	5.1E-05	2.6E-05	3.3E-04	4.2E-06	1.5E-03	1.8E+00	2.9E+00	9.7E-01	1.1E-01	1.1E-02	3.8E-01	7.9E-05	-4.7E-02	8.4E-05	5.4E-01	2.4E-04	-5.0E-02
NAT89	6.1E-05	5.1E-05	4.7E-04	5.2E-06	1.2E-03	2.1E+00	3.1E+00	9.7E-01	1.3E-01	2.0E-02	5.4E-01	5.6E-04	-5.5E-03	3.5E-04	5.3E-01	5.0E-04	5.1E-01
NAT90	4.8E-05	2.8E-05	3.2E-04	5.3E-06	1.1E-03	2.1E+00	3.1E+00	8.6E-01	9.1E-02	1.6E-02	3.8E-01	2.1E-04	-5.5E-02	9.3E-05	5.3E-01	2.4E-04	-3.8E-02
NAT91	3.6E-05	3.4E-05	2.4E-04	4.8E-06	1.0E-03	2.2E+00	3.5E+00	1.0E+00	1.3E-01	2.2E-02	2.6E-01	1.4E-03	-5.2E-02	1.2E-04	5.3E-01	2.9E-04	1.2E-01
NAT92	2.4E-05	2.7E-05	2.0E-04	2.1E-06	9.6E-04	1.8E+00	4.6E+00	1.0E+00	1.2E-01	3.8E-02	1.9E-01	1.7E-04	-4.2E-02	1.5E-04	5.4E-01	3.2E-04	2.1E-01
NAT93	2.3E-05	1.6E-05	2.5E-04	2.7E-06	6.8E-04	1.4E+00	2.5E+00	7.5E-01	9.9E-02	9.6E-03	5.3E-02	1.1E-04	-1.2E-02	4.4E-05	5.2E-01	2.4E-04	-5.5E-02
NAT94	3.9E-05	2.8E-05	2.6E-04	2.0E-06	8.1E-04	3.2E+00	3.5E+00	8.1E-01	1.4E-01	1.0E-02	3.5E-01	3.0E-04	-5.0E-02	8.3E-05	5.3E-01	3.4E-04	-6.0E-03
NAT95	3.1E-05	9.1E-06	1.7E-04	1.1E-06	6.7E-04	1.5E+00	3.2E+00	7.9E-01	7.5E-02	2.3E-02	2.4E-01	1.1E-03	-5.3E-02	6.0E-05	5.3E-01	1.2E-04	-3.2E-02
NAT96	1.5E-05	2.2E-05	1.4E-04	-5.4E-07	6.5E-04	1.1E+00	2.0E+00	6.6E-01	5.4E-02	9.2E-03	9.0E-02	1.1E-04	-5.3E-02	2.4E-05	5.1E-01	3.6E-04	-8.4E-02
NAT97	1.5E-05	1.9E-05	1.3E-04	-7.4E-07	6.8E-04	1.2E+00	2.2E+00	7.8E-01	8.2E-02	1.3E-02	7.3E-02	4.3E-04	-4.9E-02	3.7E-05	5.2E-01	3.2E-04	-4.8E-02
NAT98	2.0E-05	2.4E-05	2.4E-04	-3.6E-07	1.0E-03	2.2E+00	2.3E+00	8.9E-01	1.6E-01	5.9E-03	5.2E-02	1.2E-04	-4.0E-02	4.5E-05	5.1E-01	3.1E-04	-2.8E-02
NAT99	4.7E-05	2.7E-05	3.8E-04	-9.9E-08	1.6E-03	2.0E+00	3.9E+00	8.9E-01	1.3E-01	6.0E-02	6.1E-01	6.3E-04	-6.3E-03	8.2E-05	5.4E-01	3.8E-04	-4.9E-03
NAT100	2.5E-05	4.5E-05	2.1E-04	-1.4E-06	1.0E-03	1.5E+00	3.8E+00	9.6E-01	1.4E-01	5.6E-02	2.8E-01	2.1E-04	-4.5E-02	7.1E-05	5.4E-01	7.7E-04	1.7E-02
NAT101	2.3E-05	7.5E-05	1.6E-04	1.5E-05	7.4E-04	1.1E+00	2.2E+00	6.5E-01	1.3E-01	2.9E-02	9.3E-02	4.1E-04	-4.6E-02	4.0E-05	4.9E-01	1.4E-03	-4.7E-02
NAT102	3.3E-05	1.4E-05	2.5E-04	9.1E-06	6.3E-04	1.3E+00	3.3E+00	7.0E-01	1.2E-01	5.6E-02	3.2E-01	6.5E-04	-3.8E-02	6.2E-05	4.8E-01	2.0E-04	-5.8E-02
NAT103	3.2E-05	8.0E-05	1.9E-04	6.0E-06	9.0E-04	1.1E+00	2.7E+00	6.4E-01	9.2E-02	6.1E-02	3.3E-01	3.9E-04	-4.4E-02	4.3E-05	5.2E-01	1.6E-03	7.8E-02
NAT104	3.5E-05	9.3E-06	2.2E-04	3.4E-06	5.1E-04	1.3E+00	2.5E+00	5.9E-01	9.4E-02	3.3E-02	1.7E-01	3.2E-04	-4.9E-02	5.7E-05	5.1E-01	1.7E-04	-4.0E-02
NAT105	4.5E-05	1.8E-05	2.4E-04	3.5E-06	4.3E-04	1.7E+00	3.0E+00	5.3E-01	1.2E-01	7.4E-02	2.1E-01	6.9E-04	-4.8E-02	1.0E-04	5.2E-01	3.2E-04	5.8E-02
NAT106	2.4E-05	1.5E-05	2.2E-04	1.6E-06	5.9E-04	2.3E+00	3.8E+00	6.8E-01	1.3E-01	3.7E-02	1.4E-01	1.4E-03	-5.1E-02	1.0E-04	5.6E-01	2.5E-04	5.7E-02
NAT107	2.2E-05	1.3E-05	2.0E-04	9.6E-07	6.1E-04	1.6E+00	2.6E+00	6.3E-01	1.0E-01	1.9E-02	8.0E-02	3.3E-04	-2.9E-02	5.1E-05	5.5E-01	2.0E-04	-3.5E-02
NAT108	4.1E-05	2.5E-05	6.8E-04	1.6E-06	5.0E-04	1.7E+00	4.4E+00	7.5E-01	1.3E-01	5.5E-02	2.8E-01	8.4E-04	-4.7E-02	8.2E-05	5.5E-01	3.2E-04	-2.3E-02
NAT109	2.9E-05	1.9E-05	2.1E-04	3.2E-07	8.1E-04	1.5E+00	5.9E+00	8.0E-01	1.1E-01	2.1E-02	5.4E-02	5.7E-04	-5.2E-02	1.2E-04	5.3E-01	2.8E-04	-1.7E-03
NAT110	7.4E-05	2.5E-04	3.4E-04	5.8E-07	7.3E-04	1.7E+00	4.1E+00	8.2E-01	1.7E-01	8.7E-02	4.2E-01	3.2E-04	3.0E-02	1.3E-04	5.3E-01	4.8E-03	7.0E-02
NAT111	2.2E-05	1.5E-05	2.2E-04	3.8E-06	7.6E-04	1.5E+00	2.4E+00	6.0E-01	1.0E-01	1.3E-02	5.2E-02	1.3E-04	-4.8E-02	1.2E-04	5.5E-01	1.8E-04	1.4E-01
NAT112	6.3E-05	1.5E-05	6.0E-04	8.7E-06	6.4E-04	1.2E+00	2.6E+00	6.8E-01	8.4E-02	8.2E-02	4.7E-01	1.1E-04	-5.2E-02	1.8E-04	5.4E-01	3.2E-04	1.9E-01
NAT113	2.6E-05	3.0E-05	2.0E-04	1.0E-06	5.8E-04	1.6E+00	3.2E+00	5.3E-01	1.1E-01	1.5E-02	6.1E-02	1.1E-03	-5.0E-02	6.4E-05	5.2E-01	4.7E-04	-1.7E-02
NAT114	3.3E-05	3.3E-05	2.6E-04	2.4E-06	6.5E-04	1.9E+00	1.6E+00	5.8E-01	1.2E-01	1.1E-02	6.0E-02	5.1E-05	-4.1E-02	1.2E-04	5.3E-01	5.4E-04	8.8E-02
NAT115	5.0E-05	3.3E-05	2.8E-04	6.9E-07	7.1E-04	1.5E+00	3.7E+00	6.3E-01	1.8E-01	2.0E-02	8.6E-02	1.8E-04	1.7E-02	1.2E-04	5.6E-01	4.6E-04	7.4E-02
NAT116	3.1E-05	1.8E-05	2.2E-04	-5.0E-07	7.9E-04	1.1E+00	1.6E+00	6.3E-01	1.1E-01	1.0E-03	4.6E-02	1.8E-03	-4.3E-02	1.1E-04	5.5E-01	2.2E-04	8.9E-02
NAT117	7.7E-05	6.6E-05	3.2E-04	2.0E-06	8.0E-04	1.2E+00	2.1E+00	6.3E-01	1.1E-01	1.4E-02	7.7E-02	2.7E-04	-4.1E-02	2.0E-04	5.4E-01	1.1E-03	1.9E-01
NAT118	7.0E-05	1.2E-04	3.3E-04	1.5E-06	1.0E-03	1.3E+00	2.3E+00	7.8E-01	1.3E-01	3.3E-02	1.6E-01	1.9E-04	-2.8E-02	1.5E-04	5.4E-01	2.4E-03	6.6E-02
NAT119	7.2E-05	4.3E-05	2.8E-04	7.8E-07	9.2E-04	1.4E+00	2.7E+00	6.3E-01	1.4E-01	3.6E-02	2.6E-01	1.0E-03	-1.7E-02	1.2E-04	5.4E-01	6.6E-04	2.9E-02
NAT120	5.8E-05	2.7E-05	3.1E-04	7.9E-08	7.3E-04	1.2E+00	6.8E+00	6.3E-01	1.1E-01	8.2E-02	5.0E-01	2.8E-04	-4.3E-02	2.4E-04	5.1E-01	2.8E-04	5.7E-02

Sample Code	Y/Ca	Cd/Ca	Ba/Ca	Th/Ca	U/Ca	Na/Ca	Mg/Ca	P/Ca	S/Ca	Mn/Ca	Fe/Ca	Co/Ca	Zn/Ca	Rb/Ca	Sr/Ca	Pb/Ca	K/Ca
Mmol/mol																	
Detection limit	2.8E-05	6.6E-04	1.4E-02	5.1E-05	1.6E-06	5.6E-02	6.6E-03	2.6E-02	6.7E-01	1.3E-03	8.4E-03	2.0E-04	8.2E-03	1.4E-05	2.6E-03	3.1E-05	1.8E-02
Precision%	0.10	0.20	0.07	0.10	0.06	0.02	0.01	0.01	0.04	0.12	7.95	0.02	0.44	0.01	0.02	0.03	0.02
NAT121	3.2E-05	2.1E-05	5.9E-04	1.8E-05	9.2E-04	1.3E+00	7.8E+00	6.3E-01	1.1E-01	1.8E-02	8.1E-02	7.3E-05	-1.5E-02	1.2E-04	5.1E-01	3.2E-04	1.3E-01
NAT122	1.1E-04	7.2E-05	4.2E-04	1.4E-05	1.0E-03	1.2E+00	1.9E+00	6.5E-01	1.2E-01	2.5E-02	1.3E-01	7.3E-04	-4.4E-02	2.3E-04	5.4E-01	1.1E-03	1.1E-01
NAT123	4.9E-05	4.0E-05	3.6E-04	7.0E-06	8.1E-04	1.2E+00	2.0E+00	6.2E-01	9.6E-02	2.7E-02	1.8E-01	1.1E-04	-4.9E-02	1.1E-04	5.2E-01	5.6E-04	-7.4E-04
NAT124	4.8E-05	5.8E-05	8.6E-04	2.9E-06	5.6E-04	1.2E+00	3.6E+00	6.7E-01	1.2E-01	1.1E-01	5.1E-01	3.9E-04	-1.4E-02	1.1E-04	5.1E-01	1.0E-03	2.1E-02
NAT125	1.1E-05	9.4E-06	1.7E-03	1.8E-06	7.0E-04	1.1E+00	1.8E+00	5.1E-01	7.7E-02	2.8E-03	1.7E-02	2.2E-04	-5.4E-02	7.1E-05	5.1E-01	8.5E-05	3.4E-02
NAT126	1.8E-05	1.5E-05	3.1E-04	1.7E-06	7.5E-04	1.2E+00	2.0E+00	5.3E-01	7.9E-02	9.6E-03	2.8E-02	7.8E-05	-4.7E-02	1.4E-04	5.1E-01	1.5E-04	8.9E-02
NAT127	3.0E-05	1.8E-05	2.6E-04	1.4E-06	5.8E-04	9.7E-01	2.5E+00	6.5E-01	6.7E-02	7.9E-02	2.6E-01	4.0E-05	-5.2E-02	6.0E-05	4.8E-01	1.5E-04	-6.0E-02
NAT128	1.5E-05	1.9E-05	1.2E-04	6.4E-08	5.9E-04	9.4E-01	2.6E+00	4.9E-01	6.1E-02	2.8E-02	1.0E-01	7.7E-05	-5.2E-02	3.6E-05	5.0E-01	2.5E-04	-7.7E-02
NAT129	4.3E-05	1.3E-04	3.0E-04	1.4E-06	1.0E-03	9.4E-01	1.7E+00	6.3E-01	7.6E-02	1.4E-02	1.3E-01	6.4E-04	-3.2E-02	7.7E-05	5.4E-01	2.8E-03	-1.3E-02
NAT130	7.9E-05	5.5E-05	4.4E-04	1.7E-06	2.1E-03	7.4E-01	7.2E+00	8.8E-01	6.2E-02	7.0E-02	9.0E-01	2.6E-04	-3.2E-02	1.2E-04	4.8E-01	3.9E-04	-5.9E-02
NAT131	4.0E-05	2.1E-05	2.4E-04	3.3E-06	2.0E-03	8.5E-01	3.4E+00	7.0E-01	7.9E-02	5.5E-02	2.2E-01	2.6E-04	-3.6E-02	9.8E-05	5.2E-01	1.7E-04	7.6E-02
NAT132	2.5E-05	4.6E-05	3.4E-04	2.1E-06	2.2E-03	9.3E-01	2.7E+00	7.5E-01	6.0E-02	8.6E-03	4.3E-02	2.7E-05	-5.2E-02	6.9E-05	5.4E-01	2.3E-04	1.2E-02
NAT133	1.7E-05	1.7E-05	1.0E-04	-1.2E-06	1.7E-03	1.1E+00	2.2E+00	5.1E-01	1.1E-01	5.1E-03	2.8E-02	7.0E-05	-4.3E-02	8.1E-05	5.2E-01	1.9E-04	5.5E-02
NAT140	1.1E-05	5.8E-05	1.1E-04	-2.1E-06	1.3E-03	8.7E-01	2.2E+00	4.8E-01	7.4E-02	1.2E-03	5.5E-03	1.7E-05	-4.0E-02	1.8E-05	5.4E-01	1.1E-03	-6.6E-02
NAT141	2.2E-05	1.2E-05	2.7E-04	1.2E-05	1.1E-03	1.0E+00	2.0E+00	4.9E-01	1.3E-01	3.6E-03	2.7E-02	2.7E-05	-2.2E-04	5.0E-05	5.2E-01	1.6E-04	-4.0E-02
NAT142	1.0E-05	1.2E-05	1.7E-04	5.1E-06	1.1E-03	1.0E+00	1.7E+00	4.2E-01	9.3E-02	1.7E-03	4.4E-03	1.2E-04	-4.4E-02	7.9E-05	5.0E-01	2.0E-04	7.1E-02
NAT143	1.6E-05	2.3E-05	1.1E-04	3.3E-06	1.4E-03	9.2E-01	2.9E+00	3.8E-01	8.9E-02	2.5E-03	1.7E-02	2.3E-05	-4.5E-02	5.4E-05	5.2E-01	4.8E-04	-2.8E-02
NAT144	1.4E-05	1.7E-05	1.0E-04	1.9E-06	1.1E-03	1.7E+00	2.0E+00	4.6E-01	1.2E-01	3.8E-03	7.6E-03	3.3E-05	-4.4E-02	6.1E-05	5.0E-01	2.6E-04	1.3E-02
NAT145	1.5E-05	1.3E-05	1.0E-04	1.8E-06	1.1E-03	1.6E+00	3.5E+00	3.1E-01	1.1E-01	3.2E-03	1.5E-02	3.2E-04	-4.6E-02	6.9E-05	4.9E-01	1.9E-04	2.3E-02
NAT146	2.5E-05	2.2E-05	2.3E-04	3.2E-06	1.0E-03	1.7E+00	2.6E+00	5.3E-01	1.3E-01	6.8E-03	4.3E-02	5.5E-05	1.9E-03	8.5E-05	5.1E-01	3.3E-04	6.6E-02
NAT147	1.3E-05	2.7E-05	1.3E-04	1.3E-06	1.1E-03	1.3E+00	2.5E+00	5.1E-01	1.1E-01	3.0E-03	1.3E-02	7.7E-05	-3.6E-02	3.9E-05	5.1E-01	5.3E-04	-2.6E-02
NAT148	2.3E-05	5.1E-04	2.3E-04	4.1E-07	1.8E-03	1.5E+00	3.3E+00	6.4E-01	1.6E-01	6.2E-03	3.2E-02	2.4E-04	-2.5E-02	9.4E-05	5.0E-01	1.1E-02	9.6E-02
NAT149	4.0E-05	2.6E-05	2.8E-04	1.7E-06	2.1E-03	1.8E+00	2.6E+00	4.6E-01	1.3E-01	7.2E-03	1.7E-01	3.3E-04	-2.8E-02	8.5E-05	5.2E-01	4.3E-04	-1.2E-02
NAT150	1.4E-05	2.5E-05	1.4E-04	-1.2E-07	9.6E-04	1.2E+00	2.2E+00	4.4E-01	1.3E-01	3.3E-03	3.2E-02	7.9E-04	-2.8E-02	3.8E-05	5.1E-01	6.3E-04	-1.7E-02
NAT151	1.0E-04	2.4E-05	4.5E-04	6.2E-06	2.0E-03	1.8E+00	3.0E+00	5.6E-01	1.1E-01	2.3E-02	5.1E-01	4.7E-04	-3.2E-02	2.2E-04	5.1E-01	3.0E-04	7.1E-02
NAT152	1.1E-05	1.1E-05	1.6E-04	1.6E-07	8.9E-04	1.0E+00	2.3E+00	4.1E-01	1.3E-01	2.4E-02	2.0E-02	9.8E-05	4.0E-03	2.8E-05	4.9E-01	1.0E-04	-4.1E-02
NAT153	4.3E-05	1.2E-05	2.4E-04	1.2E-06	9.0E-04	1.7E+00	3.5E+00	5.1E-01	1.4E-01	1.1E-02	2.4E-01	5.5E-03	-2.9E-02	1.7E-04	5.1E-01	1.6E-04	2.1E-01
NAT154	2.1E-04	2.1E-05	8.2E-04	9.7E-06	2.2E-03	1.8E+00	3.6E+00	6.7E-01	1.4E-01	5.1E-02	1.4E+00	2.8E-04	-2.6E-02	3.5E-04	5.2E-01	3.0E-04	1.2E-01
NAT155	2.0E-05	8.3E-05	2.0E-04	-2.0E-07	1.6E-03	9.6E-01	2.9E+00	4.7E-01	1.1E-01	4.0E-03	7.7E-02	1.1E-04	-2.8E-02	8.4E-05	5.0E-01	1.9E-03	5.3E-02
NAT156	8.9E-05	1.1E-05	3.3E-04	2.5E-06	8.4E-04	1.4E+00	4.5E+00	5.1E-01	1.6E-01	2.6E-02	4.3E-01	1.3E-04	-4.0E-02	1.8E-04	4.9E-01	2.8E-04	8.9E-02
NAT133	3.7E-05	3.0E-05	2.3E-04	6.2E-07	1.1E-03	1.0E+00	2.1E+00	4.6E-01	9.4E-02	2.1E-02	1.2E-01	5.9E-05	-4.6E-02	9.5E-05	5.0E-01	2.5E-04	3.3E-02
NAT134	2.2E-05	2.8E-05	1.5E-04	2.6E-07	7.1E-04	9.9E-01	2.4E+00	3.9E-01	7.0E-02	5.1E-03	3.8E-02	1.9E-04	-5.0E-02	1.4E-04	4.9E-01	2.6E-04	2.0E-01
NAT135	1.2E-04	5.7E-05	6.2E-04	3.2E-06	1.2E-03	1.2E+00	1.8E+00	5.4E-01	9.9E-02	1.8E-02	1.0E-01	7.8E-05	-4.5E-02	1.8E-04	5.0E-01	5.4E-04	8.5E-02
NAT136	2.6E-05	2.9E-05	3.3E-04	-8.4E-07	1.3E-03	9.3E-01	2.4E+00	6.4E-01	8.1E-02	3.8E-03	2.3E-02	7.4E-05	-4.0E-02	6.1E-05	5.1E-01	2.9E-04	-6.6E-03
NAT137	6.8E-05	2.8E-05	3.2E-04	3.4E-07	1.6E-03	9.6E-01	2.8E+00	5.6E-01	7.6E-02	1.4E-02	8.9E-02	1.5E-04	-4.6E-02	9.6E-05	5.0E-01	4.2E-04	2.6E-02
NAT138	3.2E-05	2.3E-05	2.4E-04	-1.3E-06	1.0E-03	9.2E-01	2.6E+00	5.4E-01	8.2E-02	3.8E-02	1.8E-01	4.1E-05	-4.8E-02	8.0E-05	5.0E-01	2.6E-04	-1.1E-02
NAT157	6.2E-05	6.6E-05	3.1E-04	2.1E-06	1.6E-03	8.6E-01	3.4E+00	5.6E-01	9.6E-02	2.3E-02	1.3E-01	1.7E-04	-2.5E-02	1.3E-04	5.0E-01	1.1E-03	3.9E-02
NAT158	3.2E-05	1.3E-05	1.8E-04	-2.2E-07	1.1E-03	8.9E-01	2.5E+00	4.7E-01	1.1E-01	3.3E-02	6.9E-02	2.1E-04	-1.9E-02	1.3E-04	5.0E-01	1.4E-04	1.3E-01
NAT159	1.9E-05	1.5E-05	1.4E-04	8.5E-08	1.2E-03	8.3E-01	2.9E+00	5.5E-01	1.0E-01	9.2E-03	4.4E-02	6.2E-05	-2.8E-02	8.3E-05	4.9E-01	1.8E-04	4.7E-02
NAT160	4.1E-05	4.6E-05	2.4E-04	1.6E-06	1.3E-03	8.9E-01	2.1E+00	4.8E-01	1.1E-01	1.1E-02	6.7E-02	1.6E-04	-3.3E-02	1.1E-04	5.1E-01	7.8E-04	3.5E-02

Sample code	Y/Ca	Cd/Ca	Ba/Ca	Th/Ca	U/Ca	Na/Ca	Mg/Ca	P/Ca	S/Ca	Mn/Ca	Fe/Ca	Co/Ca	Zn/Ca	Rb/Ca	Sr/Ca	Pb/Ca	K/Ca
mmol/mol																	
Detection limit	9.1E-06	2.2E-04	4.8E-03	3.0E-05	6.5E-07	2.0E-02	3.1E-03	3.6E-03	1.8E-01	3.4E-04	1.4E-03	5.9E-05	1.4E-02	9.5E-06	7.0E-04	9.6E-06	2.1E-02
Precision %	0.04	0.03	0.01	0.02	0.01	0.01	0.01	0.02	0.01	0.03	0.34	0.016	0.05	0.01	0.01	0.01	0.01
NAT161	1.2E-04	3.8E-05	4.4E-04	1.4E-05	2.0E-03	1.2E+00	3.9E+00	6.7E-01	1.7E-01	3.5E-02	1.8E-01	1.5E-04	3.8E-02	2.9E-04	4.9E-01	3.5E-04	4.4E-01
NAT162	2.8E-05	1.9E-05	2.3E-04	9.6E-06	1.0E-03	9.7E-01	1.8E+00	5.3E-01	1.5E-01	4.7E-02	2.1E-01	2.3E-04	7.3E-03	1.3E-04	4.9E-01	4.1E-04	2.0E-01
NAT163	1.7E-05	2.4E-05	2.0E-04	6.3E-06	1.2E-03	9.4E-01	2.4E+00	5.4E-01	1.5E-01	5.4E-03	2.7E-02	2.8E-05	1.3E-02	5.7E-05	4.9E-01	4.4E-04	9.0E-02
NAT164	8.4E-05	3.3E-05	4.0E-04	9.3E-06	2.3E-03	9.1E-01	5.4E+00	5.8E-01	1.4E-01	1.7E-02	1.0E-01	9.0E-05	8.2E-03	1.9E-04	4.6E-01	3.5E-04	1.9E-01
NAT165	6.3E-05	4.8E-05	4.9E-04	7.5E-06	1.7E-03	9.2E-01	2.1E+00	5.4E-01	1.3E-01	1.2E-02	1.1E-01	7.5E-05	1.8E-02	1.7E-04	5.1E-01	6.4E-04	2.0E-01
NAT166	9.1E-05	6.5E-05	6.3E-04	8.6E-06	2.5E-03	9.8E-01	4.6E+00	7.4E-01	1.5E-01	2.0E-02	1.5E-01	1.1E-04	2.6E-02	2.0E-04	4.9E-01	8.0E-04	1.8E-01
NAT167	2.8E-05	2.2E-05	1.8E-04	2.8E-06	2.0E-03	8.6E-01	2.4E+00	5.8E-01	1.3E-01	7.8E-03	4.2E-02	4.5E-05	1.3E-02	7.6E-05	5.2E-01	3.1E-04	9.9E-02
NAT168	2.3E-05	1.1E-04	1.5E-04	2.5E-06	1.7E-03	8.5E-01	3.1E+00	5.6E-01	1.3E-01	1.1E-02	4.3E-02	2.6E-04	1.3E-02	6.2E-05	5.0E-01	2.3E-03	1.0E-01
NAT169	5.4E-05	4.7E-05	3.6E-04	6.3E-06	1.9E-03	8.0E-01	2.8E+00	5.6E-01	1.4E-01	1.8E-02	1.2E-01	1.5E-04	1.8E-02	1.1E-04	5.0E-01	7.6E-04	1.3E-01
NAT170	4.4E-05	2.9E-05	3.4E-04	3.1E-06	1.6E-03	9.3E-01	2.5E+00	5.4E-01	1.4E-01	8.4E-03	6.4E-02	1.1E-04	2.1E-02	2.0E-04	4.9E-01	3.1E-04	4.2E-01
NAT171	2.4E-05	1.6E-05	3.6E-04	4.4E-06	1.8E-03	8.3E-01	1.9E+00	4.9E-01	1.3E-01	4.9E-03	3.9E-02	5.1E-05	1.5E-02	8.4E-05	4.7E-01	2.9E-04	1.5E-01
NAT172	3.3E-05	1.8E-05	3.1E-04	2.9E-06	1.5E-03	9.6E-01	2.6E+00	5.5E-01	1.4E-01	1.2E-02	8.0E-02	6.9E-05	1.6E-02	1.3E-04	4.6E-01	1.6E-04	2.4E-01
NAT173	1.8E-05	9.8E-05	2.0E-04	3.6E-06	1.2E-03	9.4E-01	2.1E+00	4.7E-01	1.5E-01	3.0E-03	2.0E-02	5.6E-05	8.3E-02	8.5E-05	4.5E-01	3.3E-04	1.9E-01
NAT174	3.1E-05	2.4E-05	2.8E-04	2.7E-06	8.4E-04	9.2E-01	2.1E+00	3.9E-01	1.5E-01	1.2E-02	6.5E-02	5.3E-05	3.3E-02	9.8E-05	4.6E-01	3.3E-04	1.9E-01
NAT175	2.5E-05	1.9E-05	2.0E-04	2.1E-06	1.4E-03	9.5E-01	3.3E+00	4.6E-01	1.4E-01	8.7E-03	5.0E-02	5.0E-05	7.2E-03	8.8E-05	4.7E-01	1.9E-04	1.5E-01
NAT176	2.8E-05	2.0E-05	2.3E-04	1.1E-06	1.3E-03	8.2E-01	1.8E+00	4.9E-01	1.3E-01	1.2E-02	8.0E-02	3.2E-05	2.5E-02	7.9E-05	4.7E-01	2.1E-04	1.3E-01
NAT177	3.3E-05	2.1E-05	3.1E-04	2.3E-06	1.4E-03	1.1E+00	3.9E+00	5.2E-01	1.5E-01	1.8E-02	1.2E-01	4.1E-05	1.1E-02	1.1E-04	4.5E-01	2.7E-04	1.7E-01
NAT178	1.6E-05	1.6E-05	1.8E-04	9.6E-07	1.3E-03	9.4E-01	2.0E+00	4.5E-01	1.3E-01	3.8E-03	1.6E-02	5.5E-05	3.5E-02	7.5E-05	4.6E-01	2.4E-04	1.7E-01
NAT179	2.1E-05	1.6E-05	1.8E-04	1.1E-06	9.3E-04	8.8E-01	1.9E+00	4.5E-01	1.3E-01	1.3E-02	6.3E-02	3.1E-05	8.9E-03	6.6E-05	4.5E-01	2.1E-04	1.1E-01
NAT180	3.0E-05	2.6E-05	2.6E-04	1.5E-06	1.1E-03	1.3E+00	1.9E+00	4.3E-01	1.5E-01	1.3E-02	7.7E-02	5.0E-05	1.4E-02	1.9E-04	4.8E-01	2.6E-04	3.6E-01
NAT181	4.6E-05	4.1E-05	3.9E-04	1.0E-05	1.4E-03	1.1E+00	2.8E+00	5.0E-01	1.3E-01	2.4E-02	1.2E-01	5.3E-05	1.9E-02	1.5E-04	4.9E-01	4.4E-04	2.3E-01
NAT182	2.2E-05	2.2E-05	2.3E-04	5.6E-06	6.6E-04	1.4E+00	2.7E+00	3.2E-01	1.9E-01	9.3E-03	3.6E-02	5.3E-05	1.6E-01	2.5E-04	4.9E-01	1.5E-04	6.1E-01
NAT183	3.0E-05	3.5E-05	3.4E-04	4.4E-06	7.0E-04	1.3E+00	2.6E+00	3.9E-01	1.8E-01	4.3E-02	2.2E-01	5.9E-05	3.7E-02	1.3E-04	4.8E-01	5.5E-04	1.9E-01
NAT184	8.2E-05	1.5E-04	7.8E-04	7.1E-06	1.4E-03	1.1E+00	8.3E+00	6.5E-01	1.7E-01	7.9E-02	4.2E-01	1.6E-04	4.5E-02	2.2E-04	4.5E-01	1.1E-03	1.8E-01
NAT185	4.8E-05	5.9E-05	4.2E-04	3.1E-06	1.2E-03	1.1E+00	4.1E+00	5.6E-01	2.9E-01	3.7E-02	2.0E-01	1.1E-04	7.3E-02	1.3E-04	5.1E-01	5.9E-04	1.4E-01
NAT186	4.8E-05	4.6E-05	8.5E-04	2.9E-06	1.0E-03	1.3E+00	3.5E+00	5.3E-01	1.7E-01	2.2E-02	1.8E-01	5.5E-05	6.2E-02	2.2E-04	5.2E-01	1.6E-03	4.3E-01
NAT187	3.6E-05	5.7E-05	4.3E-04	4.7E-06	9.5E-04	1.2E+00	1.5E+00	4.6E-01	1.7E-01	1.1E-02	4.0E-01	7.7E-05	5.1E-02	1.2E-04	5.0E-01	4.2E-04	1.5E-01
NAT188	1.1E-04	6.3E-05	9.8E-04	3.1E-06	8.5E-04	1.9E+00	3.9E+00	9.5E-01	8.4E-01	5.1E-02	1.5E-01	5.7E-05	1.5E+00	2.0E-04	4.7E-01	6.1E-04	4.2E-01

Table 14: Trace element measurements in mmol/mol of sample stalagmite from Aklagavi. Measurements below detection limit are given in grey.

Searching for station nr 43041 in

v2.temperature.inv

JAGDALPUR INDIA (INDIA)

coordinates: 19.10N, 82.00E, 553m

WMO station code: 43041 JAGDALPUR

prcp from v2.prcp [mm/month]

Year	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	JJAS total	ONDJ total	FMAM total	Annual total
1910	0	0	0	51	56	251	503	325	301	273	26	0	1380	299	107	1786
1911	0	0	20	7	69	270	344	458	316	158	36	1	1388	195	96	1679
1912	0	57	0	67	64	37	461	373	335	50	21	0	1206	71	188	1465
1913	0	29	0	42	20	164	328	307	278	100	1	0	1077	101	91	1269
1914	0	3	20	71	66	451	363	317	405	23	0	24	1536	47	160	1743
1915	51	46	31	55	88	219	262	447	201	94	12	0	1129	157	220	1506
1916	0	1	0	33	43	130	272	362	241	71	21	0	1005	92	77	1174
1917	0	41	0	43	119	361	326	186	542	374	3	0	1415	377	203	1995
1918	39	0	11	27	106	284	296	535	196	16	5	21	1311	81	144	1536
1919	31	202	38	8	49	336	362	433	186	217	66	14	1317	328	297	1942
1920	10	1	6	65	23	155	267	281	95	50	0	0	798	60	95	953
1921	19	0	0	31	0	263	255	310	248	60	0	0	1076	79	31	1186
1922	2	0	0	8	63	260	487	260	277	104	51	0	1284	157	71	1512
1923	0	25	5	66	20	81	195	199	183	88	19	0	658	107	116	881
1924	45	0	1	44	50	152	204	405	378	119	153	0	1139	317	95	1551
1925	0	0	1	45	259	371	541	905	170	46	1	0	1987	47	305	2339
1926	88	0	25	105	60	287	346	776	405	61	0	0	1814	149	190	2153
1927	6	1	46	10	61	433	552	659	87	153	14	0	1731	173	118	2022
1928	0	1	12	17	36	155	652	314	432	98	0	0	1553	98	66	1717
1929	0	109	1	94	20	359	674	772	256	86	0	24	2061	110	224	2395
1930	0	0	44	39	20	278	237	223	305	87	108	5	1043	200	103	1346
1931	0	2	6	78	50	34	248	555	248	186	88	0	1085	274	136	1495
1932	0	25	0	34	46	114	532	480	278	13	77	0	1404	90	105	1599
1933	1	1	12	25	120	361	366	355	256	71	37	27	1338	136	158	1632
1934	0	0	1	37	4	353	533	663	304	167	25	0	1853	192	42	2087
1935	1	0	1	27	24	134	433	259	273	12	0	0	1099	13	52	1164
1936	0	82	14	2	125	498	632	452	292	98	36	0	1874	134	223	2231
1937	0	146	34	111	12	114	491	203	196	43	0	0	1004	43	303	1350
1938	1	25	28	64	69	253	265	293	253	312	37	0	1064	350	186	1600
1939	4	5	26	69	6	144	314	208	228	241	26	0	894	271	106	1271
1940	0	22	25	29	107	316	291	413	51	126	31	6	1071	163	183	1417
1941	1	0	26	14	93	358	140	233	129	51	26	0	860	78	133	1071
1942	0	38	2	126	78	138	506	393	147	17	5	0	1184	22	244	1450
1943	44	0	0	54	123	214	341	296	181	76	6	0	1032	126	177	1335
1944	14	25	78	95	93	97	483	322	289	122	11	0	1191	147	291	1629
1945	25	0	0	93	23	119	383	357	485	89	44	11	1344	169	116	1629
1946	0	4	5	111	78	194	564	398	252	112	5	0	1408	117	198	1723
1947	28	1	24	39	20	217	557	387	350	109	35	22	1511	194	84	1789
1948	0	11	19	44	40	206	214	247	351	52	113	0	1018	165	114	1297
1949	0	0	1	27	52	254	179	372	235	268	0	0	1040	268	80	1388
1950	0	29	12	26	22	120	368	318	84	21	91	0	890	112	89	1091

Year	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	JIAS total	ONDI total	FMAM total	Annual total
1951	0	0	55	22	107	184	562	336	136	74	4	0	1218	78	184	1480
1952	0	5	3	67	58	106	549	299	393	87	0	40	1347	127	133	1607
1953	23	0	0	46	31	260	195	586	215	130	8	0	1256	161	77	1494
1954	0	0	16	64	53	97	457	462	454	116	0	0	1470	116	133	1719
1955	0	2	52	65	26	165	303	515	237	246	6	0	1220	252	145	1617
1956	0	5	0	3	121	253	504	515	133	60	0	0	1405	60	129	1594
1957	0	3	38	45	62	258	497	478	74	151	0	0	1307	151	148	1606
1958	1	4	16	52	105	73	369	357	344	170	20	0	1143	191	177	1511
1959	16	0	0	17	65	411	338	383	309	115	0	9	1441	140	82	1663
1960	0	0	23	46	154	312	323	301	215	139	1	0	1151	140	223	1514
1961	1	50	50	50	109	274	358	294	255	220	49	0	1181	270	259	1710
1962	8	32	1	105	43	221	363	402	188	13	10	69	1174	100	181	1455
1963	0	0	10	104	76	114	236	429	306	191	0	0	1085	191	190	1466
1964	0	59	6	129	25	141	197	479	237	163	1	0	1054	164	219	1437
1965	8	1	24	18	79	216	408	212	191	1	0	0	1027	9	122	1158
1966	64	0	3	55	30	177	279	345	248	34	7	13	1049	118	88	1255
1967	1	0	67	48	11	328	264	364	197	32	0	122	1153	155	126	1434
1968	20	15	40	142	62	211	351	117	404	174	25	4	1083	223	259	1565
1969	0	0	7	32	64	130	615	302	367	68	31	2	1414	101	103	1618
1970	5	7	43	97	32	328	253	638	176	17	0	0	1395	22	179	1596
1971	6.6	16.8	0.1	113.1	181.1	265.9	207.7	407.1	174.7	69.4	0	0	1055.4	76	311.1	1442.5
1972	0	25.2	0	8.8	39	191.8	462.7	240.6	341.8	70.6	78.4	0	1236.9	149	73	1458.9
1973	0	0	9.2	39.7	13.4	304.7	20.4	236.4	96.3	200.6	0.5	0.1	657.8	201.2	62.3	921.3
1974	0	0	5.1	24.4	91.8	468.1	240	162.4	118.7	109.9	26.7	0	989.2	136.6	121.3	1247.1
1975	2.1	11.9	0.2	52.6	85.2	529.2	271.8	434.3	418.8	269	4.4	0	1654.1	275.5	149.9	2079.5
1976	0	0	9.6	50.9	113.8	135	418.2	407.8	198.2	0	45.3	6.8	1159.2	52.1	174.3	1385.6
1977	0	0	0.2	120.2	71.6	211.4	344.1	441.4	110.6	46.3	125.1	34	1107.5	205.4	192	1504.9
1978	21.9	16.6	19.2	75.9	60.6	275	343.1	417.3	209.9	44	50.9	0	1245.3	116.8	172.3	1534.4
1979	0	11.2	0	21	17	405.8	363.3	425.9	238.2	107.2	5.8	11.2	1433.2	124.2	49.2	1606.6
1980	0	0	5.4	40.9	42.2	432.9	471.9	217.6	249.8	33	0.1	0	1372.2	33.1	88.5	1493.8
1981	25	0	31	97	88	164	256	321	253	35	1	0	994	61	216	1271
1982	1	6	15	62	45	235	369	455	214	23	41	0	1273	65	128	1466
1983	0	26	15	8	83	216	354	321	199	75	4	8	1090	87	132	1309
1984	6	12	4	5	95	306	392	322	121	44	0	0	1141	50	116	1307
1985	39	0	4	2	45	387	296	389	237	199	0	2	1309	240	51	1600
1986	33	29	2	51	30	263	324	469	103	43	73	12	1159	161	112	1432
1987	3	0	13	23	98	179	248	338	86	51	19	0	851	73	134	1058
1988	0	0	3	69	109	204	440	282	163	31	10	2	1089	43	181	1313
1989	0	0	41	13	98	215	290	401	230	18	0	4	1136	22	152	1310
1990	4	69	60	19	342	308	370	599	187	268	28	8	1464	308	490	2262

Year	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	JJAS total	ONDJ total	FMAM total	Annual total
1991	13	0	16	46	108	275.5	433	287	226	62	29	0	1221.5	104	170	1495.5
1992	6	1	0	15	68	243	409	376	134	31	30	0	1162	67	84	1313
1993	0	0	17	20	113	229	343	221	255	186	0	0	1048	186	150	1384
1994	0	1	0	21	147	172	438	396	191	64	17	0	1197	81	169	1447
1995	6	0	57	27	127	134.5	469	251	230	162	24	0	1084.5	192	211	1487.5
1996	10	1	6	73	2	97	303	271	123	39	31	0	794	80	82	956
1997	18	0	67	84	49.5	70	230	226	198	8	85	0	724	111	200.5	1035.5
1998	0	28	0	33	97	173	265	157	162	173	113	0	757	286	158	1201
1999	0	0	0	0	87	261	160	757	191	88	1	0	1369	89	87	1545
2000	0	58	0	35	60	410	238	377	105	122	0	0	1130	122	153	1405
2001	28.5	0	4	53	111	301	345	511	113	60	60	0	1270	148.5	168	1586.5
2002	57	0	8	53	66	202	219	474	75	20	0	0	970	77	127	1174
2003	0	16	42	18	4	49	549	403	135	299	0	90	1136	389	80	1605
2004	56	11	1	34	51	332	389	321	323	120	3	0	1365	179	97	1641
2005	22	22	8	26	89	185	308	253	344	229	3	0	1090	254	145	1489
2006	0	0	44	130	90	117	488	272	311	1	91	0	1188	92	264	1544
2007	0	15	0	12	50	287	202	377	158	96	0	12	1024	108	77	1209
2008	10	18	136	18	42	287	394	292	255	6	2	0	1228	18	214	1460
2009	0	0	12	6	148	94	484	267	149	51	10	0	994	61	166	1221
2010	23	6	19	72	76	236	483	497	363	155	75	25	1579	278	173	2030
2011	0	9	0	69	173	111	245	300	305	1	0	12.5	961	13.5	251	1225.5
2012	26	0	1	126	89	148	533	546	333	42	26	0	1560	94	216	1870
2013	0	3	0	104	45	544	266	229	145	204	7	0	1184	211	152	1547
2014	0	3	40	58	95	167	359	276	457	84	2	0	1259	86	196	1541
2015	0	5	52	77	87	492	157	435	490	10	0	0	1574	10	221	1805

Table 15: GHCNM monthly rainfall amount data (in mm) for Jagdalpur sourced from KNMI Explorer. Calculated JJAS (monsoon), FMAM (summer), ONDJ (winter) and annual total rainfall amounts have been given in the last 4 columns.

Searching for station nr 43041 in ghcnm.tavg.v3.qcu v3.3.0.20160801
JAGDALPUR (INDIA)
coordinates: 19.08N, 82.03E, 553.0m (prob: 512m)
WMO station code: 43041 JAGDALPUR
tavg [Celsius] daily mean temperature (unadjusted) from GHCN-M
v3.3.0.20160801

Year	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	JJAS mean	ONDJ mean	FMAM mean	Annual mean
1910	19.4	21.5	26.7	30.9	31.8	28.4	25.9	25.4	25.8	24.7	19.7	16.8	26.4	20.2	27.7	24.8
1911	19.5	22.2	26.1	30.1	31.8	27.2	25.7	24.4	25.7	24.4	22.0	18.2	25.8	21.0	27.6	24.8
1912	19.2	22.9	27.5	29.3	31.9	30.9	25.0	25.0	25.7	24.8	21.2	17.8	26.7	20.8	27.9	25.1
1913	18.3	23.1	26.4	31.0	31.2	27.7	25.4	24.9	25.7	24.2	20.6	19.3	25.9	20.6	27.9	24.8
1914	18.5	23.5	26.9	27.6	30.2	28.1	25.1	25.2	25.4	24.3	21.4	19.2	26.0	20.9	27.1	24.6
1915	19.3	22.2	25.6	29.7	31.7	30.1	26.2	25.8	25.9	25.5	23.6	19.1	27.0	21.9	27.3	25.4
1916	18.8	22.4	26.3	30.5	30.9	26.6	26.1	25.4	25.9	25.4	22.6	18.0	26.0	21.2	27.5	24.9
1917	18.9	21.2	25.3	28.9	27.2	26.0	24.7	25.3	25.1	24.2	21.4	18.0	25.3	20.6	25.7	23.9
1918	18.7	21.3	25.8	28.9	29.2	25.7	25.9	24.6	25.8	24.1	23.3	20.0	25.5	21.5	26.3	24.5
1919	21.3	23.0	26.3	29.4	29.9	26.6	25.6	24.7	25.8	24.5	22.1	18.6	25.7	21.6	27.2	24.8
1920	19.7	22.4	26.9	29.5	30.2	29.2	25.2	25.2	26.2	25.2	21.3	18.1	26.5	21.1	27.3	24.9
1921	20.3	22.0	27.5	30.1	34.7	28.9	25.9	25.1	25.2	23.9	19.1	18.6	26.3	20.5	28.6	25.1
1922	19.8	21.9	27.2	30.9	32.1	28.5	24.8	25.6	25.4	24.2	22.1	17.4	26.1	20.9	28.0	25.0
1923	19.1	22.1	25.6	29.6	32.1	31.8	25.2	24.7	26.0	24.0	21.2	18.7	26.9	20.8	27.4	25.0
1924	19.9	23.1	27.2	30.7	31.8	30.7	25.8	25.7	25.5	24.1	21.0	18.1	26.9	20.8	28.2	25.3
1925	19.0	21.4	25.9	30.2	29.1	27.3	24.3	24.9	26.1	24.7	22.4	18.6	25.7	21.2	26.7	24.5
1926	20.8	23.1	26.7	28.7	30.1	31.8	25.7	24.9	25.8	24.1	20.7	19.0	27.1	21.2	27.2	25.1
1927	22.1	23.8	27.2	31.2	31.9	28.9	24.9	24.6	25.8	23.9	20.7	18.8	26.1	21.4	28.5	25.3
1928	19.8	22.1	26.4	29.8	31.9	28.6	25.2	25.7	25.7	25.4	20.6	19.3	26.3	21.3	27.6	25.0
1929	20.5	20.8	25.9	27.8	31.8	27.8	24.7	24.7	26.0	23.6	20.0	19.7	25.8	21.0	26.6	24.4
1930	19.3	20.9	26.3	29.2	31.3	28.7	25.1	24.9	25.4	24.7	20.2	18.8	26.0	20.8	26.9	24.6
1931	18.9	23.2	26.3	30.1	31.8	30.7	25.5	25.2	26.3	25.0	21.0	18.4	26.9	20.8	27.9	25.2
1932	18.8	20.9	26.3	29.7	31.2	29.7	24.8	25.6	25.6	25.5	22.4	18.6	26.4	21.3	27.0	24.9
1933	19.9	23.7	26.4	29.5	29.7	26.0	25.6	25.4	25.4	24.5	21.5	19.4	25.6	21.3	27.3	24.8
1934	19.3	21.8	26.5	30.2	32.7	28.7	25.3	25.2	25.4	23.8	20.4	18.5	26.2	20.5	27.8	24.8
1935	19.9	22.8	26.5	28.8	33.1	30.9	24.6	25.2	25.5	24.9	20.7	19.8	26.6	21.3	27.8	25.2
1936	22.3	22.0	26.8	29.9	31.1	25.8	25.6	24.7	26.0	24.7	23.2	19.7	25.5	22.5	27.5	25.2
1937	18.9	23.1	26.2	26.5	32.1	29.6	24.9	25.4	25.6	24.5	21.2	18.9	26.4	20.9	27.0	24.7
1938	22.2	22.3	27.9	30.0	31.4	25.9	25.4	25.7	25.7	24.1	20.1	18.4	25.7	21.2	27.9	24.9
1939	20.2	22.9	26.0	30.2	33.1	29.7	24.7	25.2	25.5	25.3	20.5	18.3	26.3	21.1	28.1	25.1
1940	17.7	22.2	25.5	29.3	30.5	27.8	24.3	25.0	26.4	25.2	22.6	19.9	25.9	21.4	26.9	24.7
1941	21.1	23.3	27.6	31.7	31.8	27.5	25.7	25.8	26.3	24.2	19.6	19.7	26.3	21.2	28.6	25.4
1942	19.7	22.6	27.1	29.8	32.3	30.2	24.5	25.3	26.7	23.4	20.7	19.9	26.7	20.9	28.0	25.2
1943	21.5	20.2	26.3	28.7	30.4	27.3	25.2	24.8	25.8	24.7	21.2	17.2	25.8	21.2	26.4	24.4
1944	19.5	21.4	24.2	27.3	30.8	29.2	24.5	24.6	24.9	24.0	19.9	18.0	25.8	20.4	25.9	24.0
1945	18.6	21.0	25.9	27.9	31.2	28.6	24.9	25.0	25.3	24.6	19.1	19.6	26.0	20.5	26.5	24.3
1946	16.7	20.5	26.9	27.1	30.4	26.9	25.2	24.7	25.7	25.1	23.5	21.1	25.6	21.6	26.2	24.5
1947	21.5	21.2	27.2	31.1	32.5	29.2	24.5	25.5	25.3	23.8	20.4	18.6	26.1	21.1	28.0	25.1
1948	20.3	23.2	25.3	29.8	31.9	29.9	26.2	25.1	25.3	24.8	23.4	17.3	26.6	21.5	27.6	25.2
1949	18.9	21.2	26.8	29.4	30.5	27.8	25.1	25.4	25.4	24.7	21.7	17.5	25.9	20.7	27.0	24.5
1950	19.0	21.9	25.3	29.9	31.8	28.3	24.5	25.5	25.7	23.8	20.2	17.6	26.0	20.2	27.2	24.5

Year	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	IJAS mean	ONDJ mean	FMAJ mean	Annual mean
1951	18.7	22.5	26.3	28.8	30.1	28.1	25.9	24.6	26.2	25.7	21.9	19.2	26.2	21.4	26.9	24.8
1952	20.1	23.1	25.9	29.6	31.1	30.1	25.9	25.1	24.9	24.7	20.5	20.2	26.5	21.4	27.4	25.1
1953	20.3	23.3	28.3	29.7	33.4	30.7	25.9	25.0	26.8	25.7	21.6	18.9	27.1	21.6	28.7	25.8
1954	19.8	23.7	26.7	30.7	31.6	29.1	25.9	25.9	25.4	24.3	20.1	20.2	26.6	21.1	28.2	25.3
1955	20.4	24.1	27.5	29.3	30.3	29.2	25.5	25.8	25.7	25.0	20.6	18.4	26.6	21.1	27.8	25.2
1956	20.9	21.6	27.8	30.9	30.7	26.8	24.9	25.3	25.7	24.5	22.6	20.2	25.7	22.1	27.8	25.2
1957	21.5	22.9	25.7	29.1	30.9	28.7	24.8	25.5	26.5	26.1	22.1	20.4	26.4	22.5	27.2	25.4
1958	20.9	23.5	26.9	30.1	30.9	31.1	24.9	26.1	25.9	25.1	23.1	19.9	27.0	22.3	27.9	25.7
1959	20.7	23.4	27.0	30.2	31.7	28.3	25.3	24.9	25.5	25.3	21.3	19.4	26.0	21.7	28.1	25.3
1960	20.6	22.7	26.0	30.1	31.1	28.5	25.5	25.1	26.4	24.5	21.7	20.9	26.4	21.9	27.5	25.3
1961	21.0	22.0	28.3	30.3	30.9	27.6	24.9	25.4	24.8	24.7	20.6	18.7	25.7	21.3	27.9	24.9
1962	18.3	21.9	24.5	28.7	30.5	27.8	24.9	25.2	26.1	25.2	21.6	19.7	26.0	21.2	26.4	24.5
1963	19.0	22.5	26.6	27.8	30.6	28.2	25.5	25.3	25.9	25.4	22.5	19.7	26.2	21.7	26.9	24.9
1964	21.8	23.8	27.6	30.5	32.3	28.5	25.8	24.5	26.0	25.3	22.0	19.6	26.2	22.2	28.6	25.6
1965	20.6	23.0	26.6	29.5	30.8	29.2	25.4	26.2	26.0	25.6	22.5	20.9	26.7	22.4	27.5	25.5
1966	20.4	23.8	27.5	30.3	33.0	28.7	26.7	25.9	26.2	25.3	24.0	19.7	26.9	22.4	28.7	26.0
1967	20.9	23.5	25.3	29.7	32.5	29.5	26.3	25.1	26.0	24.5	22.0	21.8	26.7	22.3	27.8	25.6
1968	20.0	23.3	25.4	27.6	30.8	29.3	25.8	25.3	25.9	24.5	22.4	20.2	26.6	21.8	26.8	25.0
1969	20.5	24.7	28.7	31.3	30.3	28.6	25.0	25.4	25.6	25.1	23.2	19.0	26.2	22.0	28.8	25.6
1970	20.4	24.7	27.3	29.2	31.9	26.7	25.3	25.3	25.9	25.6	20.8	17.8	25.8	21.2	28.3	25.1
1971	20.7	23.7	25.9	28.3	29.0	26.0	25.3	25.4	26.1	24.8	20.0	18.1	25.7	20.9	26.7	24.4
1972	19.3	22.4	27.7	29.6	32.2	31.2	25.9	25.6	25.8	24.3	22.0	21.4	27.1	21.8	28.0	25.6
1973	21.9	24.6	27.8	32.0	33.5	29.5	25.2	25.3	26.2	25.4	21.2	19.3	26.6	22.0	29.5	26.0
1974	19.5	24.0	28.0	31.4	30.9	28.8	26.2	25.5	26.5	25.2	21.5	18.8	26.8	21.3	28.6	25.5
1975	19.2	23.6	27.9	31.2	32.8	27.6	25.5	25.7	25.5	25.8	20.9	18.3	26.1	21.1	28.9	25.3
1976	18.4	22.9	27.5	29.7	31.5	28.8	25.0	25.3	25.8	25.7	24.6	21.4	26.2	22.5	27.9	25.6
1977	20.8	23.8	28.6	28.8	29.6	29.7	25.8	25.3	25.2	24.1	23.7	18.3	26.5	21.7	27.7	25.3
1978	18.4	21.8	26.0	29.2	31.9	28.9	25.2	24.5	25.7	24.7	22.8	18.9	26.1	21.2	27.2	24.8
1979	20.2	22.8	26.2	30.0	31.0	29.6	26.6	25.4	26.2	24.8	23.3	19.3	27.0	21.9	27.5	25.5
1980	20.5	23.2	27.3	30.8	32.1	27.2	25.1	25.3	25.5	24.0	20.9	20.0	25.8	21.4	28.4	25.2
1981	18.6	22.9	25.7	30.0	30.5	28.7	25.7	25.2	26.1	24.5	20.9	19.3	26.4	20.8	27.3	24.8
1982	20.9	23.6	27.3	29.7	30.4	29.4	26.7	24.6	25.8	24.7	22.1	19.6	26.6	21.8	27.8	25.4
1983	19.9	23.5	27.5	30.7	31.2	30.5	26.6	25.7	25.9	24.5	20.0	18.5	27.2	20.7	28.2	25.4
1984	21.3	22.8	26.2	28.6	32.1	26.8	25.4	25.0	25.2	24.8	19.6	19.6	25.6	21.3	27.4	24.8
1985	21.1	22.1	27.5	30.5	31.4	28.0	25.4	25.2	25.3	23.4	20.5	19.8	26.0	21.2	27.9	25.0
1986	18.8	22.8	26.9	30.0	32.0	27.4	25.7	25.3	26.4	25.0	21.8	20.4	26.2	21.5	27.9	25.2
1987	19.8	21.6	25.4	30.0	29.3	29.4	25.8	26.0	26.7	25.0	22.4	19.7	27.0	21.7	26.6	25.1
1988	20.3	23.4	27.1	29.4	32.0	28.7	25.3	25.5	26.0	23.7	20.6	19.7	26.4	21.1	28.0	25.1
1989	19.4	22.0	25.8	30.2	32.0	27.7	26.0	25.7	25.8	24.7	21.8	18.9	26.3	21.2	27.5	25.0
1990	20.0	22.9	25.6	29.6	27.6	26.7	25.0	25.6	26.1	24.3	22.8	20.2	25.9	21.8	26.4	24.7

Year	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	JJAS mean	ONDJ mean	FMAM mean	Annual mean
1991	20.5	24.0	27.8	30.0	31.2	28.2	25.9	25.5	26.5	25.0	21.4	19.1	26.5	21.5	28.3	25.4
1992	19.0	22.0	27.6	30.2	31.3	28.8	26.6	25.1	26.1	25.2	23.8	18.8	26.7	21.7	27.8	25.4
1993	20.6	22.2	26.4	30.1	31.4	29.1	26.3	25.7	26.0	26.0	22.1	18.9	26.8	21.9	27.5	25.4
1994	21.1	23.1	28.2	30.1	31.1	28.0	25.1	24.7	25.8	25.8	22.3	18.8	25.9	22.0	28.1	25.3
1995	19.1	23.0	26.9	29.5	28.4	29.9	25.8	26.5	26.5	25.9	22.6	20.3	27.2	22.0	27.0	25.4
1996	21.9	23.4	27.7	29.5	32.0	29.0	26.5	25.7	27.0	25.6	22.8	19.6	27.1	22.5	28.2	25.9
1997	19.2	22.0	27.1	26.6	30.4	29.7	26.6	25.6	26.4	25.4	24.8	22.7	27.1	23.0	26.5	25.5
1998	21.8	23.6	27.1	30.2	31.9	30.0	26.6	26.6	27.0	26.3	23.8	18.5	27.6	22.6	28.2	26.1
1999	18.7	24.3	27.3	31.9	30.1	27.7	25.8	25.1	25.7	26.0	22.0	19.1	26.1	21.5	28.4	25.3
2000	20.3	23.2	26.1	31.1	30.8	27.1	26.2	25.9	26.5	25.9	22.9	19.3	26.4	22.1	27.8	25.4
2001	20.3	23.7	26.7	28.9	31.3	26.5	25.4	25.3	27.1	25.9	24.1	19.7	26.1	22.5	27.7	25.4
2002	20.3	23.5	27.3	30.3	32.5	28.1	27.1	24.9	26.1	26.1	22.1	20.7	26.6	22.3	28.4	25.8
2003	20.5	24.2	26.5	29.9	33.1	31.0	25.4	25.3	25.7	25.3	21.9	19.1	26.9	21.7	28.4	25.7
2004	19.4	21.1	26.7	29.5	30.0	26.8	25.2	24.5	26.1	24.9	21.8	19.5	25.7	21.4	26.8	24.6
2005	21.0	23.5	27.5	29.9	31.3	28.9	25.7	25.6	26.3	25.7	21.3	19.9	26.6	22.0	28.1	25.6
2006	20.2	23.3	26.3	29.3	29.8	28.7	25.7	25.1	26.5	25.5	22.9	20.7	26.5	22.3	27.2	25.3
2007	20.6	22.5	26.5	29.9	31.7	28.7	26.5	26.1	26.3	25.1	22.0	21.0	26.9	22.2	27.7	25.6
2008	20.6	22.2	26.4	29.5	31.7	27.3	25.7	25.4	26.0	25.6	23.3	21.1	26.1	22.7	27.5	25.4
2009	21.5	24.6	27.1	30.9	31.1	29.9	25.4	26.5	27.5	24.8	23.7	20.3	27.3	22.6	28.4	26.1
2010	19.9	23.5	28.5	31.2	31.3	29.2	25.9	26.3	26.7	25.5	24.2	19.4	27.0	22.3	28.6	26.0
2011	19.7	22.6	26.9	28.1	30.5	28.1	26.5	26.3	25.9	25.7	22.4	19.9	26.7	21.9	27.0	25.2
2012	20.3	23.4	26.7	29.5	31.5	29.2	24.7	24.8	25.8	24.8	22.1	20.9	26.1	22.0	27.8	25.3
2013	21.1	23.1	26.6	29.1	31.9	26.7	24.7	25.3	26.1	24.6	21.7	19.2	25.7	21.7	27.7	25.0
2014	20.8	22.4	25.9	29.6	29.9	29.7	25.4	26.0	25.9	25.0	22.3	19.3	26.8	21.9	27.0	25.2
2015	19.5	23.1	26.6	27.9	30.8	26.7	26.9	25.9	26.4	25.9	23.1	22.2	26.5	22.7	27.1	25.4

Table 16: GHCNM monthly mean temperature data (in °C) for Jagdalpur sourced from KNMI Explorer. Calculated JJAS (monsoon), FMAM (summer), ONDJ (winter) and annual means have been given in the last 4 columns.

	January	February	March	April	May	June	July	August	September	October	November	December
Hyderabad	0	81	30.5	13	65	216	126	469	51	22	2	1
Jagdalpur	0	58	0	35	60	410	238	377	105	122	0	0

Table 17: Rainfall amount data for Hyderabad and Jagdalpur. Data sourced from KNMI explorer for the year 2000.

Wavenumber (cm-1)	Absorbance			Wavenumber (cm-1)	Absorbance		
	NKF1	NKF2	NKF3		NKF1	NKF2	NKF3
649.9	0.000729	0.000499	0.000707	752.1	0.001393	0.000883	0.001049
651.8	0.00075	0.000507	0.000712	754.0	0.001449	0.000928	0.00108
653.8	0.000787	0.000528	0.000729	756.0	0.001516	0.000972	0.001103
655.7	0.000815	0.000565	0.000756	757.9	0.001583	0.001006	0.00113
657.6	0.000831	0.000582	0.000777	759.8	0.001649	0.001025	0.001168
659.5	0.000861	0.000556	0.000781	761.7	0.00171	0.00104	0.001205
661.5	0.000908	0.000516	0.000769	763.7	0.001763	0.001063	0.001235
663.4	0.000944	0.000497	0.000757	765.6	0.001813	0.001097	0.001265
665.3	0.000966	0.00051	0.000784	767.5	0.001861	0.001141	0.001298
667.3	0.001005	0.000565	0.00089	769.5	0.001899	0.001188	0.001335
669.2	0.001058	0.000651	0.001014	771.4	0.001924	0.001226	0.001373
671.1	0.00109	0.000719	0.001046	773.3	0.001945	0.001245	0.001403
673.0	0.001124	0.000757	0.001039	775.2	0.001982	0.001256	0.001425
675.0	0.001174	0.000782	0.001055	777.2	0.00204	0.001269	0.001441
676.9	0.001224	0.0008	0.001102	779.1	0.002091	0.001288	0.001459
678.8	0.00127	0.000825	0.001166	781.0	0.002118	0.001317	0.001484
680.8	0.001316	0.000873	0.001226	783.0	0.002129	0.00135	0.001514
682.7	0.001359	0.000934	0.001267	784.9	0.002148	0.00138	0.001541
684.6	0.001414	0.000988	0.001295	786.8	0.002191	0.001408	0.001569
686.5	0.001495	0.00103	0.001332	788.7	0.002254	0.00144	0.001601
688.5	0.001587	0.001083	0.001389	790.7	0.002319	0.001471	0.001634
690.4	0.001685	0.00116	0.001464	792.6	0.002369	0.001493	0.001669
692.3	0.001803	0.001262	0.001555	794.5	0.0024	0.00152	0.001712
694.3	0.001953	0.00139	0.00167	796.5	0.002424	0.001556	0.00175
696.2	0.002154	0.001561	0.00183	798.4	0.002454	0.001585	0.001762
698.1	0.002429	0.001804	0.002059	800.3	0.002495	0.001598	0.001755
700.0	0.002806	0.002154	0.002381	802.2	0.002548	0.001611	0.001762
702.0	0.003358	0.002672	0.002863	804.2	0.002609	0.001647	0.001805
703.9	0.004286	0.003554	0.003672	806.1	0.002671	0.0017	0.001878
705.8	0.005967	0.005228	0.005116	808.0	0.002731	0.001747	0.001959
707.8	0.008698	0.008099	0.007427	810.0	0.002793	0.001794	0.002033
709.7	0.011804	0.011566	0.01005	811.9	0.002855	0.001857	0.002094
711.6	0.013158	0.013401	0.011316	813.8	0.002914	0.001918	0.002139
713.5	0.011203	0.01176	0.009954	815.7	0.002978	0.001955	0.002174
715.5	0.007324	0.007876	0.006894	817.7	0.003059	0.001977	0.002212
717.4	0.004006	0.004351	0.004063	819.6	0.003157	0.00201	0.002262
719.3	0.002184	0.002289	0.002346	821.5	0.003262	0.002073	0.002326
721.2	0.001446	0.001361	0.001544	823.5	0.003357	0.002166	0.002397
723.2	0.001187	0.000978	0.0012	825.4	0.003449	0.002273	0.002479
725.1	0.001083	0.000809	0.001034	827.3	0.00357	0.002385	0.002585
727.0	0.00104	0.000733	0.000952	829.2	0.00374	0.002505	0.002722
729.0	0.001047	0.000709	0.000928	831.2	0.003939	0.002639	0.002878
730.9	0.001083	0.000716	0.00094	833.1	0.004144	0.002789	0.003046
732.8	0.001117	0.000738	0.000962	835.0	0.004362	0.002952	0.003224
734.7	0.001139	0.000748	0.000971	837.0	0.004627	0.003137	0.003435
736.7	0.001156	0.000733	0.000952	838.9	0.004971	0.003377	0.003718
738.6	0.001175	0.000712	0.000925	840.8	0.00544	0.003734	0.004124
740.5	0.001203	0.000709	0.000916	842.7	0.006126	0.004329	0.00474
742.5	0.00124	0.000727	0.000926	844.7	0.007016	0.005201	0.005567
744.4	0.001277	0.000759	0.000946	846.6	0.00776	0.006006	0.006298
746.3	0.001308	0.000793	0.000968	848.5	0.008019	0.006286	0.00659
748.2	0.001332	0.00082	0.000989	850.5	0.008077	0.006217	0.00665
750.2	0.001356	0.000846	0.001015				

Table 18: FTIR measurements for stalagmite from Kotumsar cave. Only the measurements relevant for distinguishing between calcite and aragonite mineralogy have been shown, not the whole spectrum till 4000 cm⁻¹.

Lamina	Non-lam	Core/DRAW	Sample scale (mm)	Height	Lamina width	Depth	Lamina	Non-lam	Core/DRAW	Sample scale (mm)	Height	Lamina width	Depth
	mm	mm	Scale (1:2)	mm	cm	cm		mm	mm	Scale (1:2)	mm	cm	cm
	15	30	15	15	1.5	31.25	61		0.71	0.355	60.72	0.0355	25.2
1		0.15	0.075	15.075	0.0075	29.75	62		0.62	0.31	61.03	0.031	25.18
2		0.3	0.15	15.225	0.015	29.74	63		0.85	0.425	61.455	0.0425	25.14
3		0.55	0.275	15.5	0.0275	29.72	64		1.23	0.615	62.07	0.0615	25.10
4		0.42	0.21	15.71	0.021	29.70	65		0.61	0.305	62.375	0.0305	25.04
5		0.4	0.2	15.91	0.02	29.68	66		0.64	0.32	62.695	0.032	25.01
6		0.2	0.1	16.01	0.01	29.66	67		0.32	0.16	62.855	0.016	24.98
7		0.55	0.275	16.285	0.0275	29.65	68		0.46	0.23	63.085	0.023	24.96
8		0.65	0.325	16.61	0.0325	29.62	69		0.64	0.32	63.405	0.032	24.94
9		0.62	0.31	16.92	0.031	29.59	70		0.33	0.165	63.57	0.0165	24.91
10		0.38	0.19	17.11	0.019	29.56	71		0.84	0.42	63.99	0.042	24.89
11		0.46	0.23	17.34	0.023	29.54	72		1.08	0.54	64.53	0.054	24.85
12		0.56	0.28	17.62	0.028	29.51	73		0.4	0.2	64.73	0.02	24.79
13		0.5	0.25	17.87	0.025	29.49	74		0.8	0.4	65.13	0.04	24.77
14		0.45	0.225	18.095	0.0225	29.46	75		0.92	0.46	65.59	0.046	24.73
15		3	1.5	19.595	0.15	29.44	76		0.92	0.46	66.05	0.046	24.69
16		1.18	0.59	20.185	0.059	29.29	77		0.83	0.415	66.465	0.0415	24.64
17		0.86	0.43	20.615	0.043	29.23	78		0.81	0.405	66.87	0.0405	24.60
18		0.69	0.345	20.96	0.0345	29.19	79		0.32	0.16	67.03	0.016	24.56
19		0.9	0.45	21.41	0.045	29.15	80		0.3	0.15	67.18	0.015	24.54
20		0.7	0.35	21.76	0.035	29.11	81		0.45	0.225	67.405	0.0225	24.53
21		1.4	0.7	22.46	0.07	29.07	82		0.31	0.155	67.56	0.0155	24.51
22		1	0.5	22.96	0.05	29.00	83		0.32	0.16	67.72	0.016	24.49
23		0.68	0.34	23.3	0.034	28.95	84		1.5	0.75	68.47	0.075	24.48
24		0.41	0.205	23.505	0.0205	28.92	85		0.62	0.31	68.78	0.031	24.40
25		0.86	0.43	23.935	0.043	28.90	86		0.31	0.155	68.935	0.0155	24.37
26		0.98	0.49	24.425	0.049	28.85	87		0.42	0.21	69.145	0.021	24.35
27		1.12	0.56	24.985	0.056	28.80	88		1.1	0.55	69.695	0.055	24.33
28		0.82	0.41	25.395	0.041	28.75	89		1	0.5	70.195	0.05	24.28
29		0.8	0.4	25.795	0.04	28.71	90	4	8.8	4.4	74.595	0.44	24.23
30		0.6	0.3	26.095	0.03	28.67	91		0.18	0.09	74.685	0.009	23.79
31		0.53	0.265	26.36	0.0265	28.64	92		0.51	0.255	74.94	0.0255	23.78
32		0.52	0.26	26.62	0.026	28.61	93		0.53	0.265	75.205	0.0265	23.75
33		0.62	0.31	26.93	0.031	28.59	94		0.61	0.305	75.51	0.0305	23.73
34		0.41	0.205	27.135	0.0205	28.55	95		0.49	0.245	75.755	0.0245	23.70
35		0.42	0.21	27.345	0.021	28.53	96		0.32	0.16	75.915	0.016	23.67
36		0.9	0.45	27.795	0.045	28.51	97		0.68	0.34	76.255	0.034	23.66
37		0.32	0.16	27.955	0.016	28.47	98		0.69	0.345	76.6	0.0345	23.62
38		0.4	0.2	28.155	0.02	28.45	99		0.42	0.21	76.81	0.021	23.6
39		0.4	0.2	28.355	0.02	28.43	100		0.38	0.19	77	0.019	23.6
40		0.25	0.125	28.48	0.0125	28.41	101		0.4	0.2	77.2	0.02	23.5
41		0.61	0.305	28.785	0.0305	28.40	102		0.41	0.205	77.405	0.0205	23.5
42		0.78	0.39	29.175	0.039	28.37	103		0.42	0.21	77.615	0.021	23.5
43	18	39	19.5	48.675	1.95	28.33	104	8	19	9.5	87.115	0.95	23.5
44		0.7	0.35	49.025	0.035	26.38	105		0.69	0.345	87.46	0.0345	22.5
45		0.81	0.405	49.43	0.0405	26.34	106		0.73	0.365	87.825	0.0365	22.5
46		0.9	0.45	49.88	0.045	26.30	107		0.7	0.35	88.175	0.035	22.5
47		0.68	0.34	50.22	0.034	26.26	108		1.1	0.55	88.725	0.055	22.4
48		5.1	2.55	52.77	0.255	26.23	109		0.6	0.3	89.025	0.03	22.4
49		2.2	1.1	53.87	0.11	25.97	110		2	1	90.025	0.1	22.3
50		2.9	1.45	55.32	0.145	25.86	111		0.98	0.49	90.515	0.049	22.2
51		1.3	0.65	55.97	0.065	25.72	112		0.6	0.3	90.815	0.03	22.2
52		4.8	2.4	58.37	0.24	25.65	113		0.51	0.255	91.07	0.0255	22.2
53		0.4	0.2	58.57	0.02	25.41	114		0.56	0.28	91.35	0.028	22.1
54		0.41	0.205	58.775	0.0205	25.39	115		0.55	0.275	91.625	0.0275	22.1
55		0.6	0.3	59.075	0.03	25.37	116		0.64	0.32	91.945	0.032	22.1
56		0.3	0.15	59.225	0.015	25.34	117		0.98	0.49	92.435	0.049	22.1
57		0.8	0.4	59.625	0.04	25.32	118		0.8	0.4	92.835	0.04	22
58		0.31	0.155	59.78	0.0155	25.28	119		0.4	0.2	93.035	0.02	22
59		0.25	0.125	59.905	0.0125	25.27	120		0.69	0.345	93.38	0.0345	21.9
60		0.92	0.46	60.365	0.046	25.26							

Lamina	Non-lam	Core/DRAW	Sample scale (mm)	Height	Lamina width	Depth	Lamina	Non-lam	Core/DRAW	Sample scale (mm)	Height	Lamina width	Depth
	mm	mm	Scale (1:2)	mm	cm	cm		mm	mm	Scale (1:2)	mm	cm	cm
121		0.82	0.41	93.79	0.041	21.91	181		0.43	0.215	129.14	0.0215	18.4
122		0.74	0.37	94.16	0.037	21.87	182		0.44	0.22	129.36	0.022	18.3
123		0.45	0.225	94.385	0.0225	21.83	183		0.24	0.12	129.48	0.012	18.3
124		0.52	0.26	94.645	0.026	21.81	184		0.42	0.21	129.69	0.021	18.3
125		0.47	0.235	94.88	0.0235	21.78	185		0.5	0.25	129.94	0.025	18.3
126		0.61	0.305	95.185	0.0305	21.76	186		0.9	0.45	130.39	0.045	18.3
127		0.63	0.315	95.5	0.0315	21.73	187		0.63	0.315	130.71	0.0315	18.2
128		0.6	0.3	95.8	0.03	21.70	188		0.52	0.26	130.97	0.026	18.2
129		0.58	0.29	96.09	0.029	21.67	189		0.73	0.365	131.33	0.0365	18.2
130		0.7	0.35	96.44	0.035	21.64	190		0.42	0.21	131.54	0.021	18.1
131		0.86	0.43	96.87	0.043	21.60	191		0.44	0.22	131.76	0.022	18.1
132		0.75	0.375	97.245	0.0375	21.56	192		0.69	0.345	132.11	0.0345	18.1
133		0.8	0.4	97.645	0.04	21.52	193		0.43	0.215	132.32	0.0215	18
134		0.88	0.44	98.085	0.044	21.48	194		0.33	0.165	132.49	0.0165	18
135		0.7	0.35	98.435	0.035	21.44	195		0.48	0.24	132.73	0.024	18
136		1.13	0.565	99	0.0565	21.40	196		0.41	0.205	132.93	0.0205	18
137		0.86	0.43	99.43	0.043	21.35	197		0.46	0.23	133.16	0.023	18
138		0.73	0.365	99.795	0.0365	21.30	198		0.49	0.245	133.41	0.0245	17.9
139		0.7	0.35	100.15	0.035	21.27	199		0.72	0.36	133.77	0.036	17.9
140		0.71	0.355	100.5	0.0355	21.23	200		0.97	0.485	134.25	0.0485	17.9
141		0.8	0.4	100.9	0.04	21.20	201		0.76	0.38	134.63	0.038	17.8
142		0.68	0.34	101.24	0.034	21.16	202		0.38	0.19	134.82	0.019	17.8
143		0.78	0.39	101.63	0.039	21.12	203		0.32	0.16	134.98	0.016	17.8
144	13	28	14	115.63	1.4	21.08	204		0.44	0.22	135.2	0.022	17.7
145		0.81	0.405	116.04	0.0405	19.68	205		0.6	0.3	135.5	0.03	17.7
146		0.77	0.385	116.42	0.0385	19.64	206		0.31	0.155	135.66	0.0155	17.7
147		0.45	0.225	116.65	0.0225	19.61	207		0.32	0.16	135.82	0.016	17.7
148		0.67	0.335	116.98	0.0335	19.58	208		0.52	0.26	136.08	0.026	17.7
149		0.9	0.45	117.43	0.045	19.55	209		0.3	0.15	136.23	0.015	17.6
150		0.52	0.26	117.69	0.026	19.50	210		1.58	0.79	137.02	0.079	17.6
151		0.58	0.29	117.98	0.029	19.48	211		0.46	0.23	137.25	0.023	17.5
152		0.95	0.475	118.46	0.0475	19.45	212		0.82	0.41	137.66	0.041	17.5
153		0.65	0.325	118.78	0.0325	19.40	213		0.65	0.325	137.98	0.0325	17.5
154		2.15	1.075	119.86	0.1075	19.37	214		0.7	0.35	138.33	0.035	17.4
155		2.12	1.06	120.92	0.106	19.26	215		0.42	0.21	138.54	0.021	17.4
156		0.41	0.205	121.12	0.0205	19.16	216		0.95	0.475	139.02	0.0475	17.4
157		1.19	0.595	121.72	0.0595	19.14	217		0.38	0.19	139.21	0.019	17.3
158		0.58	0.29	122.01	0.029	19.08	218		0.8	0.4	139.61	0.04	17.3
159		0.55	0.275	122.28	0.0275	19.05	219		0.65	0.325	139.93	0.0325	17.3
160		0.4	0.2	122.48	0.02	19.02	220		0.53	0.265	140.2	0.0265	17.3
161		0.94	0.47	122.95	0.047	19.00	221		0.42	0.21	140.41	0.021	17.2
162		1	0.5	123.45	0.05	18.95	222		0.72	0.36	140.77	0.036	17.2
163		0.52	0.26	123.71	0.026	18.90	223		0.6	0.3	141.07	0.03	17.2
164		0.43	0.215	123.93	0.0215	18.88	224		0.78	0.39	141.46	0.039	17.1
165		0.41	0.205	124.13	0.0205	18.85	225		0.59	0.295	141.75	0.0295	17.1
166		0.9	0.45	124.58	0.045	18.83	226		0.35	0.175	141.93	0.0175	17.1
167		0.66	0.33	124.91	0.033	18.79	227		0.38	0.19	142.12	0.019	17.1
168		0.68	0.34	125.25	0.034	18.76	228		0.51	0.255	142.37	0.0255	17
169		0.43	0.215	125.47	0.0215	18.72	229		0.28	0.14	142.51	0.014	17
170		0.92	0.46	125.93	0.046	18.70	230		0.5	0.25	142.76	0.025	17
171		0.82	0.41	126.34	0.041	18.65	231		0.69	0.345	143.11	0.0345	17
172		0.73	0.365	126.7	0.0365	18.61	232		0.8	0.4	143.51	0.04	16.9
173		0.64	0.32	127.02	0.032	18.58	233		0.68	0.34	143.85	0.034	16.9
174		0.55	0.275	127.3	0.0275	18.55	234		0.62	0.31	144.16	0.031	16.9
175		0.4	0.2	127.5	0.02	18.52	235		0.59	0.295	144.45	0.0295	16.8
176		0.49	0.245	127.74	0.0245	18.50	236		0.52	0.26	144.71	0.026	16.8
177		0.66	0.33	128.07	0.033	18.47	237		0.43	0.215	144.93	0.0215	16.8
178		0.37	0.185	128.26	0.0185	18.44	238		0.4	0.2	145.13	0.02	16.8
179		0.49	0.245	128.5	0.0245	18.42	239		1.5	0.75	145.88	0.075	16.7
180		0.85	0.425	128.93	0.0425	18.40	240		0.79	0.395	146.27	0.0395	16.7

Lamina	Non-lam	Core/DRAW	Sample scale (mm)	Height	Lamina width	Depth	Lamina	Non-lam	Core/DRAW	Sample scale (mm)	Height	Lamina width	Depth
	mm	mm	Scale (1:2)	mm	cm	cm		mm	mm	Scale (1:2)	mm	cm	cm
241		0.72	0.36	146.63	0.036	16.62	301		0.6	0.3	169.71	0.03	14.3
242		0.75	0.375	147.01	0.0375	16.58	302		2.68	1.34	171.05	0.134	14.3
243		0.68	0.34	147.35	0.034	16.55	303		1.1	0.55	171.6	0.055	14.1
244		0.71	0.355	147.7	0.0355	16.51	304		0.83	0.415	172.02	0.0415	14.1
245		0.72	0.36	148.06	0.036	16.48	305		0.89	0.445	172.46	0.0445	14
246		0.5	0.25	148.31	0.025	16.44	306		0.5	0.25	172.71	0.025	14
247		0.44	0.22	148.53	0.022	16.42	307		0.62	0.31	173.02	0.031	14
248		0.66	0.33	148.86	0.033	16.39	308		0.28	0.14	173.16	0.014	13.9
249		0.42	0.21	149.07	0.021	16.36	309		0.3	0.15	173.31	0.015	13.9
250		0.5	0.25	149.32	0.025	16.34	310		0.95	0.475	173.79	0.0475	13.9
251		0.52	0.26	149.58	0.026	16.32	311		0.75	0.375	174.16	0.0375	13.9
252		0.42	0.21	149.79	0.021	16.29	312		0.45	0.225	174.39	0.0225	13.8
253		0.69	0.345	150.14	0.0345	16.27	313		1.25	0.625	175.01	0.0625	13.8
254		0.48	0.24	150.38	0.024	16.23	314		1.1	0.55	175.56	0.055	13.7
255		0.98	0.49	150.87	0.049	16.21	315		0.82	0.41	175.97	0.041	13.7
256		1.1	0.55	151.42	0.055	16.16	316		1.4	0.7	176.67	0.07	13.7
257		0.89	0.445	151.86	0.0445	16.11	317		1.18	0.59	177.26	0.059	13.6
258		1.31	0.655	152.52	0.0655	16.06	318		1.45	0.725	177.99	0.0725	13.5
259		1	0.5	153.02	0.05	16.00	319		1.1	0.55	178.54	0.055	13.4
260		0.9	0.45	153.47	0.045	15.95	320		0.45	0.225	178.76	0.0225	13.4
261		0.64	0.32	153.79	0.032	15.90	321		0.79	0.395	179.16	0.0395	13.4
262		0.62	0.31	154.1	0.031	15.87	322		0.66	0.33	179.49	0.033	13.3
263		0.5	0.25	154.35	0.025	15.84	323		0.61	0.305	179.79	0.0305	13.3
264		0.53	0.265	154.61	0.0265	15.81	324		0.68	0.34	180.13	0.034	13.3
265		0.88	0.44	155.05	0.044	15.79	325		0.81	0.405	180.54	0.0405	13.2
266		0.6	0.3	155.35	0.03	15.74	326		0.79	0.395	180.93	0.0395	13.2
267		0.35	0.175	155.53	0.0175	15.71	327		0.74	0.37	181.3	0.037	13.2
268		0.8	0.4	155.93	0.04	15.69	328		1.2	0.6	181.9	0.06	13.1
269		1.21	0.605	156.53	0.0605	15.65	329		1.2	0.6	182.5	0.06	13.1
270		0.54	0.27	156.8	0.027	15.59	330		1.01	0.505	183.01	0.0505	13
271		0.5	0.25	157.05	0.025	15.57	331		1.21	0.605	183.61	0.0605	12.9
272		0.7	0.35	157.4	0.035	15.54	332		0.96	0.48	184.09	0.048	12.9
273		0.69	0.345	157.75	0.0345	15.51	333		0.79	0.395	184.49	0.0395	12.8
274		0.45	0.225	157.97	0.0225	15.47	334		0.82	0.41	184.9	0.041	12.8
275		1.1	0.55	158.52	0.055	15.45	335		1.21	0.605	185.5	0.0605	12.8
276		0.72	0.36	158.88	0.036	15.40	336		0.35	0.175	185.68	0.0175	12.7
277		0.64	0.32	159.2	0.032	15.36	337		0.54	0.27	185.95	0.027	12.7
278		1.73	0.865	160.07	0.0865	15.33	338		0.73	0.365	186.31	0.0365	12.7
279		1.49	0.745	160.81	0.0745	15.24	339		1.78	0.89	187.2	0.089	12.6
280		1.31	0.655	161.47	0.0655	15.17	340		1.28	0.64	187.84	0.064	12.5
281		1.15	0.575	162.04	0.0575	15.10	341		0.54	0.27	188.11	0.027	12.5
282		1.15	0.575	162.62	0.0575	15.04	342		1.06	0.53	188.64	0.053	12.4
283		1.01	0.505	163.12	0.0505	14.99	343		1.05	0.525	189.17	0.0525	12.4
284		0.58	0.29	163.41	0.029	14.94	344		0.42	0.21	189.38	0.021	12.3
285		0.51	0.255	163.67	0.0255	14.91	345		0.41	0.205	189.58	0.0205	12.3
286		0.3	0.15	163.82	0.015	14.88	346		0.59	0.295	189.88	0.0295	12.3
287		0.4	0.2	164.02	0.02	14.87	347		0.7	0.35	190.23	0.035	12.3
288		0.67	0.335	164.35	0.0335	14.85	348		0.5	0.25	190.48	0.025	12.2
289		0.43	0.215	164.57	0.0215	14.81	349		0.69	0.345	190.82	0.0345	12.2
290		0.64	0.32	164.89	0.032	14.79	350		0.52	0.26	191.08	0.026	12.2
291		0.75	0.375	165.26	0.0375	14.76	351		0.56	0.28	191.36	0.028	12.1
292		1.6	0.8	166.06	0.08	14.72	352		0.75	0.375	191.74	0.0375	12.1
293		0.72	0.36	166.42	0.036	14.64	353		3	1.5	193.24	0.15	12.1
294		1.53	0.765	167.19	0.0765	14.61	354		2.9	1.45	194.69	0.145	11.9
295		0.62	0.31	167.5	0.031	14.53	355		0.56	0.28	194.97	0.028	11.8
296		0.74	0.37	167.87	0.037	14.50	356		0.34	0.17	195.14	0.017	11.8
297		0.79	0.395	168.26	0.0395	14.46	357		0.32	0.16	195.3	0.016	11.7
298		0.83	0.415	168.68	0.0415	14.42	358		0.3	0.15	195.45	0.015	11.7
299		0.85	0.425	169.1	0.0425	14.38	359		0.84	0.42	195.87	0.042	11.7
300		0.62	0.31	169.41	0.031	14.34	360		0.86	0.43	196.3	0.043	11.7

Lamina	Non-lam	Core/DRAW	Sample scale (mm)	Height	Lamina width	Depth	Lamina	Non-lam	Core/DRAW	Sample scale (mm)	Height	Lamina width	Depth
	mm	mm	Scale (1:2)	mm	cm	cm		mm	mm	Scale (1:2)	mm	cm	cm
361		0.73	0.365	196.66	0.0365	11.62	421		0.53	0.265	216.93	0.0265	9.58
362		1.81	0.905	197.565	0.0905	11.58	422		0.33	0.165	217.095	0.0165	9.55
363		0.51	0.255	197.82	0.0255	11.49	423		0.47	0.235	217.33	0.0235	9.54
364		0.32	0.16	197.98	0.016	11.47	424		0.5	0.25	217.58	0.025	9.51
365		0.62	0.31	198.29	0.031	11.45	425		0.28	0.14	217.72	0.014	9.49
366		1.51	0.755	199.045	0.0755	11.42	426		0.37	0.185	217.905	0.0185	9.47
367		1.08	0.54	199.585	0.054	11.34	427		0.6	0.3	218.205	0.03	9.46
368		0.32	0.16	199.745	0.016	11.29	428		0.38	0.19	218.395	0.019	9.43
369		0.7	0.35	200.095	0.035	11.27	429		0.56	0.28	218.675	0.028	9.41
370		0.7	0.35	200.445	0.035	11.24	430		1.02	0.51	219.185	0.051	9.38
371		0.41	0.205	200.65	0.0205	11.20	431		0.86	0.43	219.615	0.043	9.33
372		0.42	0.21	200.86	0.021	11.18	432		0.87	0.435	220.05	0.0435	9.29
373		0.25	0.125	200.985	0.0125	11.16	433		0.46	0.23	220.28	0.023	9.24
374		0.48	0.24	201.225	0.024	11.15	434		1.2	0.6	220.88	0.06	9.22
375		0.37	0.185	201.41	0.0185	11.12	435		1.3	0.65	221.53	0.065	9.16
376		0.2	0.1	201.51	0.01	11.11	436		0.69	0.345	221.875	0.0345	9.09
377		0.59	0.295	201.805	0.0295	11.10	437		0.48	0.24	222.115	0.024	9.06
378		0.25	0.125	201.93	0.0125	11.07	438		0.52	0.26	222.375	0.026	9.04
379		0.43	0.215	202.145	0.0215	11.05	439		0.49	0.245	222.62	0.0245	9.01
380		0.37	0.185	202.33	0.0185	11.03	440		0.85	0.425	223.045	0.0425	8.98
381		0.73	0.365	202.695	0.0365	11.01	441		1.07	0.535	223.58	0.0535	8.94
382		0.7	0.35	203.045	0.035	10.98	442		1.75	0.875	224.455	0.0875	8.89
383		0.69	0.345	203.39	0.0345	10.94	443		0.48	0.24	224.695	0.024	8.80
384		0.95	0.475	203.865	0.0475	10.91	444		0.55	0.275	224.97	0.0275	8.78
385		0.95	0.475	204.34	0.0475	10.86	445		0.6	0.3	225.27	0.03	8.75
386		0.79	0.395	204.735	0.0395	10.81	446		0.82	0.41	225.68	0.041	8.72
387		0.84	0.42	205.155	0.042	10.77	447		0.63	0.315	225.995	0.0315	8.68
388		0.57	0.285	205.44	0.0285	10.73	448		0.64	0.32	226.315	0.032	8.65
389		1.87	0.935	206.375	0.0935	10.70	449		0.49	0.245	226.56	0.0245	8.62
390		1.36	0.68	207.055	0.068	10.61	450		0.68	0.34	226.9	0.034	8.59
391		0.55	0.275	207.33	0.0275	10.54	451		0.52	0.26	227.16	0.026	8.56
392		0.78	0.39	207.72	0.039	10.51	452		0.6	0.3	227.46	0.03	8.53
393		0.7	0.35	208.07	0.035	10.48	453		0.5	0.25	227.71	0.025	8.50
394		0.73	0.365	208.435	0.0365	10.44	454		0.37	0.185	227.895	0.0185	8.48
395		0.82	0.41	208.845	0.041	10.40	455		0.4	0.2	228.095	0.02	8.46
396		0.68	0.34	209.185	0.034	10.36	456		0.2	0.1	228.195	0.01	8.44
397		0.88	0.44	209.625	0.044	10.33	457		1.92	0.96	229.155	0.096	8.43
398		0.82	0.41	210.035	0.041	10.28	458		1.08	0.54	229.695	0.054	8.33
399		0.93	0.465	210.5	0.0465	10.24	459		0.8	0.4	230.095	0.04	8.28
400		0.57	0.285	210.785	0.0285	10.20	460		0.64	0.32	230.415	0.032	8.24
401		0.86	0.43	211.215	0.043	10.17	461		1.9	0.95	231.365	0.095	8.21
402		0.83	0.415	211.63	0.0415	10.13	462		0.52	0.26	231.625	0.026	8.11
403		0.62	0.31	211.94	0.031	10.08	463		0.64	0.32	231.945	0.032	8.08
404		0.89	0.445	212.385	0.0445	10.05	464		0.76	0.38	232.325	0.038	8.05
405		0.43	0.215	212.6	0.0215	10.01	465		1.07	0.535	232.86	0.0535	8.01
406		1.18	0.59	213.19	0.059	9.99	466		0.5	0.25	233.11	0.025	7.96
407		0.36	0.18	213.37	0.018	9.93	467		0.51	0.255	233.365	0.0255	7.94
408		0.76	0.38	213.75	0.038	9.91	468		0.74	0.37	233.735	0.037	7.91
409		0.44	0.22	213.97	0.022	9.87	469		0.57	0.285	234.02	0.0285	7.87
410		0.4	0.2	214.17	0.02	9.85	470		0.54	0.27	234.29	0.027	7.85
411		0.45	0.225	214.395	0.0225	9.83	471		0.56	0.28	234.57	0.028	7.82
412		0.51	0.255	214.65	0.0255	9.81	472		0.29	0.145	234.715	0.0145	7.79
413		0.62	0.31	214.96	0.031	9.78	473		0.82	0.41	235.125	0.041	7.78
414		0.66	0.33	215.29	0.033	9.75	474		0.78	0.39	235.515	0.039	7.73
415		0.2	0.1	215.39	0.01	9.72	475		1.26	0.63	236.145	0.063	7.70
416		0.36	0.18	215.57	0.018	9.71	476		0.68	0.34	236.485	0.034	7.63
417		0.46	0.23	215.8	0.023	9.69	477		0.79	0.395	236.88	0.0395	7.60
418		0.57	0.285	216.085	0.0285	9.67	478		0.9	0.45	237.33	0.045	7.56
419		0.6	0.3	216.385	0.03	9.64	479		0.56	0.28	237.61	0.028	7.51
420		0.56	0.28	216.665	0.028	9.61	480		0.55	0.275	237.885	0.0275	7.49

Lamina	Non-lam	Core/DRAW	Sample scale (mm)	Height	Lamina width	Depth	Lamina	Non-lam	Core/DRAW	Sample scale (mm)	Height	Lamina width	Depth
	mm	mm	Scale (1:2)	mm	cm	cm		mm	mm	Scale (1:2)	mm	cm	cm
481		0.29	0.145	238.03	0.0145	7.46	541		0.45	0.225	258.04	0.0225	5.47
482		0.4	0.2	238.23	0.02	7.44	542		0.41	0.205	258.245	0.0205	5.44
483		0.33	0.165	238.395	0.0165	7.42	543		0.3	0.15	258.395	0.015	5.42
484		0.58	0.29	238.685	0.029	7.41	544		0.34	0.17	258.565	0.017	5.41
485		0.33	0.165	238.85	0.0165	7.38	545		0.71	0.355	258.92	0.0355	5.39
486		0.31	0.155	239.005	0.0155	7.36	546		0.38	0.19	259.11	0.019	5.36
487		1.36	0.68	239.685	0.068	7.35	547		0.28	0.14	259.25	0.014	5.34
488		0.47	0.235	239.92	0.0235	7.28	548		0.66	0.33	259.58	0.033	5.32
489		0.56	0.28	240.2	0.028	7.26	549		1.1	0.55	260.13	0.055	5.29
490		0.72	0.36	240.56	0.036	7.23	550		1.2	0.6	260.73	0.06	5.23
491		0.63	0.315	240.875	0.0315	7.19	551		1.1	0.55	261.28	0.055	5.17
492		0.8	0.4	241.275	0.04	7.16	552		1.09	0.545	261.825	0.0545	5.12
493		1.9	0.95	242.225	0.095	7.12	553		0.94	0.47	262.295	0.047	5.06
494		1.05	0.525	242.75	0.0525	7.02	554		0.77	0.385	262.68	0.0385	5.02
495		0.76	0.38	243.13	0.038	6.97	555		0.86	0.43	263.11	0.043	4.98
496		0.72	0.36	243.49	0.036	6.93	556		1.05	0.525	263.635	0.0525	4.94
497		0.42	0.21	243.7	0.021	6.90	557		1.12	0.56	264.195	0.056	4.88
498		0.2	0.1	243.8	0.01	6.88	558		0.76	0.38	264.575	0.038	4.83
499		0.71	0.355	244.155	0.0355	6.87	559		0.83	0.415	264.99	0.0415	4.79
500		0.76	0.38	244.535	0.038	6.83	560		0.92	0.46	265.45	0.046	4.75
501		0.46	0.23	244.765	0.023	6.79	561		0.62	0.31	265.76	0.031	4.70
502		0.41	0.205	244.97	0.0205	6.77	562		0.63	0.315	266.075	0.0315	4.67
503		0.52	0.26	245.23	0.026	6.75	563		0.77	0.385	266.46	0.0385	4.64
504		1	0.5	245.73	0.05	6.72	564		0.24	0.12	266.58	0.012	4.60
505		0.67	0.335	246.065	0.0335	6.67	565		0.5	0.25	266.83	0.025	4.59
506		0.9	0.45	246.515	0.045	6.64	566		0.45	0.225	267.055	0.0225	4.56
507		0.89	0.445	246.96	0.0445	6.60	567		0.38	0.19	267.245	0.019	4.54
508		0.96	0.48	247.44	0.048	6.55	568		0.32	0.16	267.405	0.016	4.52
509		0.83	0.415	247.855	0.0415	6.50	569		0.52	0.26	267.665	0.026	4.51
510		0.5	0.25	248.105	0.025	6.46	570		0.69	0.345	268.01	0.0345	4.48
511		0.86	0.43	248.535	0.043	6.44	571		0.42	0.21	268.22	0.021	4.45
512		0.33	0.165	248.7	0.0165	6.39	572		0.9	0.45	268.67	0.045	4.43
513		0.6	0.3	249	0.03	6.38	573		0.52	0.26	268.93	0.026	4.38
514		0.8	0.4	249.4	0.04	6.35	574		0.3	0.15	269.08	0.015	4.35
515		0.49	0.245	249.645	0.0245	6.31	575		0.51	0.255	269.335	0.0255	4.34
516		0.6	0.3	249.945	0.03	6.28	576		0.43	0.215	269.55	0.0215	4.31
517		0.51	0.255	250.2	0.0255	6.25	577		0.74	0.37	269.92	0.037	4.29
518		1.1	0.55	250.75	0.055	6.23	578		0.44	0.22	270.14	0.022	4.26
519		0.92	0.46	251.21	0.046	6.17	579		0.68	0.34	270.48	0.034	4.23
520		0.82	0.41	251.62	0.041	6.13	580		0.67	0.335	270.815	0.0335	4.20
521		0.6	0.3	251.92	0.03	6.09	581		0.58	0.29	271.105	0.029	4.17
522		0.45	0.225	252.145	0.0225	6.06	582		0.36	0.18	271.285	0.018	4.14
523		0.37	0.185	252.33	0.0185	6.03	583		0.42	0.21	271.495	0.021	4.12
524		0.42	0.21	252.54	0.021	6.01	584		0.41	0.205	271.7	0.0205	4.10
525		0.52	0.26	252.8	0.026	5.99	585		0.83	0.415	272.115	0.0415	4.08
526		0.6	0.3	253.1	0.03	5.97	586		0.78	0.39	272.505	0.039	4.04
527		0.57	0.285	253.385	0.0285	5.94	587		0.73	0.365	272.87	0.0365	4.00
528		0.47	0.235	253.62	0.0235	5.91	588		0.69	0.345	273.215	0.0345	3.96
529		0.57	0.285	253.905	0.0285	5.89	589		0.68	0.34	273.555	0.034	3.93
530		0.52	0.26	254.165	0.026	5.86	590		0.14	0.07	273.625	0.007	3.89
531		0.68	0.34	254.505	0.034	5.83	591		0.98	0.49	274.115	0.049	3.88
532		0.69	0.345	254.85	0.0345	5.80	592		1.48	0.74	274.855	0.074	3.84
533		0.77	0.385	255.235	0.0385	5.76	593		0.8	0.4	275.255	0.04	3.76
534		0.52	0.26	255.495	0.026	5.72	594		0.82	0.41	275.665	0.041	3.72
535		1.47	0.735	256.23	0.0735	5.70	595		0.55	0.275	275.94	0.0275	3.68
536		0.82	0.41	256.64	0.041	5.62	596		0.55	0.275	276.215	0.0275	3.65
537		0.4	0.2	256.84	0.02	5.58	597		0.5	0.25	276.465	0.025	3.63
538		1	0.5	257.34	0.05	5.56	598		0.52	0.26	276.725	0.026	3.60
539		0.3	0.15	257.49	0.015	5.51	599		0.82	0.41	277.135	0.041	3.57
540		0.65	0.325	257.815	0.0325	5.50	600		0.31	0.155	277.29	0.0155	3.53

Lamina	Non-lam	CorelDRAW	Sample scale (mm)	Height	Lamina width	Depth	Lamina	Non-lam	CorelDRAW	Sample scale (mm)	Height	Lamina width	Depth
	mm	mm	Scale (1:2)	mm	cm	cm		mm	mm	Scale (1:2)	mm	cm	cm
601		0.71	0.355	277.645	0.0355	3.52	651		0.41	0.205	290.385	0.0205	2.23
602		0.23	0.115	277.76	0.0115	3.48	652		0.53	0.265	290.65	0.0265	2.21
603		0.58	0.29	278.05	0.029	3.47	653		0.95	0.475	291.125	0.0475	2.18
604		0.72	0.36	278.41	0.036	3.44	654		0.43	0.215	291.34	0.0215	2.13
605		0.61	0.305	278.715	0.0305	3.41	655		0.65	0.325	291.665	0.0325	2.11
606		0.53	0.265	278.98	0.0265	3.38	656		0.35	0.175	291.84	0.0175	2.08
607		0.34	0.17	279.15	0.017	3.35	657		0.46	0.23	292.07	0.023	2.06
608		0.47	0.235	279.385	0.0235	3.33	658		0.23	0.115	292.185	0.0115	2.04
609		0.38	0.19	279.575	0.019	3.31	659		0.71	0.355	292.54	0.0355	2.03
610		0.39	0.195	279.77	0.0195	3.29	660		0.95	0.475	293.015	0.0475	1.99
611		0.42	0.21	279.98	0.021	3.27	661		0.4	0.2	293.215	0.02	1.95
612		0.41	0.205	280.185	0.0205	3.25	662		0.35	0.175	293.39	0.0175	1.93
613		0.43	0.215	280.4	0.0215	3.23	663		0.3	0.15	293.54	0.015	1.91
614		0.2	0.1	280.5	0.01	3.21	664		0.52	0.26	293.8	0.026	1.89
615		0.48	0.24	280.74	0.024	3.20	665		0.38	0.19	293.99	0.019	1.87
616		0.69	0.345	281.085	0.0345	3.17	666		0.63	0.315	294.305	0.0315	1.85
617		0.32	0.16	281.245	0.016	3.14	667		0.72	0.36	294.665	0.036	1.82
618		0.69	0.345	281.59	0.0345	3.12	668		0.6	0.3	294.965	0.03	1.78
619		0.42	0.21	281.8	0.021	3.09	669		0.89	0.445	295.41	0.0445	1.75
620		0.27	0.135	281.935	0.0135	3.07	670		0.62	0.31	295.72	0.031	1.71
621		0.62	0.31	282.245	0.031	3.05	671		0.81	0.405	296.125	0.0405	1.68
622		0.4	0.2	282.445	0.02	3.02	672		0.45	0.225	296.35	0.0225	1.63
623		0.33	0.165	282.61	0.0165	3.00	673		0.82	0.41	296.76	0.041	1.61
624		0.95	0.475	283.085	0.0475	2.99	674		0.72	0.36	297.12	0.036	1.57
625		0.5	0.25	283.335	0.025	2.94	675		0.31	0.155	297.275	0.0155	1.54
626		0.44	0.22	283.555	0.022	2.91	676		0.72	0.36	297.635	0.036	1.52
627		0.38	0.19	283.745	0.019	2.89	677		0.36	0.18	297.815	0.018	1.48
628		0.34	0.17	283.915	0.017	2.87	678		0.35	0.175	297.99	0.0175	1.47
629		0.56	0.28	284.195	0.028	2.86	679		0.68	0.34	298.33	0.034	1.45
630		0.92	0.46	284.655	0.046	2.83	680		0.37	0.185	298.515	0.0185	1.41
631		0.47	0.235	284.89	0.0235	2.78	681		0.94	0.47	298.985	0.047	1.40
632		0.91	0.455	285.345	0.0455	2.76	682		0.38	0.19	299.175	0.019	1.35
633		0.41	0.205	285.55	0.0205	2.71	683		1.27	0.635	299.81	0.0635	1.33
634		0.12	0.06	285.61	0.006	2.69	684		1.1	0.55	300.36	0.055	1.27
635		0.46	0.23	285.84	0.023	2.69	685		0.53	0.265	300.625	0.0265	1.21
636		0.78	0.39	286.23	0.039	2.66	686		1.22	0.61	301.235	0.061	1.18
637		0.88	0.44	286.67	0.044	2.62	687		1.71	0.855	302.09	0.0855	1.12
638		0.42	0.21	286.88	0.021	2.58	688		0.82	0.41	302.5	0.041	1.04
639		0.73	0.365	287.245	0.0365	2.56	689		0.69	0.345	302.845	0.0345	1.00
640		0.48	0.24	287.485	0.024	2.52	690		1.4	0.7	303.545	0.07	0.96
641		0.29	0.145	287.63	0.0145	2.50	691		0.62	0.31	303.855	0.031	0.89
642		0.36	0.18	287.81	0.018	2.48	692		0.89	0.445	304.3	0.0445	0.86
643		0.64	0.32	288.13	0.032	2.47	693		0.79	0.395	304.695	0.0395	0.82
644		0.83	0.415	288.545	0.0415	2.43	694		3.5	1.75	306.445	0.175	0.78
645		0.51	0.255	288.8	0.0255	2.39	695		0.42	0.21	306.655	0.021	0.60
646		0.5	0.25	289.05	0.025	2.37	696		0.44	0.22	306.875	0.022	0.58
647		0.59	0.295	289.345	0.0295	2.34	697		0.6	0.3	307.175	0.03	0.56
648		0.59	0.295	289.64	0.0295	2.31	698		0.36	0.18	307.355	0.018	0.53
649		0.48	0.24	289.88	0.024	2.28	699		0.42	0.21	307.565	0.021	0.51
650		0.6	0.3	290.18	0.03	2.26	700		0.53	0.265	307.83	0.0265	0.49
							701		2.28	1.14	308.97	0.114	0.46
							702		7	3.5	312.47	0.35	0.35

Table 19: Lamina count and lamina width measurements of sample stalagmite from Kotumsar cave using CorelDRAW software.

Sample	Age	$\delta^{18}\text{O}$	$\delta^{13}\text{C}$	Y/Ca	Ba/Ca	Pb/Ca	U/Ca	Na/Ca	Mg/Ca	P/Ca	Rb/Ca	Sr/Ca
	Years BP	‰ VPDB	‰ VPDB	mmol/mol								
DL Min				1.10E-05	1.40E-04	7.30E-06	7.50E-07	1.00E-02	1.60E-03	4.80E-03	5.80E-06	6.10E-04
DL Max				1.90E-05	5.10E-04	3.60E-05	3.70E-06	9.20E-02	1.50E-02	3.20E-02	2.10E-05	2.30E-03
P% Min				1.2	0.8	0.6	0.6	1.1	0.8	1.2	1.1	0.5
P% Max				7.2	4.0	3.9	6.1	3.1	3.2	3.1	2.5	2.7
NKT1	3449	-4.40	-10.27	4.2E-03	7.5E-02	1.5E-04	4.1E-05	4.8E-01	2.0E+00	2.8E-01	1.2E-04	6.6E-02
NKT2	3445	-4.06	-10.05	3.5E-03	7.3E-02	1.2E-04	4.0E-05	3.4E-01	2.0E+00	2.5E-01	1.0E-04	6.3E-02
NKT3	3442	-3.96	-10.29	2.8E-03	7.4E-02	1.3E-04	2.3E-05	2.8E-01	1.7E+00	2.4E-01	1.3E-04	5.0E-02
NKT4	3438	-3.84	-10.18	2.7E-03	8.3E-02	1.2E-04	3.5E-05	3.2E-01	3.5E+00	2.1E-01	1.3E-04	6.6E-02
NKT5	3434	-3.96	-10.31	2.6E-03	8.5E-02	1.0E-04	3.4E-05	3.2E-01	1.8E+00	1.8E-01	1.2E-04	6.8E-02
NKT6	3431	-3.91	-9.75	2.3E-03	9.0E-02	4.5E-05	2.1E-05	2.1E-01	1.6E+00	1.9E-01	4.8E-05	6.0E-02
NKT7	3427	-4.67	-10.79	3.8E-03	9.1E-02	6.7E-05	2.8E-05	2.4E-01	1.6E+00	1.7E-01	6.6E-05	7.0E-02
NKT8	3423	-4.67	-11.03	4.7E-03	8.3E-02	7.6E-05	2.7E-05	3.0E-01	1.6E+00	1.8E-01	8.7E-05	6.7E-02
NKT9	3419	-5.15	-11.01	3.3E-03	8.7E-02	1.0E-04	1.7E-05	5.7E-01	1.4E+00	2.4E-01	1.4E-04	5.6E-02
NKT10	3416	-5.56	-11.20	3.6E-03	9.6E-02	5.9E-05	2.5E-05	2.4E-01	1.6E+00	2.0E-01	6.4E-05	7.0E-02
NKT11	3412	-5.49	-10.92	2.8E-03	1.1E-01	7.4E-05	2.8E-05	2.6E-01	1.5E+00	1.9E-01	7.5E-05	7.6E-02
NKT12	3408	-5.11	-10.66	3.0E-03	1.0E-01	4.6E-05	1.7E-05	2.6E-01	1.5E+00	1.8E-01	7.3E-05	6.6E-02
NKT13	3404	-4.91	-10.22	3.5E-03	9.4E-02	8.6E-05	3.6E-05	3.3E-01	2.2E+00	1.9E-01	8.0E-05	7.6E-02
NKT14	3400	-4.77	-10.61	3.5E-03	9.4E-02	1.4E-04	3.2E-05	5.0E-01	1.7E+00	1.8E-01	1.7E-04	7.6E-02
NKT15	3396	-4.41	-10.85	3.0E-03	8.5E-02	8.2E-05	1.5E-05	1.8E-01	1.5E+00	1.8E-01	5.3E-05	7.6E-02
NKT16	3392	-4.28	-10.13	1.4E-03	9.6E-02	8.4E-05	3.4E-05	3.5E-01	1.7E+00	1.6E-01	9.4E-05	7.7E-02
NKT17	3389	-4.00	-9.69	5.5E-04	9.6E-02	2.3E-04	3.5E-05	4.5E-01	1.7E+00	1.5E-01	1.6E-04	7.8E-02
NKT18	3385	-3.50	-9.70	9.1E-04	1.0E-01	2.5E-04	1.9E-05	1.2E+00	1.5E+00	1.8E-01	4.1E-04	6.7E-02
NKT19	3381	-3.57	-9.85	1.3E-03	9.0E-02	9.2E-05	3.1E-05	3.7E-01	1.6E+00	1.6E-01	9.9E-05	7.3E-02
NKT20	3377	-4.22	-9.61	1.9E-03	8.6E-02	8.9E-05	3.2E-05	4.5E-01	1.7E+00	2.1E-01	1.5E-04	6.9E-02
NKT21	3374	-4.79	-9.16	2.4E-03	8.7E-02	1.0E-04	2.1E-05	7.1E-01	1.5E+00	2.8E-01	1.7E-04	5.6E-02
NKT22	3370	-4.67	-9.20	2.7E-03	9.5E-02	2.2E-04	3.5E-05	6.9E-01	2.3E+00	2.3E-01	1.7E-04	7.3E-02
NKT23	3367	-4.58	-8.93	1.5E-03	9.0E-02	1.2E-04	3.6E-05	5.6E-01	1.8E+00	2.0E-01	2.0E-04	7.3E-02
NKT24	3363	-4.03	-8.47	1.3E-03	7.2E-02	1.1E-04	2.3E-05	8.2E-01	1.8E+00	1.7E-01	1.7E-04	5.4E-02
NKT25r	3360	-3.37	-8.95	9.9E-04	7.8E-02	1.9E-04	3.5E-05	5.4E-01	2.1E+00	1.5E-01	2.5E-04	5.4E-02
NKT26	3357	-3.48	-9.92	1.1E-03	6.5E-02	4.3E-04	5.7E-05	7.4E-01	2.5E+00	2.6E-01	3.2E-04	6.5E-02
NKT27	3354	-3.24	-9.27	5.0E-04	6.9E-02	2.3E-04	3.2E-05	4.0E-01	2.1E+00	2.1E-01	1.6E-04	5.3E-02
NKT28	3351	-2.94	-8.87	6.5E-04	8.0E-02	2.6E-04	5.4E-05	4.4E-01	2.4E+00	2.0E-01	1.5E-04	7.3E-02
NKT29	3348	-2.98	-8.60	6.6E-04	7.4E-02	1.8E-04	5.3E-05	7.2E-01	2.6E+00	1.6E-01	2.0E-04	7.1E-02
NKT30	3346	-3.31	-9.18	9.1E-04	7.2E-02	5.8E-05	2.9E-05	1.8E-01	2.0E+00	1.5E-01	6.7E-05	5.3E-02
NKT31	3343	-3.12	-9.21	1.5E-03	8.0E-02	1.3E-04	4.8E-05	5.1E-01	2.5E+00	1.8E-01	1.5E-04	7.2E-02
NKT32	3341	-3.03	-9.05	9.0E-04	8.9E-02	8.9E-05	4.6E-05	4.1E-01	2.2E+00	1.9E-01	1.2E-04	7.4E-02
NKT33	3339	-3.09	-9.58	7.8E-04	9.2E-02	8.4E-05	2.5E-05	3.1E-01	1.8E+00	2.2E-01	1.4E-04	6.1E-02
NKT34	3337	-3.08	-9.53	5.7E-04	1.1E-01	6.7E-05	3.3E-05	3.0E-01	1.8E+00	1.6E-01	7.1E-05	8.1E-02
NKT35	3335	-2.76	-8.83	4.2E-04	8.9E-02	8.1E-05	3.5E-05	3.3E-01	2.0E+00	1.4E-01	8.1E-05	7.1E-02
NKT36	3333	-2.43	-8.37	3.6E-04	6.7E-02	1.0E-04	2.7E-05	2.9E-01	2.2E+00	1.5E-01	9.3E-05	5.1E-02
NKT37	3331	-2.69	-8.16	3.9E-04	7.7E-02	1.8E-04	4.8E-05	4.4E-01	2.6E+00	1.4E-01	1.2E-04	7.2E-02
NKT38	3330	-3.39	-8.43	6.1E-04	8.7E-02	9.3E-05	4.1E-05	3.3E-01	2.4E+00	1.4E-01	7.9E-05	7.3E-02
NKT39	3328	-3.94	-8.66	1.0E-03	8.9E-02	2.5E-05	2.4E-05	2.3E-01	1.9E+00	1.8E-01	6.2E-05	6.3E-02
NKT40	3327	-4.12	-8.67	8.6E-04	1.0E-01	1.9E-04	3.3E-05	3.3E-01	2.0E+00	1.4E-01	9.1E-05	8.2E-02
NKT41	3325	-4.32	-9.15	1.1E-03	9.8E-02	1.1E-04	3.8E-05	3.8E-01	1.8E+00	1.6E-01	1.3E-04	7.9E-02
NKT42	3324	-4.87	-9.10	6.2E-04	1.1E-01	4.1E-05	1.8E-05	3.8E-01	1.5E+00	2.4E-01	1.1E-04	7.1E-02
NKT43	3323	-4.86	-9.49	9.0E-04	1.1E-01	1.6E-04	3.2E-05	4.0E-01	1.5E+00	1.6E-01	9.2E-05	8.8E-02
NKT44	3322	-4.54	-9.59	1.1E-03	1.3E-01	5.4E-05	2.3E-05	2.2E-01	1.4E+00	2.3E-01	5.2E-05	8.5E-02
NKT45	3320	-4.51	-9.31	1.1E-03	1.1E-01	6.0E-05	1.2E-05	5.7E-01	1.2E+00	2.0E-01	1.6E-04	6.6E-02
NKT46	3319	-3.89	-8.67	9.6E-04	1.1E-01	3.0E-04	2.4E-05	3.6E-01	1.6E+00	2.0E-01	1.3E-04	7.5E-02
NKT47r	3318	-3.81	-8.80	9.0E-04	9.6E-02	2.9E-04	2.4E-05	2.7E-01	1.5E+00	1.4E-01	9.6E-05	6.2E-02
NKT48	3316	-3.98	-8.10	3.9E-04	7.5E-02	8.8E-05	2.2E-05	5.0E-01	1.8E+00	1.4E-01	1.4E-04	5.6E-02
NKT49	3315	-4.05	-8.47	1.8E-03	9.4E-02	6.9E-05	3.7E-05	3.0E-01	1.9E+00	1.4E-01	7.5E-05	7.5E-02
NKT50	3314	-3.85	-8.41	2.1E-03	8.8E-02	7.6E-05	4.7E-05	3.5E-01	2.1E+00	1.8E-01	9.1E-05	7.4E-02
NKT51	3312	-4.12	-8.90	6.4E-04	9.5E-02	5.5E-05	1.6E-05	1.9E-01	1.5E+00	1.2E-01	6.7E-05	6.5E-02
NKT52	3311	-4.72	-9.35	8.2E-04	1.2E-01	1.1E-04	3.0E-05	4.0E-01	1.8E+00	1.4E-01	1.2E-04	9.2E-02
NKT53	3309	-4.56	-9.24	1.2E-03	1.2E-01	1.3E-04	2.4E-05	3.8E-01	1.7E+00	1.5E-01	1.4E-04	8.8E-02
NKT54	3307	-5.02	-9.50	2.3E-03	1.1E-01	5.0E-05	1.4E-05	3.5E-01	1.3E+00	1.9E-01	1.2E-04	6.6E-02
NKT55	3305	-4.77	-9.00	2.6E-03	1.1E-01	1.0E-04	3.2E-05	3.8E-01	1.7E+00	1.5E-01	1.1E-04	8.3E-02
NKT56	3303	-3.95	-8.65	2.9E-03	1.0E-01	1.0E-04	3.6E-05	3.6E-01	2.0E+00	1.9E-01	1.2E-04	8.4E-02
NKT57	3301	-4.29	-8.72	2.3E-03	1.1E-01	2.6E-04	1.8E-05	1.1E+00	1.5E+00	2.3E-01	2.4E-04	6.6E-02
NKT58	3299	-3.59	-8.66	1.4E-03	1.1E-01	2.1E-04	3.0E-05	4.1E-01	1.9E+00	1.4E-01	1.3E-04	8.5E-02
NKT59	3297	-3.80	-8.12	1.0E-03	1.1E-01	1.7E-04	3.6E-05	3.4E-01	2.4E+00	1.3E-01	9.0E-05	8.2E-02
NKT60	3295	-4.40	-8.08	1.3E-03	1.0E-01	1.4E-04	2.6E-05	1.0E+00	2.0E+00	1.4E-01	3.8E-04	6.6E-02

Sample	Age	$\delta^{18}O$	$\delta^{13}C$	Y/Ca	Ba/Ca	Pb/Ca	U/Ca	Na/Ca	Mg/Ca	P/Ca	Rb/Ca	Sr/Ca
	Years BP	‰ VPDB	‰ VPDB	mmol/mol								
DL Min				1.10E-05	1.40E-04	7.30E-06	7.50E-07	1.00E-02	1.60E-03	4.80E-03	5.80E-06	6.10E-04
DL Max				1.90E-05	5.10E-04	3.60E-05	3.70E-06	9.20E-02	1.50E-02	3.20E-02	2.10E-05	2.30E-03
P% Min				1.2	0.8	0.6	0.6	1.1	0.8	1.2	1.1	0.5
P% Max				7.2	4.0	3.9	6.1	3.1	3.2	3.1	2.5	2.7
NKT61r	3292	-3.95	-8.84	2.2E-03	1.1E-01	2.4E-05	3.1E-05	2.4E-01	2.3E+00	3.0E-01	6.8E-05	7.0E-02
NKT62	3290	-3.87	-9.34	2.5E-03	1.1E-01	1.2E-04	4.4E-05	4.1E-01	2.3E+00	3.3E-01	1.3E-04	8.2E-02
NKT63	3287	-3.81	-9.03	1.7E-03	9.9E-02	4.8E-05	2.7E-05	1.2E-01	2.1E+00	2.9E-01	3.7E-05	6.5E-02
NKT64	3285	-3.92	-9.11	1.5E-03	1.3E-01	1.1E-04	4.8E-05	4.7E-01	2.6E+00	2.6E-01	1.2E-04	9.4E-02
NKT65	3282	-3.68	-8.73	1.3E-03	1.3E-01	2.7E-04	4.3E-05	4.0E-01	2.8E+00	2.5E-01	1.2E-04	9.5E-02
NKT66	3279	-3.52	-8.06	1.5E-03	1.4E-01	4.2E-05	2.5E-05	6.7E-01	2.3E+00	2.2E-01	2.1E-04	8.5E-02
NKT67	3276	-4.09	-8.56	1.8E-03	1.2E-01	6.7E-05	3.5E-05	3.3E-01	2.3E+00	1.7E-01	7.1E-05	8.6E-02
NKT68	3273	-3.74	-8.46	1.8E-03	9.5E-02	1.1E-04	4.5E-05	5.6E-01	2.9E+00	4.0E-01	2.6E-04	8.2E-02
NKT69	3270	-3.67	-8.23	6.1E-04	9.2E-02	1.4E-04	3.9E-05	2.8E-01	3.4E+00	4.0E-01	1.5E-04	6.8E-02
NKT70	3266	-3.58	-8.13	6.7E-04	9.2E-02	1.3E-04	4.6E-05	3.3E-01	3.6E+00	3.2E-01	1.4E-04	7.5E-02
NKT71	3263	-3.71	-8.14	7.2E-04	9.2E-02	1.3E-04	5.3E-05	3.8E-01	3.7E+00	2.4E-01	1.3E-04	8.3E-02
NKT72	3260	-4.00	-8.60	6.8E-04	1.3E-01	1.2E-04	3.5E-05	4.4E-01	2.9E+00	2.7E-01	1.7E-04	8.2E-02
NKT73	3256	-3.47	-8.43	7.1E-04	9.6E-02	3.7E-04	4.7E-05	5.9E-01	3.6E+00	3.2E-01	1.9E-04	7.3E-02
NKT74	3252	-3.02	-8.42	3.2E-04	9.6E-02	1.6E-04	4.8E-05	3.5E-01	3.2E+00	2.1E-01	1.0E-04	7.5E-02
NKT75	3249	-3.61	-9.15	9.5E-04	1.3E-01	1.6E-04	3.2E-05	9.2E-01	3.1E+00	2.8E-01	3.0E-04	7.9E-02
NKT76	3245	-3.56	-9.19	2.4E-03	1.5E-01	6.4E-05	3.0E-05	2.0E-01	2.2E+00	2.0E-01	3.7E-05	9.2E-02
NKT77	3241	-4.14	-10.37	5.0E-03	1.6E-01	1.3E-04	3.4E-05	3.9E-01	1.5E+00	2.4E-01	1.4E-04	9.4E-02
NKT78	3237	-4.11	-9.76	4.1E-03	1.5E-01	9.1E-05	3.0E-05	7.5E-01	1.7E+00	5.3E-01	1.8E-04	8.0E-02
NKT79	3233	-4.26	-10.49	4.4E-03	1.5E-01	1.1E-04	4.4E-05	6.9E-01	1.9E+00	7.0E-01	3.4E-04	9.5E-02
NKT80r	3229	-4.56	-10.38	4.8E-03	1.6E-01	4.2E-05	2.5E-05	4.2E-01	1.6E+00	3.9E-01	1.9E-04	8.5E-02
NKT81	3225	-5.05	-9.95	3.9E-03	1.6E-01	5.9E-05	2.2E-05	6.4E-01	1.6E+00	2.9E-01	2.0E-04	8.2E-02
NKT82	3221	-4.44	-10.01	3.5E-03	1.5E-01	8.8E-05	4.0E-05	3.9E-01	2.0E+00	2.6E-01	9.0E-05	1.0E-01
NKT83	3217	-4.68	-10.29	4.6E-03	1.2E-01	1.2E-04	3.7E-05	3.8E-01	2.0E+00	3.0E-01	9.9E-05	8.4E-02
NKT84	3213	-5.07	-10.24	5.2E-03	9.9E-02	5.5E-05	2.0E-05	3.0E-01	1.9E+00	3.0E-01	9.6E-05	6.0E-02
NKT85	3209	-4.71	-10.14	5.6E-03	9.7E-02	8.3E-05	3.5E-05	4.4E-01	2.1E+00	3.0E-01	1.3E-04	7.2E-02
NKT86	3205	-4.65	-10.08	4.6E-03	1.1E-01	1.0E-04	3.6E-05	4.0E-01	2.1E+00	2.5E-01	1.2E-04	8.2E-02
NKT87	3200	-4.32	-9.90	4.0E-03	1.1E-01	5.2E-05	2.0E-05	3.0E-01	1.8E+00	2.6E-01	8.0E-05	6.3E-02
NKT88	3196	-4.36	-10.03	5.5E-03	1.1E-01	8.4E-05	3.3E-05	3.7E-01	2.1E+00	3.0E-01	1.3E-04	7.5E-02
NKT89	3192	-4.39	-9.89	4.4E-03	1.1E-01	9.3E-05	4.0E-05	3.9E-01	2.1E+00	2.7E-01	9.6E-05	8.6E-02
NKT90	3188	-4.06	-10.20	4.4E-03	8.7E-02	4.8E-05	2.7E-05	2.4E-01	2.1E+00	2.7E-01	6.4E-05	5.8E-02
NKT91	3184	-3.60	-10.14	6.0E-03	8.7E-02	1.2E-04	4.8E-05	3.9E-01	2.2E+00	3.2E-01	9.9E-05	7.0E-02
NKT92r	3181	-3.35	-9.70	2.9E-03	8.0E-02	1.7E-04	4.5E-05	4.6E-01	2.5E+00	4.8E-01	2.8E-04	5.4E-02
NKT93	3177	-3.29	-9.79	2.2E-03	7.4E-02	1.9E-04	3.5E-05	6.0E-01	2.4E+00	3.2E-01	2.2E-04	5.1E-02
NKT94r	3173	-3.35	-9.68	2.3E-03	8.8E-02	9.3E-05	3.5E-05	1.8E-01	2.3E+00	2.8E-01	6.0E-05	5.8E-02
NKT95	3169	-3.57	-9.67	3.4E-03	9.6E-02	2.9E-04	5.2E-05	3.3E-01	2.5E+00	4.1E-01	1.3E-04	7.2E-02
NKT96	3165	-3.41	-9.50	2.3E-03	9.4E-02	7.6E-05	3.5E-05	4.4E-01	2.2E+00	3.0E-01	1.1E-04	6.2E-02
NKT97	3162	-3.22	-9.32	2.4E-03	8.7E-02	2.1E-04	5.8E-05	5.3E-01	2.9E+00	3.2E-01	1.9E-04	7.6E-02
NKT98	3158	-3.10	-8.90	1.6E-03	7.3E-02	2.4E-04	5.2E-05	5.0E-01	2.5E+00	2.6E-01	1.9E-04	6.3E-02
NKT99	3155	-2.98	-8.59	8.7E-04	6.6E-02	9.7E-05	3.9E-05	2.4E-01	2.8E+00	2.1E-01	6.4E-05	5.1E-02
NKT100	3151	-3.05	-8.47	9.7E-04	7.1E-02	2.5E-04	5.9E-05	6.7E-01	3.1E+00	2.5E-01	2.8E-04	6.8E-02
NKT101	3148	-3.23	-8.90	2.2E-03	1.1E-01	1.4E-04	5.1E-05	3.7E-01	2.7E+00	3.1E-01	9.2E-05	7.9E-02
NKT102	3144	-3.27	-9.94	2.1E-03	1.5E-01	5.2E-05	2.7E-05	3.6E-01	1.9E+00	4.6E-01	8.2E-05	8.4E-02
NKT103	3141	-3.93	-10.61	1.6E-03	1.6E-01	2.0E-04	4.3E-05	5.7E-01	1.8E+00	4.8E-01	2.3E-04	9.8E-02
NKT104	3138	-4.46	-10.91	2.8E-03	1.3E-01	8.4E-05	3.2E-05	2.6E-01	1.7E+00	3.1E-01	6.5E-05	8.4E-02
NKT105	3134	-4.36	-11.03	3.5E-03	1.1E-01	2.9E-05	2.1E-05	2.4E-01	1.6E+00	2.7E-01	6.5E-05	6.8E-02
NKT106	3131	-3.45	-11.55	4.6E-03	9.5E-02	1.0E-04	3.3E-05	3.0E-01	2.3E+00	3.2E-01	1.1E-04	7.0E-02
NKT107	3128	-3.50	-11.12	4.1E-03	1.1E-01	8.3E-05	3.6E-05	2.9E-01	2.1E+00	2.8E-01	6.9E-05	7.6E-02
NKT108	3125	-3.74	-10.67	3.6E-03	1.2E-01	6.9E-05	2.5E-05	5.3E-01	2.0E+00	2.8E-01	1.9E-04	6.8E-02
NKT109	3121	-4.19	-9.97	3.3E-03	1.2E-01	2.8E-04	3.8E-05	6.6E-01	2.3E+00	2.8E-01	3.3E-04	8.6E-02
NKT110	3118	-3.71	-10.44	3.4E-03	1.4E-01	9.0E-05	3.6E-05	3.1E-01	1.9E+00	2.7E-01	7.7E-05	9.0E-02
NKT111	3115	-3.85	-10.65	3.7E-03	1.6E-01	3.2E-05	2.1E-05	2.4E-01	1.6E+00	2.7E-01	5.5E-05	8.8E-02
NKT112	3112	-3.43	-10.20	3.2E-03	1.4E-01	6.1E-05	3.0E-05	2.7E-01	2.1E+00	2.5E-01	6.5E-05	9.1E-02
NKT113	3109	-3.20	-9.42	2.8E-03	1.3E-01	9.0E-05	3.8E-05	3.0E-01	2.5E+00	2.3E-01	7.5E-05	9.5E-02
NKT114	3106	-3.66	-9.56	1.3E-03	1.2E-01	4.4E-05	2.6E-05	3.4E-01	2.3E+00	2.1E-01	9.4E-05	8.1E-02
NKT115	3103	-4.55	-9.74	1.2E-03	9.3E-02	3.8E-05	3.1E-05	3.3E-01	2.9E+00	2.2E-01	9.7E-05	7.7E-02
NKT116	3100	-4.90	-9.55	1.2E-03	8.6E-02	4.8E-05	4.0E-05	3.6E-01	2.8E+00	2.5E-01	1.3E-04	7.6E-02
NKT117	3097	-3.95	-9.41	1.2E-03	1.0E-01	3.3E-05	2.6E-05	5.9E-01	2.5E+00	2.2E-01	2.3E-04	7.3E-02
NKT118	3094	-4.40	-9.66	1.8E-03	1.2E-01	5.9E-05	3.5E-05	2.6E-01	2.5E+00	2.4E-01	9.2E-05	8.5E-02
NKT119	3091	-4.73	-9.44	1.5E-03	1.2E-01	1.4E-04	4.3E-05	4.7E-01	2.7E+00	2.6E-01	1.4E-04	9.6E-02
NKT120	3088	-3.68	-7.71	6.6E-03	1.1E-01	1.3E-04	5.3E-05	4.6E-01	2.9E+00	9.8E-01	1.2E-04	8.9E-02

Sample	Age	$\delta^{18}\text{O}$	$\delta^{13}\text{C}$	Y/Ca	Ba/Ca	Pb/Ca	U/Ca	Na/Ca	Mg/Ca	P/Ca	Rb/Ca	Sr/Ca
	Years BP	‰ VPDB	‰ VPDB	mmol/mol								
DL Min				1.10E-05	1.40E-04	7.30E-06	7.50E-07	1.00E-02	1.60E-03	4.80E-03	5.80E-06	6.10E-04
DL Max				1.90E-05	5.10E-04	3.60E-05	3.70E-06	9.20E-02	1.50E-02	3.20E-02	2.10E-05	2.30E-03
P% Min				1.2	0.8	0.6	0.6	1.1	0.8	1.2	1.1	0.5
P% Max				7.2	4.0	3.9	6.1	3.1	3.2	3.1	2.5	2.7
NKT121	3086	-4.19	-10.29	1.2E-02	9.7E-02	1.2E-04	6.3E-05	4.5E-01	3.1E+00	1.7E+00	1.0E-04	8.2E-02
NKT122	3083	-4.87	-11.55	1.0E-02	1.2E-01	1.6E-04	4.6E-05	4.4E-01	2.5E+00	4.6E-01	1.6E-04	8.6E-02
NKT123	3080	-4.89	-11.56	5.6E-04	1.2E-01	6.4E-05	5.0E-05	4.2E-01	3.2E+00	5.1E-01	1.0E-04	8.5E-02
NKT124	3077	-4.91	-11.83	1.1E-02	1.3E-01	1.3E-04	4.9E-05	3.9E-01	2.4E+00	5.5E-01	9.8E-05	8.8E-02
NKT125	3074	-4.63	-10.96	8.5E-03	1.4E-01	1.2E-04	5.2E-05	4.5E-01	2.5E+00	4.4E-01	1.0E-04	1.0E-01
NKT126	3071	-4.93	-11.50	8.3E-03	1.1E-01	3.4E-05	2.9E-05	4.3E-01	2.4E+00	4.0E-01	8.7E-05	6.7E-02
NKT127	3068	-4.10	-11.38	9.4E-03	1.2E-01	9.6E-05	4.5E-05	5.1E-01	2.6E+00	4.0E-01	1.1E-04	9.3E-02
NKT128	3066	-4.87	-11.09	1.3E-02	9.2E-02	1.2E-04	4.8E-05	4.2E-01	2.8E+00	5.2E-01	8.9E-05	7.8E-02
NKT129	3063	-4.59	-11.10	7.6E-03	1.4E-01	9.4E-05	3.3E-05	7.0E-01	2.5E+00	4.6E-01	1.8E-04	8.0E-02
NKT130	3060	-4.82	-11.04	8.9E-03	8.5E-02	1.1E-04	4.4E-05	3.8E-01	2.8E+00	5.0E-01	9.6E-05	7.2E-02
NKT131	3057	-4.89	-10.92	6.9E-03	1.1E-01	2.1E-04	4.2E-05	4.0E-01	2.7E+00	4.1E-01	1.4E-04	8.5E-02
NKT132	3054	-4.77	-11.02	5.9E-03	9.4E-02	8.1E-05	2.9E-05	9.1E-01	2.6E+00	3.7E-01	3.5E-04	6.3E-02
NKT133	3051	-4.82	-11.08	4.4E-03	1.0E-01	7.5E-05	3.3E-05	2.0E-01	2.4E+00	3.3E-01	7.3E-05	7.0E-02
NKT134	3049	-4.88	-11.11	7.7E-03	1.0E-01	1.1E-04	4.2E-05	3.5E-01	2.3E+00	3.9E-01	1.3E-04	7.5E-02
NKT135	3046	-4.25	-10.34	4.7E-03	9.6E-02	4.7E-05	2.6E-05	6.4E-01	2.2E+00	3.5E-01	1.7E-04	6.2E-02
NKT136	3043	-4.86	-10.56	2.1E-03	2.1E-01	9.6E-05	4.6E-05	4.1E-01	2.2E+00	5.8E-01	1.1E-04	1.2E-01
NKT137	3040	-4.70	-10.10	2.5E-03	1.8E-01	1.7E-04	4.0E-05	3.7E-01	2.2E+00	3.0E-01	1.1E-04	1.1E-01
NKT138	3037	-3.98	-9.28	3.2E-03	1.7E-01	1.0E-04	6.8E-05	1.7E-01	2.0E+00	1.6E+00	5.6E-05	9.3E-02
NKT139	3034	-4.32	-10.29	3.8E-03	1.5E-01	9.9E-05	4.4E-05	3.7E-01	2.3E+00	3.8E-01	8.5E-05	9.6E-02
NKT140	3031	-3.81	-9.89	2.9E-03	1.4E-01	1.2E-04	4.5E-05	4.3E-01	2.5E+00	3.3E-01	1.1E-04	9.9E-02
NKT141	3027	-3.40	-9.59	2.3E-03	1.8E-01	5.0E-05	2.6E-05	3.2E-01	2.1E+00	2.9E-01	9.2E-05	9.8E-02
NKT142	3024	-3.54	-9.82	3.1E-03	1.5E-01	1.0E-04	4.7E-05	4.0E-01	2.8E+00	2.7E-01	8.0E-05	1.0E-01
NKT143	3021	-3.18	-9.65	2.5E-03	1.5E-01	9.9E-05	3.8E-05	3.7E-01	2.9E+00	2.2E-01	1.1E-04	1.1E-01
NKT144	3018	-3.62	-10.50	2.3E-03	1.6E-01	4.0E-05	2.6E-05	3.5E-01	2.3E+00	2.5E-01	1.1E-04	9.2E-02
NKT145	3014	-3.65	-10.99	6.0E-03	1.1E-01	1.1E-04	3.5E-05	3.6E-01	2.4E+00	3.3E-01	1.1E-04	8.1E-02
NKT146	3011	-3.68	-9.65	3.2E-03	1.6E-01	1.1E-04	4.8E-05	5.4E-01	2.6E+00	2.9E-01	9.7E-05	1.1E-01
NKT147	3007	-3.59	-10.17	4.0E-03	1.5E-01	8.0E-05	2.8E-05	9.7E-01	2.3E+00	4.2E-01	2.7E-04	8.4E-02
NKT148	3003	-3.73	-9.76	4.5E-03	1.9E-01	2.1E-04	1.5E-04	5.5E-01	3.3E+00	5.5E-01	1.9E-04	1.2E-01
NKT149	3000	-3.45	-10.04	4.0E-03	1.6E-01	1.4E-04	5.5E-05	3.9E-01	2.8E+00	6.8E-01	1.4E-04	1.0E-01
NKT150	2996	-3.58	-10.71	2.2E-03	1.6E-01	6.3E-05	3.2E-05	6.5E-01	2.3E+00	5.1E-01	1.7E-04	9.5E-02
NKT151	2992	-3.72	-10.13	4.0E-03	1.4E-01	1.3E-04	6.0E-05	4.4E-01	3.0E+00	5.0E-01	1.3E-04	1.0E-01
NKT152	2988	-3.92	-10.59	3.8E-03	1.3E-01	1.2E-04	5.7E-05	4.2E-01	2.5E+00	4.4E-01	1.2E-04	9.9E-02
NKT153	2983	-3.97	-10.61	5.1E-03	1.3E-01	1.8E-04	3.5E-05	1.2E+00	2.6E+00	5.2E-01	6.3E-04	8.1E-02
NKT154	2979	-3.32	-10.06	2.8E-03	1.5E-01	7.5E-05	4.0E-05	3.0E-01	2.5E+00	2.5E-01	7.9E-05	9.7E-02
NKT155	2975	-3.67	-11.03	3.6E-03	1.4E-01	9.6E-05	4.1E-05	3.2E-01	2.3E+00	2.5E-01	6.6E-05	9.5E-02
NKT156	2970	-3.44	-10.48	3.5E-03	1.4E-01	7.4E-05	3.0E-05	5.6E-01	2.3E+00	3.4E-01	2.0E-04	8.6E-02
NKT157	2965	-3.45	-10.48	4.2E-03	1.7E-01	1.1E-04	5.9E-05	4.3E-01	2.5E+00	7.5E-01	1.0E-04	1.1E-01
NKT158	2961	-3.72	-10.53	4.9E-03	1.4E-01	1.0E-04	6.3E-05	3.1E-01	3.1E+00	9.0E-01	8.5E-05	9.4E-02
NKT159	2956	-3.93	-10.28	3.7E-03	1.7E-01	3.3E-05	3.7E-05	3.2E-01	2.1E+00	6.3E-01	1.2E-04	9.3E-02
NKT160	2951	-4.44	-10.58	3.7E-03	1.2E-01	8.7E-05	5.8E-05	3.7E-01	3.4E+00	6.9E-01	1.1E-04	8.8E-02
NKT161	2946	-4.85	-10.61	2.9E-03	1.4E-01	8.0E-05	5.1E-05	3.3E-01	2.7E+00	5.7E-01	9.6E-05	9.7E-02
NKT162	2941	-4.16	-10.34	2.6E-03	1.3E-01	9.4E-05	3.6E-05	1.7E-01	2.5E+00	5.2E-01	3.1E-05	8.4E-02
NKT163	2936	-4.06	-10.50	3.9E-03	1.8E-01	1.1E-04	4.6E-05	4.3E-01	2.4E+00	6.5E-01	1.6E-04	1.0E-01
NKT164	2931	-3.88	-10.46	3.6E-03	1.4E-01	9.6E-05	4.0E-05	2.9E-01	2.9E+00	4.4E-01	1.0E-04	8.9E-02
NKT165	2926			2.9E-03	1.4E-01	3.1E-05	3.9E-05	3.0E-01	2.9E+00	8.1E-01	7.2E-05	8.8E-02
NKT166r	2921	-3.48	-9.52	2.0E-03	1.7E-01	7.4E-05	3.9E-05	3.1E-01	3.1E+00	7.1E-01	9.6E-05	9.8E-02
NKT167	2915	-3.82	-9.32	4.4E-03	1.4E-01	1.5E-04	5.3E-05	3.7E-01	3.7E+00	6.0E-01	1.1E-04	1.0E-01
NKT168	2910	-3.85	-10.09	1.8E-03	1.4E-01	2.5E-05	2.9E-05	1.1E-01	2.7E+00	3.5E-01	2.9E-05	8.8E-02
NKT169	2905	-4.12	-10.27	3.2E-03	1.3E-01	1.0E-04	3.8E-05	3.8E-01	2.5E+00	1.7E-01	1.2E-04	9.2E-02
NKT170r	2899	-4.40	-9.93	3.6E-03	1.3E-01	3.4E-05	3.1E-05	1.4E-01	2.8E+00	3.0E-01	2.4E-05	8.2E-02
NKT171	2894	-4.23	-10.03	4.5E-03	1.1E-01	4.8E-05	2.7E-05	3.8E-01	2.8E+00	2.9E-01	1.5E-04	7.1E-02
NKT172	2888	-4.47	-9.87	8.2E-03	7.1E-02	1.4E-04	3.7E-05	3.5E-01	3.3E+00	3.3E-01	1.7E-04	5.0E-02
NKT173	2883	-4.73	-10.13	8.3E-03	6.7E-02	6.8E-05	3.4E-05	3.2E-01	3.1E+00	3.6E-01	1.3E-04	4.8E-02
NKT174	2877	-4.49	-10.01	4.7E-03	1.0E-01	4.3E-05	2.9E-05	2.7E-01	2.8E+00	2.5E-01	8.1E-05	6.9E-02
NKT175	2872	-4.22	-9.68	5.7E-03	6.5E-02	1.5E-04	3.5E-05	8.3E-01	3.4E+00	3.0E-01	4.8E-04	5.3E-02
NKT176	2866	-4.19	-8.46	3.5E-03	8.4E-02	6.4E-05	3.9E-05	1.6E-01	3.6E+00	2.9E-01	2.9E-05	6.0E-02
NKT177	2861	-4.51	-8.25	8.7E-03	6.2E-02	2.5E-05	3.6E-05	2.9E-01	3.2E+00	3.6E-01	8.1E-05	4.8E-02
NKT178	2855	-3.77	-7.62	2.4E-03	7.8E-02	2.2E-04	3.2E-05	1.7E-01	3.9E+00	2.3E-01	4.8E-05	6.0E-02
NKT179	2849	-4.83	-8.25	3.2E-03	7.3E-02	1.2E-04	3.0E-05	3.6E-01	3.2E+00	2.5E-01	1.4E-04	5.5E-02
NKT180	2844	-5.04	-8.45	2.9E-03	7.7E-02	4.2E-05	2.8E-05	4.5E-01	3.6E+00	2.6E-01	1.1E-04	6.0E-02

Sample	Age	$\delta^{18}\text{O}$	$\delta^{13}\text{C}$	Y/Ca	Ba/Ca	Pb/Ca	U/Ca	Na/Ca	Mg/Ca	P/Ca	Rb/Ca	Sr/Ca
	Years BP	‰ VPDB	‰ VPDB	mmol/mol								
DL Min				1.10E-05	1.40E-04	7.30E-06	7.50E-07	1.00E-02	1.60E-03	4.80E-03	5.80E-06	6.10E-04
DL Max				1.90E-05	5.10E-04	3.60E-05	3.70E-06	9.20E-02	1.50E-02	3.20E-02	2.10E-05	2.30E-03
P% Min				1.2	0.8	0.6	0.6	1.1	0.8	1.2	1.1	0.5
P% Max				7.2	4.0	3.9	6.1	3.1	3.2	3.1	2.5	2.7
NKT181	2838	-4.53	-8.23	3.1E-03	6.0E-02	3.6E-03	3.6E-05	3.0E-01	3.5E+00	4.1E-01	8.5E-05	4.7E-02
NKT182	2832	-4.04	-7.84	1.9E-03	7.1E-02	1.4E-04	3.3E-05	3.0E-01	3.8E+00	3.8E-01	2.0E-04	5.3E-02
NKT183	2826	-3.95	-7.73	1.9E-03	8.7E-02	1.1E-04	3.0E-05	5.4E-01	3.6E+00	3.2E-01	3.0E-04	6.2E-02
NKT184	2821	-4.35	-8.45	1.8E-03	1.0E-01	8.4E-05	2.7E-05	7.9E-01	3.3E+00	2.6E-01	4.1E-04	7.0E-02
NKT185	2815	-4.90	-9.52	3.6E-03	6.7E-02	3.3E-05	3.2E-05	2.1E-01	3.5E+00	2.6E-01	3.8E-05	5.3E-02
NKT186	2809	-4.63	-10.06	2.6E-03	7.7E-02	9.6E-05	2.7E-05	3.9E-01	3.2E+00	2.6E-01	1.3E-04	6.3E-02
NKT187	2803	-3.94	-8.11	1.9E-03	7.7E-02	8.2E-05	3.1E-05	4.9E-01	3.8E+00	2.7E-01	2.3E-04	6.0E-02
NKT188	2797	-3.91	-8.17	1.9E-03	9.1E-02	6.9E-05	3.1E-05	2.8E-01	3.7E+00	2.8E-01	5.0E-05	6.5E-02
NKT189	2791	-4.06	-9.57	1.6E-03	7.1E-02	6.3E-05	2.8E-05	2.0E-01	3.9E+00	3.1E-01	8.1E-05	5.7E-02
NKT190	2785	-4.21	-9.53	3.4E-03	8.5E-02	9.0E-05	3.3E-05	3.1E-01	3.1E+00	2.6E-01	5.6E-05	6.0E-02
NKT191	2778	-4.61	-9.40	3.5E-03	9.4E-02	4.3E-05	2.6E-05	5.0E-01	3.0E+00	2.6E-01	5.3E-05	6.4E-02
NKT192	2772	-4.53	-9.15	4.6E-03	6.0E-02	4.3E-05	3.0E-05	1.8E-01	3.4E+00	2.8E-01	5.5E-05	4.9E-02
NKT193	2766	-4.16	-10.41	7.0E-03	6.2E-02	7.1E-05	3.6E-05	2.5E-01	2.5E+00	6.3E-01	4.6E-05	4.4E-02
NKT194	2760	-4.18	-10.18	4.0E-03	1.2E-01	4.4E-04	2.8E-05	1.9E-01	2.2E+00	3.4E-01	6.2E-05	7.0E-02
NKT195	2753	-4.21	-12.16	2.8E-03	8.3E-02	7.3E-05	2.8E-05	6.1E-01	3.6E+00	2.7E-01	2.3E-04	6.3E-02
NKT196	2747	-4.34	-12.09	4.1E-03	1.8E-01	3.1E-05	2.6E-05	3.4E-01	1.7E+00	3.4E-01	6.5E-05	9.2E-02
NKT197	2740	-4.07	-10.56	5.3E-03	9.2E-02	6.5E-05	3.3E-05	2.5E-01	2.6E+00	3.0E-01	4.4E-05	5.7E-02
NKT198	2734	-3.71	-10.01	2.7E-03	8.9E-02	5.7E-05	3.2E-05	2.5E-01	3.2E+00	5.7E-01	9.9E-05	6.5E-02
NKT199	2727	-4.00	-11.00	3.2E-03	1.6E-01	6.7E-05	3.2E-05	1.8E-01	1.9E+00	3.3E-01	4.6E-05	8.7E-02
NKT200	2720	-4.53	-11.42	3.2E-03	1.3E-01	5.8E-05	2.5E-05	2.4E-01	2.0E+00	2.6E-01	3.9E-05	8.0E-02
NKT201	2714	-4.16	-10.22	5.6E-03	1.3E-01	1.0E-04	2.6E-05	8.3E-01	2.0E+00	3.6E-01	2.2E-04	7.4E-02
NKT202	2707	-4.44	-10.33	2.2E-03	1.9E-01	4.4E-05	4.2E-05	2.5E-01	2.1E+00	5.6E-01	6.3E-05	1.1E-01
NKT203	2700	-4.68	-11.10	3.7E-03	2.0E-01	5.6E-05	3.2E-05	2.7E-01	1.7E+00	4.5E-01	4.8E-05	1.0E-01
NKT204	2694	-4.37	-10.60	2.3E-03	1.6E-01	4.9E-05	3.7E-05	3.8E-01	2.6E+00	5.4E-01	1.6E-04	9.4E-02
NKT205	2687	-5.87	-10.65	3.7E-03	8.9E-02	2.3E-04	3.6E-05	2.6E-01	2.4E+00	3.6E-01	7.2E-05	6.1E-02
NKT206	2680	-5.72	-10.00	5.6E-03	9.4E-02	5.8E-04	4.0E-05	3.3E-01	2.7E+00	5.3E-01	8.8E-05	6.4E-02
NKT207	2673	-4.45	-10.33	2.4E-03	1.8E-01	5.1E-05	4.8E-05	4.0E-01	2.5E+00	1.2E+00	1.0E-04	1.0E-01
NKT208	2666	-4.53	-10.12	3.3E-03	1.1E-01	2.9E-04	2.6E-05	7.1E-01	2.3E+00	3.2E-01	1.1E-04	7.2E-02
NKT209	2659	-4.64	-9.77	2.9E-03	1.3E-01	3.6E-05	3.0E-05	1.8E-01	2.4E+00	3.2E-01	4.2E-05	7.8E-02
NKT210	2652	-4.82	-9.52	2.4E-03	1.1E-01	3.6E-05	2.9E-05	4.2E-01	2.3E+00	2.8E-01	1.8E-04	7.7E-02
NKT211	2645	-6.49	-10.57	5.5E-03	8.2E-02	4.6E-05	3.2E-05	2.1E-01	2.2E+00	4.8E-01	5.1E-05	5.6E-02
NKT212	2638	-5.25	-9.74	5.3E-03	9.3E-02	2.7E-04	3.1E-05	3.6E-01	2.2E+00	4.0E-01	2.1E-04	6.0E-02
NKT213	2631	-4.22	-9.65	3.4E-03	9.9E-02	2.8E-05	2.3E-05	1.5E-01	2.4E+00	2.5E-01	6.3E-05	7.0E-02
NKT214	2624	-4.13	-9.13	3.0E-03	1.1E-01	5.3E-05	2.8E-05	3.0E-01	2.4E+00	2.5E-01	7.6E-05	7.4E-02
NKT215	2617	-4.04	-9.00	2.3E-03	9.2E-02	8.2E-05	2.3E-05	3.9E-01	2.6E+00	1.8E-01	8.6E-05	6.8E-02
NKT216	2610	-3.89	-9.10	2.4E-03	1.3E-01	5.8E-05	5.4E-05	4.3E-01	2.8E+00	1.2E+00	1.5E-04	8.3E-02
NKT217	2602	-4.31	-10.23	4.6E-03	1.3E-01	8.0E-05	4.5E-05	6.2E-01	2.0E+00	8.9E-01	1.5E-04	7.5E-02
NKT218	2595	-3.88	-9.36	3.2E-03	1.3E-01	3.0E-03	8.2E-05	4.3E-01	2.6E+00	2.2E+00	9.0E-05	8.4E-02
NKT219	2588	-4.24	-9.51	3.3E-03	1.1E-01	6.0E-05	2.3E-05	7.4E-01	2.2E+00	2.6E-01	2.3E-04	7.5E-02
NKT220	2581	-4.52	-9.42	2.8E-03	1.1E-01	3.0E-05	3.6E-05	1.7E-01	2.4E+00	3.8E-01	4.5E-05	7.1E-02
NKT221	2573	-4.28	-9.55	2.7E-03	1.3E-01	6.6E-05	4.4E-05	3.4E-01	2.2E+00	5.5E-01	5.4E-05	7.6E-02
NKT222	2566	-4.24	-10.10	1.8E-03	1.3E-01	9.3E-05	2.3E-05	7.9E-01	2.2E+00	2.4E-01	2.8E-04	8.9E-02
NKT223	2558	-4.28	-10.23	4.2E-03	1.2E-01	1.8E-04	3.7E-05	2.4E-01	2.2E+00	5.5E-01	1.0E-04	7.1E-02
NKT224	2551	-3.96	-10.37	5.6E-03	1.1E-01	1.1E-04	5.4E-05	7.3E-01	2.4E+00	7.7E-01	1.7E-04	7.4E-02
NKT225	2543	-3.92	-10.89	2.9E-03	1.5E-01	7.3E-05	2.7E-05	6.7E-01	2.3E+00	3.0E-01	3.3E-04	9.9E-02
NKT226	2536	-4.19	-10.38	3.8E-03	1.0E-01	9.4E-05	4.0E-05	1.8E-01	2.6E+00	5.8E-01	5.2E-05	6.5E-02
NKT227	2528	-4.12	-10.35	3.5E-03	1.0E-01	3.4E-03	4.3E-05	5.6E-01	2.7E+00	6.1E-01	1.6E-04	6.7E-02
NKT228	2520	-3.88	-10.29	3.4E-03	9.1E-02	4.0E-05	3.4E-05	3.9E-01	2.4E+00	5.1E-01	1.3E-04	6.4E-02
NKT229	2513	-3.89	-9.87	2.9E-03	1.0E-01	4.0E-04	4.3E-05	2.0E-01	2.7E+00	5.8E-01	5.2E-05	6.8E-02
NKT230	2505	-3.80	-9.98	3.2E-03	1.0E-01	5.7E-05	3.7E-05	3.1E-01	2.6E+00	3.9E-01	6.1E-05	7.2E-02
NKT231	2497	-3.66	-9.73	4.8E-03	1.2E-01	3.5E-05	4.5E-05	3.5E-01	2.4E+00	7.3E-01	9.5E-05	7.4E-02
NKT232	2489	-3.62	-10.17	3.4E-03	1.1E-01	2.4E-05	3.8E-05	2.9E-01	2.7E+00	5.1E-01	4.4E-05	6.9E-02
NKT233	2481	-3.61	-9.71	2.2E-03	1.5E-01	4.4E-05	3.5E-05	2.9E-01	2.4E+00	4.0E-01	9.9E-05	8.8E-02
NKT234	2474	-3.80	-9.98	3.4E-03	1.2E-01	2.7E-05	3.7E-05	3.1E-01	2.4E+00	5.2E-01	9.5E-05	7.9E-02
NKT235	2466	-3.66	-9.83	2.6E-03	1.5E-01	4.6E-05	7.3E-05	3.5E-01	2.7E+00	1.5E+00	1.2E-04	8.5E-02
NKT236	2457	-3.61	-9.77	4.0E-03	1.2E-01	3.2E-05	3.7E-05	1.7E-01	2.7E+00	5.4E-01	2.9E-05	7.1E-02
NKT237	2449	-3.43	-9.33	3.2E-03	1.2E-01	3.9E-05	3.1E-05	4.8E-01	2.5E+00	3.8E-01	1.5E-04	8.0E-02
NKT238	2441	-3.41	-9.82	2.2E-03	1.6E-01	7.2E-04	4.4E-05	5.8E-01	2.6E+00	6.8E-01	1.2E-04	9.6E-02
NKT239	2433	-3.43	-9.70	2.2E-03	1.6E-01	4.7E-05	4.6E-05	4.6E-01	3.0E+00	6.6E-01	1.1E-04	9.8E-02
NKT240	2425	-4.07	-9.37	2.7E-03	1.3E-01	4.0E-05	3.8E-05	4.1E-01	2.5E+00	5.9E-01	1.1E-04	8.4E-02

Sample	Age	$\delta^{18}\text{O}$	$\delta^{13}\text{C}$	Y/Ca	Ba/Ca	Pb/Ca	U/Ca	Na/Ca	Mg/Ca	P/Ca	Rb/Ca	Sr/Ca
	Years BP	‰ VPDB	‰ VPDB	mmol/mol								
DL Min				1.10E-05	1.40E-04	7.30E-06	7.50E-07	1.00E-02	1.60E-03	4.80E-03	5.80E-06	6.10E-04
DL Max				1.90E-05	5.10E-04	3.60E-05	3.70E-06	9.20E-02	1.50E-02	3.20E-02	2.10E-05	2.30E-03
P% Min				1.2	0.8	0.6	0.6	1.1	0.8	1.2	1.1	0.5
P% Max				7.2	4.0	3.9	6.1	3.1	3.2	3.1	2.5	2.7
NKT241	2416	-3.70	-9.70	1.8E-03	1.5E-01	5.6E-05	3.5E-05	2.0E-01	2.9E+00	3.1E-01	3.7E-05	9.6E-02
NKT242	2408	-3.86	-10.09	2.6E-03	1.8E-01	7.1E-05	3.3E-04	5.0E-01	3.0E+00	1.5E+01	6.4E-05	9.8E-02
NKT243	2399	-4.25	-10.01	2.1E-03	1.7E-01	2.4E-05	4.3E-05	2.8E-01	2.6E+00	6.7E-01	1.1E-04	1.0E-01
NKT244	2391	-4.01	-10.62	6.7E-04	1.0E-01	6.4E-04	5.3E-05	3.0E-01	4.3E+00	1.9E-01	8.1E-05	7.9E-02
NKT245	2382	-4.14	-10.71	3.7E-04	9.9E-02	7.3E-05	5.6E-05	7.7E-01	4.1E+00	1.4E-01	1.3E-04	8.0E-02
NKT246	2373	-3.82	-10.67	7.2E-04	1.2E-01	1.7E-04	5.0E-05	5.0E-01	3.6E+00	2.1E-01	1.0E-04	8.6E-02
NKT247	2364	-3.69	-10.19	1.1E-03	1.3E-01	2.8E-04	4.4E-05	2.3E-01	3.1E+00	2.9E-01	7.4E-05	9.2E-02
NKT248	2356	-3.58	-9.65	2.4E-03	1.4E-01	1.1E-04	4.8E-05	2.4E-01	3.0E+00	3.0E-01	6.4E-05	9.6E-02
NKT249	2347	-3.89	-10.37	2.0E-03	1.3E-01	4.1E-05	3.4E-05	3.8E-01	3.4E+00	3.3E-01	8.4E-05	9.3E-02
NKT250	2338	-3.55	-10.60	3.9E-03	1.2E-01	5.0E-05	4.7E-05	1.8E-01	2.7E+00	2.4E-01	2.3E-05	7.9E-02
NKT251	2328	-3.56	-9.42	2.9E-03	1.2E-01	1.1E-04	4.7E-05	3.9E-01	3.0E+00	1.8E-01	1.0E-04	8.6E-02
NKT252	2319	-4.42	-10.41	1.7E-04	1.4E-01	3.6E-05	5.2E-05	2.5E-01	3.2E+00	1.1E+00	8.0E-05	9.6E-02
NKT253	2310	-3.50	-10.49	3.3E-03	1.6E-01	8.7E-05	7.3E-05	1.3E-01	2.6E+00	8.3E-01	2.3E-05	9.4E-02
NKT254	2301	-3.64	-10.34	2.6E-03	1.6E-01	1.6E-04	5.5E-05	9.2E-01	2.7E+00	3.7E-01	7.3E-05	9.8E-02
NKT255	2291	-4.17	-10.47	8.5E-04	1.1E-01	5.1E-05	5.1E-05	4.2E-01	3.7E+00	1.9E-01	1.2E-04	8.3E-02
NKT256	2282	-3.90	-10.73	4.2E-03	1.6E-01	3.1E-04	6.4E-05	1.8E-01	2.6E+00	5.0E-01	3.5E-05	9.7E-02
NKT257	2272	-3.41	-11.36	3.4E-03	1.5E-01	6.7E-05	5.9E-05	5.3E-01	2.8E+00	3.4E-01	5.5E-05	9.6E-02
NKT258	2263	-4.60	-11.02	5.2E-03	1.1E-01	2.4E-05	4.8E-05	2.7E-01	2.8E+00	2.9E-01	5.4E-05	7.7E-02
NKT259	2253	-4.51	-9.94	3.0E-03	1.2E-01	3.2E-03	5.5E-05	2.4E-01	2.9E+00	3.0E-01	5.2E-05	8.3E-02
NKT260	2244	-4.32	-9.18	2.7E-03	1.2E-01	8.8E-04	5.5E-05	3.0E-01	3.3E+00	3.0E-01	9.4E-05	7.9E-02
NKT261	2235	-3.44	-8.02	3.2E-03	1.4E-01	1.1E-04	4.9E-05	8.0E-01	2.8E+00	2.7E-01	2.0E-04	9.8E-02
NKT262	2225	-3.44	-8.53	2.6E-03	1.4E-01	1.0E-04	7.3E-05	2.2E-01	4.6E+00	3.2E-01	5.7E-05	8.8E-02
NKT263	2216	-3.53	-8.17	1.7E-03	1.4E-01	9.5E-05	8.1E-05	2.1E-01	4.1E+00	6.7E-01	4.2E-05	8.4E-02
NKT264	2207	-3.27	-8.54	5.2E-03	1.6E-01	5.8E-05	1.4E-04	3.5E-01	2.8E+00	2.2E+00	7.9E-05	9.6E-02
NKT265	2198	-3.50	-7.73	1.7E-03	1.1E-01	1.4E-04	5.7E-05	5.3E-01	5.0E+00	3.9E-01	6.3E-05	7.6E-02
NKT266	2189	-3.56	-8.85	3.0E-03	8.2E-02	1.1E-04	4.2E-05	1.1E+00	3.8E+00	2.4E-01	6.9E-04	6.2E-02
NKT267	2180	-2.68	-6.84	4.4E-03	1.5E-01	5.5E-05	5.6E-05	7.1E-01	2.5E+00	3.8E-01	2.1E-04	9.8E-02
NKT268	2171	-3.57	-7.68	3.2E-03	1.0E-01	4.7E-05	5.8E-05	1.0E-01	4.6E+00	3.4E-01	5.2E-05	7.3E-02
NKT269	2162	-4.02	-10.59	1.1E-02	8.2E-02	1.4E-04	4.7E-05	1.5E-01	2.6E+00	2.9E-01	5.7E-05	6.0E-02
NKT270	2154	-3.20	-7.63	7.1E-04	1.4E-01	5.6E-05	6.1E-05	2.4E-01	4.4E+00	4.2E-01	9.1E-05	1.0E-01
NKT271	2145	-3.27	-7.02	2.1E-03	1.3E-01	2.3E-05	8.9E-05	2.1E-01	5.3E+00	5.3E-01	2.8E-05	9.1E-02
NKT272	2137	-4.27	-10.07	6.5E-03	1.4E-01	4.4E-05	5.1E-05	9.6E-02	2.5E+00	2.4E-01	2.4E-05	9.5E-02
NKT273	2129	-4.70	-10.75	1.2E-03	1.4E-01	3.5E-05	7.2E-05	2.6E-01	4.4E+00	7.5E-01	6.4E-05	8.8E-02

Table 20: Stable isotope and trace element ratio measurements for sample stalagmite from Kotumsar cave.

Subsample	Years BP	S/Ca	Precision	DL	S/Ca	Subsample	Years BP	S/Ca	Precision	DL	S/Ca
		All			ADL			All			ADL
NKT1	3449	2.3682	0.0609	0.3049	2.3682	NKT61r	3292	0.1216	0.0264	0.1119	2.3367
NKT2	3445	2.0724	0.0609	0.3049	2.0724	NKT62	3290	2.3488	0.0171	0.1037	
NKT3	3442	0.1742	0.0056	0.2923		NKT63	3287	0.1688	0.0147	0.3522	1.3389
NKT4	3438	1.6364	0.0609	0.3049	1.6364	NKT64	3285	2.8438	0.0171	0.1037	1.7212
NKT5	3434	1.6549	0.0609	0.3049	1.6549	NKT65	3282	2.0470	0.0171	0.1037	
NKT6	3431	0.1598	0.0056	0.2923		NKT66	3279	0.1948	0.0147	0.3522	0.8827
NKT7	3427	1.5658	0.0609	0.3049	1.5658	NKT67	3276	1.6063	0.0171	0.1037	1.6199
NKT8	3423	1.8603	0.0609	0.3049	1.8603	NKT68	3273	2.2547	0.0171	0.1037	
NKT9	3419	0.1922	0.0056	0.2923		NKT69	3270	0.1800	0.0147	0.3522	2.4421
NKT10	3416	1.2738	0.0609	0.3049	1.2738	NKT70	3266	638.0502	0.0171	0.1037	
NKT11	3412	1.5241	0.0609	0.3049	1.5241	NKT71	3263	2.3367	0.0171	0.1037	
NKT12	3408	0.2191	0.0056	0.2923		NKT72	3260	0.2066	0.0147	0.3522	2.5453
NKT13	3404	2.1121	0.0609	0.3049	2.1121	NKT73	3256	1.3389	0.0171	0.1037	2.2634
NKT14	3400	2.2326	0.0609	0.3049	2.2326	NKT74	3252	1.7212	0.0171	0.1037	
NKT15	3396	0.1717	0.0056	0.2923		NKT75	3249	0.2054	0.0147	0.3522	1.9146
NKT16	3392	2.3941	0.0609	0.3049	2.3941	NKT76	3245	0.8827	0.0171	0.1037	2.2662
NKT17	3389	2.2636	0.0609	0.3049	2.2636	NKT77	3241	1.6199	0.0171	0.1037	
NKT18	3385	0.2646	0.0056	0.2923		NKT78	3237	0.2311	0.0147	0.3522	1.7317
NKT19	3381	2.2334	0.0609	0.3049	2.2334	NKT79	3233	2.4421	0.0171	0.1037	2.6190
NKT20	3377	2.1037	0.0609	0.3049	2.1037	NKT80r	3229	0.1756	0.0264	0.1119	
NKT21	3374	0.3126	0.0056	0.2923		NKT81	3225	0.1863	0.0147	0.3522	2.3437
NKT22	3370	1.9349	0.0609	0.3049	1.9349	NKT82	3221	2.5453	0.0171	0.1037	0.1577
NKT23	3367	2.0213	0.0609	0.3049	2.0213	NKT83	3217	2.2634	0.0171	0.1037	
NKT24	3363	0.3015	0.0056	0.2923		NKT84	3213	0.1731	0.0147	0.3522	0.1327
NKT25r	3360	0.1691	0.0264	0.1119	0.1691	NKT85	3209	1.9146	0.0171	0.1037	1.8048
NKT26	3357	2.3967	0.0609	0.3049	2.3967	NKT86	3205	2.2662	0.0171	0.1037	
NKT27	3354	0.1990	0.0056	0.2923		NKT87	3200	0.1861	0.0147	0.3522	2.5138
NKT28	3351	2.4487	0.0609	0.3049	2.4487	NKT88	3196	1.7317	0.0171	0.1037	1.7498
NKT29	3348	2.6539	0.0609	0.3049	2.6539	NKT89	3192	2.6190	0.0171	0.1037	
NKT30	3346	0.1660	0.0056	0.2923		NKT90	3188	0.1746	0.0147	0.3522	2.1363
NKT31	3343	2.3132	0.0609	0.3049	2.3132	NKT91	3184	2.3437	0.0171	0.1037	1.7783
NKT32	3341	2.1147	0.0609	0.3049	2.1147	NKT92r	3181	0.1577	0.0264	0.1119	
NKT33	3339	0.1705	0.0056	0.2923		NKT93	3177	0.1989	0.0147	0.3522	2.0707
NKT34	3337	1.8654	0.0609	0.3049	1.8654	NKT94r	3173	0.1327	0.0264	0.1119	1.5615
NKT35	3335	1.6862	0.0609	0.3049	1.6862	NKT95	3169	1.8048	0.0171	0.1037	
NKT36	3333	0.1604	0.0056	0.2923		NKT96	3165	0.1892	0.0147	0.3522	1.5478
NKT37	3331	2.3747	0.0609	0.3049	2.3747	NKT97	3162	2.5138	0.0171	0.1037	1.7501
NKT38	3330	2.0243	0.0609	0.3049	2.0243	NKT98	3158	1.7498	0.0171	0.1037	
NKT39	3328	0.1509	0.0056	0.2923		NKT99	3155	0.1826	0.0147	0.3522	2.0016
NKT40	3327	2.2771	0.0609	0.3049	2.2771	NKT100	3151	2.1363	0.0171	0.1037	1.6763
NKT41	3325	2.3055	0.0609	0.3049	2.3055	NKT101	3148	1.7783	0.0171	0.1037	
NKT42	3324	0.1646	0.0056	0.2923		NKT102	3144	0.2658	0.0147	0.3522	
NKT43	3323	2.5047	0.0609	0.3049	2.5047	NKT103	3141	2.0707	0.0171	0.1037	1.5804
NKT44	3322	0.9676	0.0609	0.3049	0.9676	NKT104	3138	1.5615	0.0171	0.1037	
NKT45	3320	0.2052	0.0056	0.2923		NKT105	3134	0.1979	0.0147	0.3522	1.1733
NKT46	3319	0.9051	0.0609	0.3049	0.9051	NKT106	3131	1.5478	0.0171	0.1037	1.7062
NKT47r	3318	0.1518	0.0264	0.1119	0.1518	NKT107	3128	1.7501	0.0171	0.1037	
NKT48	3316	0.2135	0.0056	0.2923		NKT108	3125	0.2001	0.0147	0.3522	1.2083
NKT49	3315	1.4035	0.0609	0.3049	1.4035	NKT109	3121	2.0016	0.0171	0.1037	2.4196
NKT50	3314	1.9977	0.0609	0.3049	1.9977	NKT110	3118	1.6763	0.0171	0.1037	2.7614
NKT51	3312	0.1549	0.0056	0.2923		NKT111	3115	0.1908	0.0147	0.3522	1.9715
NKT52	3311	2.6893	0.0171	0.1037	2.6893	NKT112	3112	1.1516	0.0171	0.1037	
NKT53	3309	1.8669	0.0171	0.1037	1.8669	NKT113	3109	1.5804	0.0171	0.1037	1.8808
NKT54	3307	0.1822	0.0056	0.2923		NKT114	3106	0.2592	0.0147	0.3522	2.7259
NKT55	3305	2.2087	0.0171	0.1037	2.2087	NKT115	3103	1.1733	0.0171	0.1037	
NKT56	3303	1.7904	0.0171	0.1037	1.7904	NKT116	3100	1.7062	0.0171	0.1037	1.9001
NKT57	3301	0.3531	0.0056	0.2923		NKT117	3097	0.1907	0.0147	0.3522	2.1057
NKT58	3299	1.7940	0.0171	0.1037	1.794	NKT118	3094	1.2083	0.0171	0.1037	
NKT59	3297	1.7696	0.0171	0.1037	1.7696	NKT119	3091	2.4196	0.0171	0.1037	1.6692
NKT60	3295	0.1929	0.0147	0.3522		NKT121	3088	2.7614	0.0171	0.1037	1.8450

Subsample	Years BP	S/Ca	Precision	DL	S/Ca	Subsample	Years BP	S/Ca	Precision	DL	S/Ca
		All			ADL			All			ADL
NKT122	3086	1.9715	0.0171	0.1037		NKT181	2844	0.1923	0.0344	0.2848	
NKT123	3083	0.2252	0.0147	0.3522	0.7452	NKT182	2838	0.1297	0.0344	0.2848	
NKT124	3080	1.8808	0.0171	0.1037	1.7159	NKT183	2832	0.2895	0.0147	0.3522	
NKT125	3077	2.7259	0.0171	0.1037		NKT184	2826	0.2308	0.0344	0.2848	
NKT126	3074	0.1934	0.0147	0.3522	2.0957	NKT185	2821	0.1410	0.0344	0.2848	
NKT127	3071	1.9001	0.0171	0.1037	2.0542	NKT186	2815	0.2242	0.0147	0.3522	
NKT128	3068	2.1057	0.0171	0.1037		NKT187	2809	0.2290	0.0344	0.2848	
NKT129	3066	0.3462	0.0147	0.3522	2.4442	NKT188	2803	0.1399	0.0344	0.2848	
NKT130	3063	1.6692	0.0171	0.1037	2.5972	NKT189	2797	0.1908	0.0147	0.3522	
NKT131	3060	1.8450	0.0171	0.1037		NKT190	2791	0.1900	0.0344	0.2848	
NKT132	3057	0.2089	0.0147	0.3522	0.121638	NKT191	2785	0.3022	0.0344	0.2848	
NKT133	3054	0.7452	0.0171	0.1037	2.348832	NKT192	2778	0.1654	0.0147	0.3522	
NKT134	3051	1.7159	0.0171	0.1037		NKT193	2772	0.2001	0.0344	0.2848	
NKT135	3049	0.1875	0.0147	0.3522	2.843844	NKT194	2766	0.1973	0.0344	0.2848	
NKT136	3046	2.0957	0.0171	0.1037	2.046974	NKT195	2760	0.1692	0.0147	0.3522	
NKT137	3043	2.0542	0.0171	0.1037		NKT196	2753	0.2454	0.0344	0.2848	
NKT138	3040	0.2793	0.0147	0.3522	1.606259	NKT197	2747	0.1985	0.0344	0.2848	
NKT139	3037	2.4442	0.0171	0.1037	2.25473	NKT198	2740	0.2030	0.0147	0.3522	
NKT140	3034	2.5972	0.0171	0.1037		NKT199	2734	0.1846	0.0344	0.2848	
NKT141	3031	0.22890	0.01469	0.35219		NKT200	2727	0.1602	0.0344	0.2848	
NKT142	3027	2.11131	0.01708	0.10371	2.11131	NKT201	2720	0.3303	0.0147	0.3522	
NKT143	3024	1.82209	0.01708	0.10371	1.822095	NKT202	2714	0.2189	0.0344	0.2848	
NKT144	3021	0.21848	0.01469	0.35219		NKT203	2707	0.2236	0.0344	0.2848	
NKT145	3018	1.60089	0.01708	0.10371	1.600891	NKT204	2700	0.2738	0.0147	0.3522	
NKT146	3014	2.48927	0.01708	0.10371	2.489269	NKT205	2694	0.1943	0.0344	0.2848	
NKT147	3011	0.22122	0.01469	0.35219		NKT206	2687	0.4785	0.0344	0.2848	0.478506
NKT148	3007	2.28429	0.01708	0.10371	2.28429	NKT207	2680	0.2517	0.0147	0.3522	
NKT149	3003	1.78600	0.01708	0.10371	1.786005	NKT208	2673	0.3826	0.0344	0.2848	0.382582
NKT150	3000	0.18970	0.01469	0.35219		NKT209	2666	0.1718	0.0344	0.2848	
NKT151	2996	2.90448	0.01708	0.10371	2.904483	NKT210	2659	0.2273	0.0147	0.3522	
NKT152	2992	2.87979	0.01708	0.10371	2.879787	NKT211	2652	0.1997	0.0344	0.2848	
NKT153	2988	0.22658	0.01469	0.35219		NKT212	2645	0.1693	0.0344	0.2848	
NKT154	2983	1.53106	0.01708	0.10371	1.531063	NKT213	2638	0.1765	0.0147	0.3522	
NKT155	2979	2.18646	0.01708	0.10371	2.186455	NKT214	2631	0.1934	0.0344	0.2848	
NKT156	2975	0.27445	0.01469	0.35219		NKT215	2624	0.2034	0.0344	0.2848	
NKT157	2970	2.42652	0.01708	0.10371	2.426517	NKT216	2617	0.2459	0.0147	0.3522	
NKT158	2965	1.73012	0.01708	0.10371	1.730124	NKT217	2610	0.3413	0.0344	0.2848	0.341349
NKT159	2961	0.27854	0.01469	0.35219		NKT218	2602	0.3131	0.0344	0.2848	0.313069
NKT160	2956	2.11923	0.01708	0.10371	2.119233	NKT219	2595	0.1957	0.0147	0.3522	
NKT161	2951	2.24960	0.01708	0.10371	2.249598	NKT220	2588	0.1739	0.0344	0.2848	
NKT162	2946	0.22861	0.01469	0.35219		NKT221	2581	0.2782	0.0344	0.2848	
NKT163	2941	1.64093	0.01708	0.10371	1.640929	NKT222	2573	0.2709	0.0147	0.3522	
NKT164	2936	0.86421	0.01708	0.10371	0.864209	NKT223	2566	0.1996	0.0344	0.2848	
NKT165	2931	0.22317	0.01469	0.35219		NKT224	2558	0.4340	0.0344	0.2848	0.434032
NKT166r	2926	0.24796	0.02637	0.11186	0.247959	NKT225	2551	0.2120	0.0147	0.3522	
NKT167	2921	2.00112	0.01708	0.10371	2.001118	NKT226	2543	0.1506	0.0344	0.2848	
NKT168	2915	0.22871	0.01469	0.35219		NKT227	2536	1.0009	0.0344	0.2848	1.000914
NKT169	2910	2.05545	0.01708	0.10371	2.055449	NKT228	2528	0.2389	0.0147	0.3522	
NKT170r	2905	0.14077	0.02637	0.11186	0.140765	NKT229	2520	0.2453	0.0344	0.2848	
NKT171	2899	0.22703	0.01469	0.35219		NKT230	2513	0.2440	0.0344	0.2848	
NKT172	2894	0.16955	0.03439	0.28483		NKT231	2505	0.2121	0.0147	0.3522	
NKT173	2888	0.16920	0.03439	0.28483		NKT232	2497	0.2187	0.0344	0.2848	
NKT174	2883	0.19674	0.01469	0.35219		NKT233	2489	0.2304	0.0344	0.2848	
NKT175	2877	0.18947	0.03439	0.28483		NKT234	2481	0.2238	0.0147	0.3522	
NKT176	2872	0.14975	0.03439	0.28483		NKT235	2474	0.2213	0.0344	0.2848	
NKT177	2866	0.17746	0.01469	0.35219		NKT236	2466	0.1702	0.0344	0.2848	
NKT178	2861	0.11282	0.03439	0.28483		NKT237	2457	0.2112	0.0147	0.3522	
NKT179	2855	0.16248	0.03439	0.28483		NKT238	2449	0.5087	0.0344	0.2848	0.508684
NKT180	2849	0.20807	0.01469	0.35219		NKT239	2441	0.6332	0.0344	0.2848	0.633211
						NKT240	2433	0.2178	0.0147	0.3522	

Subsample	Years BP	S/Ca	Precision	DL	S/Ca	Subsample	Years BP	S/Ca	Precision	DL	S/Ca
		All			ADL			All			ADL
NKT241	2425	0.1375	0.0344	0.2848		NKT261	2253	0.2399	0.0147	0.3522	
NKT242	2416	0.3882	0.0344	0.2848	0.388212	NKT262	2244	0.2921	0.0344	0.2848	0.292108
NKT243	2408	0.2835	0.0147	0.3522		NKT263	2235	0.2366	0.0344	0.2848	
NKT244	2399	0.1569	0.0344	0.2848		NKT264	2225	0.3562	0.0147	0.3522	0.35624
NKT245	2391	0.3531	0.0344	0.2848	0.353123	NKT265	2216	0.3008	0.0344	0.2848	0.300761
NKT247	2382	0.1877	0.0344	0.2848		NKT266	2207	0.1723	0.0344	0.2848	
NKT248	2373	0.1805	0.0344	0.2848		NKT267	2198	0.2604	0.0147	0.3522	
NKT249	2364	0.1829	0.0147	0.3522		NKT268	2189	0.1405	0.0344	0.2848	
NKT250	2356	0.1526	0.0344	0.2848		NKT269	2180	0.3002	0.0344	0.2848	0.300203
NKT251	2347	0.1885	0.0344	0.2848		NKT270	2171	0.2055	0.0147	0.3522	
NKT252	2338	0.2762	0.0147	0.3522		NKT271	2162	0.1828	0.0344	0.2848	
NKT253	2328	0.1364	0.0344	0.2848		NKT272	2154	0.1255	0.0344	0.2848	
NKT254	2319	0.5384	0.0344	0.2848	0.538445	NKT273	2145	0.2444	0.0147	0.3522	
NKT255	2310	0.2230	0.0147	0.3522							
NKT256	2301	0.1792	0.0344	0.2848							
NKT257	2291	0.1644	0.0344	0.2848							
NKT258	2282	0.2318	0.0147	0.3522							
NKT259	2272	0.2417	0.0344	0.2848							
NKT260	2263	0.2061	0.0344	0.2848							

Table 21: S/Ca mmol/mol measurements for sample stalagmite from Kotumsar cave. Precision and detection limits for S/Ca measurements have also been given. DL: Detection Limit. ADL: Above Detection Limit. Every third subsample was measured in a single run first before measuring the remaining subsamples giving the regular pattern observed in detection limits in the data.

<i>Sample</i>	$\delta^{18}O$	$\delta^{13}C$
NKHTS-1	-3.86	-12.30
NKHTS-2	-3.72	-11.51
NKHTS-3	-3.84	-11.90
NKHTS-4	-4.33	-8.61
NKHTS-5	-4.71	-9.08
NKHTS-6	-4.83	-9.44
NKHTS-7	-5.12	-9.75

Table 22: Hendy test measurements for sample stalagmite from Kotumsar cave. They are referred by a shorter code name of Ht1, Ht2, Ht3 etc in the chapter.

Published fractionation equation	T (C)	T (K)	1000lna	1000/T(K)	a	Drip water	Rwater	Rcalc	dcalcVSMOW	Calculated Calcite
Kim and O'Neill, 1997 ($10^3 \ln a = 18.03 * 10^3 / T(K) - 32.42$)	28.25	302.4	27.20	3.31	1.0272	-1.5	0.002002	0.002057	25.66	-5.09
	28.25	302.4	27.20	3.31	1.0272	-3.1	0.001999	0.002053	24.02	-6.68
	26.33	300.48	27.58	3.33	1.0276	-1.5	0.002002	0.002057	26.04	-4.72
Coplen, 2007 ($10^3 \ln a = 17.4 * 10^3 / T(K) - 28.6$)	26.33	300.48	27.58	3.33	1.0276	-3.1	0.001999	0.002054	24.40	-6.32
	28.25	302.4	28.94	3.31	1.0289	-1.5	0.002002	0.00206	27.40	-3.41
	28.25	302.4	28.94	3.31	1.0289	-3.1	0.001999	0.002057	25.75	-5.01
	26.33	300.48	29.31	3.31	1.0293	-1.5	0.002002	0.002061	27.76	-3.05
	26.33	300.48	29.31	3.31	1.0293	-3.1	0.001999	0.002058	26.12	-4.65

Table 23: Measured $\delta^{18}\text{O}$ of sample stalagmite from Kotumsar cave compared to expected $\delta^{18}\text{O}$ values from published fractionation equations.

Wavenumber (cm-1)	Absorbance						
	N3VS3	N3VS4	N3VS5	N3VS6	N3VS7	N3VS8	N3VS9
649.7787	0.0008	0.004849	0.000556	-0.002403	0.001021	0.001138	0.001489
651.7068	0.0008	0.004851	0.000558	-0.002389	0.001007	0.001126	0.001508
653.6349	0.0008	0.004858	0.000566	-0.002363	0.001016	0.00113	0.001532
655.5630	0.0009	0.004882	0.000572	-0.002364	0.001045	0.001158	0.001542
657.4912	0.0009	0.004887	0.000572	-0.002398	0.001083	0.001195	0.001546
659.4193	0.0009	0.00484	0.000562	-0.002434	0.001104	0.001223	0.001567
661.3474	0.0009	0.004777	0.000559	-0.002443	0.001102	0.001235	0.001607
663.2755	0.0009	0.004865	0.000575	-0.002427	0.001098	0.001244	0.001656
665.2037	0.0009	0.005347	0.000604	-0.002419	0.001102	0.001255	0.001696
667.1318	0.0010	0.006129	0.000632	-0.002453	0.001107	0.00126	0.001695
669.0599	0.0010	0.006258	0.000643	-0.0025	0.001109	0.001263	0.001664
670.9880	0.0010	0.005609	0.000643	-0.00249	0.001119	0.001287	0.00166
672.9162	0.0010	0.005144	0.000643	-0.002444	0.00114	0.001328	0.001683
674.8443	0.0010	0.005036	0.000643	-0.002391	0.001164	0.001376	0.001719
676.7724	0.0010	0.005058	0.000648	-0.002345	0.001182	0.001409	0.001766
678.7006	0.0010	0.005071	0.000657	-0.00232	0.001195	0.001423	0.001812
680.6287	0.0011	0.005071	0.000664	-0.0023	0.001215	0.001441	0.001847
682.5568	0.0011	0.005078	0.000678	-0.002261	0.001249	0.001476	0.001884
684.4849	0.0012	0.005095	0.000715	-0.002203	0.001292	0.001519	0.001943
686.4131	0.0012	0.005115	0.000768	-0.002135	0.001345	0.001574	0.002033
688.3412	0.0013	0.005132	0.000822	-0.002045	0.001409	0.001655	0.002157
690.2693	0.0013	0.005152	0.000874	-0.001912	0.001494	0.001774	0.002326
692.1974	0.0015	0.00523	0.000936	-0.001695	0.001642	0.001964	0.002597
694.1256	0.0018	0.005529	0.001036	-0.001224	0.001976	0.002357	0.003174
696.0537	0.0025	0.006212	0.001217	-0.000285	0.002647	0.003115	0.004291
697.9818	0.0032	0.007014	0.001466	0.000809	0.00344	0.003979	0.005581
699.9099	0.0035	0.007219	0.001681	0.001153	0.003706	0.004228	0.005988
701.8381	0.0030	0.006617	0.001826	0.000452	0.003215	0.003648	0.005156
703.7662	0.0023	0.005897	0.002053	-0.000442	0.002567	0.002946	0.004089
705.6943	0.0022	0.005799	0.002604	-0.000613	0.002439	0.002862	0.003892
707.6225	0.0030	0.006606	0.003678	0.000316	0.003121	0.003683	0.005023
709.5506	0.0044	0.008156	0.005163	0.002211	0.004511	0.005268	0.007293
711.4787	0.0056	0.009462	0.0063	0.003889	0.005751	0.00663	0.009277
713.4068	0.0054	0.009213	0.006145	0.00367	0.005623	0.006411	0.008996
715.3350	0.0039	0.007521	0.004755	0.001629	0.004161	0.004708	0.00658
717.2631	0.0023	0.005777	0.003109	-0.00051	0.002602	0.002938	0.004065
719.1912	0.0014	0.004779	0.001923	-0.001737	0.001703	0.001933	0.002625
721.1193	0.0011	0.004347	0.001274	-0.002243	0.001339	0.001535	0.002034
723.0475	0.0009	0.004163	0.000971	-0.002442	0.001202	0.001396	0.001804
724.9756	0.0009	0.004104	0.000827	-0.002526	0.001146	0.001348	0.001714
726.9037	0.0009	0.004105	0.000742	-0.00256	0.001129	0.001327	0.001689
728.8318	0.0009	0.004116	0.000693	-0.002574	0.001134	0.001319	0.001693
730.7600	0.0009	0.00413	0.000678	-0.002589	0.001142	0.001321	0.001703
732.6881	0.0009	0.00415	0.000686	-0.002609	0.001138	0.001326	0.00171
734.6162	0.0009	0.004167	0.000698	-0.002628	0.001123	0.001329	0.001709
736.5444	0.0009	0.004178	0.000698	-0.002641	0.001113	0.001334	0.001709
738.4725	0.0009	0.004185	0.000685	-0.002648	0.001119	0.001345	0.001718
740.4006	0.0009	0.004191	0.000664	-0.002646	0.001131	0.001351	0.001733
742.3287	0.0009	0.004199	0.000643	-0.002633	0.00114	0.001349	0.001755
744.2569	0.0009	0.004217	0.000634	-0.002615	0.001146	0.001349	0.001778
746.1850	0.0009	0.004238	0.000641	-0.002598	0.001156	0.001352	0.001794
748.1131	0.0009	0.004255	0.000648	-0.002591	0.001173	0.001352	0.001802
750.0412	0.0010	0.004262	0.000649	-0.002595	0.001199	0.001364	0.001807

Wavenumber (cm-1)	Absorbance						
	N3VS3	N3VS4	N3VS5	N3VS6	N3VS7	N3VS8	N3VS9
751.9694	0.0010	0.004265	0.000657	-0.002601	0.00122	0.001402	0.001818
753.8975	0.0010	0.004278	0.000684	-0.002607	0.001221	0.001453	0.001839
755.8256	0.0011	0.004303	0.000725	-0.002618	0.001218	0.001492	0.001866
757.7537	0.0011	0.004328	0.00076	-0.002622	0.00123	0.001508	0.001894
759.6819	0.0011	0.004347	0.000777	-0.002604	0.001248	0.001506	0.001917
761.6100	0.0011	0.004361	0.000782	-0.002565	0.001262	0.001501	0.001935
763.5381	0.0011	0.004375	0.000787	-0.002527	0.001276	0.001501	0.001955
765.4663	0.0011	0.004393	0.000798	-0.002505	0.001295	0.001514	0.001978
767.3944	0.0011	0.004413	0.00082	-0.002494	0.001309	0.001541	0.001997
769.3225	0.0011	0.004437	0.000847	-0.002483	0.001306	0.001573	0.002009
771.2506	0.0011	0.004474	0.000864	-0.002463	0.001302	0.001599	0.002027
773.1788	0.0012	0.004519	0.000863	-0.002441	0.001316	0.001616	0.00206
775.1069	0.0012	0.004558	0.000851	-0.002425	0.001348	0.001636	0.002099
777.0350	0.0012	0.004585	0.00084	-0.00241	0.001383	0.00167	0.002127
778.9631	0.0012	0.004608	0.000847	-0.002387	0.0014	0.001708	0.002148
780.8913	0.0012	0.00463	0.000874	-0.002357	0.001401	0.001729	0.002175
782.8194	0.0013	0.004648	0.000906	-0.002341	0.001403	0.001735	0.00221
784.7475	0.0013	0.004671	0.000929	-0.00234	0.001414	0.001744	0.002245
786.6756	0.0013	0.004716	0.000948	-0.002335	0.001431	0.001765	0.002278
788.6038	0.0013	0.004776	0.000961	-0.002316	0.001453	0.001795	0.002316
790.5319	0.0013	0.004829	0.000962	-0.00229	0.001474	0.001823	0.002356
792.4600	0.0014	0.00487	0.000957	-0.002269	0.001488	0.001844	0.002387
794.3881	0.0014	0.004917	0.000958	-0.002256	0.001502	0.001868	0.00241
796.3163	0.0014	0.00498	0.000966	-0.002245	0.001524	0.00191	0.002439
798.2444	0.0014	0.005044	0.000975	-0.002225	0.001556	0.001958	0.002481
800.1725	0.0014	0.005091	0.000991	-0.002191	0.001592	0.001986	0.002535
802.1007	0.0015	0.005124	0.001015	-0.002147	0.001629	0.002005	0.002601
804.0288	0.0015	0.005164	0.001032	-0.002094	0.001672	0.002039	0.002676
805.9569	0.0016	0.005225	0.001035	-0.002038	0.001723	0.002088	0.002757
807.8850	0.0016	0.005298	0.001042	-0.001979	0.001771	0.00214	0.002844
809.8132	0.0017	0.005358	0.001069	-0.001913	0.001815	0.002187	0.002928
811.7413	0.0018	0.005405	0.001107	-0.001838	0.001865	0.002232	0.003005
813.6694	0.0018	0.005467	0.001138	-0.001755	0.001928	0.00229	0.003094
815.5975	0.0019	0.00556	0.001159	-0.001663	0.002003	0.002384	0.003212
817.5257	0.0020	0.005675	0.001175	-0.001562	0.002083	0.002507	0.003363
819.4538	0.0020	0.005797	0.001195	-0.001443	0.002163	0.002632	0.003537
821.3819	0.0021	0.005935	0.001223	-0.001293	0.002249	0.002753	0.003736
823.3100	0.0023	0.006093	0.00126	-0.001095	0.002351	0.002888	0.003974
825.2382	0.0025	0.006278	0.001307	-0.000854	0.002482	0.003057	0.004263
827.1663	0.0026	0.006504	0.001365	-0.000581	0.002655	0.003264	0.004612
829.0944	0.0029	0.006775	0.001434	-0.000246	0.002879	0.003517	0.00503
831.0226	0.0031	0.007091	0.001512	0.000196	0.003158	0.003839	0.005552
832.9507	0.0035	0.007493	0.001597	0.000784	0.003514	0.004258	0.006232
834.8788	0.0040	0.008054	0.0017	0.001556	0.003998	0.004817	0.00714
836.8069	0.0046	0.00886	0.001853	0.002606	0.004694	0.00559	0.008383
838.7351	0.0056	0.009993	0.002088	0.004075	0.005708	0.00669	0.010109
840.6632	0.0067	0.011369	0.002415	0.005882	0.006983	0.008058	0.01222
842.5913	0.0078	0.012625	0.002804	0.007543	0.008166	0.009318	0.014154
844.5194	0.0087	0.013674	0.003235	0.008921	0.009148	0.010346	0.015736
846.4476	0.0100	0.015167	0.003727	0.010851	0.010559	0.011804	0.017928
848.3757	0.0123	0.017729	0.004308	0.014123	0.01304	0.014382	0.021671
850.3038	0.0154	0.021047	0.005064	0.018269	0.016286	0.017807	0.026482

Wavenumber (cm-1)	Absorbance						
	N3VS10	N3VS11	N3VS12	N3VS13	N3VS14	N3VS15	N3VS16
649.7787	0.001619	0.002684	0.0021	0.003004	0.003348	0.003433	0.002917
651.7068	0.00161	0.002554	0.002009	0.002658	0.003057	0.003425	0.002747
653.6349	0.001726	0.002521	0.002035	0.002382	0.002875	0.003333	0.002625
655.5630	0.001869	0.002492	0.002076	0.002173	0.002712	0.003102	0.002538
657.4912	0.001916	0.002416	0.002022	0.002066	0.002536	0.00283	0.002482
659.4193	0.001815	0.002237	0.001919	0.002062	0.00239	0.002641	0.002408
661.3474	0.001668	0.001961	0.001863	0.002053	0.002331	0.002583	0.002278
663.2755	0.001591	0.001711	0.001829	0.001966	0.00232	0.002573	0.002133
665.2037	0.001566	0.001584	0.001766	0.001844	0.002273	0.002511	0.002036
667.1318	0.001533	0.001523	0.0017	0.00173	0.002171	0.002376	0.001961
669.0599	0.001513	0.001457	0.001677	0.001659	0.002044	0.002188	0.001863
670.9880	0.001539	0.001462	0.001667	0.001692	0.001957	0.002008	0.001817
672.9162	0.001541	0.001543	0.001603	0.00173	0.001928	0.001905	0.001822
674.8443	0.001488	0.001601	0.001506	0.001658	0.001914	0.001877	0.001761
676.7724	0.001427	0.001603	0.001443	0.001514	0.001889	0.001898	0.001638
678.7006	0.001396	0.001551	0.001416	0.001396	0.001848	0.001925	0.001524
680.6287	0.001372	0.00146	0.001379	0.001328	0.001796	0.001916	0.00143
682.5568	0.001317	0.001374	0.001327	0.001272	0.001731	0.001857	0.001345
684.4849	0.001233	0.001332	0.001301	0.001201	0.001653	0.00177	0.001306
686.4131	0.001159	0.001308	0.001311	0.001143	0.001588	0.00168	0.001328
688.3412	0.001113	0.001257	0.001321	0.001132	0.001562	0.001591	0.001364
690.2693	0.001076	0.001195	0.001301	0.001157	0.001561	0.001505	0.001381
692.1974	0.001044	0.00118	0.001256	0.001185	0.001562	0.001438	0.001368
694.1256	0.001063	0.001193	0.001211	0.001182	0.001556	0.001383	0.001316
696.0537	0.001135	0.00116	0.001174	0.001147	0.001506	0.001315	0.001247
697.9818	0.001186	0.001071	0.001134	0.001116	0.001397	0.001276	0.00119
699.9099	0.001185	0.000978	0.00109	0.001097	0.001296	0.001315	0.001146
701.8381	0.001171	0.000929	0.001054	0.001064	0.001267	0.001375	0.001114
703.7662	0.001172	0.000946	0.001032	0.001025	0.001287	0.001371	0.001096
705.6943	0.001161	0.000993	0.001	0.001019	0.001296	0.001309	0.001084
707.6225	0.00111	0.001008	0.000936	0.001036	0.001286	0.001248	0.001071
709.5506	0.001048	0.000988	0.000887	0.001015	0.001274	0.001215	0.001057
711.4787	0.001002	0.000995	0.000891	0.000952	0.001248	0.001198	0.001033
713.4068	0.00097	0.001033	0.00091	0.000908	0.001201	0.001187	0.001
715.3350	0.00096	0.001039	0.00092	0.000915	0.001156	0.001171	0.000989
717.2631	0.000973	0.000988	0.000935	0.000941	0.001127	0.001147	0.001016
719.1912	0.000975	0.000935	0.00096	0.000937	0.001109	0.001118	0.001039
721.1193	0.000938	0.000922	0.000973	0.000909	0.001117	0.001096	0.001005
723.0475	0.000899	0.000923	0.000965	0.000907	0.001156	0.001084	0.000932
724.9756	0.000918	0.000901	0.000965	0.000933	0.001173	0.001065	0.000888
726.9037	0.000991	0.000875	0.000984	0.000946	0.001138	0.001048	0.000894
728.8318	0.001044	0.000864	0.001	0.00093	0.001079	0.001051	0.000916
730.7600	0.001031	0.000853	0.000993	0.000898	0.001017	0.001059	0.000908
732.6881	0.000974	0.000825	0.000968	0.000867	0.000976	0.001052	0.000848
734.6162	0.000924	0.000803	0.000946	0.000844	0.000982	0.001047	0.000788
736.5444	0.000891	0.00081	0.000938	0.000817	0.001026	0.001051	0.000793
738.4725	0.000859	0.000824	0.000932	0.000778	0.001077	0.001037	0.000839
740.4006	0.000843	0.000822	0.000928	0.000742	0.001101	0.001006	0.000864
742.3287	0.000863	0.000815	0.000935	0.000718	0.001082	0.000988	0.00086
744.2569	0.000897	0.000811	0.000958	0.000708	0.00104	0.000975	0.000843
746.1850	0.000907	0.000788	0.000974	0.000715	0.001007	0.000947	0.000822
748.1131	0.000895	0.000748	0.000947	0.000741	0.000994	0.000936	0.000816
750.0412	0.000882	0.000715	0.000884	0.000768	0.000991	0.000959	0.000838

Wavenumber (cm ⁻¹)	Absorbance						
	N3VS10	N3VS11	N3VS12	N3VS13	N3VS14	N3VS15	N3VS16
751.9694	0.000883	0.0007	0.000836	0.000766	0.000983	0.000981	0.000862
753.8975	0.000891	0.000708	0.000833	0.000734	0.000952	0.000969	0.000855
755.8256	0.000883	0.00074	0.000858	0.000711	0.0009	0.000928	0.00082
757.7537	0.000857	0.000764	0.000882	0.000734	0.000858	0.000888	0.000784
759.6819	0.000826	0.000738	0.000893	0.000787	0.000849	0.000874	0.00076
761.6100	0.000798	0.000681	0.000896	0.000825	0.000853	0.000883	0.000747
763.5381	0.0008	0.00065	0.000894	0.000821	0.000832	0.000886	0.000738
765.4663	0.000849	0.000661	0.00089	0.000778	0.000783	0.000866	0.000729
767.3944	0.000892	0.000686	0.000889	0.00072	0.000739	0.000834	0.000714
769.3225	0.000876	0.000719	0.000893	0.000667	0.00073	0.000816	0.000693
771.2506	0.000837	0.000756	0.000895	0.000627	0.000757	0.000817	0.000681
773.1788	0.000827	0.000768	0.000897	0.000603	0.000802	0.000823	0.000693
775.1069	0.000848	0.000748	0.000912	0.000597	0.000825	0.000828	0.00072
777.0350	0.000868	0.000714	0.000936	0.000597	0.000797	0.000846	0.000737
778.9631	0.000867	0.000678	0.000937	0.000601	0.000751	0.000878	0.000725
780.8913	0.000847	0.000641	0.000901	0.000614	0.000742	0.000892	0.000692
782.8194	0.000825	0.000611	0.000867	0.000625	0.000767	0.000873	0.000661
784.7475	0.000813	0.000598	0.000872	0.000614	0.000792	0.000845	0.000647
786.6756	0.000811	0.000595	0.000896	0.000592	0.000808	0.000841	0.000635
788.6038	0.000812	0.000592	0.000906	0.000594	0.000813	0.000864	0.000615
790.5319	0.000811	0.000584	0.00091	0.00062	0.000789	0.000875	0.000619
792.4600	0.000817	0.000582	0.000931	0.000651	0.000744	0.000849	0.000668
794.3881	0.000836	0.000598	0.000967	0.000654	0.000716	0.000811	0.00073
796.3163	0.000856	0.000616	0.000988	0.000614	0.000713	0.000793	0.000761
798.2444	0.000863	0.000598	0.000968	0.000566	0.000709	0.000785	0.000759
800.1725	0.000857	0.000557	0.000926	0.000553	0.000701	0.00076	0.000742
802.1007	0.000847	0.000535	0.000903	0.00056	0.000704	0.000729	0.000731
804.0288	0.000842	0.000544	0.000902	0.000559	0.000716	0.000726	0.000738
805.9569	0.000853	0.000562	0.000912	0.000557	0.000719	0.000746	0.000754
807.8850	0.000868	0.000574	0.000926	0.000572	0.000717	0.000769	0.000763
809.8132	0.000876	0.000582	0.000942	0.000594	0.000719	0.000779	0.000759
811.7413	0.00088	0.00059	0.000953	0.000609	0.000719	0.000777	0.000753
813.6694	0.000887	0.000604	0.000948	0.000618	0.000721	0.000783	0.000753
815.5975	0.000891	0.000625	0.000933	0.000627	0.000737	0.0008	0.000753
817.5257	0.000885	0.000648	0.000938	0.000635	0.000765	0.000825	0.00075
819.4538	0.000871	0.000669	0.000968	0.000629	0.000784	0.000864	0.000755
821.3819	0.00087	0.000676	0.000981	0.00062	0.00077	0.000902	0.000762
823.3100	0.000882	0.000664	0.000966	0.000629	0.000726	0.000905	0.000747
825.2382	0.000893	0.000646	0.000956	0.000648	0.000686	0.00087	0.00072
827.1663	0.000902	0.000632	0.000968	0.000644	0.000683	0.000839	0.000718
829.0944	0.000913	0.000628	0.000983	0.000611	0.00072	0.00084	0.000735
831.0226	0.000914	0.000648	0.000983	0.000596	0.000772	0.000856	0.000745
832.9507	0.00091	0.00069	0.000979	0.000636	0.0008	0.000864	0.00076
834.8788	0.000917	0.00072	0.000987	0.000694	0.000796	0.000873	0.000787
836.8069	0.000924	0.000715	0.000995	0.000706	0.000784	0.000887	0.000796
838.7351	0.000913	0.000681	0.000992	0.000683	0.000778	0.000888	0.000776
840.6632	0.0009	0.000639	0.000994	0.000667	0.000769	0.00088	0.00075
842.5913	0.000908	0.00061	0.001013	0.000663	0.000765	0.000884	0.000744
844.5194	0.000927	0.000608	0.00104	0.000656	0.000772	0.000905	0.00076
846.4476	0.000926	0.000621	0.00106	0.000648	0.000779	0.000922	0.000786
848.3757	0.000903	0.000628	0.001067	0.000646	0.000772	0.000922	0.000811
850.3038	0.000884	0.000633	0.001069	0.000657	0.000763	0.000915	0.000832

Table 24: FTIR measurements for stalagmite from Valmiki cave. Only the measurements relevant for distinguishing between calcite and aragonite mineralogy have been shown (i.e. 650 to 850 cm⁻¹), not the whole spectrum till 4000 cm⁻¹. Subsamples have simply been referred to as S3 to S16 in the chapter.

<i>Sample Number</i>	<i>Calcite %</i>	<i>Aragonite %</i>	<i>Hydroxylapatite %</i>
S17	54	46	
S18	87	13	
S19	91	9	
S20	85	15	
S21	2	98	
S22	3	97	
S23	3	97	
S24	1	99	
S25	90	10	
S26	78	22	
S27	4	96	
S28	5	95	
S29	91	9	
S30	87	13	
S31	3	97	
S32	8	92	
S33	87	13	
S34	2	98	
S35	85	15	
S36	79	21	
S37	86	14	
S38	4	96	
S39	80	20	
S40	4	96	
S41	73	14	14

Table 25: XRD measurements for stalagmite from Valmiki cave.

Aragonite		T (C)	T (K)	1000 ln a	1000/T(K)	a	Drip water	R _{water}	R _{arag}	drag/VSMOW	Calculated Aragonite
Grossman and Ku, 1986	$10^3 \ln a = 18.34 * 10^3 / T(K) - 31.954$	32.8	306.95	27.8	3.26	1.0278	-1.59	0.002002	0.002058	26.161	-4.61
Patterson et al, 1993	$10^3 \ln a = 18.56 * 10^3 / T(K) - 33.49$	32.8	306.95	27.0	3.26	1.0270	-1.59	0.002002	0.002056	25.343	-5.40
Thorold et al, 1997	$10^3 \ln a = 18.56 * 10^3 / T(K) - 32.54$	32.8	306.95	27.9	3.26	1.0279	-1.59	0.002002	0.002058	26.291	-4.48
Kim et al, 2007b	$10^3 \ln a = 17.88 * 10^3 / T(K) - 30.76$	32.8	306.95	27.5	3.26	1.0275	-1.59	0.002002	0.002057	25.857	-4.90
Grossman and Ku, 1986	$10^3 \ln a = 18.34 * 10^3 / T(K) - 31.954$	32.8	306.95	27.8	3.26	1.0278	-3.25	0.001999	0.002054	24.455	-6.26
Patterson et al, 1993	$10^3 \ln a = 18.56 * 10^3 / T(K) - 33.49$	32.8	306.95	27.0	3.26	1.0270	-3.25	0.001999	0.002053	23.638	-7.05
Thorold et al, 1997	$10^3 \ln a = 18.56 * 10^3 / T(K) - 32.54$	32.8	306.95	27.9	3.26	1.0279	-3.25	0.001999	0.002054	24.585	-6.14
Kim et al, 2007b	$10^3 \ln a = 17.88 * 10^3 / T(K) - 30.76$	32.8	306.95	27.5	3.26	1.0275	-3.25	0.001999	0.002054	24.151	-6.56
Calcite		T (C)	T (K)	1000 ln a	1000/T(K)	a	Drip water	R _{water}	R _{calc}	dcalc/VSMOW	Calculated Calcite
Kim and O'Neill, 1997	$10^3 \ln a = 18.03 * 10^3 / T(K) - 32.42$	32.8	306.95	26.3	3.26	1.0263	-1.59	0.002002	0.002055	24.687	-6.04
Coplen, 2007	$10^3 \ln a = 17.4 * 10^3 / T(K) - 28.6$	32.8	306.95	28.1	3.26	1.0281	-1.59	0.002002	0.002058	26.452	-4.32
Kim and O'Neill, 1997	$10^3 \ln a = 18.03 * 10^3 / T(K) - 32.42$	32.8	306.95	26.3	3.26	1.0263	-3.25	0.001999	0.002051	22.984	-7.69
Coplen, 2007	$10^3 \ln a = 17.4 * 10^3 / T(K) - 28.6$	32.8	306.95	28.1	3.26	1.0281	-3.25	0.001999	0.002055	24.745	-5.98

Table 26: Calculation of expected $\delta^{18}\text{O}$ values from published equilibrium fractionation equations for sample stalagmite from Valmiki cave. Associated formulas in table 11 of Appendix 3.

	k_{Mg}	k_{Sr}	k_{Ba}	k_U	k_{Mn}	k_{Na}	k_P
<i>Day and Henderson, 2013</i>	0.0099E0.02 [+/-0.004]T	0.13E-0.0011 [+/-0.005]T	0.11E0.0011 [+/-0.01]T	0.14E-0.025 [+/-0.01]T			
<i>Rinstidt et al, 1998</i>	0.012E0.023T	0.09E-0.003T	0.02E0.0004T				
<i>Wassenberg et al, 2016</i>	1.01E-04 [+/-9E-5]	1.38 [+/-0.53]	0.91 [+/-0.53]	6.26 [+/-4.53]			
<i>This study, Chapter 5</i>	5.3E-04 [+/-4.1E-04]	2.8 [+/-0.12]		14.39 [+/-6.45]	0.30 [+/-0.22]	8.4E-03 [2.5E-03]	2.24 [+/-0.44]

Table 27: Published partition coefficient (distribution coefficient) values used to compare measurements of sample stalagmite from Valmiki cave.

Sample Code	kMg	kSr	kBa	kU	kNa	kP	kMn
S3	5.75E-04	1.97E+00	8.30E-02	2.10E+00	3.07E-03	7.34E-01	7.27E-02
S4	6.18E-04	1.61E+00	9.16E-02	1.49E+00	2.75E-03	1.02E+00	3.81E-01
S5	3.50E-03	9.97E-01	1.85E-02	1.05E+00	1.26E-03	1.18E+00	2.37E-01
S6	3.56E-04	1.94E+00	7.90E-02	2.28E+00	3.35E-03	5.38E-01	3.80E-02
S7	3.00E-04	2.21E+00	8.73E-02	3.30E+00	3.43E-03	2.17E+00	1.96E-01
S8	5.20E-04	1.91E+00	1.07E-01	2.31E+00	3.77E-03	6.90E-01	2.29E-01
S9	2.50E-04	2.31E+00	1.09E-01	2.88E+00	2.68E-03	8.20E-01	6.36E-02
S10	2.69E-04	2.17E+00	1.24E-01	3.72E+00	4.58E-03	9.03E-01	8.03E-02
S11	1.00E-03	1.30E+00	3.61E-02	3.29E+00	8.09E-04	6.48E-01	4.15E-02
S12	1.11E-03	1.96E+00	9.58E-02	2.88E+00	4.12E-03	1.20E+00	3.41E-01
S13	1.90E-03	1.09E+00	4.50E-02	2.43E+00	6.34E-04	9.45E-01	5.20E-01
S14	1.99E-03	1.16E+00	2.96E-02	2.62E+00	4.25E-03	1.16E+00	2.81E-01
S15	1.40E-02	7.09E-01	1.02E-02	3.82E-01	3.10E-03	2.62E+00	9.35E-01
S16	1.40E-02	8.75E-02	1.41E-01	1.59E-01	1.34E-03	6.24E+00	2.41E+00
S17	1.65E-03	1.77E+00	4.81E-02	2.72E+00	1.40E-03	7.19E-01	5.41E-02
S18	1.95E-03	1.38E+00	2.63E-02	1.77E+00	6.02E-04	6.28E-01	6.18E-02
S19	3.53E-03	1.02E+00	2.85E-02	1.02E+00	2.57E-04	5.51E-01	3.34E-02
S20	5.26E-03	9.41E-01	2.16E-02	8.79E-01	3.89E-04	1.11E+00	8.33E-02
S21	3.16E-04	2.48E+00	8.72E-02	3.46E+00	2.85E-03	7.02E-01	4.29E-02
S22	3.13E-04	2.56E+00	9.33E-02	4.54E+00	2.91E-03	1.10E+00	4.69E-02
S23	4.20E-04	2.60E+00	1.33E-01	4.53E+00	2.77E-03	1.10E+00	6.75E-02
S24	3.56E-04	2.53E+00	9.34E-02	4.11E+00	2.86E-03	8.29E-01	5.56E-02
S25	1.85E-03	1.03E+00	2.40E-01	2.39E+00	3.08E-04	8.80E-01	1.70E-01
S26	1.84E-03	1.21E+00	3.33E-02	3.75E+00	7.29E-04	7.32E-01	2.57E-02
S27	3.28E-04	1.83E+00	9.45E-02	3.50E+00	2.50E-03	7.63E-01	9.44E-02
S28	5.33E-04	1.85E+00	7.95E-02	3.30E+00	2.54E-03	7.66E-01	1.94E-01
S29	2.09E-03	9.93E-01	1.93E-02	2.90E+00	6.12E-04	6.52E-01	4.87E-02
S30	1.16E-03	1.04E+00	1.33E-02	3.13E+00	6.36E-04	6.81E-01	6.30E-02
S31	2.79E-04	2.29E+00	1.43E-01	3.39E+00	2.38E-03	9.62E-01	1.22E-02
S32	8.32E-04	1.58E+00	1.07E-01	3.01E+00	2.29E-03	7.23E-01	1.49E-01
S33	2.40E-03	9.89E-01	6.02E-02	2.68E+00	4.21E-04	7.13E-01	2.00E-01
S34	3.63E-04	1.93E+00	8.80E-02	4.02E+00	2.89E-03	1.13E+00	4.03E-01
S35	1.66E-03	1.09E+00	1.36E-02	3.13E+00	4.92E-04	5.97E-01	3.74E-02
S36	1.33E-03	1.16E+00	2.85E-02	2.25E+00	8.25E-04	8.91E-01	1.91E-01
S37	2.34E-03	1.38E+00	1.43E-01	3.02E+00	9.17E-04	1.88E+00	2.22E+00
S38	5.42E-04	2.63E+00	1.20E-01	3.63E+00	2.70E-03	1.55E+00	1.40E-01
S39	2.08E-03	1.30E+00	7.50E-02	3.16E+00	7.21E-04	1.19E+00	7.19E-01
S40	4.83E-04	2.61E+00	1.06E-01	3.53E+00	3.15E-03	1.09E+00	2.19E-01
S41	3.75E-03	6.85E-01	1.35E-01	2.84E+00	2.52E-03	3.00E+02	5.27E+01
ValMod	3.23E-02	1.19E-01	2.01E-01	2.31E-01	2.51E-03	7.72E+01	2.44E+01

Table 28: Calculated k values for subsamples from Valmiki sample stalagmite. Drip water measurements have been given in table 8.3, sample trace element ratios are in table 8.2.

Sample	^{238}U	sd	$^{238}\text{U}/^{235}\text{U}$	sd	Aprox $^{238}\text{U}/^{230}\text{Th}$	sd	Aprox $^{230}\text{Th}/^{238}\text{U}$
	volts		Atomic Ratio		Atomic Ratio		Atomic Ratio
S20	0.052022	0.000787	141.629	3.63587	58540.8	6852	1.70821E-05
S20	0.051844	0.00066	140.472	5.00625	58978.8	4415.34	1.69552E-05
S20	0.051312	0.000775	147.837	4.83678	60131.1	5790.89	1.66303E-05
S20	0.050013	0.000897	140.371	5.80525	62207	6156.86	1.60754E-05
S19	0.061006	0.00107	143.896	3.33718	65279	5620.63	1.53189E-05
S19	0.061497	0.000867	139.177	3.34773	62739	5180.83	1.5939E-05
S19	0.059713	0.00102	145.954	3.49706	60733.3	6292.02	1.64654E-05
S19	0.059323	0.001199	141.37	3.50329	62341.8	5658.54	1.60406E-05
S18	0.105161	0.001941	139.733	1.91888	90448.2	6689.92	1.10561E-05
S18	0.104186	0.001296	139.407	1.54921	94203.2	4875.3	1.06154E-05
S18	0.103176	0.001339	141.136	2.92182	95109.9	13239.5	1.05142E-05
S18	0.103656	0.001317	140.425	1.06902	95668.1	6566.14	1.04528E-05
S17	0.167952	0.002463	141.558	1.72696	123955	11712	8.06744E-06
S17	0.165711	0.002564	141.643	1.3574	128098	12379.1	7.80652E-06
S17	0.163933	0.002315	140.166	1.5248	129063	7591.94	7.74815E-06
S17	0.160396	0.002038	140.463	1.85185	122811	7768.38	8.14259E-06
S21	0.292435	0.00405	140.867	0.620374	172632	9648.51	5.79267E-06
S21	0.291231	0.00337	140.05	1.14363	174221	13766.1	5.73984E-06
S21	0.29173	0.003154	141.662	0.688758	175500	12334.7	5.69801E-06
S21	0.287587	0.011448	141.216	0.662919	171380	10085.6	5.83499E-06
S22	0.416518	0.006601	141.178	0.494603	181082	16183.7	5.52236E-06
S22	0.374248	0.008757	141.254	0.514104	183950	18213.7	5.43626E-06
S22	0.380592	0.008632	140.609	0.475942	181347	7265.42	5.51429E-06
S22	0.386643	0.003687	140.468	0.252902	175504	11196.4	5.69788E-06
S23	0.333922	0.003278	140.407	0.821367	173317	15690.9	5.76977E-06
S23	0.33029	0.002201	141.633	0.755684	176751	6912.66	5.65768E-06
S23	0.323784	0.00423	140.359	0.516015	181345	9540.22	5.51435E-06
S23	0.32231	0.004057	140.327	0.790896	180512	15370.5	5.5398E-06
S24	0.178944	0.018155	140.678	0.811465	177756	14202.1	5.62569E-06
S24	0.298172	0.026469	139.417	0.607285	186761	17846.4	5.35444E-06
S24	0.36108	0.01039	139.799	0.540604	175290	14964.2	5.70483E-06
S24	0.371173	0.004145	140.687	0.70356	174654	7747.17	5.72561E-06

Table 29 (A): Approximate $^{230}\text{Th}/^{238}\text{U}$ measurements for sample stalagmite from Valmiki cave.

Sample	^{238}U	sd	$^{238}\text{U}/^{235}\text{U}$	sd	Aprox $^{238}\text{U}/^{230}\text{Th}$	sd	Aprox $^{230}\text{Th}/^{238}\text{U}$
	volts		Atomic Ratio		Atomic Ratio		Atomic Ratio
S25	0.101672	0.002731	137.26	3.7352	130680	10521.5	7.65228E-06
S25	0.103537	0.00347	139.717	2.07023	132541	12798.9	7.54484E-06
S25	0.104342	0.002338	138.766	2.33773	131851	7324.22	7.58432E-06
S25	0.104688	0.004338	138.201	1.1026	142227	9204.79	7.03101E-06
S26	0.164766	0.004837	140.552	1.30017	183399	13487.5	5.45259E-06
S26	0.16691	0.005007	140.048	1.36138	184206	24388.6	5.4287E-06
S26	0.16745	0.006383	142.791	1.24826	192894	16635.5	5.18419E-06
S26	0.171201	0.006022	140.516	1.57877	200488	24763.4	4.98783E-06
S27	0.135809	0.004565	139.301	1.24703	182820	19643.6	5.46986E-06
S27	0.13747	0.006423	139.981	0.941874	179479	17914.6	5.57168E-06
S27	0.137539	0.00565	141.315	1.45597	179339	17521.6	5.57603E-06
S27	0.140189	0.006013	141.255	1.15688	174862	14271.1	5.7188E-06
S28	0.104775	0.003739	139.18	1.97425	176287	17916.1	5.67257E-06
S28	0.107795	0.004132	138.058	0.979037	179038	25881	5.58541E-06
S28	0.109574	0.004114	139.098	1.70842	168547	15797.9	5.93306E-06
S28	0.111292	0.004905	139.162	1.513	170204	15816.6	5.8753E-06
S29	0.158855	0.006169	138.378	1.87536	155713	13764.5	6.42207E-06
S29	0.169283	0.006227	140.737	0.867651	163549	15249	6.11438E-06
S29	0.179413	0.006668	141.367	1.42875	163140	12851.5	6.1297E-06
S29	0.187178	0.009212	142.532	0.873155	156645	15646.1	6.38386E-06
S30	0.203528	0.00825	140.992	1.34173	192986	17678.7	5.18172E-06
S30	0.221278	0.009764	140.429	0.415728	186587	13948.9	5.35943E-06
S30	0.237717	0.01219	139.949	0.683347	189644	16548.4	5.27304E-06
S30	0.256334	0.009613	139.816	0.605893	180708	25439.4	5.53379E-06

Table 29 (B): Approximate $^{230}\text{Th}/^{238}\text{U}$ measurements for sample stalagmite from Valmiki cave.

Sample	^{238}U	sd	$^{238}\text{U}/^{235}\text{U}$	sd	Aprox $^{238}\text{U}/^{230}\text{Th}$	sd	Aprox $^{230}\text{Th}/^{238}\text{U}$
	volts		Atomic Ratio		Atomic Ratio		Atomic Ratio
S31	0.40243	0.016228	140.599	0.2076	180624	11007.9	5.53636E-06
S31	0.42436	0.007473	140.421	0.382404	180392	13785	5.54348E-06
S31	0.438692	0.012559	140.147	0.63001	180973	11619.3	5.52569E-06
S31	0.442017	0.011775	139.992	0.559742	179452	13066.9	5.57252E-06
S32	0.209656	0.005937	139.748	1.03924	173268	8108.88	5.77141E-06
S32	0.207398	0.008019	141.106	1.40188	167737	10807.7	5.96171E-06
S32	0.206158	0.010387	139.261	0.758961	165733	13899.1	6.0338E-06
S32	0.196514	0.018061	140.439	1.56615	167833	11321.9	5.9583E-06
S28	0.104775	0.003739	139.18	1.97425	176287	17916.1	5.67257E-06
S28	0.107795	0.004132	138.058	0.979037	179038	25881	5.58541E-06
S28	0.109574	0.004114	139.098	1.70842	168547	15797.9	5.93306E-06
S28	0.111292	0.004905	139.162	1.513	170204	15816.6	5.8753E-06
S34	0.209347	0.007547	142.179	0.701857	176729	15878.9	5.65838E-06
S34	0.196162	0.009044	141.354	1.06295	177484	16277.7	5.63431E-06
S34	0.185481	0.00792	140.941	1.2789	183548	23388.3	5.44817E-06
S34	0.170253	0.008435	141.17	0.608063	181063	11153.5	5.52294E-06
S33	0.224974	0.008298	139.671	0.775589	126664	6827.14	7.8949E-06
S33	0.218742	0.010386	140.673	0.846179	123609	7572.8	8.09003E-06
S33	0.205374	0.007265	141.516	0.590214	132432	13083	7.55105E-06
S33	0.190767	0.011549	140.589	1.63384	125016	9025.64	7.99898E-06
S29	0.158855	0.006169	138.378	1.87536	155713	13764.5	6.42207E-06
S29	0.169283	0.006227	140.737	0.867651	163549	15249	6.11438E-06
S29	0.179413	0.006668	141.367	1.42875	163140	12851.5	6.1297E-06
S29	0.187178	0.009212	142.532	0.873155	156645	15646.1	6.38386E-06
S35	0.196405	0.006628	139.675	0.928402	196664	15444	5.08481E-06
S35	0.160395	0.023599	139.423	1.2834	187755	14060.5	5.32609E-06
S35	0.145565	0.008886	140.797	1.23838	197546	12214.4	5.06211E-06
S35	0.125663	0.004676	140.639	2.21792	198704	21124.7	5.03261E-06
S36	0.044747	0.001856	138.765	4.34716	175327	18023.2	5.70363E-06
S36	0.14199	0.095285	139.197	1.56501	176403	19600.4	5.66884E-06
S36	0.235626	0.005802	140.373	0.942574	187855	11866.4	5.32325E-06
S36	0.231699	0.00504	140.826	1.20399	178892	14740.3	5.58996E-06

Table 29 (C): Approximate $^{230}\text{Th}/^{238}\text{U}$ measurements for sample stalagmite from Valmiki cave.

Sample	^{238}U	sd	$^{238}\text{U}/^{235}\text{U}$	sd	Aprox $^{238}\text{U}/^{230}\text{Th}$	sd	Aprox $^{230}\text{Th}/^{238}\text{U}$
	volts		Atomic Ratio		Atomic Ratio		Atomic Ratio
S37	0.180666	0.001957	141.528	0.619615	112368	8758.8	8.89933E-06
S37	0.177745	0.002093	143.087	0.943205	115639	7670.39	8.6476E-06
S37	0.173706	0.002939	141.712	1.26082	114230	9543.91	8.75427E-06
S37	0.171908	0.00173	139.185	1.35315	114358	7382.38	8.74447E-06
S38	0.158059	0.003239	140.662	1.54614	158202	15505.3	6.32103E-06
S38	0.155856	0.002184	142.883	1.573	167795	12162.8	5.95965E-06
S38	0.154345	0.002414	142.095	1.19536	169883	4266.41	5.8864E-06
S38	0.151904	0.002115	142.259	1.25547	151271	151271	6.61065E-06
S38	0.156769	0.007337	140.236	0.007337	152994	9149.69	6.5362E-06
S38	0.152114	0.00339	142.45	1.09935	154414	9918.25	6.4761E-06
S39	0.150245	0.001874	140.278	1.59703	156447	9950.23	6.39194E-06
S39	0.148537	0.002792	144.262	1.39138	151884	19635.2	6.58397E-06
S39	0.145	0.002155	142.129	1.57273	148585	8384.77	6.73015E-06
S39	0.143643	0.003597	140.604	1.00827	148322	15054.1	6.74209E-06
S40	0.181157	0.002124	140.137	1.53504	157438	10102.3	6.35171E-06
S40	0.174005	0.00503	139.611	1.36431	162353	9161.69	6.15942E-06
S40	0.166136	0.004844	139.814	0.794417	154246	10445.5	6.48315E-06
S40	0.158889	0.004347	144.05	1.34193	155653	8088.23	6.42455E-06
S40	0.138919	0.005146	140.24	1.80884	143455	12037.5	6.97083E-06
S40	0.144755	0.004735	140.24	1.95819	153647	13426.7	6.50843E-06
S40	0.14321	0.00426	142.382	1.16867	153516	14221.6	6.51398E-06
S40	0.143364	0.003834	139.487	2.06867	158033	24154.3	6.32779E-06
S41	0.184993	0.004437	140.395	0.747551	84781	3875.33	1.17951E-05
S41	0.184577	0.005201	140.834	0.415978	85362.6	4191.81	1.17147E-05
S41	0.180705	0.004971	140.307	1.24182	86378.4	4793.56	1.1577E-05
S41	0.18546	0.004708	140.101	1.52748	85815.5	6157.89	1.16529E-05

Table 29 (C): Approximate $^{230}\text{Th}/^{238}\text{U}$ measurements for sample stalagmite from Valmiki cave.

Sample	Average $^{238}\text{U}/^{230}\text{Th}$	Average ^{238}U	volts	^{238}U ppb (ng/g)	Sample weight g	^{238}U ng	^{238}U g	^{238}U moles	^{238}U No. of atoms	^{230}Th No. of atoms
S24	1.79E+05	3.02E-01	3.02E-01	3.02E+00	7.12E-03	2.15E-02	2.15E-11	9.04E-14	5.45E+10	3.05E+05
S23	1.78E+05	3.28E-01	3.28E-01	3.28E+00	8.17E-03	2.68E-02	2.68E-11	1.12E-13	6.77E+10	3.80E+05
S22	1.80E+05	3.90E-01	3.90E-01	3.90E+00	6.86E-03	2.67E-02	2.67E-11	1.12E-13	6.76E+10	3.74E+05
S21	1.73E+05	2.91E-01	2.91E-01	2.91E+00	7.84E-03	2.28E-02	2.28E-11	9.58E-14	5.77E+10	3.32E+05
S17	1.26E+05	1.64E-01	1.64E-01	1.64E+00	5.13E-03	8.44E-03	8.44E-12	3.55E-14	2.13E+10	1.69E+05
S18	9.39E+04	1.04E-01	1.04E-01	1.04E+00	5.64E-03	5.87E-03	5.87E-12	2.47E-14	1.48E+10	1.58E+05
S19	6.28E+04	6.04E-02	6.04E-02	6.04E-01	5.80E-03	3.50E-03	3.50E-12	1.47E-14	8.86E+09	1.41E+05
S20	6.00E+04	5.13E-02	5.13E-02	5.13E-01	6.32E-03	3.24E-03	3.24E-12	1.36E-14	8.20E+09	1.37E+05
S37	1.14E+05	1.76E-01	1.76E-01	1.76E+00	8.00E-03	1.41E-02	1.41E-11	5.92E-14	3.56E+10	3.12E+05
S38	1.59E+05	1.55E-01	1.55E-01	1.55E+00	6.80E-03	1.05E-02	1.05E-11	4.42E-14	2.66E+10	1.67E+05
S39	1.51E+05	1.47E-01	1.47E-01	1.47E+00	6.17E-03	9.06E-03	9.06E-12	3.81E-14	2.29E+10	1.51E+05
S40	1.55E+05	1.56E-01	1.56E-01	1.56E+00	9.11E-03	1.42E-02	1.42E-11	5.98E-14	3.60E+10	2.33E+05
S25	1.34E+05	1.04E-01	1.04E-01	1.04E+00	7.00E-03	7.25E-03	7.25E-12	3.05E-14	1.83E+10	1.37E+05
S26	1.90E+05	1.68E-01	1.68E-01	1.68E+00	5.72E-03	9.59E-03	9.59E-12	4.03E-14	2.42E+10	1.27E+05
S27	1.79E+05	1.38E-01	1.38E-01	1.38E+00	6.52E-03	8.98E-03	8.98E-12	3.77E-14	2.27E+10	1.27E+05
S28	1.74E+05	1.08E-01	1.08E-01	1.08E+00	6.38E-03	6.91E-03	6.91E-12	2.90E-14	1.75E+10	1.01E+05
S29	1.60E+05	1.74E-01	1.74E-01	1.74E+00	6.32E-03	1.10E-02	1.10E-11	4.61E-14	2.78E+10	1.74E+05
S30	1.87E+05	2.30E-01	2.30E-01	2.30E+00	6.38E-03	1.47E-02	1.47E-11	6.16E-14	3.71E+10	1.98E+05
S31	1.80E+05	4.27E-01	4.27E-01	4.27E+00	7.00E-03	2.99E-02	2.99E-11	1.26E-13	7.56E+10	4.19E+05
S32	1.69E+05	2.05E-01	2.05E-01	2.05E+00	8.02E-03	1.64E-02	1.64E-11	6.91E-14	4.16E+10	2.47E+05
S33	1.27E+05	2.10E-01	2.10E-01	2.10E+00	9.16E-03	1.92E-02	1.92E-11	8.08E-14	4.86E+10	3.83E+05
S34	1.80E+05	1.90E-01	1.90E-01	1.90E+00	6.58E-03	1.25E-02	1.25E-11	5.26E-14	3.17E+10	1.76E+05
S35	1.95E+05	1.57E-01	1.57E-01	1.57E+00	9.28E-03	1.46E-02	1.46E-11	6.12E-14	3.69E+10	1.89E+05
S36	1.80E+05	1.64E-01	1.64E-01	1.64E+00	1.14E-02	1.87E-02	1.87E-11	7.85E-14	4.72E+10	2.63E+05
S41	8.56E+04	1.84E-01	1.84E-01	1.84E+00	8.95E-03	1.65E-02	1.65E-11	6.92E-14	4.16E+10	4.87E+05

Table 29 (D): Calculating atomic ratios and number of atoms from the approximate $^{230}\text{Th}/^{238}\text{U}$ measurements for sample stalagmite from Valmiki cave.