

Carbon burial in continental and marine settings:
Lacustrine and marine records of
major environmental change in deep time and their
depositional and diagenetic consequences



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**Thesis submitted to the University of Oxford
for the degree of Doctor of Philosophy**

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University of Oxford

Trinity Term, 2016

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Declaration

The contents of this thesis are all my own work, except where otherwise stated. The views and opinions expressed herein are mine and not necessarily those of any other person or body unless so attributed.

Abstract

Carbon burial in continental and marine settings: Lacustrine and marine records of major environmental change in deep time and their depositional and diagenetic consequences

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The Early Jurassic Toarcian Oceanic Anoxic Event (T-OAE; ~183 Ma) is recognized as possibly the most extreme oceanographic and global climatic change event of the Phanerozoic. The T-OAE was marked by massive carbon release into the ocean-atmosphere system, widespread oceanic de-oxygenation, global organic-matter burial, and a strongly perturbed global carbon cycle. Although effects of the T-OAE are extensively studied in the marine realm, the environmental and climatic response on the continents is effectively unknown. In this thesis, I identify the first lacustrine record of the T-OAE, in the Da'anzhai Member of the Sichuan Basin (China), and demonstrate that a major lake system developed contemporaneously with the T-OAE, likely due to enhanced hydrological cycling under elevated atmospheric $p\text{CO}_2$. Increased lacustrine organic productivity from elevated fluvial nutrient supply resulted in ~460 Gt of organic carbon burial in the palaeo-Sichuan lake alone, representing a major, but hitherto overlooked, carbon sink and negative feedback in the T-OAE global carbon cycle, and likely other similar events. Algal dominated biomass, deposited under a stratified water column during lake level rise, marks the Da'anzhai Member as potential hydrocarbon source rock. Given the challenges associated with Mesozoic stratigraphic correlation, I further present the first integrated (marine) stratigraphic reference framework for the complete Toarcian Stage from the Llanbedr (Mochras Farm) Borehole (Cardigan Bay Basin, UK), which allows precise correlation between the T-OAE and coeval Karoo-volcanism. I also show that accelerated global weathering rates during the T-OAE resulted in widespread mass transport deposits at different palaeolatitudes and changes in ocean chemistry leading to pronounced marine siderite deposition. Periodic smaller-magnitude carbon cycle perturbations in the Hettangian and Sinemurian were possibly in phase with short (~100kyr) and long (~405kyr) eccentricity astronomical forcing, with the formation of organic-rich laminated black shales in the Bristol Channel Basin, similar to Mediterranean sapropels in the Pleistocene.

Extended Abstract

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The Early Jurassic (~201–174 Ma) was marked by a series of rapid perturbations in climate, the environment, and global geochemical cycles, which have been linked to volcanic outgassing and the release of biogenic or thermogenic methane into the ocean–atmosphere system. The most significant event during the Early Jurassic, and arguably the entire Mesozoic, was the early Toarcian Oceanic Anoxic Event (T-OAE; ~183 Ma), marked by marine anoxia–euxinia and globally significant organic-matter burial, accompanied by a major global carbon-cycle perturbation. Although the T-OAE is well studied in the marine realm, accompanying climatic and environmental change on the continents is poorly understood. In this thesis, major palaeoenvironmental changes of the Early Jurassic have been studied to better constrain what happened in marine and lacustrine settings during the T-OAE, and specifically what role lacustrine systems played in the recovery of a perturbed global carbon-cycle, but also to calibrate possible carbon cycle and environmental change, with associated black-shale deposition and seafloor methane release, in response to astronomical forcing. Three geological localities spanning two Early Jurassic time-intervals have been studied: (1) the marine Toarcian in the western Cardigan Bay Basin (UK; Llanbedr (Mochras farm) Borehole), (2) the upper Lower Jurassic lacustrine Da'anzhai Member of the Sichuan Basin (China; two Shell/PetroChina cores), and (3) the marine lower Sinemurian in the Bristol Channel Basin (outcrop successions at Kilve, Somerset, UK).

In **Chapter 2**, the “Llanbedr (Mochras Farm)” Borehole from West Wales, UK, one of the biostratigraphically most complete and expanded marine successions known of the Early Jurassic, is studied. The Mochras core contains a continuous ~260-m-thick Toarcian succession, formed in the relatively deep, open-marine, Cardigan Bay shelf basin. Here, I present high-resolution $\delta^{13}\text{C}_{\text{TOC}}$ analysis, inorganic petrology, molecular and bulk organic-geochemistry, XRD mineral characterization, major- and trace-elemental concentration analyses, and detailed core sedimentary description, to construct (1) a high-resolution chemostratigraphic reference record for the complete Toarcian Stage, and (2) palaeoceanographic and depositional conditions in response to climatically induced changes in global weathering rates. The T-OAE interval in the Mochras core is marked by mass-transport deposits, comparable to coeval marine successions from low–mid palaeolatitudes. Siderite beds frequently formed from the Pliensbachian–Toarcian boundary up to the end of the T-OAE in the Cardigan Bay Basin, directly associated with elevated global continental weathering, as evidenced by elevated $^{187}\text{Os}/^{188}\text{Os}$ values. Both phenomena may be a response to high atmospheric $p\text{CO}_2$ -induced climatic change, with increased hydrological cycling, intensified continental weathering, elevated organic carbon and pyrite burial, and an associated decrease in seawater sulfate concentration, during the T-OAE.

In **Chapter 3**, magnetic polarity analyses have been undertaken on the Toarcian succession of the Mochras core. Palaeomagnetic reversals provide a precise and accurate stratigraphic correlation proxy between marine, and also continental, sedimentary archives, and even to records of major (flood) basalt emplacement. Here, I present the first high-resolution magnetostratigraphic record for the complete Toarcian Stage, that is bio- and chemostratigraphically well constrained, from the biostratigraphically complete and expanded Mochras (Llanbedr) Borehole (Cardigan Bay Basin, UK). With this, I construct an integrated Toarcian stratigraphic reference framework for correlation between Toarcian

marine and continental sedimentary basins worldwide. This high-resolution record of dominant magnetic polarity evolution throughout the Toarcian Stage also allows accurate and precise correlation between the T-OAE and associated climatic change, and the record of major basalt emplacement in the Karoo Large Igneous Province.

In **Chapter 4**, I present radio-isotopic (Re-Os), palynological and geochemical data from the upper Lower Jurassic lacustrine black shales of the Da'anzhai Member in the Sichuan Basin, China. I demonstrate that a major lake system developed contemporaneously with the T-OAE, likely due to enhanced hydrological cycling under elevated atmospheric $p\text{CO}_2$. I present a model in which increased lacustrine organic productivity from elevated fluvial nutrient supply resulted in the additional burial of ~460 Gt of organic carbon in the Sichuan Basin alone, creating an important negative feedback in the global exogenic carbon cycle, which significantly shortened global $\delta^{13}\text{C}$ recovery. Coeval accelerated organic-carbon burial in both marine and lacustrine basins suggests nutrient delivery as the prime cause for global carbon-cycle recovery during the T-OAE.

In **Chapter 5**, I present a comprehensive geochemical study, comprising Rock-Eval, molecular biomarker analysis, palynology and organic petrography, on the upper Lower Jurassic lacustrine black shales of the Da'anzhai Member in the Sichuan Basin, China, to (1) constrain the evolution of the depositional environment and redox conditions in the palaeo-Sichuan Lake preceding and during the T-OAE and (2) characterize the biomass produced and preserved in the palaeo-Sichuan Lake.

In **Chapter 6**, I investigate the state of the global carbon cycle and prevailing climatic and environmental conditions that existed during the (Early Jurassic) early Sinemurian Stage, as recorded in the Bristol Channel Basin (UK). The sedimentary successions of the lower Sinemurian *Arietites bucklandi* ammonite zone, in the coastal exposures at Kilve (Somerset, UK), show the occurrence of ~2 m thick laminated organic-rich black shale interval that is marked by a 2–3‰ negative excursion in $\delta^{13}\text{C}_{\text{TOC}}$ and $\delta^{13}\text{C}_{\text{CARB}}$, and

distinct changes in terrestrial vegetation and marine primary productivity, with the blooming of marine prasinophyte green algae. This event does not represent a single perturbation of the regional environment, but follows in a sequence of eccentricity-modulated, precession-paced perturbations that occur throughout the preceding Lower Jurassic Hettangian and lower Sinemurian Stages, with the periodic (astronomically forced) formation of organic-rich laminated black shales in the (possibly restricted) Bristol Channel Basin. However, the early Sinemurian event studied herein is more extreme in nature, with sedimentary total organic carbon (TOC) values of 5–11% persisting over ~2 m (~100 kyr), possibly in phase with maximum short (~100 kyr) and long (~405 kyr) eccentricity forcing.

The formation of methane seep carbonate cemented mounds at the early Sinemurian seabed of the Bristol Channel Basin occurred relatively soon after deposition of the laminated black shales. In this chapter, I also present a model in which biogenic methane was possibly generated by microbial methanogenesis in the organic-rich sub-seafloor sediments, and channeled to the sediment-water interface approximately ~200 kyr after deposition, to form seabed methane seepage and the associated formation of cemented carbonate mounds.

Acknowledgements

I sincerely thank my supervisors Hugh Jenkyns and Steve Hesselbo, who accepted me 4 years ago to work on this fantastic project, for their dedicated supervision and genuine guidance during my DPhil study. I am very grateful for their great support during the course of my PhD throughout which I was able to attend different conferences, workshops and summer schools. This introduced me to experts from different research areas, which not only broadened my scientific views, but also allowed extensive collaborations that significantly improved the outcome of my research. I acknowledge the full scholarship from Shell International Exploration & Production B.V. for my DPhil study at the Department of Earth Sciences, University of Oxford. I am grateful to Geoff Pike, Xudong Jing and Anusha Surendra, who helped and supported me in the application to Oxford, which has changed my life dramatically.

I would like to thank Shell China Exploration & Production Co. Ltd. and PetroChina Southwest Oil and Gasfield Company for enabling access to core materials and the initial expertise and knowledge they provided. Thanks specifically go to Malcolm Dransfield, Sanjoy Ghosh, Tai-Ran Jiang, Xue-Yan Li, Haibin Xu, and Zhiping Tang and Qinggao Zeng. I would also like to thank the British Geological Survey (BGS) for enabling access to the Mochras core. I acknowledge the approval from Shell and PetroChina for publishing the results from the Da'anzhai cores and from the Executive Director of BGS (NERC) for publishing the collaborative study. I acknowledge CGG Robertson and Shell for providing the palaeogeographic reconstruction used in the thesis.

I feel very lucky to have met Erdem Idiz, Bruce Levell, who were previously at Shell and are now in Oxford, Joe Brannan, Sander van den Boorn, James Eldrett, Keith Gerdes, Olaf Podlaha, Jack Russell, Euphrasia Wong (all at Shell), who have helped and contributed so much during the course of this collaborative study, through their scientific input, facilitating access to Shell materials, laboratories and data, and arranging permissions for publication.

Thanks especially also go to my scientific collaborators: Johan Weijers and Erik Tegelaar (Shell Global Solutions International B.V.) for allowing me into the research labs in Rijswijk and teaching me biomarker geochemistry; to Conall MacNiocaill for introducing me into the world of magnetostratigraphy; to Jim Riding (BGS), Rich Pancost and David Naafs (Bristol), David Selby (Durham), for their insights and discussions during our

collaborative studies; to Jenny Huggett, who taught me to use SEM and assisted in interpreting my XRD data; to Nick Tosca (Oxford) for allowing me to use the XRD lab; to Olga Gorbanenko (Oxford) and Georgios Siavalas (Shell) for their help with the organic petrographical studies; to Melanie Leng (Nottingham) for performing part of the $\delta^{13}\text{C}$ analyses; to Lawrence Percival for collaborating in research and publications; to Clemens Ullmann (CSM/ Exeter University) for discussions and help with sampling of the Mochras core; to Helmut Weissert for inviting me to his and Hugh's scientific party.

I am thankful to all the other PIs of the Oxford-Shell project, Joe Cartwright, Gideon Henderson, Don Porcelli, who have contributed with their insights in my research. I also thank Alex, Allison, Ben, Claudia, Israa, James, John, Luke, Marisa, Martino, Matteo, Mel, Olga, Qingfeng, Sietske and Tim (all PhD-students and post-docs in the Oxford-Shell research group), for all the scientific discussions, field trips, pubs and dinners.

Many thanks to Alice Barroll, Norman Charnley, Peter Ditchfield, Owen Green, Jon Wells, Steve Wyatt (Oxford) and Mabs and Simona (OU) for help with the measurement or assistance in the lab; to Elaine, Emma, Steve (Usher), Yasuko and all other people in the department who have helped me throughout my PhD-project.

I would like to thank postgrad12, Ash, Brendan, Dave, Fern, Hanne, Helen, Joan, Mike, Nikita, Qingfeng, Renee, Tim, Will, Yu; and other friends Ana, Chao, Fan, Feifei, Frey, Jianxin, Jie, Jin, Jo, Laura, Leo, Linhao, Kuangdai, Maya, Meng, Sally, Roy and Marie White, Wen, Xiaojia, Yijing, Xinyuan and many others who have made my life in Oxford full of joy; to my special friend Yue, who has always been supporting me.

I've been so lucky to have met Micha in the early days of my time in Oxford and our shared life and all the travels to 9 countries across 4 continents. Thank you for sharing the happiness and to always cheer me up. I appreciate all the scientific discussions and your reading of my manuscripts/chapters. I am grateful to Jose, Wim, Sanne, Antal and all his other family and friends, who have made me feel at home in Europe.

I am the most grateful to my parents, who have always been very caring, loving, supportive and considerate throughout my whole life, and who always encouraged me to make the most of my life. I am also grateful to my cousin Chen Chi and the other families and friends who have always been taking care and supporting me.

Last but not least, I thank Stuart and Alex for doing my transfer and confirmation of status evaluations. I would like to thank Stuart Robison and François Baudin for their willingness to read my thesis, and the great and insightful discussions during my viva that further contributed to the success of this thesis.

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Publications

The work presented in this thesis is (partly) based on the following publications and manuscripts:

- **Xu, W.**, Ruhl, M., Jenkyns, H.C., Hesselbo, S.P., Riding, J.B., Selby, D., Naafs, B.D.A., Weijers, J.W.H., Pancost, R.D., Tegelaar, E.W., Idiz, E.F., Lake expansion forms major carbon sink during the Toarcian Oceanic Anoxic Event. *Nature Geoscience*, 10, 129–134. (2017; Chapter 4 in this thesis)
- **Xu, W.**, Ruhl, M., Hesselbo, S.P., Riding, J.B., Jenkyns, H.C., Orbital pacing of the Early Jurassic carbon cycle, black shale formation and seabed methane seepage. *Sedimentology*, 64, 127–149. (2017; Chapter 6 in this thesis)
- Ruhl, M., Hesselbo, S.P., Hinnov, L., Jenkyns, H.C., **Xu, W.**, Riding, J.B., Storm, M.S., Minisini, D., Ullmann, C.V. and Leng, M.J. Astronomical constraints on the duration of the Early Jurassic Pliensbachian Stage and global climatic fluctuations. *Earth and Planetary Science Letters*, 455, 149–165 (2016).
- Percival, L.M.E., Cohen, A.S., Davies, M.K., Dickson, A.J., Hesselbo, S.P. Jenkyns, H.C., Leng, M.J., Mather, T.A., Storm, M.S., **Xu, W.** Osmium isotope evidence for two pulses of increased continental weathering linked to Early Jurassic volcanism and climate change. *Geology*, 44, 759–762 (2016).
- Percival, L.M.E., Witt, M.L.I., Mather, T.A., Hermoso, M., Jenkyns, H.C., Hesselbo, S.P., Al-Suwaidi, A.H., Storm, M.S., **Xu, W.**, Ruhl, M. Globally enhanced mercury deposition during the end-Pliensbachian extinction and Toarcian OAE: A link to the Karoo–Ferrar Large Igneous Province. *Earth and Planetary Science Letters*, 428, 267–280 (2015).
- Hesselbo, S.P., Bjerrum, C.J., Hinnov, L.A., MacNiocaill, C., Miller, K.G., Riding, J.B., van de Schootbrugge, B., and **the Mochras Revisited Science Team**. Mochras borehole revisited: A new global standard for Early Jurassic earth History. *Scientific Drilling*, 16, 81–91 (2013).
- **Xu et al.**, Evolution of the Early Jurassic Toarcian carbon-cycle and global climatic controls on local sedimentary processes (Cardigan Bay Basin, UK). *Earth and Planetary Science Letters*, in preparation (Chapter 2 in this thesis).
- **Xu et al.**, Lower Jurassic Toarcian magnetostratigraphy (Mochras Borehole, Cardigan Bay Basin, UK), and its implications for linking Karoo volcanism with the T-OAE. *Journal of the Geological Society, London*, in preparation (Chapter 3 in this thesis).
- **Xu et al.**, Organic geochemistry and organic petrography of the Lower Jurassic Toarcian lacustrine Da'anzhai Member, Sichuan Basin, China. *Organic Geochemistry*, in preparation (Chapter 5 in this thesis).

Chapter 1

Introduction

1.1 The early Toarcian Oceanic Anoxic Event

The Toarcian Stage, the final stage of the Early Jurassic, has an estimated duration of 8.3–8.6 Myrs (2014 Geological Time Scale; Boulila et al., 2014)). The early Toarcian Oceanic Anoxic Event (T-OAE at ~183 Ma), arguably the warmest time-interval of the Jurassic Period, is recognized as one of the most intense and geographically extensive events of oceanic redox change and accompanying organic-carbon burial in the Mesozoic Era (Jenkyns, 1985, 1988; Dera et al., 2011a; Korte et al., 2015). The T-OAE is marked by major changes in global geochemical cycles, with an apparently rapid negative shift of as much as ~7‰ in bulk marine and terrestrial organic-carbon isotope records and a typically smaller (3–6‰) negative excursion in carbonate archives and specific organic compounds (Hesselbo et al., 2000, 2007; Schouten et al., 2000; Sælen et al., 2000; Jenkyns et al., 2002; Kemp et al., 2005; Hermoso et al., 2009a; Al-Suwaidi et al., 2010, 2016; French et al., 2014; Suan et al., 2015). The observed early Toarcian perturbation to the exogenic carbon cycle has been linked to volcanism of the Karoo-Ferrar large igneous province (LIP) and associated release of volcanogenic CO₂, thermogenic methane (CH₄) from sill intrusion into Gondwanan coals and shales, and/or biogenic methane from dissociation of sub-seafloor clathrates (Duncan et al., 1997; Hesselbo et al., 2000; Kemp et al., 2005; McElwain et al., 2005; Svensen et al., 2007, 2012; Burgess et al., 2015; Percival et al., 2015).

Early Toarcian elevated atmospheric $p\text{CO}_2$ likely induced climatic and environmental change (Jenkyns et al., 2002; McElwain et al., 2005; Dera et al., 2011a; Ullmann et al., 2014; Brazier et al., 2015) by accelerating the global hydrological cycle and increasing silicate weathering, thereby increasing delivery of riverine nutrients to the oceans and potentially also to large inland lakes (Jenkyns, 2010). In the marine

realm, the consequential increase in primary productivity and carbon flux to the sea floor is credited with enhancing the burial of planktonic material in relatively deep continental-margin sites, whereas in shallower water semi-restricted marine basins, chemical and physical water-column stratification likely aided the burial of organic matter (Jenkyns, 2010). Particularly in northern Europe, the evidence points to regional to global development of anoxic/euxinic (sulphide-rich) bottom waters that strongly affected palaeoceanographic conditions and marine ecosystems (Jenkyns, 2003, 2010; Ullmann et al., 2014). Globally significant burial of ^{13}C -depleted photosynthetically derived organic matter commonly produced an overarching positive carbon-isotope excursion (CIE) interrupted by the characteristic stepwise negative shift that invariably characterizes the T-OAE (early Toarcian *tenuicostatum*–*falciferum* ammonite zones) (Jenkyns, 1985, 1988, 2003). The overall positive shift is attributed to globally accelerated organic-carbon burial whereas the superimposed stepped negative shift suggests that the release of isotopically light carbon took place in pulses that have been attributed to astronomical forcing of the global carbon cycle (Kemp et al., 2005). Astronomical interpretation of periodic fluctuations in chemical and physical proxy records provides an estimate on the duration of the early Toarcian negative CIE of 300–900 kyr depending on the assignment of Milankovitch periodicity to the observed facies and geochemical oscillations and/or potential sedimentation gaps/hiatus in the sedimentary records studied (Kemp et al., 2005, 2011; Suan et al., 2008; Boulila et al., 2014; Huang and Hesselbo, 2014).

The T-OAE was likely preceded by an earlier carbon-cycle perturbation at the Pliensbachian–Toarcian boundary, with a smaller 2–3‰ negative CIE in marine carbonate, organic matter and fossil wood, and also marked by marine benthic extinctions (Hesselbo et al., 2007; Littler et al., 2010; Percival et al., 2015, 2016;

Bodin et al., 2016). This earlier event has been suggested to have been similar in kind to the T-OAE, possibly closely coupled to an earlier distinct phase of Karoo-Ferrar LIP volcanism as suggested by elevated sedimentary Hg concentrations and climatic repercussions as suggested by elevated $^{187}\text{Os}/^{188}\text{Os}$ (Percival et al., 2015; 2016). Elevated atmospheric $p\text{CO}_2$ -induced global temperature increase in the ocean–atmosphere system caused disruption of marine ecosystems as well as enhanced hydrological cycling and continental weathering on land (Cohen et al., 2004; Ullmann et al., 2014; Korte et al., 2015; Percival et al., 2016).

Stratigraphic studies on the Toarcian have primarily focused on the lower part of the stage, specifically on the T-OAE interval, utilizing biological and geochemical proxies. Integrated stratigraphic approach, including bio-, chemo- and magnetostratigraphy, combined with radio-isotopic dating of volcanoclastic deposits enables accurate and precise correlation of global biological, physical and geochemical events, as recorded in the marine and terrestrial sedimentary archives, with the emplacement of Large Igneous Province volcanism at that time. Due to the lack of oceanic crustal sediments of that age, a magnetostratigraphic record of the Toarcian Stage has to be reconstructed from bio- and chemostratigraphically well constrained core and outcrop sections, without the availability of an independent seafloor M-sequence. Magnetostratigraphic study of the Toarcian Stage has been confined to only a few localities. Not many of these existing magnetostratigraphic records cover the upper Toarcian, or sampling resolution in this interval is often relatively low and affected by hiatuses or poor (ammonite) biostratigraphy. The studied records include the Toarcian of southern Switzerland (Breggia Gorge; Horner and Heller, 1983), the Toarcian in Thouars and Airvault (France; Galbrun et al., 1988), in the Iznalloz section (Spain; Galbrun et al. 1990), in the Neuquén Basin (Argentina; Iglesia Llanos and

Riccardi, 2000); and the lower and middle Toarcian in the Iberian Range of Spain (Osete et al., 2007; Comas-Rengifo et al., 2010). Additionally, a long-duration magnetostratigraphic record, spanning the Pliensbachian to base-Cretaceous interval was obtained from the Northern Apennines in Italy (Satolli et al., 2015), but (ammonite) biostratigraphy is, relatively poorly constrained in this succession. Palaeomagnetic data from the lower and middle Toarcian in the Iberian Range were subsequently synthesized (Osete et al., 2007; Comas-Rengifo et al., 2010), and adopted for the Geological Time Scale 2012 (GTS2012). Utilization of magnetostratigraphy for Toarcian stratigraphic correlation has also been compromised by the lack of integration of magnetostratigraphy with both (ammonite) biostratigraphy and (carbon-isotope) chemostratigraphy. Integrated Toarcian stratigraphy and palaeo-climatic and environmental change will be presented and explored in Chapters 2 and 3 of this thesis.

1.2 Importance of the lacustrine realm

Lacustrine shale successions are important not only as potential hydrocarbon source rocks, but also as archives of environmental change in continental interiors. Previous studies on lacustrine basins have attributed the controlling factors of lacustrine deposits to either local tectonic activity and/or and climatic conditions (sediment+water supply), affecting the accommodation space (Carroll and Bohacs, 1999), while few of them have linked lacustrine black shale formation to global climatic forcing (Suarez et al., 2013; Chen et al., 2014; Zhang et al., 2016). Marine records of the T-OAE have been identified and well studied from numerous outcrops and cores in both the northern and southern hemispheres, which are marked by the apparently coeval occurrence of organic-rich shales (Jenkyns, 1985, 1988, 2003, 2010;

Hesselbo et al., 2000, 2007; Jenkyns et al., 2002; Kemp et al., 2005; Hermoso et al., 2009a; Al-Suwaidi et al., 2010, 2016). Climatic and environmental change on the continents at this time is, however, very poorly understood. Intriguingly, lacustrine records that are associated with the Paleocene–Eocene Thermal Maximum (PETM) and Oceanic Anoxic Event 1a have been identified in China with the characteristic carbon-isotope excursions that are identical to coeval marine records (Chen et al., 2014; Suarez et al., 2013; Zhang et al., 2016).

The lack of knowledge of early Toarcian lacustrine systems stems firstly from the lack of known, or described, upper Lower Jurassic lacustrine records. Secondly, it is compromised by poorly constrained continental stratigraphy prohibiting a direct lacustrine–marine correlation, especially due to the lack of marine macrofossils and volcanic ash beds that could provide high-precision (numerical) age dating.

Sedimentary archives from continental interiors in China (e.g. the Tarim, Ordos and Sichuan basins) are consistently marked by the occurrence of organic-rich black shales that are latest Early Jurassic in age (Huang et al., 2003; Yang et al., 2005; He and Zhu, 2012). Formation of these geographically and stratigraphically expanded lacustrine shales may be linked to the global climatic perturbations associated with the T-OAE. Thus, these sequences potentially provide crucial sedimentary archives of major climatic change at this time, on land.

Termination of the global carbon cycle perturbation, or at least the negative carbon-isotope excursion, associated with the T-OAE has mainly been attributed to enhanced silicate weathering and globally accelerated organic and inorganic carbon burial in different marine basins. The role of continental basins in the drawdown of carbon is often considered to be limited to chemical weathering of silicate minerals, while the amount of carbon burial in lacustrine systems is largely unexplored.

Therefore, identification of lacustrine records that are associated with the T-OAE provides significant new insight into palaeoclimatic and palaeoenvironmental change in continental interiors, and their importance as drivers of poorly constrained negative feedback mechanisms in the global exogenic carbon cycle. This will be explored in Chapters 4 and 5 of this thesis.

1.3 Astronomical pacing of Early Jurassic environmental change and black shale deposition

The Early Jurassic (~201–174 Ma) was punctuated by several major and minor fluctuations in climate, the palaeoenvironment, and global geochemical cycles (Jenkyns et al., 2002; Dera et al., 2011a; Korte and Hesselbo, 2011; Ullmann et al., 2014; Brazier et al., 2015). The most significant one of these perturbations is the T-OAE (Jenkyns, 1985, 1988). However, several recent studies have demonstrated that the T-OAE was preceded by smaller-magnitude global carbon-cycle perturbations, during the Early Jurassic, e.g. in the Late Sinemurian (*Asteroceras obtusum* to *Oxynoticeras oxynotum* ammonite biozones) and at the Sinemurian–Pliensbachian and the Pliensbachian–Toarcian stage boundaries (Hesselbo et al., 2007; Littler et al., 2010; Korte and Hesselbo, 2011; Jenkyns and Weedon, 2013; Riding et al., 2013; Duarte et al., 2014; Porter et al., 2014). Causal mechanisms for these carbon cycle perturbations are yet not well constrained.

Carbon-isotope fluctuations have been observed in sedimentary records throughout the earliest Jurassic (Hettangian) in the marine sediments of the Bristol Channel Basin (Hesselbo et al., 2002; Clémence et al., 2010; Ruhl et al., 2010), but also in the continental sedimentary archives of the Newark and Hartford Basins in the eastern USA (Whiteside et al., 2010). Observed periodic Early Jurassic environmental

and carbon-isotope (and potentially global carbon cycle) fluctuations may be causally related to (orbital and non-orbital) astronomical forcing. This is extensively explored in Chapter 6 of this thesis.

1.4 Ancient methane seepage

Global palaeoenvironmental change events are often marked by global carbon cycle change and a negative carbon-isotope excursion in organic and inorganic sedimentary archives that are often been attributed to methane hydrate dissociation or the release of thermogenic methane into the ocean–atmosphere system, e.g. the Toarcian Oceanic Anoxic Event and the Paleocene–Eocene Thermal Maximum (Hesselbo et al., 2000; Kemp et al., 2005; Dickens et al., 1995). Marine methane seepage and the formation of authigenic carbonates in and on the seabed have occurred preceding and throughout the Phanerozoic, in a variety of palaeo-depositional environments and with different (shallow and deep) sources for the biogenic and thermogenic methane (Tryon et al., 2002; Jiang et al., 2003; Niemann et al., 2006; Walter Anthony et al., 2012; Kiel et al., 2013; Nesbitt et al., 2013; Skarke et al., 2014). Seep mounds of Jurassic age have been observed in several localities in Europe, including Lower Sinemurian outcrops at Kilve (Somerset, UK) (*this thesis*; Whittaker and Green, 1983; Cornford, 2003; Allison et al., 2008; Price et al., 2008), Upper Pliensbachian outcrops in southern France (van de Schootbrugge et al., 2010), and Lower Toarcian coastal Jet Rock outcrops at Ravenscar (Yorkshire, UK) (*this thesis*; Hesselbo et al., 2013). One of the best-studied Jurassic methane seeps formed in the Oxfordian, at ~160 Ma, at Beauvoisin, southeast France (Peckmann et al., 1999). Highly depleted $\delta^{13}\text{C}_{\text{carb}}$ values of down to -30‰ in calcite nodules within the Oxfordian section likely result from hydrocarbon-sourced methane seepage (Louis-

Schmid et al., 2007). The mound-forming authigenic carbonate at Kilve also has depleted carbon-isotope signatures of -11.5‰ to -32.3‰ , which have been interpreted to originate from anaerobic methane oxidation, and mixing of the liberated carbon with seawater DIC (Allison et al., 2008; Price et al., 2008). The source of methane and the mechanism of the methane seepage are yet poorly constraint. Improved understanding on the fluxes of carbon through methane seepage may facilitate better constraints on changes in the local, regional and global methane-carbon budget, especially in response to preceding and coeval environmental change. The source of biogenic methane seeping at the Early Jurassic seabed in the Bristol Channel Basin, and its link to preceding environmental change, is also explored in Chapter 6 of this thesis.

1.5 Aims of the thesis

The work presented in this thesis studies both marine and lacustrine sedimentary records, with the aim to identify differences and similarities in climatic, environmental and depositional drivers for organic-carbon burial in both realms, during past major perturbations in the Earth system. The main objectives are:

(1) The Toarcian marine Mochras core (Cardigan Bay Basin, Wales, UK), which comprises arguably the most expanded and biostratigraphically well-calibrated Lower Jurassic marine succession in NW Europe, is studied to (a) construct a reference stratigraphic correlation framework for the complete Toarcian Stage, (b) reconstruct Toarcian palaeoceanographic and palaeoenvironmental change and its depositional expression, in the Cardigan Bay Basin and beyond, in response to the T-OAE (*Chapters 2 and 3*).

(2) The upper Lower Jurassic lacustrine Da'anzhai Member of the Sichuan Basin (China) is studied to (a) determine the precise age of the Da'anzhai Member, (b) determine the depositional context of the lacustrine black shales, (c) explore the role of major lake system formation in the context of global carbon cycle change during the Early Toarcian Oceanic Anoxic Event (T-OAE), and (d) test whether the T-OAE, known from the marine realm, had a predictable impact on organic-carbon burial in continental basins (*Chapters 4 and 5*).

(3) The Lower Jurassic Sinemurian *bucklandi* zone (Blue Lias at Kilve, Somerset Basin, UK) is studied to constrain (a) a potential Early Sinemurian global carbon-cycle perturbation and palaeoenvironmental change leading to black-shale deposition in the Bristol Channel Basin; (b) its link to astronomical pacing of the Early Jurassic climate; and (c) the subsequent genesis of Early Jurassic seabed methane seepage (*Chapter 6*).

Chapter 2

Depositional and palaeoenvironmental implications of enhanced continental weathering during the Early Jurassic Toarcian Stage: Mochras Borehole, UK

This chapter is modified from **Xu et al.**, Evolution of the Early Jurassic Toarcian carbon-cycle and global climatic controls on local sedimentary processes (Cardigan Bay Basin, UK). *Earth and Planetary Science Letters*, in preparation. Jenny Huggett contributed to the quantification of mineral concentrations with the XRD data. Clemens Ullmann counted the belemnite occurrence.

2.1 Introduction

The Toarcian Stage is suggested to have been the warmest period of the Jurassic (Dera et al., 2011a; Korte et al., 2015). The Toarcian is also marked by arguably the most intense and geographically extensive event of oceanic redox change of the Mesozoic, termed the Early Toarcian Oceanic Anoxic Event (T-OAE, at ~183 Ma), with large-scale organic-carbon burial in many marine basins (Jenkyns, 1985, 1988). As discussed in Chapter 1, the T-OAE was associated with the release of volcanogenic CO₂, and/or thermogenic methane (CH₄) from sill intrusion into Gondwanan coals, and/or biogenic methane from dissociation of sub-seafloor methane clathrates in response to the emplacement of the Karoo–Ferrar large igneous province (LIP) (Duncan et al., 1997; Hesselbo et al., 2000; Kemp et al., 2005; McElwain et al., 2005; Svensen et al., 2007, 2012; Burgess et al., 2015). Enhanced volcanism is expressed by elevated mercury concentration relative to total organic carbon (TOC) as a fingerprint in the marine sediments at the T-OAE (Percival et al., 2015, 2016). The observed early Toarcian perturbation to the exogenic carbon cycle, with elevated atmospheric *p*CO₂, likely induced climatic and environmental change, with positive and negative feedback mechanisms, e.g. an accelerating global hydrological cycle and globally increased silicate weathering, leading to enhanced delivery of riverine nutrients to the oceans and large inland lakes (Jenkyns et al., 2002; Cohen et al., 2004; McElwain et al., 2005; Jenkyns, 2010; Dera et al., 2011a; Kemp et al., 2011; Ullmann et al., 2014; Brazier et al., 2015; Percival et al., 2016; Xu et al., 2017). The consequential increase in primary productivity and enhanced organic-matter preservation aided by anoxic–euxinic bottom waters in the oceans and lakes led to regional/global deposition of black shales. Globally significant burial of isotopically depleted, photosynthetically derived organic matter is credited with producing an

overarching positive carbon-isotope excursion (CIE) interrupted by the characteristic abrupt negative shift that occurred synchronously with the T-OAE (Early Toarcian *tenuicostatum*–*falciferum* ammonite biozones) (Jenkyns, 1985, 1988, 2003).

The T-OAE was preceded by an isotopic event at the Pliensbachian–Toarcian boundary, with a smaller 2–3‰ negative carbon isotope excursion and marine benthic extinctions (Hesselbo et al., 2007; Littler et al., 2010; Percival et al., 2015; Bodin et al., 2016). It has been suggested to have been similar in kind to the T-OAE, possibly closely coupled to an early but distinct phase of Karoo–Ferrar LIP volcanism, evidenced by elevated sedimentary Hg concentrations (Percival et al., 2015; 2016).

The Llanbedr (Mochras Farm) Borehole from the Cardigan Bay Basin (Wales, UK), hereafter named ‘Mochras’ or ‘Mochras core’, penetrates the relatively homogenous and continuous limestones and mudstones of the complete Lower Jurassic. Here, we present geochemical and biological data spanning the Toarcian Stage, to (1) construct a high-resolution geochemical reference record for the complete Toarcian Stage, (2) reconstruct palaeoceanographic and palaeoenvironmental change in the relatively open-marine Cardigan Bay Basin, in response to the T-OAE and throughout the Toarcian Stage, and (3) constrain the depositional expression of increased continental weathering.

2.2 Geological setting and stratigraphy

The Mochras core contains the most expanded and biostratigraphically complete Lower Jurassic succession known, covering ~27 Myr across the Hettangian to Toarcian Stages (2012 GTS). The Mochras Farm area in the Cardigan Bay Basin during the Early Jurassic was located at a palaeo-latitude of ~42°N (based on the reference data from Torsvik et al., 2012), at the southern end of the European epi-

continental seaway (Figure 2.1), linking the northwestern Tethys Ocean to the Boreal realm.

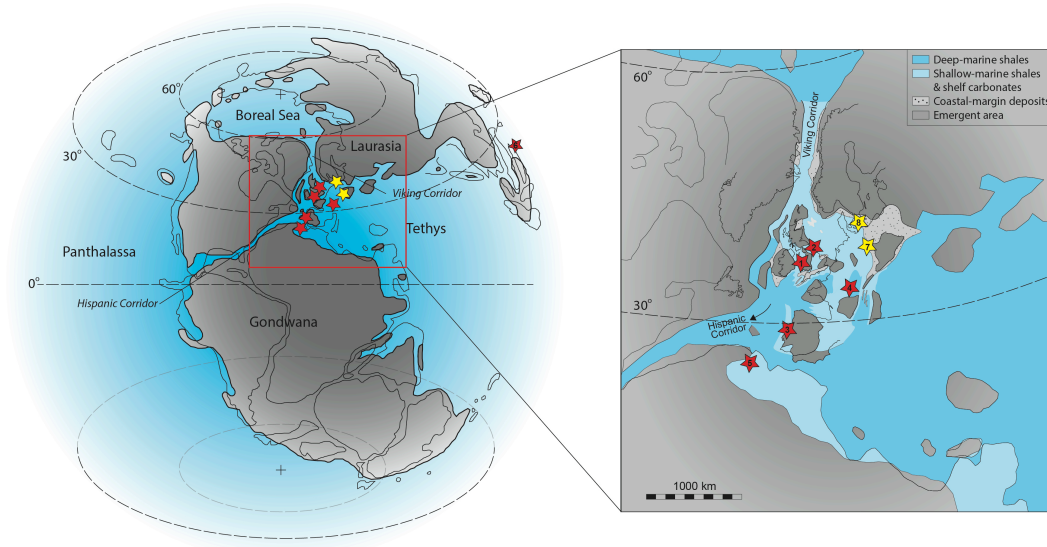


Figure 2.1 Geographical maps. (A) Early Jurassic global palaeogeography, modified after Dera et al. (2011b) and Korte et al. (2015). (B) Zoom-in map of the red-square-marked area in map A, showing the palaeogeographic positions of Mochras (1), Yorkshire (2), Portugal (3), France (4), and Morocco (5) with shallow- and deep-marine environments shown by red stars; and Denmark (7) and Poland (8), deposited under marginal-marine conditions, shown by yellow stars. Japan (6) is marked in the map on the left.

The Mochras core was drilled onshore by the British Geological Survey (BGS) in 1967–1969, at the Cardigan Bay coast in western Wales, UK (Woodland 1971; Hesselbo et al., 2013). The core penetrates down to the continental Triassic and the Jurassic section is overlain unconformably by a Quaternary/Cenozoic sequence. The Cardigan Bay Basin was downthrown against the Lower Palaeozoic Welsh Massif because of a major normal fault system, comprising the Mochras, Tonfanau and Bala faults at the eastern and southeastern margins of the basin (Tappin et al., 1994). The Lower Jurassic sequence in this onshore borehole has a remarkable thickness of about 1300 m (601.83–1906.78 meters below surface, mbs), much thicker than coeval onshore sections in other parts of the UK and continental Europe (Ruhl et al., 2016). In

comparison, the well-studied Lower Jurassic sequences along the Dorset coast (Wessex Basin) are ~360m; and along the Yorkshire coast (Cleveland Basin) they are ~450 m (Simms et al., 2004), albeit with well-known and described sedimentary gaps and intervals of condensation.

The Mochras core is biostratigraphically complete and is well studied for ammonite and foraminiferal biostratigraphy (Ivimey-Cook, 1971; Copestake & Johnson, 2014). The 8 ammonite zones of the Toarcian Stage in NW Europe have all been recognized (Ivimey-Cook, 1971; Page, 2003) and, in addition, belemnites, brachiopods, bivalves and crinoids, occur regularly throughout the core. Macro-scale plant debris also occurs throughout the entire Lower Jurassic sequence, but is especially enriched in the Lower Toarcian, coevally with siliciclastic-rich levels at around 809–826 mbs, suggesting relatively close proximity to nearby landmasses (Cope, 1984). The dominant moderately homogenous lithology of darker mudstones and marls alternating with lighter coloured muddy limestones indicates a relatively open- and deep-marine sedimentary environment (Sellwood and Jenkyns, 1975).

Earlier chemostratigraphic and geochemical analysis on the Toarcian in the Mochras core (1) showed a clear negative carbon-isotope excursion (CIE) in bulk organic matter ($\delta^{13}\text{C}_{\text{TOC}}$) and bulk carbonate ($\delta^{13}\text{C}_{\text{CARB}}$) (Jenkyns and Clayton, 1997; Jenkyns et al., 2001, 2002; van de Schootbrugge et al., 2005); (2) suggested a direct correlation between large igneous province (LIP) volcanism and the Early Toarcian negative CIE based on Hg/ TOC ratios (Percival et al., 2015); and (3) suggested an accelerated global continental weathering flux in response to LIP volcanism (based on an increase in Os-isotope ($^{187}\text{Os}/^{188}\text{Os}$) ratios; Percival et al., 2016).

2.3 Materials and methods

The Mochras core and disaggregated samples are housed in the collections of the British Geological Survey, Keyworth, Nottingham (UK). The Toarcian Stage in the Mochras core, studied here, occurs in the depth interval of 863.5 to 601.83 mbs. The core slabs of the Toarcian are reasonably well preserved, especially in comparison with the Hettangian and Sinemurian intervals, for which core slabs are only sporadically available (Hesselbo et al., 2013). Samples were collected from the complete Toarcian of the slabbed core, at ~25 cm resolution from the depth-interval of 843.3–809.6 mbs and at ~33 cm resolution from 863.5 to 843.3 mbs and 809.6 to 601.83 mbs. From the 923 collected samples, 648 samples were analyzed by X-ray fluorescence (XRF), 427 samples were analyzed for bulk organic carbon-isotope ratios ($\delta^{13}\text{C}_{\text{TOC}}$), 248 samples were analyzed by Rock-Eval, 21 samples were analyzed by scanning electron microscopy (SEM) and 70 samples were analyzed by X-ray diffraction (XRD).

2.3.1 Rock-Eval

Rock-Eval analyses were performed with a Rock-Eval 6 Standard Analyzer unit from Vinci Technologies, at the Department of Earth Sciences (University of Oxford), with pyrolysis and oxidation ovens and a flame ionization detector and infra-red cell, to measure the S1, S2, TMax, S3co/ S3co₂ (New Oxygen Index), S4co/ S4co₂ (Residual Organic Carbon), S5 (Mineral Carbon), to calculate the Total Organic Carbon (TOC, in %), Hydrogen Index (HI, in mg HC/ g TOC) and to characterize kerogen type and rock parameters. Laboratory procedures were followed from Behar et al. (2001). ~50 mg of homogenized sample were weighed into crucibles and measured following a temperature profile of 300–650 and 300–850°C for the pyrolysis and oxidation ovens, respectively. The IFP 160000 Reference Standard and the in-house

SAB134 (Blue Lias organic-rich marl) standard were regularly measured (every 10 samples for the in-house standard). The standard deviation on TOC and HI of the in-house SAB134 and the reference IFP160000 standards is, respectively, 0.07% and 0.07% (TOC) and 22.7 mg HC/g TOC and 10.6 mg HC/g TOC (HI).

2.3.2 $\delta^{13}\text{C}_{\text{TOC}}$

For $\delta^{13}\text{C}_{\text{TOC}}$ analyses, homogenized sample material (0.5g) was decarbonated in 50 mL of 5% HCl, for up to 24 hours. Samples were subsequently rinsed a few times with distilled water to reach neutral *pH*. Samples were then oven-dried at 40°C, and ground with an agate mortar for further analysis. $\delta^{13}\text{C}_{\text{TOC}}$ analyses were performed at the British Geological Survey (Keyworth, UK), by combustion in a Costech Elemental Analyser (EA) on-line to a VG TripleTrap and Optima dual-inlet mass spectrometer, with $\delta^{13}\text{C}_{\text{org}}$ values reported relative to V-PDB following a within-run laboratory standards calibration, with NBS-18, NBS-19 and NBS-22. Replicate analysis of well-mixed samples showed a precision of $\pm <0.1\text{‰}$ (1 SD).

2.3.3 Scanning Electron Microscopy

Polished thin-sections were carbon-coated and analyzed with a FEI Quanta FEG 650 Scanning Electron Microscope (SEM) at the Department of Earth Sciences, University of Oxford. Samples were selected from local red-coloured levels and from coarser grained beds, and analyzed using the backscatter electron detector. Back-Scattered Electron Imaging (BSEI) was displayed with brighter regions representing areas of higher average atomic number.

2.3.4 X-ray diffraction

Powder X-ray diffraction was performed on bulk-rock samples that were powdered and homogenized by hand in an agate mortar. Samples were bottom-loaded and pressed into circular cavity holders. Powders were analyzed using a Panalytical Empyrean Series 2 diffractometer at the Department of Earth Sciences, University of Oxford, operating at 40 kV and 40 mA, and with a Co K α source. Samples were analyzed under continuous rotation and data were acquired from 5–85 degrees 2-theta using a step size of 0.026 degrees. The diffractometer used a multiple-strip detector, to minimize scan rates compared to a single detector by a factor of 255. Diffraction data were reduced using the HighScore Plus software suite. Statistically significant peaks and diffraction profiles (after background subtraction) were determined and mineral identifications were based on correspondence to the ICDD Powder Diffraction File 4+ (PDF-4+) database. Quantification of mineral abundances was performed based on the reference intensity ratio method and appropriate scale factors were also obtained from the PDF-4+ database. However, individual peak intensities from certain minerals in small quantities (e.g. pyrite) were tabulated for each sample, as a relative measure of mineral variation between samples. This method works well in this study because all the samples were prepared in exactly the same way with exactly the same quantity, so small variations in peak intensity are likely to originate from abundances of the mineral rather than other factors (Moore and Reynolds, 1997).

2.3.5 X-ray fluorescence

X-ray fluorescence (XRF) analysis was performed at the flat surface of bulk-rock samples, using a handheld (HH) Olympus Innov-X Delta Premium DP6000C XRF Alloy Analyzer. The HH-XRF was run in Geochem Mode (DS-6000) and standard calibration to a manufacturer-delivered standard metal clip was performed at

the onset of each run. The analyzer included a powerful 4W X-ray tube for light-element analysis and a large-area Silicon Drift Detector (SDD). X-ray absorption spectra were recorded in scanning mode from 3 to 40 keV and absorption peaks were automatically identified using the Innov-X “soil mode” software. A wide range of elements are automatically detected and quantified during HH-XRF analysis, including Mg, Al, Si, P, S, K, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Rb, Sr, Y, Zr, Nb, Mo, Ag, Cd, Sn, Sb, Ta, W, Hg, Pb, Bi, Th, U, among which Ca, S, Fe, Si, Al, Ti, Zr, Rb are investigated. Ca, Al and Fe concentrations are compared with results measured by ICP-MS (method see below).

2.3.6 ICP-MS

High-resolution XRF element concentration analysis was additionally checked by ICP-MS using a Thermo-Finnigan Element 2 magnetic-sector ICP-MS at the University of Oxford (methods reported in Percival et al., 2016). It is important to note, however, that HH-XRF analyses was performed on a ~4 mm spot on the flat-surface of a bulk-rock sample, while ICP-MS elemental concentration analysis is performed on homogenized and processed powders of the same sample, potentially resulting in slightly different measured concentrations.

2.3.7 Molecular biomarker analyses

Seven samples from the Mochras core were processed for biomarker analyses. Sample preparation and biomarker analysis were performed at the Organic Geochemistry Laboratory facilities at Shell Global Solutions International in Rijswijk (The Netherlands).

2.3.7.1 Total lipid extraction

The total lipid fraction of each sample was obtained via extraction using a Dionex ASE® 350 Accelerated Solvent Extractor (ASE). First, individual ASE-cells were cleaned with dichloromethane (DCM) and methanol. Then, about 10 grams of powdered and dried sample material was weighed into a cleaned and dried ASE-cell and lipids were subsequently extracted with a 9:1 DCM:methanol solvent mixture in 3 cycles over 45 minutes, at a temperature and pressure of 125°C and 1500 psi, respectively. A blank ASE-cell was run at the beginning of each run and retrieved solvent was checked for molecular contamination. The total lipid extracts (TLEs) were concentrated to 1 ml in a TurboVap 500 using a helical gas flow and sensor endpoint detection technology (Activated Cu was also added to the extracts to remove any elemental sulphur, which turned out not to be present). Aliquots of the TLE were used for further column chromatography.

2.3.7.2 Column chromatography

An aliquot of TLE was separated over AgNO₃-impregnated silica gel columns into saturate, aromatic and resin fractions. After pre-conditioning of the column with cyclohexane and application of the TLE, the saturate fraction was eluted with *n*-hexane, the aromatic fraction with toluene and the resin fraction with acetone (3 column volumes each). A mixture of known amounts of standard compounds was added to the aromatic fraction at this stage prior to analysis using Gas Chromatography/Mass Selective Detection. The retrieved saturate fraction of each sample was subsequently separated into *n*-alkane and branched/cyclic (b/c) alkane fractions (method described in section 2.3.7.3).

2.3.7.3 *n*-alkane extraction

n-alkanes were extracted from the saturate fraction of each sample using zeolite molecular sieve beads (0.5 nm). The molecular sieve beads were activated in the oven for 3 hours at 120°C, added to the saturate fraction and left standing overnight in cyclo-hexane to trap the *n*-alkane fraction. The cyclohexane, containing the branched/cyclic (b/c) fraction, was transferred to a separate vial and beads were rinsed a few times with cyclohexane, which was added to the b/c fraction. A known amount of standard mixture was added to the b/c fraction at this stage. The b/c fraction was subsequently analyzed using Gas Chromatography/tandem mass spectrometry (GC/MSxMS).

2.3.7.4 Biomarker analysis

Aromatic fractions were analyzed for their biomarker content using an Agilent 7890B GC system coupled to an Agilent 5973 mass selective detector (MSD). Separation of compounds was achieved on a J&W DB-1 phase column (60 m × 250 µm, 0.25 µm film thickness) using the following temperature program: 50°C (1 min) - 20°C/min - 120°C - 2°C/min - 320°C (20 min.). The source temperature of the MSD was set at 250°C and it was run in selective ion mode (SIM) scanning for the masses of interest. Compounds were identified in the respective mass chromatograms by comparison of their retention time and elution order with standard samples.

B/c fractions were analyzed for their biomarker content using an Agilent 7890A GC system coupled to an Agilent 7000 Triple Quadrupole Mass Spectrometer. Separation of compounds was achieved on a J&W DB-1 phase column (60 m × 250 µm, 0.25 µm film thickness) using the following temperature program: 50°C (1 min) - 4°C/min - 220°C - 1.2 °C/min - 280°C - 3°C/m - 310°C (20 min). The temperature of

the ion source was set at 250°C and the collision energy in the second quadrupole was set at 10. A selected set of parent–daughter mass transitions was scanned to monitor the compounds of interest. Compounds were identified in the respective mass-transition chromatograms by comparison of their retention times and elution order to standard samples. For selected samples the system was run in full scan GC/MS mode to confirm identifications with full mass spectra.

2.4 Sedimentology of the Mochras core

The Toarcian interval in the Mochras core is ~262m thick and generally marked by ~ metre-scale alternations of marly limestone to carbonate-rich marl to mudstone. The sediments become darker with increasing clay content. In detail, the Lower Toarcian in the Mochras core, from 863.5 to 750 mbs covering the Upper *tenuicostatum* ammonite zone and the *exaratum* ammonite subzone of the *serpentinum* ammonite zone, is marked by carbonate-poor mudstone with local centimetre-thick laminated black shale. The *exaratum* subzone exhibits several intervals of coarser grained (silty) sediments, commonly with macroscopic wood fragments, as well as sedimentary structures such as wave ripples and levels of soft- sediment deformation. Ironstone nodules regularly occur throughout the *tenuicostatum* and the *falciferum* ammonite zones, and are especially pronounced from 852.58 to 819.90 mbs (Woodland, 1971; O’Sullivan et al., 1971). The overlying *bifrons*, *variabilis* and lower *thouarsense* ammonite zones are generally richer in carbonate and record the more pronounced metre-scale primary lithological bundles between marly limestone/carbonate-rich mudstone and carbonate-poor mudstone, similar to what is observed in the Pliensbachian of the Mochras core (Ruhl et al., 2016).

Mochras borehole, Wales, UK

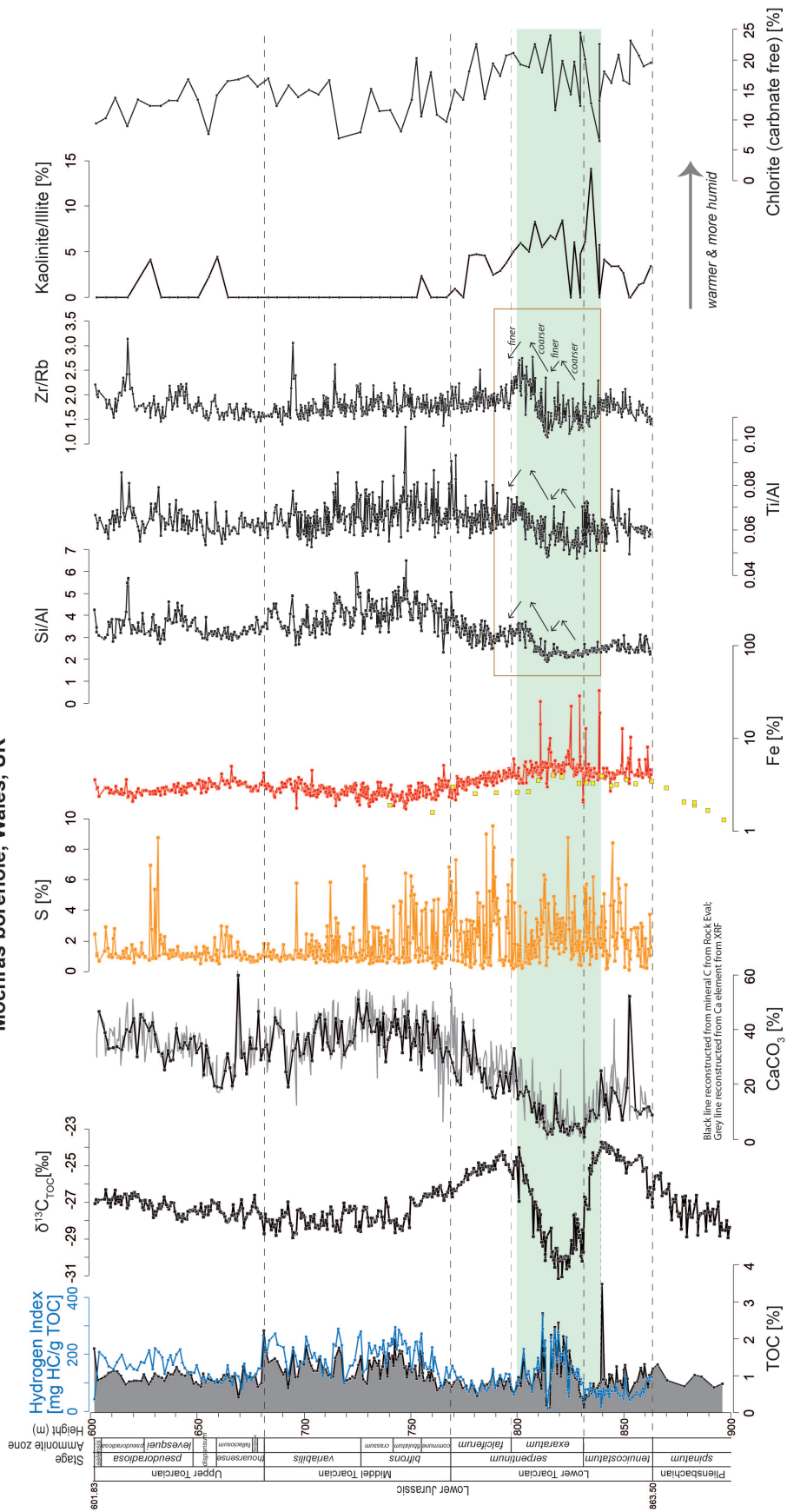


Figure 2.2 High-resolution geochemical data for the complete Toarcian Stage (Mochras core, UK). TOC and HI measured by Rock Eval are in black and dark blue squares, respectively. Concentrations of Fe (in red squares), sulphur (in yellow squares), ratios of Si/Al, Ti/Al and Rb/Zr (in black squares) are measured by handheld XRF; Fe concentrations, marked by yellow squares, are measured by ICP-MS; % $CaCO_3$ in black squares is reconstructed from Rock-Eval-based mineral carbon concentration (assuming all the mineral carbon is from $CaCO_3$); % $CaCO_3$ in grey lines is reconstructed from Ca concentration analyzed by HH-XRF.

2.5 Results and discussions

2.5.1 High-resolution chemostratigraphic reference record for the Toarcian Stage

The new organic carbon-isotope ($\delta^{13}\text{C}_{\text{TOC}}$) record presented here for the complete Toarcian Stage in the Mochras core shows a stratigraphically short-lived, relatively modest ($\sim 2\text{‰}$), negative CIE at the Pliensbachian–Toarcian boundary, followed by a strong and stratigraphically prolonged $\sim 7\text{‰}$ Lower Toarcian negative CIE of -24 to -31‰ , which is marked by a step-wise onset at the *tenuicostatum*–*serpentinum* transition (Figure 2.2). The Lower Toarcian negative CIE in the Mochras core is superimposed on a long-term positive excursion, which started in the upper *spinatum* ammonite zone and lasted until the middle of the *bifrons* zone. The Mochras $\delta^{13}\text{C}_{\text{TOC}}$ record is further marked by metre-scale $\sim 1\text{‰}$ fluctuations superimposed on the long-term trend (Figure 2.2). The observed steps at the onset of the T-OAE were previously observed in both organic and inorganic matter in other marine successions (Kemp et al., 2005, Hesselbo et al., 2007, Hesselbo and Pieńkowski, 2011, Hermoso et al., 2009a). Although the T-OAE interval in the Mochras core is mostly represented by (weakly organic-rich) mudstone or (marly) limestone, with only a few intervals of sub-centimetre-thick laminated black shale, the total organic carbon (TOC) content is elevated up to 2.5% during the most negative part of the CIE (Figures 2.2 and 2.3), as also indicated by Jenkyns and Clayton (1997). TOC values fluctuate between 0.5–1.5% during the rest of the Toarcian Stage in the Mochras core, with on average slightly higher values in the *bifrons* and *variabilis* ammonite zones (Figure 2.2).

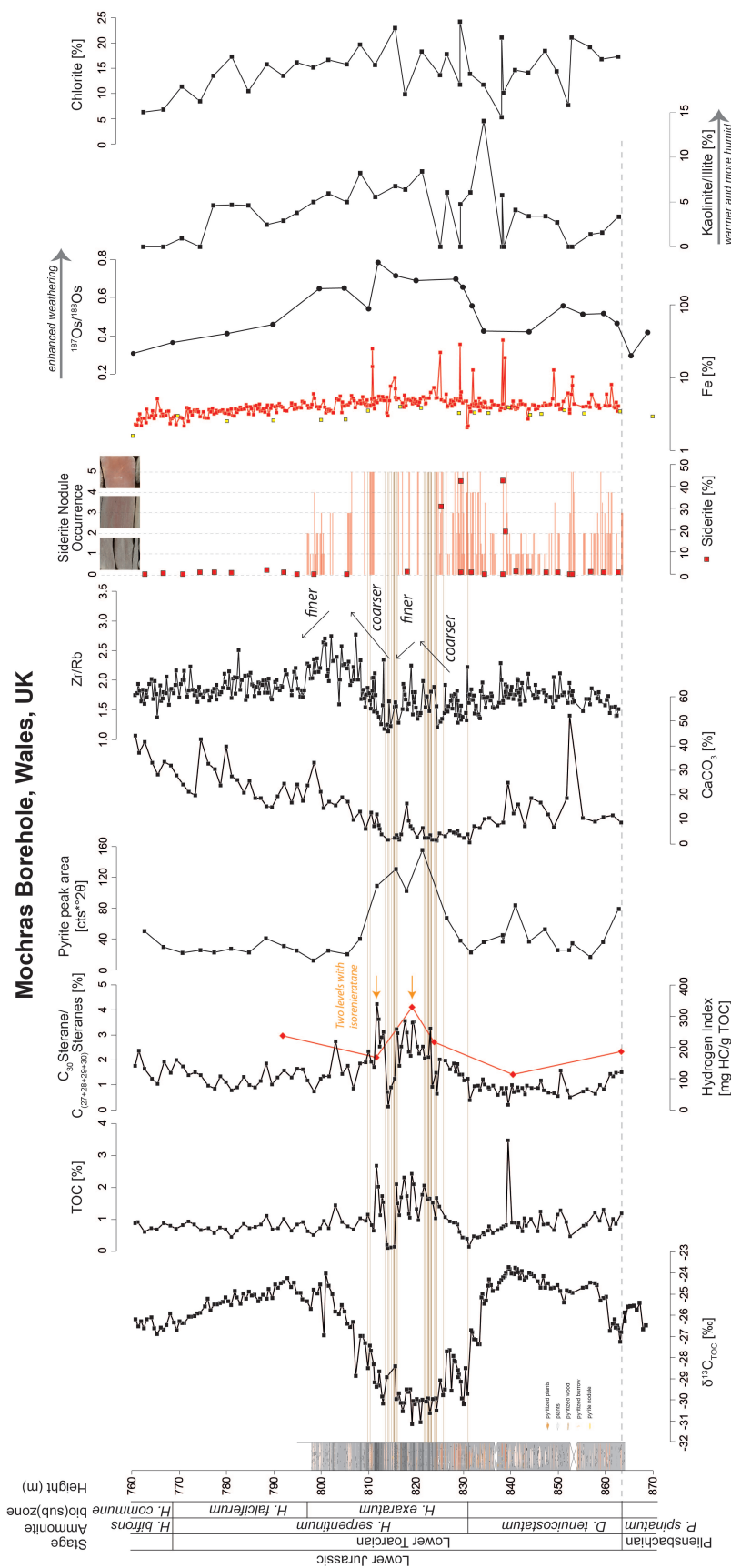


Figure 2.3 Lithological log and geochemical records from the Lower Toarcian succession of the Mochras core. The occurrences of fine-scale turbidites and debris flows in the core are marked by brown lines. $\delta^{13}C_{TOC}$, TOC, HI, % $CaCO_3$, Rb/Zr, kaolinite/illite ratios, %chlorite are plotted in black squares. C_{30} Sterane indices are plotted in red diamonds on top of HI. The occurrences of siderite nodules have been visually described based on the degree of red colour on the core from 0 to 5 illustrated by core photos marked by red lines. %siderite has been measured by XRD analysis. Fe concentrations measured by XRF and ICP-MS are plotted in red squares and yellow squares, respectively, on a log scale. $^{187}Os/^{188}Os$ ratios (Percival et al., 2016) are in full black circles. Pyrite concentration changes have been illustrated by the variations of the peak areas of XRD spectra.

Hydrogen Index (HI) values are elevated up to 339 mg HC/g TOC during the negative CIE, compared to pre-excursion values of less than 100 mg HC/g TOC, possibly reflecting an elevated marine (algae) primary productivity and organic-carbon supply into the sedimentary environment (Figures 2.2 and 2.3). C_{30} -Sterane Indices ($C_{30}/(C_{27}+C_{28}+C_{29}+C_{30})$), reflecting the percentage of marine algal organic-matter supply (Moldowan et al., 1985), are between 1.4% and 4.1%, with relatively elevated concentrations during the T-OAE negative CIE, coinciding with relatively elevated HI (Figure 2.3). C_{30} - $\beta\beta$ -Hopanes are also observed in the branched-cyclic fractions of the lipid extractions of the analyzed samples, with the ratios of C_{30} - $\beta\beta$ -Hopanes/ C_{30} -Hopanes of 0.14–0.49 (Appendix A). The presence of C_{30} - $\beta\beta$ -Hopanes suggests an immature to early mature burial history for the sedimentary organic matter in the Mochras core (Seifert and Moldowan, 1980), which is further confirmed by dominant T_{max} values of 425–441°C.

Stratigraphic correlation between the Mochras core and coeval strata from Yorkshire based on ammonite biostratigraphy shows similar magnitude negative CIEs in both sections, at the Pliensbachian–Toarcian boundary and the interval of the T-OAE. Absolute $\delta^{13}C_{org}$ values of the T-OAE negative CIE are, however, different, with $\delta^{13}C_{org}$ ranging from -24‰ to -31‰ in the Mochras record, and from -25‰ to -33‰ in the Yorkshire sections (Figure 2.2). The observed offset between the two successions is likely caused by the different compositions of the bulk organic matter. In the Mochras core, terrestrial organic matter counts for a higher percentage of the total organic matter, as indicated by the abundant macrofossil wood and HI values of only up to 339 mg HC/g TOC (Figures 2.2 and 2.3). The bulk sedimentary organic matter in the Yorkshire coast successions likely contains a higher % of algae sourced organic matter, as evidenced by HI values of up to 734 mg HC/g TOC (Sælen et al., 2000;

French et al., 2014). Marine algae generally fractionate more strongly for light carbon than terrestrial higher plants (especially the ligno-cellulose components of terrestrial higher plants), resulting in a more negative $\delta^{13}\text{C}_{\text{org}}$ signature (van Bergen and Poole, 2002). Following the broad positive CIE during the *tenuicostatum* and *serpentinum* ammonite zones, the $\delta^{13}\text{C}_{\text{org}}$ composition of sedimentary organic matter shifted towards more negative values in the *bifrons* and *variabilis* zones, where TOC contents generally increased up to 2.21% and HI values up to 296 mg HC/g TOC (Figure 2.2).

In contrast to many coeval marine basins that are marked by globally significant burial of organic matter during the T-OAE, the Cardigan Bay Basin was characterized by exceptionally organic-lean deposits and a lack of distinct black shales, which might be related to the high sedimentation rate and the siliciclastic dilution. However, because of the globally synchronous burial of organic carbon elsewhere in the World Ocean, the broad positive excursion in $\delta^{13}\text{C}$, interrupted by a negative excursion recording input of isotopically light carbon, is very distinctly recorded in the Mochras core.

2.5.2 Depositional environment and palaeoenvironmental change in the Cardigan Bay Basin

The bottom waters of the Cardigan Bay Basin during the Toarcian was generally well oxygenated as evidenced by commonly observed bioturbation throughout most of the succession. The studied concentration of gammacerane throughout the Toarcian part of the Mochras core, is very low, even in the darker mudstone successions of the *tenuicostatum* and *falciferum* ammonite zones. Gammacerane/ C_{30} -hopane ratios are between 0.01 and 0.05 (Appendix A). Gammacerane is a biomarker derived from tetrahymanol that forms in abundance

under conditions of high bacterial productivity within stratified water columns, often in lakes or isolated marine basins (Sinninghe Damsté et al., 1995). The near absence of gammacerane biomarkers suggests the lack of stratification in the water column. However, the biomarker isorenieratane was detected at two horizons during the most negative part of the T-OAE negative CIE, at ~811.66 m and ~819.10 mbs in the *exaratum* subzone (Figure 2.3). Isorenieratane is a pigment of the photosynthetic green sulphur bacteria *Chlorobiaceae*, which perform photosynthesis utilizing hydrogen sulfide and light (Koopmans et al., 1996). Hence, the presence of isorenieratane or its diagenetic and catagenetic products in sedimentary rocks or crude oils is an indication for photic- zone euxinia in the water column (Koopmans et al., 1996). The two stratigraphic intervals where isorenieratane was detected are darker in colour and laminated, suggesting little to no bioturbation at the time of deposition. These levels also have higher organic-carbon contents, with TOC values of up to 2.67%, suggesting both the increased aquatic organic productivity and the elevated preservation as possible primary controls on the enrichment of organic matter.

Geochemical conditions in the water column in the Cardigan Bay Basin may, however, have been less than favourable (oxygen, temperature, pH, etc) at certain times. Belemnite occurrence in the whole Toarcian Stage of the Mochras core has been counted by Clemens Ullmann. Belemnites occur in most of the Toarcian Stage, except the two intervals of the lower *tenuicostatum* zone and the lower *exaratum* subzone (Figure 2.4). The observed belemnite gap in the Mochras core occurs stratigraphically coevally with observed belemnite gaps in other Lower Toarcian marine successions in north-western and southern Europe (Figure 2.4), suggesting water-column conditions prohibiting the occurrence of certain large marine organisms. In the Mochras core, abundant belemnites occur in the upper Pliensbachian *spinatum* ammonite zone, but

become rare in the darker mudstones of the lowermost Toarcian *tenuicostatum* zone and the lower half of the *serpentinum* zone (*exaratum* subzone) (Figure 2.4). Belemnite occurrence in the Cleveland Basin (UK) and the Lusitanian Basin (Portugal), however, only significantly decreases at the onset of the T-OAE negative CIE (Figure 2.4). In contrast, belemnites apparently are present throughout the Lower Toarcian sedimentary successions of other marine basins across the European continental seaway, e.g. southern Germany (Bailey et al., 2003), although average belemnite abundance in these successions may also have decreased. The reappearance of belemnites stratigraphically differs between marine basins, but generally coincides with the end of the T-OAE negative CIE (Figure 2.4). The temporary disappearance of belemnites in the Lusitanian and Cleveland Basin successions was previously ascribed to unfavourable anoxic–euxinic water-column conditions (Hesselbo et al., 2007; Ullmann et al., 2014). Hence, the brief episodes of possible photic-zone euxinia, with elevated levels of isorenieratane, and possibly enhanced water-column stratification, during the T-OAE negative CIE (Figure 2.3) suggests at least episodically deteriorating conditions throughout much of the water column in the Cardigan Bay Basin that were possibly unfavorable for belemnites. Belemnites are suggested to live in the ocean bottoms, e.g. indicated by a consistent offset of the seawater temperature reconstructed from belemnites and the sea-surface temperature (TEX₈₆) (Jenkyns et al., 2012). The fact that ammonites were still present in the intervals where belemnites were rare indicates that the lack of oxygen in the deeper part of the water column played a major role in limiting the belemnite occurrence, despite the fact that the Cardigan Bay Basin was likely much less restricted compared to the Cleveland and Lusitanian Basins (Percival et al., 2016), with less extreme water-column redox change over the T-OAE. Other factors, such as preservation or other physical or chemical

conditions (e.g. temperature, pH) may also have played a minor role in the observed decrease in belemnite abundance. Similarly, crinoidal fragments, abundant throughout the Pliensbachian of the Mochras core, disappear at the Pliensbachian–Toarcian boundary and are not present throughout the Toarcian Stage, further suggesting unfavourable environmental bottom-water conditions in the Cardigan Bay Basin.

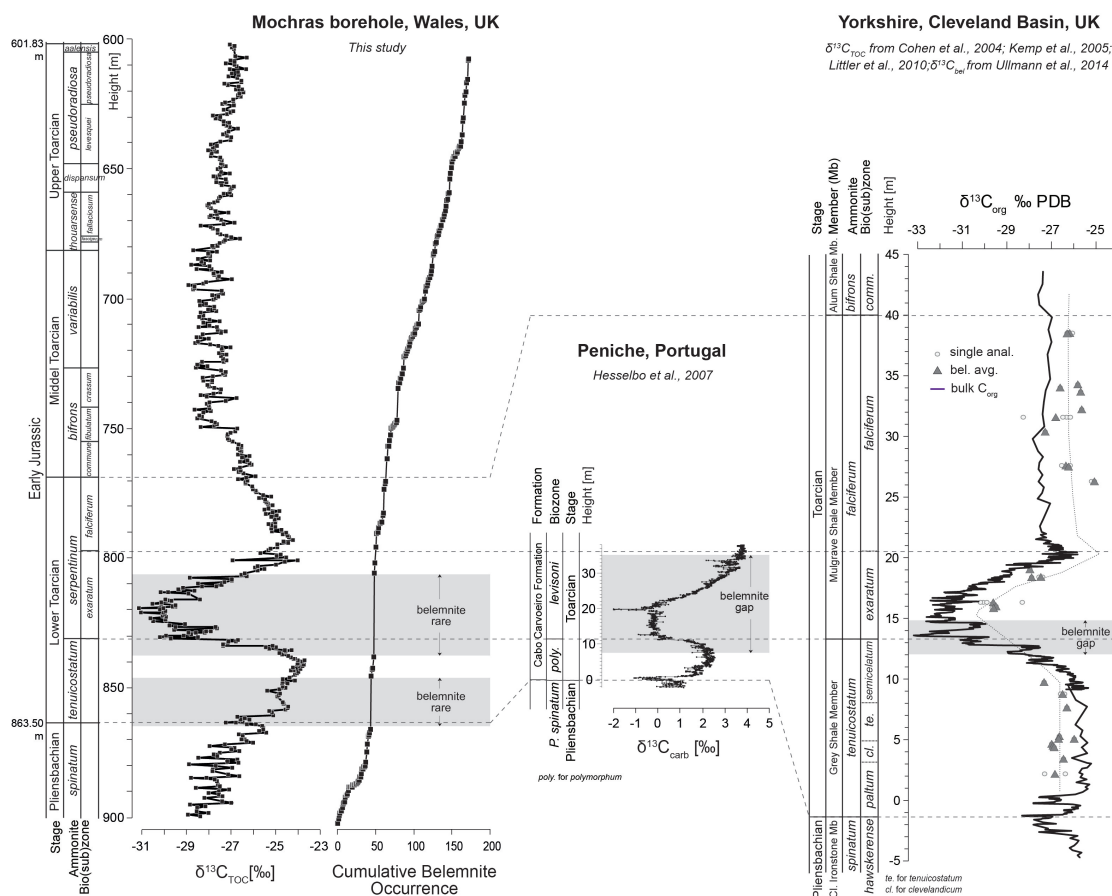


Figure 2.4 Comparison of the stratigraphic intervals where belemnites are rare (not found) based on carbon-isotope and biostratigraphic correlation between the Mochras core, and outcrops at Peniche in Portugal (Hesselbo et al., 2007) and in Yorkshire (Cleveland Basin) in the UK. Yorkshire $\delta^{13}\text{C}_{\text{TOC}}$ data are from Cohen et al. (2004); Kemp et al. (2005) and Littler et al. (2010); $\delta^{13}\text{C}_{\text{bel}}$ data are from Ullmann et al. (2014). The belemnite occurrence data at Mochras are generated by Clemens Ullmann. The belemnite rare/gap intervals are shaded in grey.

More extreme water-column conditions, possibly with increased seawater temperatures and/or elevated CO₂ concentration, in response to Early Toarcian super-

greenhouse conditions, may have made low–mid latitude (shallow) marine basins, including the relatively open-marine Cardigan Bay Basin, temporally unfavourable for micro- and macroscopic fauna to thrive, or possibly not to be preserved.

Calcium-carbonate (CaCO_3) concentrations, as reconstructed from mineral carbon contents measured by Rock Eval (assuming all the mineral carbon was sourced from CaCO_3) and from Ca-element concentrations measured by hand-held XRF (assuming all the Ca was sourced from CaCO_3), and directly by XRD (Appendix A), show very low values in the Early Toarcian of the Mochras core, especially during the most negative part of the T-OAE negative CIE. Values increase again to up to 50% in the middle Toarcian (Figure 2.2). The observed distinct minimum in CaCO_3 concentrations during the T-OAE negative CIE may have resulted from siliciclastic dilution, strongly reduced primary productivity of marine calcifiers, possibly linked to surface ocean acidification due to the increase of $p\text{CO}_2$ in the ocean–atmosphere system (McElwain et al., 2005), or from global ocean acidification and the extreme rise of the carbonate compensation depth (CCD) onto continental shelves and into deeper shelf basins, or alternatively from abundant riverine nutrient supply discouraging the productivity of coccoliths as they were outcompeted by other planktons (Wignall, 2015).

Kaolinite concentrations in the Toarcian of the Mochras core vary between 0 and ~5% and illite (mica) concentrations vary between 18% and 36%. The kaolinite cannot be clearly imaged in BSEI or analysed by Energy-dispersive X-ray spectroscopy (EDS), possibly because of the tiny size of the detrital mineral particles. Authigenic kaolinite generally has a larger particle size, and was not observed. A detrital source for the kaolinite is also evidenced by broad XRD peak-profiles, confirming the small particle size and/or poor crystallinity. XRD analysis indicates that

the illite-rich illite-smectite in the studied samples has a small proportion of swelling layers (<20%), which is characteristic of detrital clay weathered and reworked from mature rocks into fine-grained sediments.

The formation of kaolinite in soils is favoured under warm and humid climatic conditions (Millot, 1970, Thiry, 2000). The composition of detrital clay mineral assemblages may therefore constitute the prevalent climatic condition in the hinterland and detrital kaolinite/illite (K/I) ratios may thus be used as a proxy to reconstruct relative temperature and humidity changes, e.g. as in the Upper Jurassic Kimmeridge Clay (Hesselbo et al., 2009) and across the Palaeocene–Eocene boundary on Antarctica (Robert and Kennett, 1994). Increased Lower Toarcian (relative) kaolinite abundance was likely a regional phenomenon, given that it has been observed in many marine sections in northern and central Europe (e.g. France, Hungary, Poland, Portugal, Switzerland), suggesting a change to warmer and more humid conditions in the hinterland and increased continental weathering (Deconinck and Bernoulli, 1991; Duarte, 1998; Raucsik and Varga, 2008; Brański, 2010; Hermoso and Pellenard, 2014). In the Mochras core, K/I ratios are distinctly elevated during the T-OAE negative CIE, with a return to around zero for the remainder of the Toarcian (Figure 2.2). During the Early Toarcian, elevated atmospheric $p\text{CO}_2$ likely caused climatic and environmental change with accelerated hydrological cycling and increased silicate weathering (Jenkyns et al., 2002; Cohen et al., 2004; McElwain et al., 2005; Dera et al., 2011a; Kemp et al., 2011; Brazier et al., 2015; Percival et al., 2016). The increase in K/I values observed here over the T-OAE negative CIE interval confirms earlier indicators for warmer and more humid climatic conditions as well as elevated siliciclastic input from weathering, which likely impacted oceanographic and

depositional conditions and the expression of the T-OAE in the more open-marine Cardigan Bay Basin.

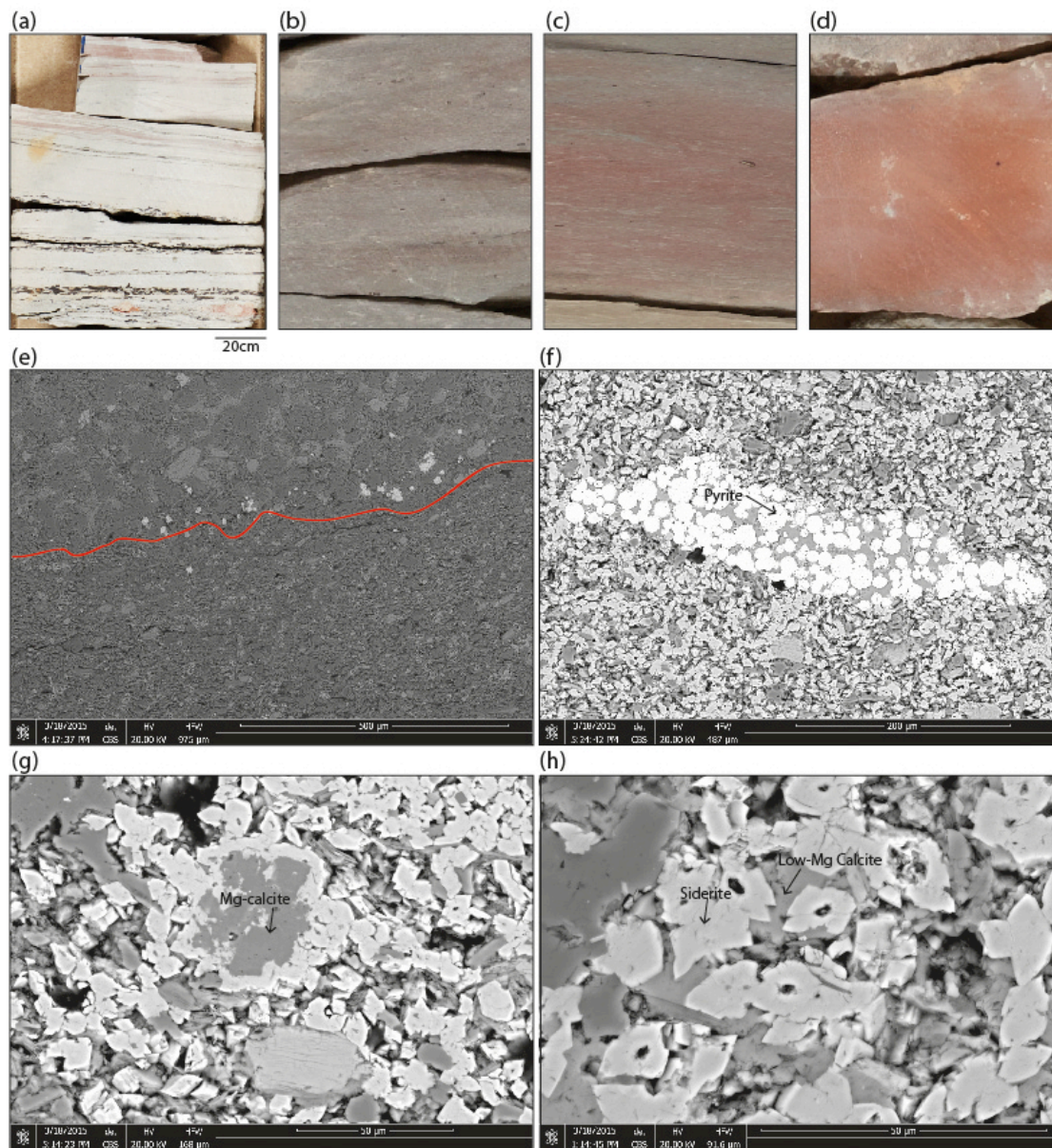


Figure 2.5 Core photos (a, b, c, d) and SEM images (e, f, g, h) of siderite-bearing beds. Image (a) contains cm-scale wave ripples with thin red-coloured layers due to the presence of oxidized siderite in the upper photo and turbidity-current deposits with wood fragments in the lower part (815.59 m); (b), (c) and (d) show varying degrees of red from the oxidation of siderite, which have also been used to illustrate the degrees of colour changes in Figure 2.3; (e) is the BSEM image of (a). The red dashed line marks the distinction between finer grained sediments below and coarser grained sediments above. In the finer grained region, the lightest colour mineral is siderite, whereas in the upper coarser grained region, no siderite is observed; (f) pyrite framboids are observed within the bioclast and siderite is present in the enclosing sediments; (g) Mg-calcite enclosed by siderite; (h) holes are present within the siderite minerals and the surrounding matrix is a low-Mg calcite cement.

2.5.3 Siderite formation in the Cardigan Bay Basin pre- and during the T-OAE

Pinkish- to reddish-coloured nodules commonly appear, with varying intensities and concentrations of iron minerals, from the Pliensbachian–Toarcian boundary up until the top of the T-OAE negative CIE (from 796.8–863.6 mbs; Figure 2.3). Although the original rock colour of the fresh surfaces (newly cut) of these nodules is brown, probable oxidation of iron minerals in the nodules resulted in the red colour on the slabbed surfaces and the outside of the core (Figure 2.5), which has developed over the past 40 years since the core was drilled (and slabbed). X-ray diffraction (XRD) analyses performed on 4 of the red nodular horizons that are rich in ferrous minerals quantitatively show that 19%–43% of the total mineral content in the nodules consists of siderite (Figure 2.3). Hand-held X-ray fluorescence (XRF) analyses on the same red nodules also show Fe elemental concentrations of up to 33% (Figure 2.3).

The siderite, however, not only occurs in distinct nodules, but also in the finer and coarser grained lithologies throughout the interval of the T-OAE negative CIE. Centimetre-scale wave ripples with fine, reddish-coloured, siderite-rich drapes occur for example at (but are not limited to) around 815.59 mbs in the core (Figure 2.5-a). The morphology of the siderite minerals and the diagenetic pathways along which they may have formed, studied here by SEM (Figure 2.5), shows that the oxidized siderite within these fine wave-ripples is concentrated in the finer grained layers, whereas the coarser grained layers contain no siderite minerals (Figure 2.5-e). Siderite formed preferentially in the fine-grained intervals, possibly due to a more reducing pore fluid environment, than existed in the coarser grained sediments. Individual siderite crystal growth in the Early Toarcian sediments of the Cardigan Bay Basin possibly initiated around Mg-calcite crystals (Figure 2.5-g: evidence of Mg-calcite overgrown by

siderite), which acted as a nucleus. The observed holes in the centre of the siderite crystals (Figure 2.5-h) may originally have consisted of these Mg-calcite nuclei that were subsequently dissolved (c.f. Huggett et al., 2000).

Siderite has been previously observed in other marine successions, e.g. in the Carboniferous Coal Measure sediments (Curtis and Spears, 1968) and the upper Pliensbachian Cleveland Ironstone Formation (Sellwood, 1971) of Yorkshire, the Cretaceous Cardium Formation in the Pembina area, US (Machemer and Hutcheon, 1988), the Upper Triassic/Lower Jurassic Sag River and Shublik Formations in the North Slope Basin of Alaska (Mozley and Hoernle, 1990) and the Eocene succession at Whitecliff Bay of the Hampshire Basin, UK (Huggett et al., 2000). Siderite generally forms as an early diagenetic product in a reducing environment with a low sulphate concentration and sufficient iron and CO_3^{2-} availability (Curtis and Spears, 1968; Huggett et al., 2000, and references therein). The Cleveland ironstone, which is mainly composed of siderite and chamosite, is thought to have precipitated during intervals of low sedimentation rates to ensure sufficient iron concentrations in the pore waters, but with a diminished supply of sulphate (Curtis and Spears, 1968; Sellwood, 1971). Siderite cements in the Eocene of Whitecliff Bay have different facies associations and formed in a weakly oxidizing depositional environment, also with low sedimentation rates and during an interval directly preceding stratigraphic breaks or hiatuses (Huggett et al., 2000). Siderite nodule formation in the Mochras core occurs over a ~60 m stratigraphic interval, from the Pliensbachian–Toarcian boundary to the end of the T-OAE negative CIE (Figure 2.3). The sedimentation rate in the Cardigan Bay Basin at the time of deposition was relatively high, and 2–3 times higher than in coeval successions from the Cleveland and Lusitanian Basins (Peniche ~35 m; Yorkshire ~22 m). Considering the broader and finer-scale sedimentary features in the

Mochras core, with periodic, metre-scale, lithological alternations on precessional time-scales observed throughout the core (Ruhl et al., 2016), sedimentation rate changes may, however, have occurred over these lithological couplets and played a role in siderite (nodule) formation.

Although siderite is associated with low sulphate concentrations, pyrite framboids are, however, also observed, especially within bioclasts that are enclosed by siderite-rich sediment or nodules (Figure 2.5-f). Pyrite framboids likely formed first during early diagenesis in response to the oxidation of organic matter in these bioclasts, with the reduction of Fe^{3+} and sulphate. Subsequent depletion of sulphate in the pore waters resulted in the further generation of Fe^{2+} , which, together with the available CO_3^{2-} in the pore waters, may have initiated the formation of siderite. In marine environments, with the abundant supply of sulphate, pyrite is commonly formed either directly in the water column under euxinic (sulphidic) conditions or during early diagenesis as a result of microbial sulphate reduction (Wilkin et al., 1996).

Sulphur elemental concentration in the Lower Toarcian of the Mochras core is broadly relatively elevated, suggesting the presence of significant pyrite (Figure 2.2, as confirmed by XRD analyses, reflected by pyrite peak areas) stratigraphically associated with elevated TOC concentrations over the interval of the T-OAE negative CIE (Figure 2.3). Similarly, elevated sulphur concentrations were also observed for other marine T-OAE successions (e.g. Kemp et al., 2011), suggesting major sulphur drawdown from the global ocean reservoir, and massive pyrite burial in the European epicontinental seaway and on the continental margins and in the open ocean basins of the Tethys, resulting in a major perturbation of the global sulphur cycle registered by an increase in the $\delta^{34}\text{S}$ ratio of seawater (Gill et al., 2011; Newton et al., 2011). The estimated rate and magnitude change in the global sulphur cycle suggests significantly

lower sulphate concentrations globally that could have facilitated early diagenetic siderite generation in sulphate-poor pore-waters of the Cardigan Bay Basin.

Iron (Fe) elemental concentrations in the Toarcian of the Mochras core, measured by hand-held XRF and inductively-coupled mass-spectrometry (ICP-MS), show elevated concentrations of up to 6% in the non-siderite-bearing beds of the T-OAE negative CIE interval, significantly higher than the average values of ~2% in the non-siderite-bearing beds underlying and overlying the T-OAE negative CIE interval (Figures 2.2 and 2.3). Fe-concentrations even peak at ~33% in the observed siderite nodules (Figure 2.3). Elevated average Fe concentrations during the T-OAE were also observed in the coeval Peniche section of the Lusitanian Basin (Hermoso et al., 2009b). In the Mochras core, Fe in non-siderite-bearing beds largely exists in Fe-rich chlorite minerals (chamosite), likely reflecting enhanced detrital iron-rich clay mineral supply from the hinterland, suggesting either intensified continental weathering, possibly under higher atmospheric CO₂ concentrations and/or enhanced hydrological cycling, or alternatively, a shift in provenance. The abundant detrital Fe-rich chlorite, observed under SEM, was likely sourced from nearby Lower Palaeozoic metamorphic rocks of the Welsh massif.

The degree of red colouring, siderite mineral and Fe and S elemental concentrations is intensified at the Pliensbachian–Toarcian boundary and during the T-OAE negative CIE, directly matching changes in the osmium-isotope composition of the seawater, as recorded in the Mochras core (Figure 2.3; Percival et al., 2016). Changes in ¹⁸⁷Os/¹⁸⁸Os ratios of global seawater are thought to reflect changes in global weathering rates, showing enhanced continental weathering at the Pliensbachian–Toarcian boundary and during the Toarcian OAE negative CIE (Percival et al., 2016). Globally enhanced weathering rates and the likely increased

supply of Fe to the global ocean, together with lower global ocean sulphate concentrations and favourable redox conditions and sedimentation rates, may have been instrumental for the formation of siderite nodules during the Early Toarcian in the Cardigan Bay Basin.

2.5.4 Coarse-grained sediment supply and continental weathering during the T-OAE

The Lower Toarcian in the Mochras core is characterized by pale-coloured, faintly laminated or rippled quartzose siltstones, some of which include cm-scale woody fragments in discrete layers (Figure 2.6 A-1, A-2, B-1, B-2). These 1–10 cm thick siltstones commonly appear in two ~3 m stratigraphic intervals in the lower half of the *faciferum* zone, at around 815 and 823 mbs (Figure 2.3). These mass-transport deposits may have formed from turbidity currents or debris flows from the basin-margins and indicate relatively vigorous transportation during the time of deposition.

Elevated elemental concentrations and elemental ratios, measured by HH-XRF and ICP-MS, suggest changes in detrital supply and grain size. Elemental silicon (Si) in sedimentary rocks is commonly sourced either from coarser-grain quartz or from finer-grain aluminosilicates, whereas aluminium (Al) is generally sourced from aluminosilicates (Calvert and Pedersen, 2007). The Al normalized Si concentration in the studied sediments therefore likely reflects the ratio between quartz and aluminosilicate phases in the sediments. Titanium (Ti) also resides in aluminosilicates as a substituent for other major elements, but also in discrete Ti-oxide and silicate mineral phases. Zirconium (Zr) occurs almost exclusively in sediments in zircon minerals (ZrSiO_4), especially in the fine sand and silt fractions. Rubidium (Rb) substitutes readily for potassium (K) in aluminosilicate minerals. Ti/Al and Zr/Rb

ratios may therefore represent a proxy for grain-size (Calvert and Pedersen, 2007). The Si/Al, Ti/Al, Rb/Zr coevally decreased from the onset of the T-OAE negative CIE to the middle of the *exaratum* ammonite subzone, which is directly followed by a strong increase and peak at around 823 mbs, at the most extreme interval of the negative CIE, suggesting an increasing supply of coarser grained minerals as a primary control on sedimentation at this time (Figure 2.2). During the subsequent recovery of the $\delta^{13}\text{C}_{\text{TOC}}$ signal to more positive values, the observed elemental ratios also gradually increase, suggesting a second interval of coarser grained sediment (Figure 2.2). This interval is subsequently followed by a shift to lower elemental ratios following the negative CIE and throughout the rest of the Toarcian, with only generally more positive values in Si/Al during the *bifrons* zone, where Ti/Al ratios are also more scattered (Figure 2.2).

XRD analysis on the Toarcian samples from the Mochras core showed the presence of quartz, calcite, chamosite, illite & mica, illite-rich illite-smectite, a minor (in places near absent) kaolinite, K-feldspar, plagioclase, Fe dolomite, siderite and pyrite (Appendix A). Detrital silt-sized quartz, calcite, chamosite and mica were also observed by SEM-EDS analyses (Figure 2.6-C). The silt-sized detrital minerals were possibly sourced from Palaeozoic rocks of the nearby Welsh massif, and they likely account for a large part of the minerals in the sediments of the Cardigan Bay Basin. Deposition of these silt-sized detrital minerals, together with the common presence of fragmental wood and plant debris, strongly suggests a depositional environment not far from land.

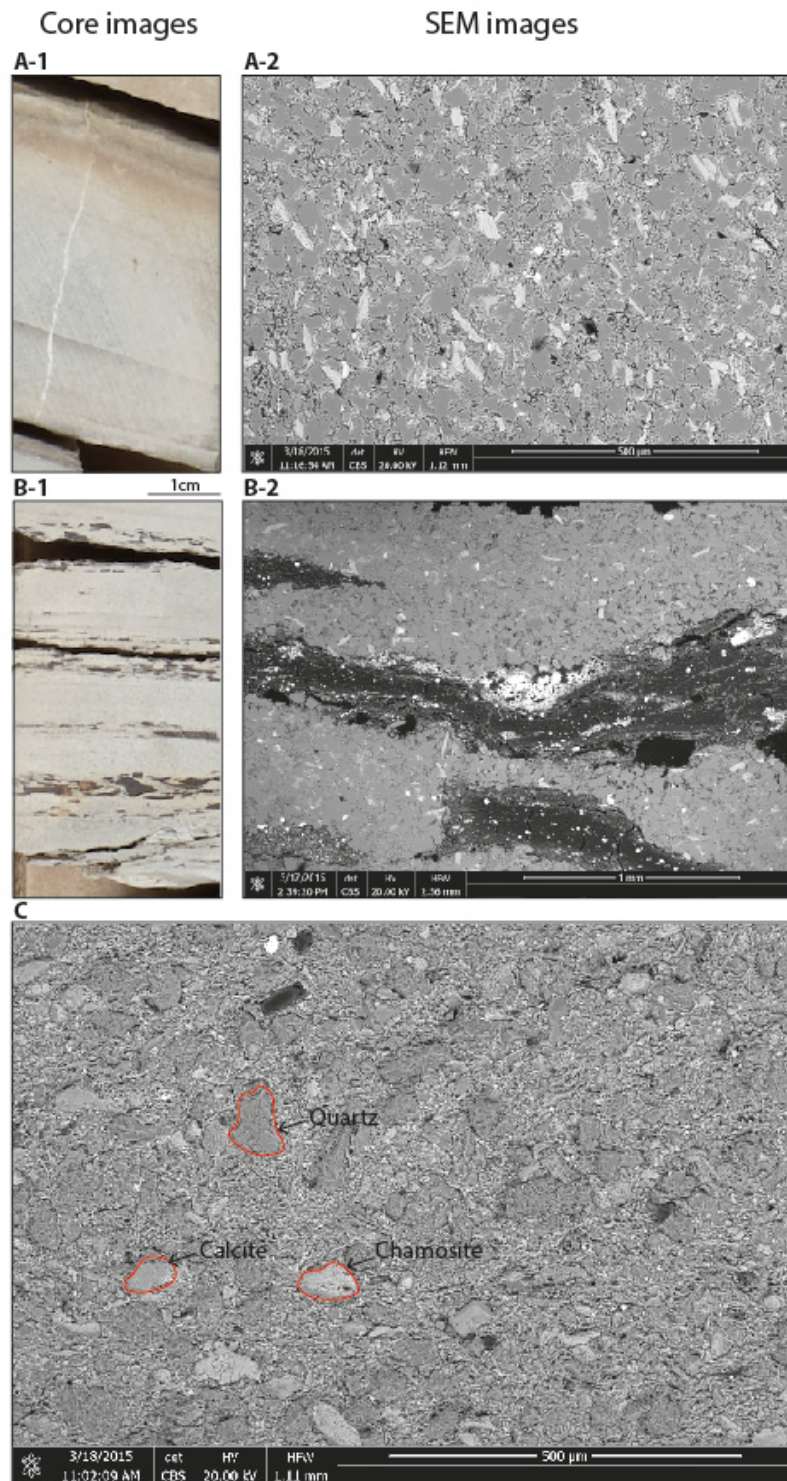


Figure 2.6 Core photos and BSEM images of turbidity-current and debris-flow deposits. (A-1) and (A-2) are core images of a turbidity-current deposit (the upper brown interval) with accompanying BSEM image showing that this layer is dominantly composed of fine silt-sized quartz; (B-1) and (B-2) are the core image of another turbidite, which consists of a large amount of macrofossil wood fragments, and its SEM image, which contains wood (black colour) surrounded by fine silt-sized detrital quartz; (C) Silt-sized detrital quartz, calcite and Fe-rich chlorite from a normal mudstone horizon (842.04m);

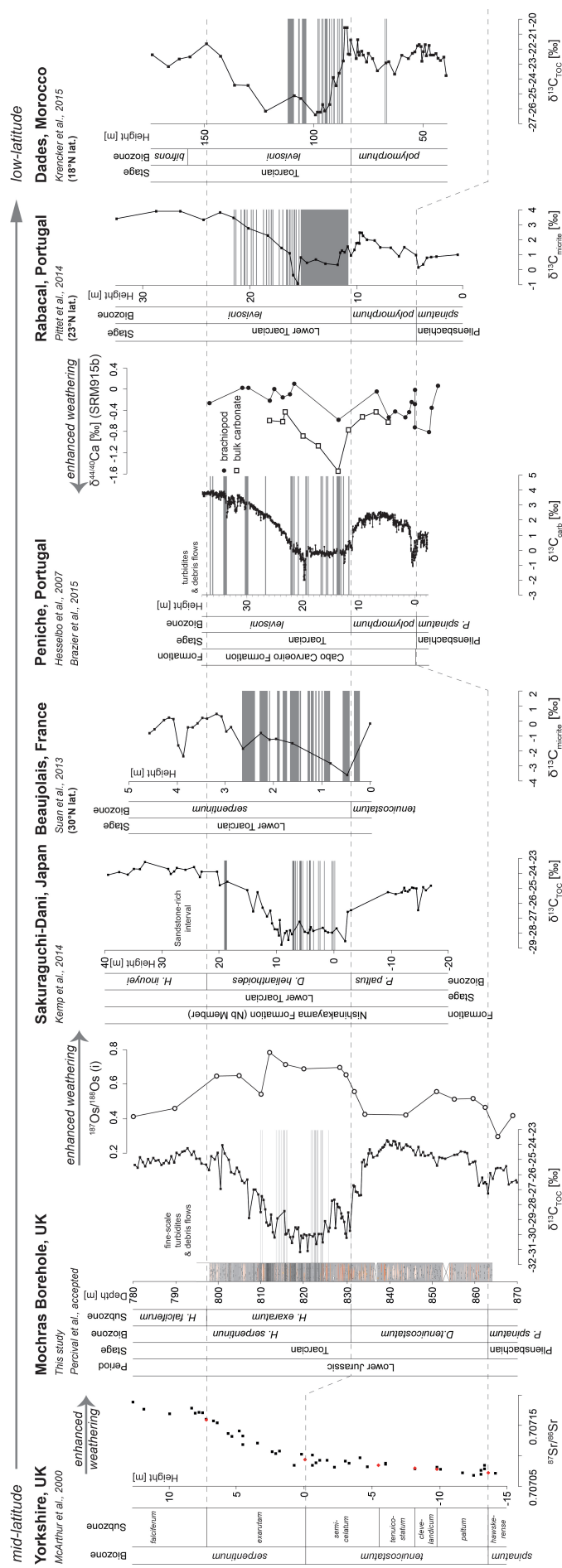


Figure 2.7 Comparison of the stratigraphic intervals where turbidites/debris flows/sandstones/storm deposits (stratigraphic horizons marked in grey) are present in a series of successions extending from mid-latitudes on the left to low-latitudes on the right. Correlations among the different sections are based on ammonite biostratigraphy and carbon-isotope stratigraphy. $^{187}\text{Os}/^{188}\text{Os}$ ratios from Mochras are in black circles (Percival et al., 2016). $\delta^{44/40}\text{Ca}$ measured on brachiopod and bulk carbonates are illustrated in filled black circles and black squares as shown in the key.

The occurrence of coarser grained deposits during the most negative interval of the T-OAE negative CIE in the Mochras core directly coincides with the deposition of coarser grained lithologies in other shallower and deeper marine basins, from different palaeo-latitudes, as recorded, for example, in the Sakuraguchi-Dani section (Japan), Beaujolais (France), the Lusitanian Basin (Portugal), and the High Atlas Basin (Morocco) (Figures 2.1 and 2.7), which possibly resulted from turbidity currents/debris flows in response to increased run-off or storm-driven currents (Hesselbo et al., 2007; Suan et al., 2013; Kemp et al., 2014; Pittet et al., 2014; Brazier et al., 2015; Krencker et al., 2015). Similar observations were also made in the coastal and marginal marine basinal settings of southwest Bornholm (Denmark) and the Polish basin (Figure 2.1; McElwain et al., 2005; Hesselbo and Pieńkowski, 2011). The mineral grain-size in the observed coarser-grained (mass-transport) deposits in the Lower Toarcian of the Mochras core is, however, much finer and the individual beds are much thinner than those in the Lower Toarcian of the Peniche (Portugal).

Globally enhanced continental weathering during the T-OAE has been suggested by different geochemical proxies. Strontium-isotope ($^{87}\text{Sr}/^{86}\text{Sr}$) values from Early Toarcian seawater, as recorded in belemnite calcite, show an Early Jurassic low at ~ 0.7071 (normalized to the NBS987 standard), at around the Pliensbachian–Toarcian transition (Jones et al., 1994; McArthur et al., 2000). Values remained low during the Early Toarcian *tenuicostatum* zone, suggesting a balance between the supply of radiogenic strontium from the global weathering of continental crustal materials to the global oceans, and the supply of unradiogenic strontium from the weathering of island arcs and hydrothermal circulation through mid-ocean ridges (Palmer and Edmond, 1989, 1992; Allègre et al., 2010). The subsequent rapid increase in $^{87}\text{Sr}/^{86}\text{Sr}$ to values of ~ 0.70725 during the lower *falciferum* (*serpentinum*) zone

(*exaratum* subzone), suggests a change in this balance, which, given the rate of change, likely represents an enhanced radiogenic strontium flux to the global oceans, possibly by enhanced Early Toarcian hydrological cycling and increased weathering of continental crust. The Early Toarcian seawater $^{187}\text{Os}/^{188}\text{Os}$ record, derived from the Mochras core, initially increased at the Pliensbachian–Toarcian boundary, followed by a stronger and more prolonged shift during the T-OAE negative CIE (Percival et al., 2016), also reflecting the supply of more radiogenic Os-isotopes to the global oceans due to elevated continental weathering. The observed T-OAE negative excursion in seawater $\delta^{44/40}\text{Ca}$, recorded at Peniche, Portugal (Brazier et al., 2015) is interpreted to reflect a drop in the carbonate accumulation rate due to ocean acidification, followed by a climatically controlled increase in the rate of continental weathering.

The stratigraphic correspondence between changes in Early Toarcian seawater $^{87}\text{Sr}/^{86}\text{Sr}$, $^{187}\text{Os}/^{188}\text{Os}$, $\delta^{44/40}\text{Ca}$, increase in relative abundance of kaolinite sections, and the sudden occurrence of coarser-grained turbiditic/ mass-transport deposits in geographically widespread, shallow- and deeper marine basins suggests enhanced hydrological cycling. This change in hydrology was likely a response to greenhouse-gas-induced climatic warming during the T-OAE that accelerated continental weathering and caused increased supply of sediment to continental-margin and intra-marginal marine basins. The data also suggest that the highest rate of hydrological cycling occurred coevally, and at different palaeo-latitudes, when the carbon-isotope composition of the global ocean-atmosphere system was at its most negative, when the rate of ^{12}C -enriched CO_2/CH_4 release was higher than the rate of ^{12}C -enriched organic-carbon burial.

2.6 Conclusions

A new high-resolution chemostratigraphic reference record for the complete Toarcian Stage, from the Mochras (Llanbedr) core (Wales, UK), shows a major ~7‰ negative excursion in $\delta^{13}\text{C}_{\text{TOC}}$, synchronous with the Toarcian Oceanic Anoxic Event (T-OAE) and superimposed on a broader Lower Toarcian positive excursion.

The T-OAE in the lower *falciferum* zone (*exaratum* subzone), in the hemipelagic Cardigan Bay Basin, in contrast to many other Lower Toarcian epicontinental European marine successions, was marked by a lack of prominent black-shale deposition. Total Organic Carbon (TOC) is, however, enriched during the T-OAE, albeit only up to ~2.5 %. Enhanced productivity, and the elevated supply of marine algal material as a component of marine sedimentary organic matter during the T-OAE is illustrated by increased hydrogen index (HI) values of up to ~300 mg HC/g TOC and the increased C_{30} sterane indices, possibly in response to relatively elevated nutrient supply. The biomarker isorenieratane, sourced from a pigment of green sulphur bacteria, has been detected in two, stratigraphically constrained, organic-rich horizons during the most negative interval of the T-OAE negative CIE, suggesting episodic photic-zone euxinia.

Belemnites regularly occur throughout the Pliensbachian and Toarcian deposits of the Mochras core, but their appearance is severely diminished in the Lower Toarcian, from the Pliensbachian–Toarcian boundary to the top level of the T-OAE negative CIE, coevally with a lack of belemnite occurrences in other NW European successions, possibly due to regionally extensive unfavourable water-column conditions.

Nodular siderite beds also occur from the Pliensbachian–Toarcian boundary up to the level of the end-point of the T-OAE negative CIE. Diagenetic siderite minerals

in the relatively open-marine Cardigan Bay Basin possibly formed in response to elevated iron (Fe) supply from continental weathering and relatively low oceanic sulphate concentrations due to abundant pyrite fixation in the globally deposited organic-rich sediments that are the hallmark of the T-OAE.

Coarser grained, cm-thick silt to fine-sand mass-transport deposits and abundant macroscopic terrestrial wood particles, occur in two ~3 m stratigraphic intervals during the most negative interval of the T-OAE negative CIE, in the *exaratum* subzone, possibly in response to enhanced hydrological cycling and intensified continental weathering under enhanced Early Toarcian super-greenhouse conditions. Mass-transport deposits in the hemi-pelagic Cardigan Bay Basin occur coevally with similar deposits in geographically widespread Early Toarcian shallow to deeper marine basins at mid–low palaeo-latitudes.

The coeval changes of the Early Toarcian seawater $^{87}\text{Sr}/^{86}\text{Sr}$, $^{187}\text{Os}/^{188}\text{Os}$, $\delta^{44/40}\text{Ca}$, increase in relative abundance of kaolinite sections, and the broadly synchronous occurrence of coarser-grained turbiditic/ mass-transport deposits in geographically widespread, shallow- and deeper marine basins suggests accelerated continental weathering likely resulted from enhanced hydrological cycling in response to greenhouse-gas-induced climatic warming during the T-OAE.

Chapter 3

Lower Jurassic Toarcian magnetostratigraphy (Mochras Borehole, Cardigan Bay Basin, UK), and its implications for linking Karoo volcanism with the T-OAE

This chapter is modified from **Xu et al.**, Lower Jurassic Toarcian magnetostratigraphy (Mochras Borehole, Cardigan Bay Basin, UK), and its implications for linking Karoo volcanism with the T-OAE. *Journal of the Geological Society, London, in preparation*.
Conall MacNiocaill helped with the palaeomag data analysis.

3.1 Introduction

The Toarcian Stage, the final stage of the Early Jurassic, has a previously estimated duration of 8.3–8.6 Myrs (2014 Geological Time Scale; Boulila et al., 2014), with the Pliensbachian–Toarcian boundary dated at ~182.7 Ma (Duncan et al., 1997). The Early Toarcian was marked by the widespread development of anoxic/euxinic conditions that led to substantial organic-carbon burial, an event termed the Early Toarcian Oceanic Anoxic Event (T-OAE; Jenkyns, 1985, 1988). The T-OAE is marked by major changes in global geochemical cycles, with an apparently rapid ~7‰ negative shift in marine and terrestrial organic-carbon isotope records and a smaller (3–6‰) negative excursion in carbonate and compound-specific archives (Hesselbo et al., 2000, 2007; Sælen et al., 2000; Schouten et al., 2000; Jenkyns et al., 2002; Kemp 2005; Hermoso et al., 2009; Al-Suwaidi et al., 2010, 2016; French et al., 2014; Suan et al., 2015). The observed early Toarcian perturbation to the exogenic carbon cycle has been linked to volcanic activity of the Karoo-Ferrar large igneous province (LIP) and associated release of volcanogenic CO₂, thermogenic methane (CH₄) from sill intrusion into Gondwanan coals and shales, and biogenic methane from dissociation of sub-seafloor clathrates (Duncan et al., 1997; Hesselbo et al., 2000; Kemp et al., 2005; McElwain et al., 2005; Svensen et al., 2007; Percival et al., 2015). The Pliensbachian–Toarcian boundary was also marked by global carbon-cycle change, with a ~2–3‰ negative carbon-isotope excursion in marine carbonate, organic matter and fossil wood (Hesselbo et al., 2007; Littler et al., 2010; Bodin et al., 2016; Percival et al., 2016).

Stratigraphic studies on the Toarcian have primarily focused on the lower part of the stage, specifically on the T-OAE interval, utilizing bio- and chemostratigraphy. Magnetostratigraphic study of the Toarcian Stage has been confined to only a few localities, including southern Switzerland (Breggia Gorge; Horner and Heller, 1983),

Thouars and Airvault (France; Galbrun et al., 1988), the Iznalloz section (Spain; Galbrun et al. 1990), the Neuquén Basin (Argentina; Llanos and Riccardi, 2000); and the Iberian Range of Spain (Osete et al., 2007; Comas-Rengifo et al., 2010). Additionally, a long-duration magnetostratigraphic record, spanning the Pliensbachian to base-Cretaceous interval was obtained from the Northern Apennines in Italy (Satolli et al., 2015), but (ammonite) biostratigraphy is, unfortunately, relatively poorly constrained in this sequence. Palaeomagnetic data from the lower and middle Toarcian in the Iberian Range were subsequently synthesized (Osete et al., 2007; Comas-Rengifo et al., 2010), and adopted for the Geological Time Scale 2012 (GTS2012). Not many of the existing magnetostratigraphic records cover the upper Toarcian, and sampling resolution in this interval is often relatively low, affected by hiatuses, or the (ammonite) biostratigraphy is not well defined. The utilization of magnetostratigraphy for stratigraphic correlation in the Toarcian has also been relatively restricted because no published record integrates magnetostratigraphy with both (ammonite) biostratigraphy and (carbon-isotope) chemostratigraphy for the complete Toarcian Stage. The arguably best example of an integrated Toarcian stratigraphy is a high-resolution magnetostratigraphy combined with carbon-, oxygen- and strontium-isotope data in the biostratigraphically well-constrained Almonacid De La Cuba Section (Spain; Comas-Rengifo et al., 2010; Rocha et al., 2016), but this study was confined to only the Pliensbachian–Toarcian boundary. Integrated stratigraphy for the T-OAE stratigraphic interval, combining the above-mentioned proxies, has not yet been presented.

The Llanbedr (Mochras Farm) core, hereafter referred to as Mochras, drilled in the Cardigan Bay Basin, West Wales (UK), presents one of the biostratigraphically most complete and expanded marine successions known of Early Jurassic age

(Woodland, 1971; Dobson and Whittington, 1987; Hesselbo et al., 2013; Copestake and Johnson, 2014; Ruhl et al., 2016). The ~260 m thick Toarcian succession in this core is much thicker than other coeval European core and outcrop sequences, and generally characterized by periodic alternations between limestone and mudstone (Hesselbo et al., 2013; Xu et al., in preparation in Chapter 2). The Toarcian interval of the Mochras core is biostratigraphically complete, with the recognition of 8 ammonite zones and 9 ammonite subzones (Page, 2003; 15 subzones following the classification of Ivimey-Cook, 1971). Furthermore, detailed foraminiferal biostratigraphy allows for the recognition of 5 zones (Copestake and Johnson, 2014). Carbon-isotope analyses of bulk organic matter shows an overall positive excursion of 3–4‰ in $\delta^{13}\text{C}_{\text{TOC}}$, relative to Upper Pliensbachian and Upper Toarcian values of -27 to -28‰, which spans the upper *spinatum* (Upper Pliensbachian) to middle *bifrons* (Toarcian) ammonite zones (Jenkyns et al., 2001; Xu et al., in preparation in Chapter 2). This Early Toarcian long-term positive trend in $\delta^{13}\text{C}_{\text{TOC}}$, presumably linked to globally significant burial of isotopically depleted organic carbon, is interrupted by the major negative carbon-isotope excursion (CIE) in marine and terrestrial organic matter and marine calcite that typically marks the main phase of the T-OAE. The negative CIE in the Mochras core is recorded as a distinct >7‰ and ~6.5‰ negative shift in bulk $\delta^{13}\text{C}_{\text{TOC}}$ and $\delta^{13}\text{C}_{\text{CARB}}$, respectively (Jenkyns and Clayton, 1997; Jenkyns, 2003; van de Schootbrugge et al., 2005; Xu et al., in preparation in Chapter 2). An initial pilot study on the Mochras core proved the feasibility of a magnetic-polarity study on this expanded and bio- and chemostratigraphically well-constrained sedimentary archive (Hesselbo et al., 2013). Here, we present the first high-resolution magnetostratigraphic record for the complete Toarcian Stage and use this to construct an integrated Toarcian stratigraphic framework. The integrated stratigraphic data presented here provide a reference

framework for correlation between Toarcian marine and continental sedimentary basins worldwide. This study also allows accurate and precise correlation between the T-OAE and associated climatic change and coeval Karoo-volcanism.

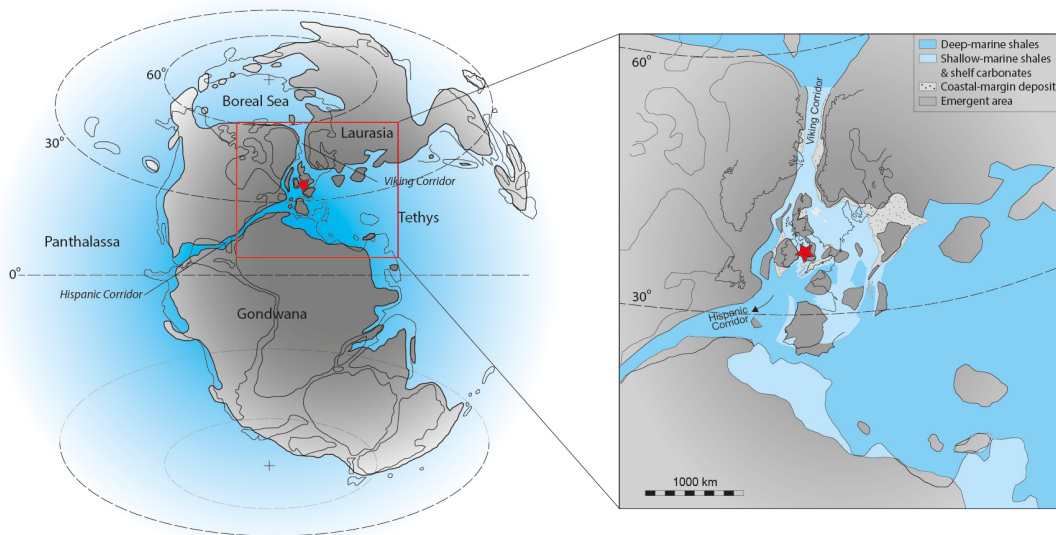


Figure 3.1 Geographical maps. (A) Early Jurassic global palaeogeography, modified after Dera et al. (2011b) and Korte et al. (2015). (B) Zoom-in map of the area within the red square in map A, showing the palaeogeographic position of the Llanbedr (Mochras Farm) Borehole (red star).

3.2 Geological setting

The sediments recorded in the Toarcian (~183 Ma) part of the Llanbedr (Mochras Farm) Borehole were deposited at a palaeo-latitude of ~42°N, at the southern end of the transcontinental seaway, at the northwestern end of the Tethys Ocean (Figure 3.1; Torsvik et al., 2012; Hesselbo et al., 2013). The onshore borehole was drilled by the British Geological Survey (BGS) from 1967–1969, on the coast of Cardigan Bay, in western Wales (Woodland 1971; Dobson and Whittington, 1987; Hesselbo et al., 2013; Copestake and Johnson, 2014). The Lower Jurassic sequence in this onshore borehole has a remarkable thickness of about 1300 m, suggesting a high sedimentation rate throughout this time interval. The relatively homogenous lithology

is dominated by alternating muddy limestone, marl and mudstone.

3.3 Materials and methods

Samples for magnetic-polarity analysis were selected at 2–5 m resolution, spanning the complete Toarcian Stage, from 601.83–863.5 mbs (metres below surface) in the Mochras Borehole. In total, 122 cubes ($2.3 \times 2.3 \times 2.3 \text{ cm}^3$) from the core sections, predominantly of marl or mudstone, were prepared.

Measurements of the natural remanent magnetisation (NRM) were made using a 3-axis 2G cryogenic magnetometer, housed in a magnetically shielded room at the University of Oxford palaeomagnetic laboratory. Specimens were stepwise demagnetised using progressive alternating field (AF) techniques through at least 12 steps, until they became unstable, or up to a maximum of 100 mT. Demagnetization results were visually inspected in orthogonal and stereographic projections; characteristic remanence components were identified using least-squares algorithms (e.g. Kirschvink, 1980). Components were considered stable where they were defined by at least 3 consecutive points on orthogonal projections and had a maximum angular deviation not exceeding 20° .

3.4 Results

Natural remanent magnetization (NRM) intensities of the measured samples ranged from 0.06 to 1.6 mA/m, with a mean of 0.26 mA/m. During progressive AF demagnetization 3 different classes of behaviour were identified: (A) samples for which demagnetization trajectories tended towards the origin, and lines could be fitted to the demagnetization trajectories (66 samples in total); (B) samples for which the polarity could be determined, but with very poor line-fits and Maximum Angular

Deviation $>30^\circ$ (28 samples in total; NRM intensities were generally very low); (C) samples that demonstrated unstable behavior during demagnetization, or where the NRM intensities were too low to provide meaningful demagnetization data (28 samples in total). Examples of Class A and B behaviour are given in Figure 3.2. The magnetostratigraphy constructed here is primarily based on data from ‘Class A’ samples, but the polarities of ‘Class B’ samples have been used as supporting evidence. Because the original Mochras core is azimuthally unoriented, only ‘inclination-only’ statistics (following the method of McFadden & Reid 1982) have been conducted on the dataset presented here. Of the 66 samples with ‘Class A’ behaviour, 37 yield downward pointing inclinations, which are interpreted as normal polarity given the northern hemisphere location of the sampling site in the Toarcian. These samples yield a mean inclination of $+37.0^\circ$ ($\alpha_{95} = 7.4^\circ$; $k = 8.48$). The remaining 29 samples yield negative inclinations, which are interpreted as reversed polarity, with a mean inclination of -37.7° ($\alpha_{95} = 5.3^\circ$; $k = 18.17$). Normal- and reverse-polarity data thus yield inclinations that are almost identical, and constitute a positive ‘inclination-only’ reversal test. When both polarities are combined we obtain an overall mean inclination of $+37.3^\circ$ ($\alpha_{95} = 5.1^\circ$; $k = 11.16$), suggesting a palaeo-latitude of 21°N . The inclination obtained here is considerably shallower than the expected inclination of $\sim+61^\circ$ for the Mochras locality at $\sim 183\text{Ma}$ (based on a reference palaeo-latitude of 42°N ; Torsvik et al. (2012)). The location of the Mochras Borehole has likely not been at palaeo-latitudes south of 42°N since the Toarcian, so it is unlikely that a multi-polarity remagnetization post-dating deposition of the Mochras sedimentary sequence has over-printed the original signal. Instead, it may be more likely that the original remanence has undergone inclination-shallowing due to post-depositional compaction of the mudstones. This is a well-documented phenomenon in

sedimentary rocks (Kodama, 2012 and references therein). Correction for this inclination shallowing, with a flattening factor (f') of 0.6 (which is often taken as a standard value; Kodama, 2012) corrects the apparent palaeo-latitude from 21°N to a 'true' palaeo-latitude of 33°N . An alternative f' -value of 0.5 corrects the apparent palaeo-latitude from 21°N to 38°N , which is within error of the previously reconstructed palaeo-latitude for this side. Incidentally, the fact that inclination shallowing is observed also provides a constraint on the age of magnetization as it was recorded by the sediments before compaction. Hence, the observed inclination shallowing, together with a positive inclination-only reversal test suggests that the sedimentary-rocks of the Mochras core record a primary Early Jurassic remanence.

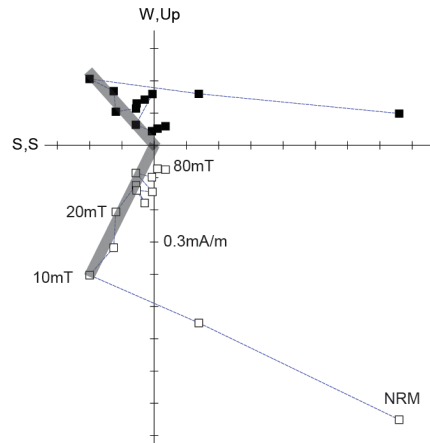
3.5 Discussion

3.5.1 Toarcian Magnetic Polarity Record in the Mochras core

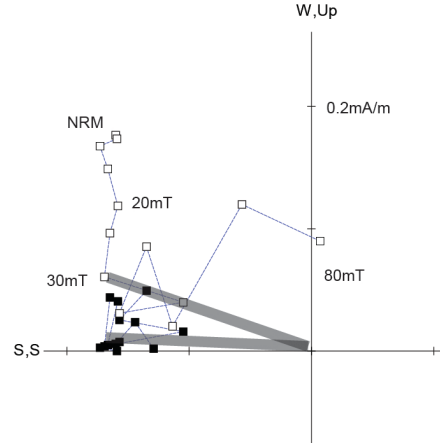
A magnetic-polarity column for the complete Toarcian Stage (except the *aalensis* ammonite zone, which is thin and likely truncated at the top in the Mochras core) has been constructed primarily based on data from 'Class A' samples, with the polarities obtained from 'Class B' samples mainly as supporting evidence (Figure 3.3). Identified magnetic polarity in more than one consecutive sample is marked by a full-width bar, whereas polarity identified by only one sample is marked by a half-width bar (e.g. Figure 3.3).

Figure 3.2 Orthogonal vector diagrams showing AF demagnetization of 8 typical samples (a–h) in stratigraphic order. (a, d, e, g, h) normal polarity (N); (b, c, f) reversed polarity (R). Closed and open symbols: projections onto horizontal and vertical planes, respectively. The grey bars represent approximate fits.

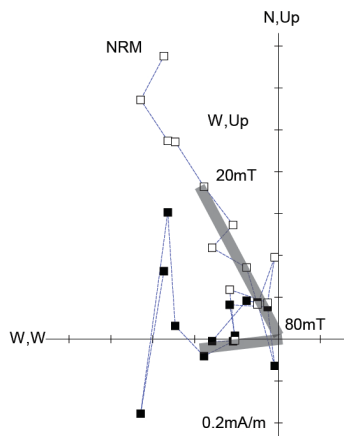
(a) 611.43 m (N)



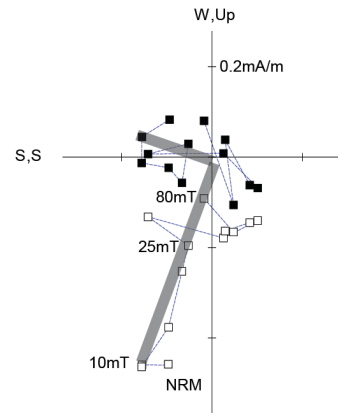
(b) 644.82 m (R)



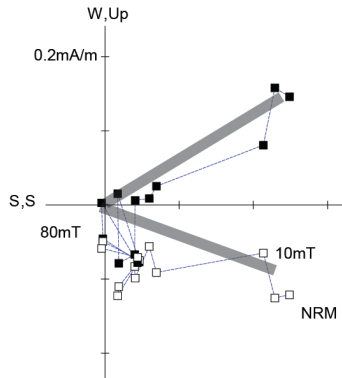
(c) 673.10 m (R)



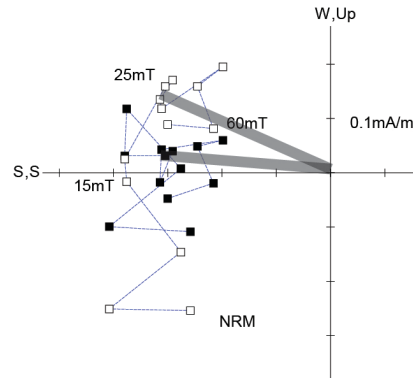
(d) 687.32 m (N)



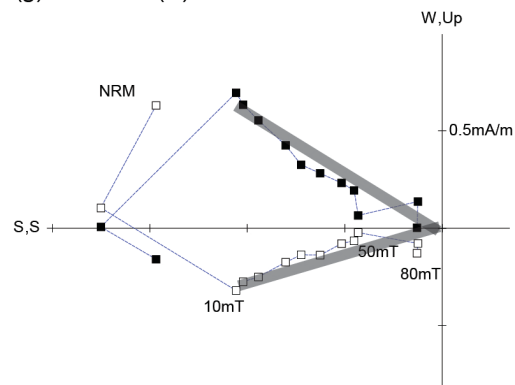
(e) 762.64 m (N)



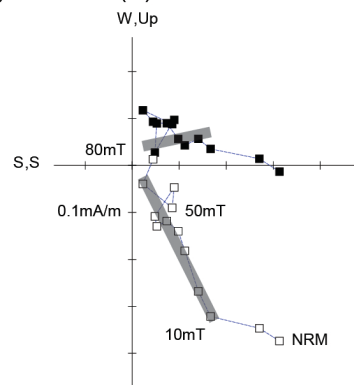
(f) 797.36 m (R)



(g) 807.21 m (N)



(h) 863.19 m (N)



Mochras Borehole, Wales, UK

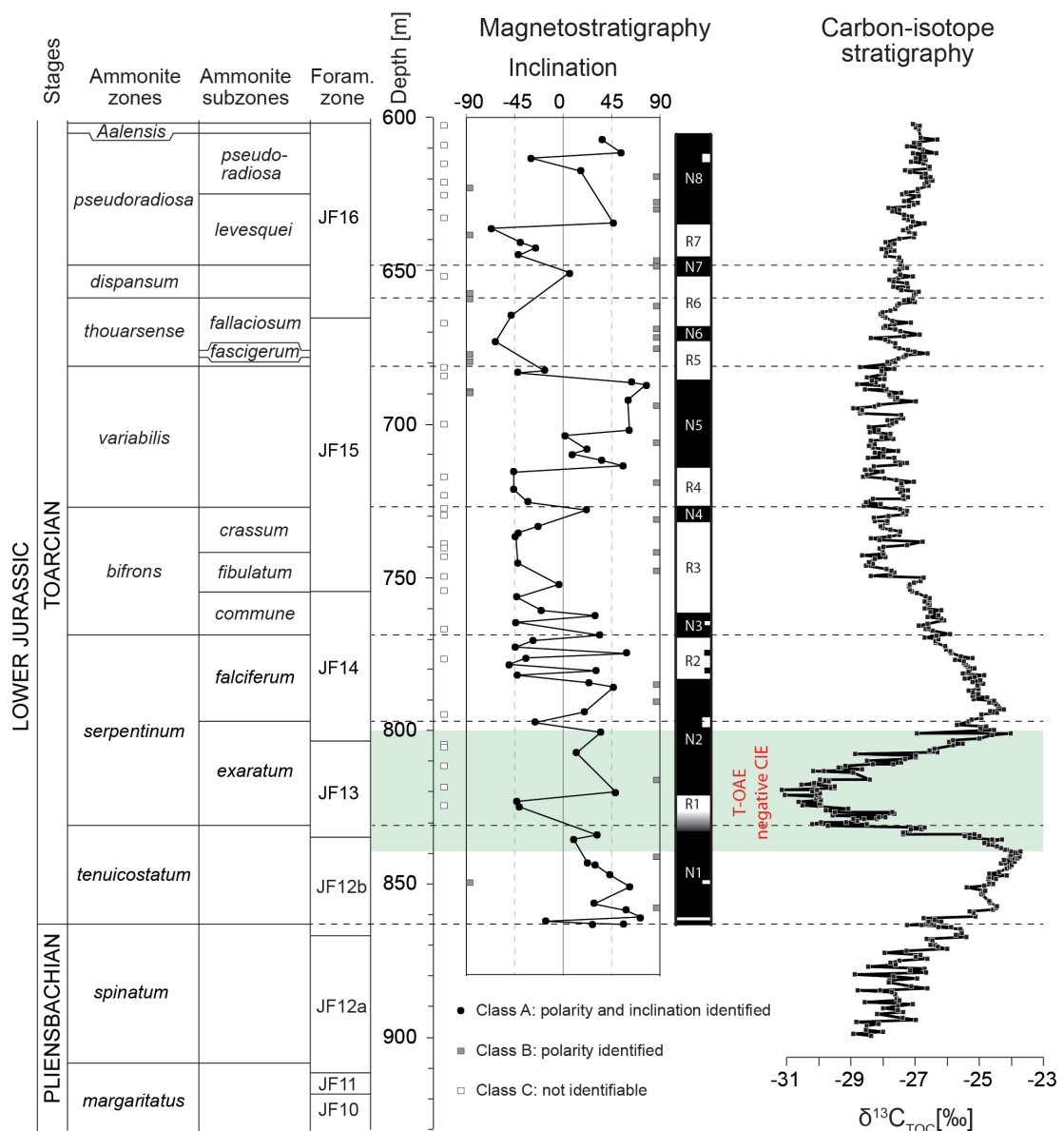


Figure 3.3 Synthesis of the (ammonite and foraminifera) bio-, magneto- and carbon-isotope stratigraphy of the complete Toarcian succession in the Mochras core. Inclination values and the magnetostratigraphic column (normal polarity in black and reversed polarity in white) are plotted. The full round black circles represent samples with identified inclinations (Class A samples) that form the basis for the construction of the magnetic-polarity record. The dark grey squares represent (Class B) samples, for which only polarity was identified (points located next to -90° indicate reversed polarity and points located next to 90° indicate normal polarity). Grey shaded zones in the reconstructed magnetic record reflect stratigraphic intervals with uncertain polarity due to a lack of sample data.

Nine normal- and eight reversed-polarity magnetozones were identified and numbered N0–N8 and R0–R7, respectively (Figure 3.3). N1, N2, N5 and N8 represent four long magnetozones of normal polarity dominating the *tenuicostatum*, *serpentinum*, *variabilis* and *pseudoradosa* ammonite zones, respectively (Figure 3.3). R3 is the stratigraphically thickest magnetozones of reversed polarity, and covers most of the *bifrons* zone (Figure 3.3). N0 and R0, at the base of the studied succession, cover the thinnest interval relative to the rest of the Toarcian in the Mochras core. The interval of normal polarity (N0) extends down into the Pliensbachian (Figure 3.3). R0, the stratigraphically lowest observed reversal in the Toarcian of the Mochras core is the only magnetozones that is identified based on only one sample.

Chemostratigraphic correlation of the Pliensbachian–Toarcian boundary between the Mochras succession and the sedimentary archive of the Lusitanian Basin (Peniche, Portugal), and subsequent biostratigraphic correlation to the magnetostratigraphic record of the Almonacid De La Cuba Section (Spain), shows that this stratigraphically thin reversed-polarity interval is also observed in the Spanish succession (Figure 3.4; Hesselbo et al., 2007; Comas-Rengifo et al., 2010; Rocha et al., 2016). At the Almonacid De La Cuba Section, the reversed-polarity magnetozones is identified within the *mirabile* ammonite subzone, which occurs within the Pliensbachian–Toarcian negative carbon-isotope excursion at Peniche (Hesselbo et al., 2007; Figure 3.4). Although ammonite subzones in the *tenuicostatum* zone have not yet been defined in the Mochras core, chemo- and magnetostratigraphic correlation between the Mochras, Peniche and the Almonacid De La Cuba successions suggest that the top of the *mirabile*-equivalent subzone is stratigraphically below ~861 mbs in the Mochras core (Figure 3.4).

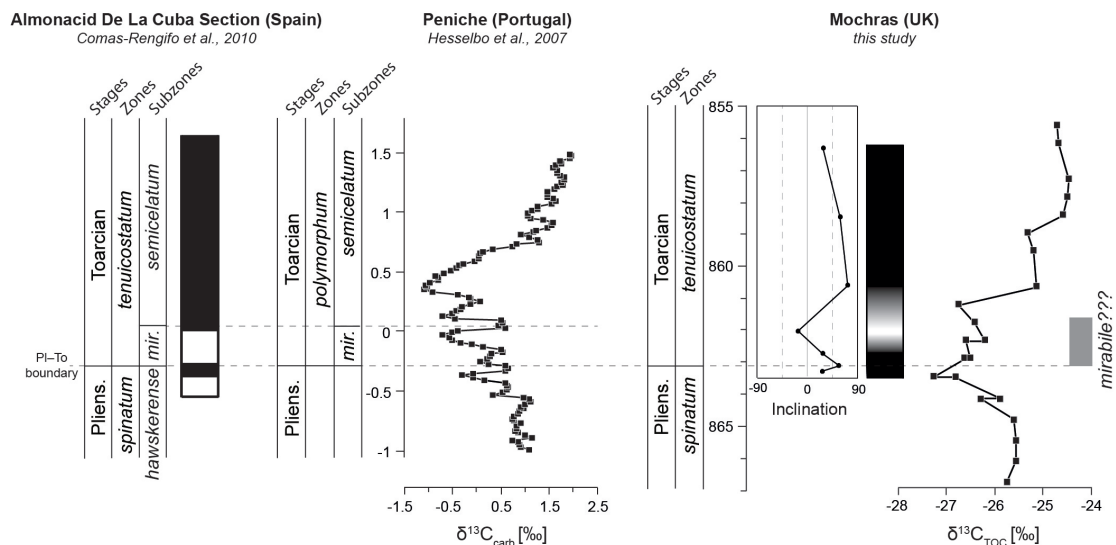


Figure 3.4 Bio-, magneto- and chemostratigraphic correlation, across the Pliensbachian–Toarcian boundary, between the Mochras core, the Peniche, and the Almonacid De La Cuba sedimentary successions (dashed lines). The grey-shaded stratigraphic intervals in the reconstructed magnetic record of the Mochras core reflects uncertain magnetic polarity due to low-resolution sample data. All three records are aligned at the Pliensbachian–Toarcian boundary. Abbreviations: Pliens.: Pliensbachian; *mir.*: *mirabile*.

3.5.2 Magnetostratigraphic correlations

Magnetostratigraphy from the Mochras Borehole can be correlated with other magnetostratigraphic sequences defined in coeval European successions, including the Breggia Gorge section of Switzerland (Horner and Heller, 1983) and the Iznalloz section (Galbrun et al., 1990), the Iberian Range Sierra Palomera and Ariño section (Osete et al., 2007) and the Almonacid De La Cuba Section (Comas-Rangifo et al., 2010) of Spain. Integration of the magnetostratigraphy from Switzerland and Spain was adopted as a constructed magnetic-polarity-scale for the Toarcian Stage in the 2012 Geological Time Scale (GTS; Ogg and Hinnov, 2012) (Figure 3.5).

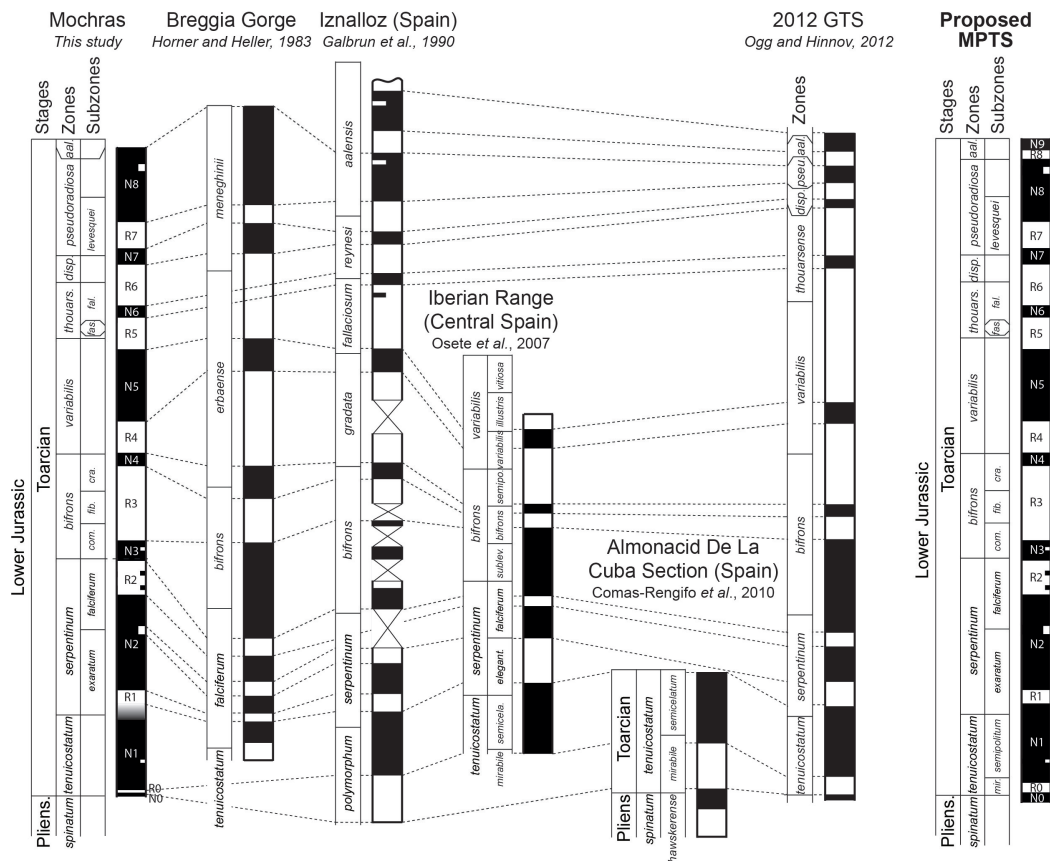


Figure 3.5 Magnetostratigraphic correlations between the different European successions. A proposed Toarcian magnetostratigraphic polarity time scale (MPTS) is shown on the right. The grey shaded zone in the magnetic record of the Mochras core reflects uncertainty in the position of the polarity zonal boundary due to the lack of analyzed samples in this interval. Stratigraphy in the Mochras core, Breggia Gorge, Iznalloz, Iberian Range and the Almonacid De La Cuba sedimentary records follows the relative thickness in each section. The vertical scale for the 2012 GTS is proportional to time. Stratigraphy in the proposed MPTS follows relative thickness of the Mochras core. Abbreviations: Pliens: Pliensbachian; *mir*: *mirabile*; *com*: *commune*; *fib*: *fibulatum*; *cra*: *crassum*; *thouars*: *thouarsense*; *fas*: *fascigerum*; *fal*: *fallaciosum*; *disp*: *dispansum*; *aal*: *aalensis*.

The Mochras core is a thicker (~260 m), stratigraphically more expanded and bio- and chemostratigraphically better constrained Toarcian succession relative to all previous studied successions, and carries a clear magnetic-polarity signal. The Breggia Gorge and the Iznalloz sections are also relatively biostratigraphically expanded, but are each less than 20 m thick (Horner and Heller, 1983; Galbrun et al., 1990), relatively condensed relative to the Mochras core. Biostratigraphic constraints on the

upper Toarcian at Breggia are also relatively poor, and the Iznalloz section exhibits several stratigraphic discontinuities. The composite magnetic-polarity column from the Iberian Range starts within the *mirabile* subzone of the *tenuicostatum* zone and ends in the *illustris* subzone of the *variabilis* zone (Osete et al., 2007). The Almonacid De La Cuba section, however, probably best characterizes the base of the Toarcian Stage among all the existing magnetic-polarity records (Comas-Rangifo, et al., 2010). This section records normal magnetic polarity across the Pliensbachian–Toarcian boundary, followed by a reversed magnetic-polarity zone through most of the *mirabile* ammonite subzone (Figure 3.5; Comas-Rangifo, et al., 2010). This reversed magnetic-polarity zone likely equates to the R0 magnetozone recognized in the Mochras core, based on chemo- and biostratigraphic correlation (see section 5.1 and Figure 3.4) and has also been recorded in the Iznalloz section (Galbrun et al., 1990). The long normal (N1) in the *tenuicostatum* zone in the Mochras core is also well documented in the magnetostratigraphic records from Iznalloz, the Iberian Range composite and the Almonacid De La Cuba sections of Spain (Figure 3.5; Galbrun et al., 1990; Osete et al., 2007; Comas-Rengifo et al., 2010). This normal-polarity (N1) magnetozone extends up to the lowermost *serpentinum* zone, followed by a reversed-polarity interval (R1) in the lower *exaratum* subzone, starting between 825–833 mbs in the Mochras core (Figure 3.3).

The R1 magnetic reversal biostratigraphically directly matches the magnetic reversals observed in both the Iznalloz and the Iberian Range sections (Figure 3.5). Normal magnetic polarity follows the magnetic reversal zone R1 throughout the remaining *exaratum* and lower *falciferum* subzones (Figure 3.2). One sample shows reversed polarity at the *exaratum*–*falciferum* subzone boundary, which is therefore marked by a half-width bar. The upper *falciferum* subzone is marked by magnetic-

polarity reversal (R2), which is matched by coeval reversed magnetic polarity in the Breggia Gorge and Iznalloz sections and the Iberian Range composite record. The Breggia Gorge section contains one more reversed-polarity magnetozone in the middle of the *falciferum* zone, which might be time-equivalent to the potential short reversed interval within the N2 magnetozone in the Mochras core (Figure 3.5). This reversal has, however, not been recorded in the Iberian Range composite, and detailed magnetostratigraphic correlation to the Iznalloz section is problematic due to the stratigraphic discontinuity in this interval (Figure 3.5). We tentatively correlate the reversed-polarity interval characterized by one sample in the Mochras core to the upper reversed-polarity magnetozone in the *serpentinum* zone in the Iznalloz section, implying that the R2 magnetozone-equivalent is within the stratigraphic gap in this section.

The *serpentinum*–*bifrons* zone boundary is, in all studied successions, marked by normal polarity (magnetozone N3 in the Mochras core; Figure 3.5). This magnetic-normal zone is, however, relatively thin in the Mochras core and only covers the lower *commune* subzone of the lower *bifrons* zone (Figure 3.3). The following reversed magnetozone (R3) in the Mochras core starts halfway through the *commune* subzone and continues through the *fibulatum* and into the upper *crassum* subzone (all in the *bifrons* zone; Figure 3.3). In the Iberian Range, this magnetic reversal is constrained to the *bifrons* subzone of the *bifrons* zone (Figure 3.5). This difference possibly reflects distinct biological provincialism between different European marine basins, with diachroneity between the ammonite subzone boundaries in the *bifrons* ammonite zone. The normal-polarity magnetozone (N4) straddles the *bifrons*–*variabilis* ammonite zone boundary in the Mochras Core and the Breggia Gorge and Iznalloz sections, and it is tentatively correlated to the short normal-polarity magnetozone in the upper part of the

bifrons zone in the Iberian Range composite (Figure 3.5). Minor differences in the biostratigraphic position of the N4 magnetozone in the different European successions possibly indicates diachroneity also for the *bifrons*–*variabilis* zonal boundary, or alternatively, may reflect a historic difference in the definition of the base of the *variabilis* zone, depending on either the first occurrence of *Haugia* or the last occurrence of *Hildoceras semipolatum*/ *Catacoeloceras* spp. (Page, 2003).

Magnetostratigraphic correlation of intervals stratigraphically above the *bifrons* zone is less precise because of the less well-constrained biostratigraphic correlation between different European ammonite provinces and associated ammonite-zone boundaries. The *erbaense* and *meneghinii* ammonite zones, recorded in the Breggia Gorge section (Switzerland), probably equate to the *variabilis*–*thouarsense* and the *pseudoradiosa*–*aalensis* (*levesquei*) ammonite zones in northwest Europe, as recorded in the Mochras core (Page 2003). In the Iznalloz section, the *gradata* zone equals the northwest European *variabilis* zone, the *fallaciosum* zone is likely partly coeval with the northwest European *thouarsense* zone, the *reynesi* zone is likely partly coeval with the northwest European *dispansum* zone and the *aalensis* zone is likely equal to the northwest European *aalensis* zone (Page 2003). The integrated stratigraphic framework proposed here for the Upper Toarcian therefore follows the correlation between the local palaeo-magnetic polarity records, with consideration of the ammonite zonal biostratigraphy (Figure 3.5). The upper Toarcian magnetic-polarity record of the Mochras core closely resembles the GTS2012 composite record; the thickness of the *pseudoradiosa* zone in the Mochras core is, greater than would be expected if sedimentation rates were constant and the duration of the zone in the GTS2012 is correct (Figure 3.5). The precise onset and termination of magnetic-polarity reversals in the different upper Toarcian sedimentary successions, relative to

ammonite zone boundaries, is also not always consistent (Figure 3.5). This difference potentially suggests that diachroneity between ammonite zonal boundaries in different biological (ammonite) provinces complicates high-resolution biostratigraphic correlation, not only in the middle, but also in the upper Toarcian. The last, *aalensis*, ammonite zone of the Toarcian Stage in the Mochras core is only very thin (~3 m), and no palaeomagnetic samples were analyzed. The *aalensis* ammonite zone in the Iznalloz-section is marked by two further palaeomagnetic reversals (Figure 3.5; Galbrun et al., 1990).

3.5.3 Proposed geomagnetic polarity time scale (MPTS) for the Toarcian Stage

A geomagnetic polarity time scale for the complete Toarcian Stage is proposed based on the new data from the Mochras core, integrated with previously published data (Figure 3.5).

The *mirabile* ammonite subzone (*tenuicostatum* zone) is marked in the proposed MPTS to show where the position of the R0 magnetozone is, based on data from the Almonacid De La Cuba Section (Comas-Rengifo et al., 2010). The base of the R1 magnetozone is assigned at above the base of the *exaratum* subzone, according to the results of the Iznalloz section and the Iberian Range composite (Galbrun et al., 1990; Osete et al., 2007). The R8 and N9 magnetozones in the *aalensis* zone, which are not recorded in the Mochras core, are added at the top of the column following GTS2012 (Ogg and Hinnov, 2012). In this way, we propose a geomagnetic polarity time scale (MPTS) for the complete Toarcian Stage (Figure 3.5).

The relative stratigraphic thicknesses of the Toarcian ammonite zones differ between sections and from those defined in GTS2012. The stratigraphic thicknesses of Toarcian ammonites zones used for the MPTS proposed here are combinations of the

zonal thickness from the Mochras core and the data as represented in GTS2012 and do not directly reflect relative time spans (Figure 3.5). The stratigraphic thickness of the *mirabile* subzone (*tenuicostatum* zone) in the Almonacide De La Cuba section is possibly more expanded than in the Mochras core. Assuming constant sedimentation rates, the *serpentinum* and the *pseudoradiosa* ammonite zones are relatively longer and the *bifrons*, *variabilis* and *thouarsense* zones are relatively shorter in the Mochras core, compared to the time-calibrated GTS2012 (Figure 3.5). This difference may either suggest changes in sedimentation rate throughout the Toarcian in the Mochras core, or a disproportionate representation of thickness relative to time in GTS2012, resulting from changes in sedimentation rate within, or between, the Spanish Iznalloz, Iberian Range and Almonacid De La Cuba sections. Since the duration of individual Toarcian ammonite zones is not yet accurately determined, future integration with astrochronological and geochronological data is required to accurately and precisely constrain the relative and numerical Toarcian time scale.

3.5.4 Linking Karoo volcanism with the Toarcian OAE

The carbon-cycle perturbations at the Pliensbachian–Toarcian boundary and in the early Toarcian have been linked to the Karoo-Ferrar large igneous province (LIP) and associated release of volcanogenic CO₂ and biogenic and seafloor-clathrate methane (Duncan et al., 1997; McElwain et al., 2005; Svensen et al., 2007; Percival et al., 2015, 2016). Elevated sedimentary mercury concentrations at the Pliensbachian–Toarcian boundary and sedimentary intervals recording the Early Toarcian OAE provided further evidence of enhanced volcanic activity at these times (Percival et al., 2015, 2016). Linking Karoo-Ferrar basalt emplacement to the T-OAE was previously based on the radiometric ages dated from the Karoo basalt and the volcanic ashes

interbedded in sedimentary sequences with ammonite biostratigraphy. The exact timing of the Karoo volcanism and its relation to the T-OAE is, however, not yet well constrained relative to European sections due to (a) relatively large uncertainties on earlier radio-isotopic Ar-Ar ages and (b) poor biostratigraphy for marine sedimentary records that yield accurate and precise U-Pb ages from contained volcanoclastic deposits.

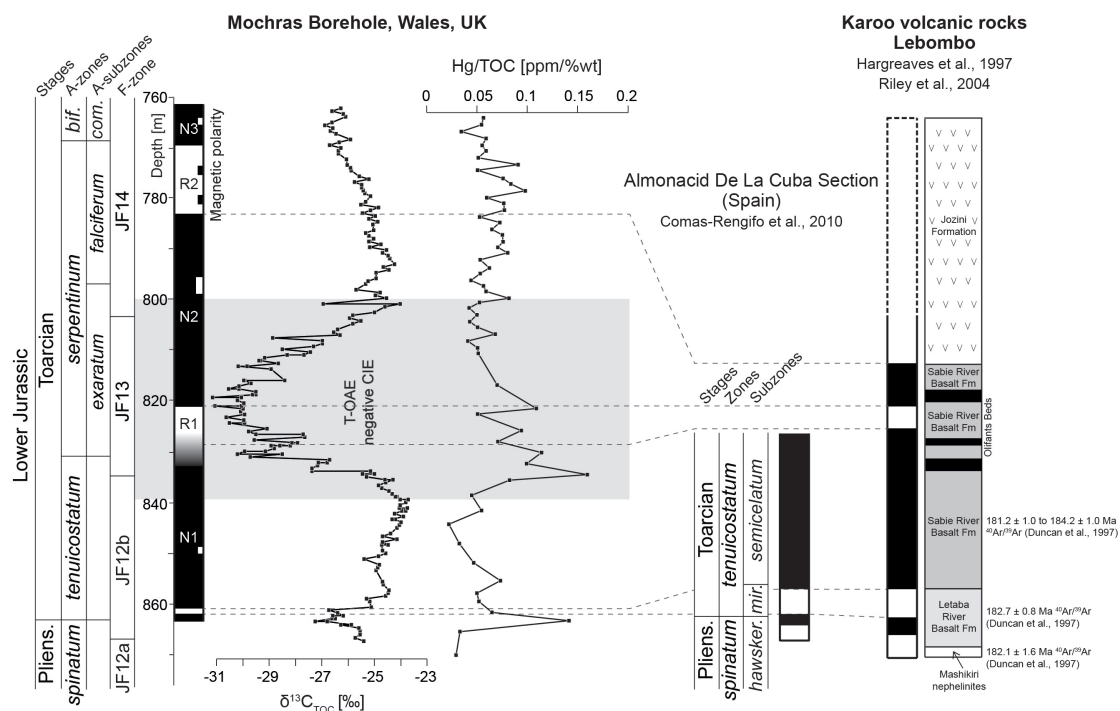


Figure 3.6 Magnetostratigraphic correlation between the Mochras core (this study), the Almonacid De La Cuba Section (Comas-Rengifo et al., 2010) and the Karoo volcanic rocks at Lebombo (South Africa; Hargreaves et al., 1997). The lithology column of the Lebombo region from the bottom to the top contains Mashikiri Nephelinite, Letaba Picrite, Sabie River Basalt and Jozini Rhyolite (Hargreaves et al., 1997). High-resolution bulk organic-carbon isotope record (this study) and the Hg/TOC record (Percival et al., 2015, 2016) from the Mochras core illustrate the carbon-cycle perturbation and the fingerprint of enhanced volcanism at the Pliensbachian–Toarcian boundary and the T-OAE.

High-resolution integrated magnetostratigraphic data from the marine realm may potentially be correlated to the geomagnetic polarity record obtained from Karoo sequences in South Africa (Hargreaves et al., 1997; Moulin et al., 2011). The onset of

accumulation of the Karoo volcanic sequence was previously correlated to the Pliensbachian–Toarcian boundary interval at Almonacid De La Cuba Section (Spain) based on magnetostratigraphy (Rocha et al., 2016). Bio- and magnetostratigraphic correlation of the Pliensbachian–Toarcian boundary between the Mochras succession and the Almonacid De La Cuba Section (Spain), and subsequent magnetostratigraphic correlation to the Karoo volcanic sequence from the Lebombo volcanic rift margin (South Africa), suggests that the three normal-polarity magnetozones in the Lebombo sequence correspond to the N0, N1 and N2 magnetozones in the Mochras core (Figure 3.6; Comas-Rengifo et al., 2010; Hargraves et al., 1997; Riley et al., 2004; Rocha et al., 2016). Based on this correlation, emplacement of the Karoo large igneous province had already begun in the late Pliensbachian, and continued until after the T-OAE negative CIE. Karoo basalt emplacement in the Karoo Basin in South Africa might actually have persisted throughout the duration of the overarching positive carbon-isotope excursion of the early Toarcian, suggesting prolonged climatic and oceanographic change, brought about by elevated atmospheric $p\text{CO}_2$, as the cause of the prolonged and large-scale extraction of isotopically depleted carbon from the global ocean-atmosphere system. The youngest normal-polarity magnetozones in the Lebombo sequence, which may correlate with the N2 magnetozones in the Mochras core, is less thick than the preceding normal-polarity magnetozones in the same sequence (Figure 3.6). The N1 and N2 normal-polarity zones have a comparable thickness in the Mochras core. Assuming the sedimentation rate at Mochras is constant, the difference may be explained by the relatively sporadic and unequal accumulation rate during emplacement of Karoo lava flows.

3.6 Conclusions

A high-resolution magnetostratigraphic record is presented, spanning the complete Toarcian succession of the Mochras Borehole, and providing a bio- and chemostratigraphically integrated and refined geomagnetic polarity time scale for the Toarcian Stage. The combined bio- (ammonite, foraminifera), magneto-, and chemo- (carbon-isotope) stratigraphic framework for the complete Toarcian Stage comprises an important stratigraphic reference record for future correlations between marine–marine and marine–terrestrial successions. This framework also provides potentially accurate and precise correlation to the basalt lava sequence of the Karoo large igneous province, linking the Pliensbachian–Toarcian boundary and T-OAE climatic and environmental perturbations directly to this episode of major volcanic activity.

Chapter 4

Lake expansion forms major carbon sink during the Toarcian Oceanic Anoxic Event

This chapter is modified from **Xu, W.**, Ruhl, M., Jenkyns, H.C., Hesselbo, S.P., Riding, J.B., Selby, D., Naafs, B.D.A., Weijers, J.W.H., Pancost, R.D., Tegelaar, E.W., Idiz, E.F., Carbon sequestration in an expanded lake system during the Toarcian Oceanic Anoxic Event. *Nature Geoscience*, *accepted*. W.X. and M.R. performed core description and sampling. W.X. performed all the analyses, except that J.B.R. performed palynological analysis; D.S. performed Re-Os dating; B.D.A.N. performed compound-specific carbon-isotope analysis. All authors contributed to data analysis and interpretation and writing and/or refinement of the manuscript.

4.1 Introduction

The early Toarcian Oceanic Anoxic Event (T-OAE at ~183 Ma) is recognized as one of the most intense and geographically extensive events of oceanic redox change and accompanying organic-carbon burial in the Mesozoic Era (Jenkyns, 1985, 1988). The T-OAE is marked by major changes in global geochemical cycles, with an apparently rapid negative shift of as much as ~7‰ in bulk marine and terrestrial organic-carbon isotope records and a typically smaller (3–6‰) negative excursion in carbonate archives and specific organic compounds (Hesselbo et al., 2000, 2007; Sælen et al., 2000; Jenkyns et al., 2002; Kemp et al., 2005; Hermoso et al., 2009a; French et al., 2014; Suan et al., 2015). Early Toarcian elevated atmospheric $p\text{CO}_2$ likely induced climatic and environmental change (Jenkyns et al., 2002; McElwain et al., 2005; Dera et al., 2011a; Ullmann et al., 2014; Brazier et al., 2015) by accelerating the global hydrological cycle and increasing silicate weathering, thereby increasing delivery of riverine nutrients to the oceans and potentially also to large inland lakes (Jenkyns, 2010). In the marine realm, the consequential increase in primary productivity and carbon flux to the sea floor is credited with enhancing the burial of planktonic material in relatively deep continental-margin sites, whereas in shallower water semi-restricted marine basins, chemical and physical water-column stratification likely aided the burial of organic matter (Jenkyns, 2010).

Marine records of the T-OAE, based on the presence of apparently coeval organic-rich shales, have now been identified from many outcrops in both the northern and southern hemispheres (Jenkyns, 1988; Jenkyns et al., 2002), but climatic and environmental change on the continents is still poorly understood. Intriguingly, however, sedimentary archives from continental interiors in China (e.g. the Tarim, Ordos and Sichuan Basins) are consistently marked by the occurrence of organic-rich

black shales that are latest Early Jurassic in age (Huang et al., 2003; Yang et al., 2005; He and Zhu, 2012). This stratigraphic evidence suggests that major inland lakes potentially formed or expanded contemporaneously with the T-OAE. Here, we (1) determine the precise age of the upper Lower Jurassic lacustrine organic-rich black shales in the Sichuan Basin; (2) determine their depositional context; and (3) explore the possible relevance of major lake formation as an additional sink for carbon in the context of the major disturbance in the early Toarcian exogenic carbon cycle.

4.2 Geological setting of the Sichuan Basin

The present-day topographic Sichuan Basin covers a total area of ~230,000 km² (Cai et al., 2003), almost three times the size of Lake Superior (82,100 km²), the most extensive modern freshwater lake in the world. The Early Jurassic Sichuan Basin (and the palaeo-Sichuan lake system) is thought to have been even larger than its present-day confines (Guo et al., 2011) (Figure 4.1). The basin formed on the western part of the Yangtze Platform and sedimentation commenced with the Neoproterozoic Sinian Sequence (850–570 Ma) (Ryder, 1991). Shallow-marine carbonates formed from the Tonian to the Middle Triassic, with occasional epeirogenic events, e.g. widespread basalt emplacement due to extension of the western margin of the Yangtze Platform, in the Late Palaeozoic (Ryder, 1991). Sedimentation switched from marine to continental in the Middle to Late Triassic with Indosinian tectonic uplift due to closure of the Palaeotethys and collision of the North and South China cratonic blocks (Cai et al., 2003). Siliciclastic sediments were deposited as alluvial fans and lakeshore–deltaic plain facies in the Early Jurassic, particularly along the southern front of the Longmen and Micang-Daba mountain ranges at the northwestern and northern margins of the Sichuan Basin (He and Zhu, 2012; Guo et al., 2011; Ryder,

1991; Zou, 2013) (Figure 4.1). Continental/fluvial deposits and green/red pedogenic horizons with soil carbonate nodules mark the Ma'anshan Member (middle Ziliujing Formation) and underlie the lacustrine facies of the upper Lower Jurassic Da'anzhai Member (uppermost Ziliujing Formation). The Da'anzhai Member represents the development of dominantly lacustrine conditions and the formation of a major lake. Lacustrine conditions may, however, have persisted through most of the Early Jurassic in the most central and deepest part of the basin, although their onset and termination are still poorly dated (Li and He, 2014).

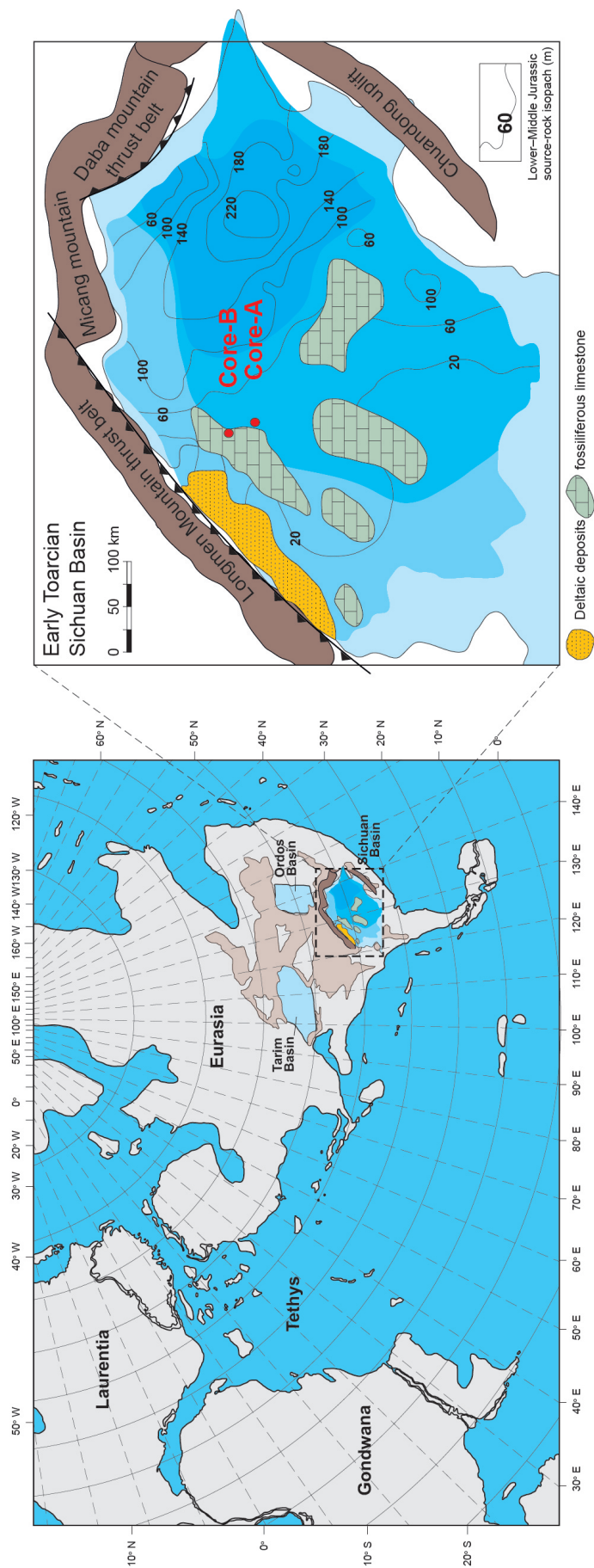


Figure 4.1 Size and location of the palaeo-Sichuan lake at 179 Ma. The map on the left shows a regional tectonic plate reconstruction at 179 Ma (edited from a map provided by CGG Robertson and Shell), with positions of the latest Early Jurassic lacustrine Sichuan, Tarim and Ordos Basins marked (Guo et al., 2011; He and Zhu, 2012; Zou, 2013). The map on the right illustrates the location of the two cores studied within the Sichuan Basin; relative variations in lake depth are illustrated in blue, with the darker shade representing deeper water areas; the green brickwork represents fossiliferous limestone and the yellow dotted ornaments represent deltaic deposits; palaeo-mountain ranges are marked in brown and the Da'anzhai Member isopachs are also indicated.

4.3 Materials and Methods

4.3.1 Materials

Two cores, named A and B, (Figure 4.1) were taken from the more proximal, northwestern part of the Sichuan Basin. Core A is 53.92 m long (from 2665.00 to 2718.92m core-depth), with core gaps from 2681.44–2682.84 m and 2699.64–2700.62 m. Core A was sampled at ~25cm resolution. Core B is 72.10 m long (from 3087.00 to 3159.10 m core-depth), with core gaps from 3113.64–3114.25 m and 3141.66–3142 m. Core B was sampled at ~80 cm resolution.

4.3.2 Rock-Eval pyrolysis

The Rock-Eval 6 Standard Analyser unit from Institut Français du Pétrole (manufacturer), at the Department of Earth Sciences (University of Oxford), was used to measure the S1, S2, $T_{\max}$, S3co/S3co₂ (New Oxygen Index), S4co/S4co₂ (Residual Organic Carbon), S5 (Mineral Carbon), to calculate the Hydrogen Index (HI, in mg HC/g TOC) and to characterize kerogen type and rock parameters. Laboratory procedures and measurement precisions have been described in section 2.3.1 of Chapter 2.

4.3.3 Hand-Held X-Ray fluorescence (HH-XRF)

Hand-held X-Ray Fluorescence analysis was performed with the *Innov-X* Delta XRF Analyzer, under climate-controlled laboratory conditions. HH-XRF analyses were executed directly on the flat surface of the slabbed Core A and Core B, at ~5cm resolution throughout the section. The HH-XRF was run in 2 Beam Mining Mode (DS-6000) and standard calibration to a manufacturer-delivered standard metal clip was performed at the onset of each run. Additionally, the NIST-2702 and NIST-2781 certified reference standards were regularly measured for quality control on the measurements and for calibration for long-term drift, measurement offset and to

constrain measurement error. Frequent measurements of the NIST-2702 standard show for calcium an average of 0.35% (NIST-2702 = 0.34%), with a standard deviation of 0.01%; for sulphur an average of 0.83% (NIST-2702 = 1.5%), with a standard deviation of 0.01%; and for molybdenum an average of 11ppm (NIST-2702 = 11.4ppm), with a standard deviation of 1.1ppm. Frequent measurements of the NIST-2781 standard show for calcium an average of 4.72% (NIST-2781 = 3.9%), with a standard deviation of 0.05%; for sulphur an average of 1.10%, with a standard deviation of 0.02%, and for molybdenum an average of 26.0ppm (NIST-2781 = 46.7ppm), with a standard deviation of 1.7ppm.

4.3.4 Bulk organic $\delta^{13}\text{C}$ analysis

One gram of homogenized sample was treated with 40mL cold HCl (3 molar) to dissolve the carbonate. Samples (dissolved in 3 molar HCl) were then put on a hot plate for 2 hours at 60°C. Samples were subsequently rinsed 4 times with distilled water to reach neutral pH. Samples were then oven-dried (at 40°C) and then again powdered. Around 1-15mg (depending on organic-carbon concentration) of homogenized de-carbonated sample residue was weighed into 8×5-mm tin capsules for $\delta^{13}\text{C}_{\text{org}}$ analyses. The $\delta^{13}\text{C}_{\text{org}}$ of the samples was measured at the Stable Isotope Laboratory at Open University (Milton Keynes, UK), with a Thermo Scientific Flash 2000 HT Elemental Analyser (EA) coupled to a Thermo Scientific MAT253 isotope ratio mass spectrometer via a Conflo IV open split interface. The Thermo Scientific Flash 2000 HT EA has a MAS2000 carousel and between the carousel and the EA sits a Thermo No Blank Device (NBD), allowing for the single sample purging with helium. The EA is also equipped with a Thermal Conductivity Detector (TCD). Automated dilution of sample gas with the Conflo IV open split interface allows for

high dynamic range of C+N content and controls the introduction of the “reference” gases. Isotope ratios are reported in standard delta notation relative to Vienna PDB. Analytical precision based on routine analysis of four internal and referenced laboratory standards (urea 020914MAG, IAEA-CH-6, NIST 8573, IR-R041), with measured average $\delta^{13}\text{C}$ values of -45.24‰, -10.39‰, -26.52‰, -23.58‰, respectively, and standard deviations of 0.85‰, 0.12‰, 0.28‰, 0.49‰.

4.3.5 Biomarker analyses

19 samples from Core A were processed for biomarker and compound-specific ($\text{C}_{23}\text{-C}_{33}$ *n*-alkane) $\delta^{13}\text{C}$ analyses. Sample preparation and biomarker analysis were undertaken at the Organic Geochemistry Lab facilities at Shell Global Solutions International in Rijswijk (The Netherlands).

4.3.5.1 Total lipid extraction

The total lipid fraction of each sample was obtained via extraction using a Dionex ASE® 350 Accelerated Solvent Extractor (ASE). Detailed methodology has been described in section 2.3.7.1 of Chapter 2.

4.3.5.2 Column chromatography

An aliquot of TLE was separated over AgNO_3 -impregnated silica gel columns into saturate, aromatic and resin fractions. Detailed methodology has been described in section 2.3.7.2 of Chapter 2.

4.3.5.3 *n*-alkane extraction

n-alkanes were extracted from the saturate fraction of each sample using zeolite molecular sieve beads (0.5 nm). The molecular sieve beads were activated in the oven for 3 hours at 120°C, added to the saturate fraction and left standing overnight in cyclo-hexane to trap the *n*-alkane fraction. The cyclohexane, containing the branched/cyclic (b/c) fraction, was transferred to a separate vial and beads were rinsed

a few times with cyclohexane, which was added to the b/c fraction. A known amount of standard mixture was added to the b/c fraction at this stage. The b/c fraction was subsequently analyzed using Gas Chromatography/tandem mass spectrometry (GC/MSxMS). A *n*-pentane:cyclo-hexane mixture (88:12) was added to the molecular sieve beads (containing the entrapped *n*-alkanes) and left overnight to release the *n*-alkanes. The *n*-alkane fraction of each sample, dissolved in the *n*-pentane:cyclo-hexane solution, was concentrated and transferred to an autosampler vial. Individual *n*-alkanes were identified using GC/MS and their carbon-isotope composition was determined using Gas Chromatography/Isotope Ratio Mass Spectrometry (GC/IRMS) (see section [4.3.6]).

4.3.5.4 Biomarker analysis

Aromatic fractions were analysed for their biomarker content using an Agilent 7890B GC system coupled to an Agilent 5973 mass selective detector (MSD). Column and temperature program have been described in section 2.3.7.4 of Chapter 2. It was run in selective ion mode (SIM) scanning for the masses of interest. Compounds were identified in the respective mass chromatograms by comparison of their retention time and elution order with standard samples.

B/c fractions were analysed for their biomarker content using an Agilent 7890A GC system coupled to an Agilent 7000 Triple Quadrupole Mass Spectrometer. Column and temperature program have been described in section 2.3.7.4 of Chapter 2. A selected set of parent-daughter mass transitions was scanned to monitor the compounds of interest. Compounds were identified in the respective mass transition chromatograms by comparison of their retention times and elution order to standard samples. For selected samples the system was run in full scan GC/MS mode to confirm identifications with full mass spectra.

4.3.6 Compound-specific (long-chain *n*-alkane) $\delta^{13}\text{C}$ analysis

The *n*-alkane fraction was measured for compound-specific $\delta^{13}\text{C}$ using an Isoprime 100 GC-combustion-isotope ratio MS (GC-CIRMS) system at the Organic Geochemistry Unit, University of Bristol. Samples were measured in duplicate and $\delta^{13}\text{C}$ values were converted to Vienna Peedee Belemnite (VPDB) by bracketing with an in-house gas (CO_2) of known $\delta^{13}\text{C}$ value. The reported values are the average of the duplicate measurements. Instrument stability was monitored by regular analysis of an in-house fatty acid methyl ester standard mixture; long-term precision is $\pm 0.3\text{‰}$. After injection of 1 or 2 μl onto a Zebron-I non-polar column (50 m length $\times$ 0.32 mm diameter $\times$ 0.10 μm film thickness), the GC oven program was: 70°C (hold for 1 min) to 130°C at 20°C/min, then to 300°C at 4°C/min, and hold for 25 min. Samples were automatically integrated using the IonVantage software package.

4.3.7 Scanning electron microscopy (SEM)

Polished thin sections (from 2680.4 and 2713.12 m in Core A) were analysed with a FEI Quanta FEG 650 Scanning Electron Microscope (SEM) at the Department of Earth Sciences, University of Oxford. Back-Scattered Electron Imaging (BSEI) was displayed with brighter regions representing areas with higher average atomic number.

4.4 Results

4.4.1 Carbon-isotope and Rock Eval results

$\delta^{13}\text{C}_{\text{TOC}}$ analyses of Core A reveal $<3\text{‰}$ fluctuations in the basal 15 m of the Da'anzhai Member, followed by a transient $\sim 4\text{‰}$ negative excursion (Figure 4.2; Appendix C). Core B similarly shows a $\sim 4\text{‰}$ negative excursion in $\delta^{13}\text{C}_{\text{TOC}}$ (Figure 4.2), followed by a full positive return to initial base values. The long-chain ($\text{C}_{23}\text{--}\text{C}_{33}$) *n*-alkane distribution of Core A does not show an odd-over-even predominance.

Compound-specific long-chain *n*-alkane (C_{23} – C_{33}) $\delta^{13}C$ analyses of Core A also show a distinct $\sim 4\text{‰}$ negative excursion, similar in magnitude to the bulk organic-matter $\delta^{13}C_{\text{TOC}}$ from the same stratigraphic interval (Figures 4.2 and 4.7). The ~ 2 – 3‰ carbon-isotope fluctuations in $\delta^{13}C_{\text{TOC}}$ in the lower Da'anzhai Member of Core A (2702–2715m in the core) are not repeated in the $\delta^{13}C_{n\text{-alkane}}$ record.

Total organic carbon (TOC) contents in the lower part of Core A are $\sim 1\%$, in comparison to values of up to $\sim 3.3\%$ in the black shale interval of the upper part of the core. In Core B, the TOC values are in general low, with higher values in the lower part of the core ($\sim 1\%$) and lower values in the upper part of the core (less than 0.5%) (Figure 4.2).

In Core A, hydrogen index (HI) values are lower in the lower Da'anzhai Member, and are especially low (< 100 mg HC/g TOC) at 2711.4–2712.3m and 2703.5–2706.6m. By contrast, HI values of the upper Da'anzhai Member go up to 450 mg HC/g TOC (Figure 4.2). In Core B, the HI values are less than 200 mg HC/g TOC throughout the whole Da'anzhai Member (Figure 4.2). T_{max} values of Core A are 438–460°C and those of Core B are 430–518°C.

4.4.2 Elemental concentrations

Major and trace elemental concentrations are measured by HH-XRF. Calcium (Ca) concentrations in Core A are $\sim 0\%$ – 42.0% and in Core B are $\sim 0\%$ – 43.5% (Figure 4.2). Sulphur (S) concentrations vary between $\sim 0\%$ and $\sim 6.4\%$ and are higher in the black shale interval in the upper part of Core A. Several horizons in Core A also contain Molybdenum (Mo) of 9–21 ppm (Figure 4.7).

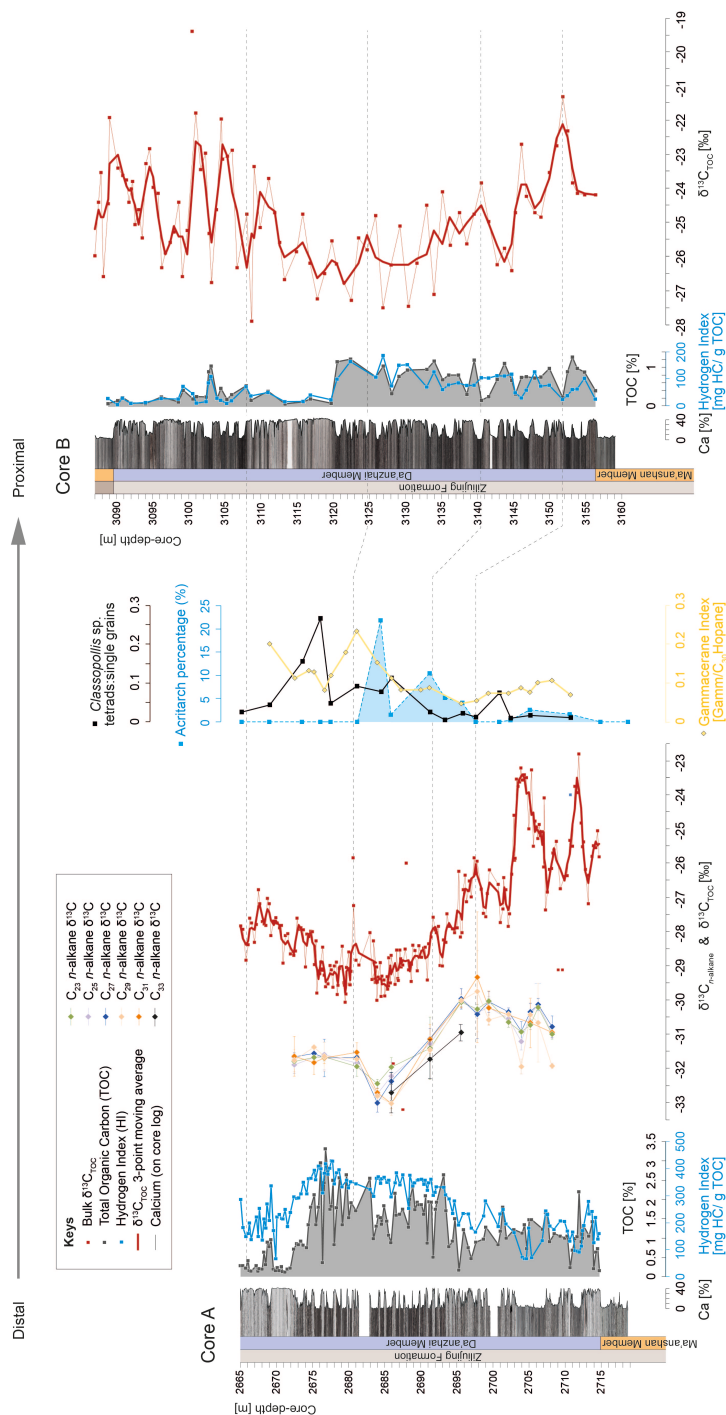


Figure 4.2 Stratigraphic correlation of cores A and B and the palaeoenvironmental proxies in the Sichuan Basin (China). Stratigraphic changes in lithology from each core are illustrated by calcium (Ca) concentrations (from XRF measurements on the cores) superimposed on the combined core photos, with light colours representing limestone and dark colours representing shale. $\delta^{13}C_{TOC}$ from both cores are plotted in red squares and the three-point moving averages are plotted in thick red lines. $\delta^{13}C_{n-alkane}$ data from different chain-lengths are plotted in diamonds of different colours, as illustrated in the legend. Error bars on $\delta^{13}C_{n-alkane}$ data reflect the 1 σ standard deviation of replicates. TOC and HI values from Rock-Eval pyrolysis are plotted for both cores in black and dark blue squares, respectively (note similar pattern of TOC enrichment). The Gamma Index values (Gamma Index / C₃₀ hopane) are plotted in yellow diamonds. Marine acritarch percentages (%) are plotted in the larger blue squares with light blue shades. Ratios of *Classopollis* sp. tetrads vs single grains are plotted in black squares.

4.4.3 Back-scattered scanning electron imaging (BSEI) of pyrite

Pyrite (FeS_2) framboids have been observed as a replacement of organic matter or shell fossils (Figure 4.3 a, c). They are also observed in tiny sizes (5–10 μm) (Figure 4.3 b, d).

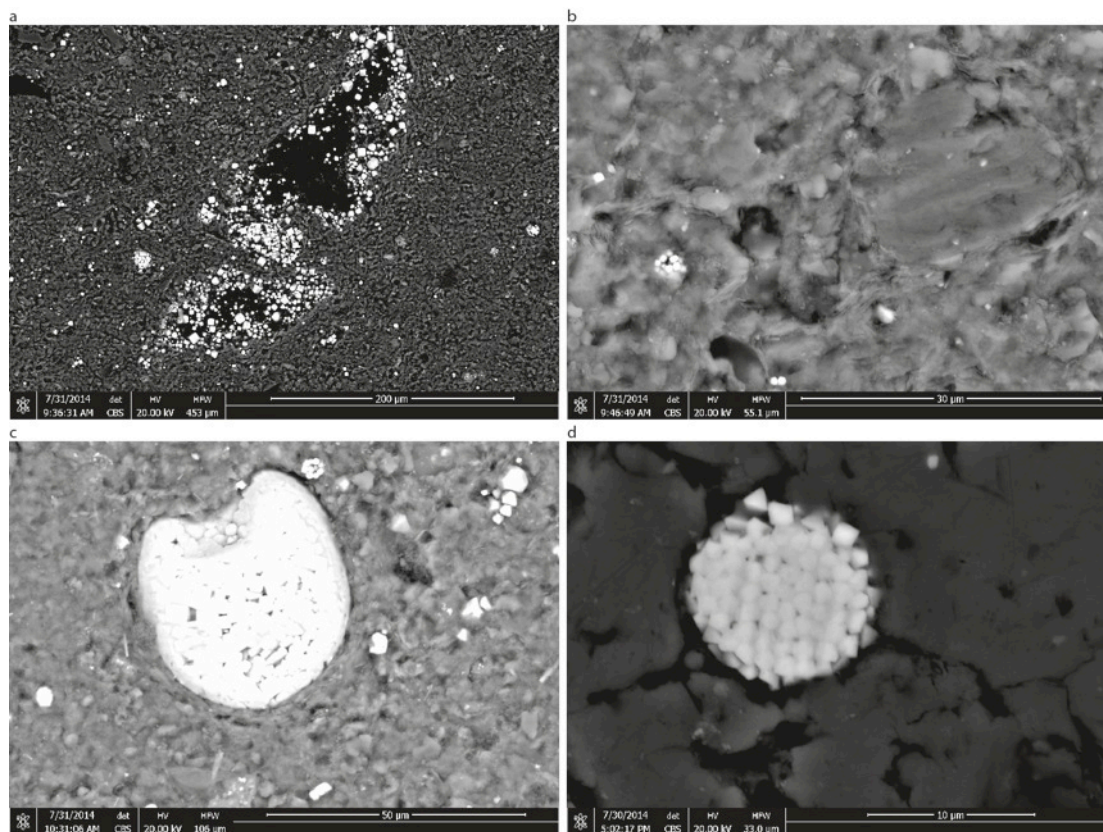


Figure 4.3 Examples of pyrite framboids from 2680.4 m (a, b, c) and 2713.12 m (d) in Core A, imaged with a back-scattered electron beam detector. (a) Pyrite likely generated by pore-water sulphate reduction due to the oxidation of organic matter. (b) Small (<5 μm) pyrite framboids which may have formed in a euxinic (sulphide-rich) water-column. (c) A fully pyritized shell fragment surrounded by small pyrite framboids. (d) A larger (>5 μm) pyrite framboid, possibly formed during early diagenesis.

4.4.4 Molecular compounds

Gammacerane biomarker has been identified by GC/MSxMS parent-daughter mass transition m/z 412 $\rightarrow$ 191, which also quantifies the 17 α -hopane (C_{30} hopane) required for the gammacerane index.

C₃₀ tetracyclic polyprenoids (TPP) were detected and analysed by GC/MSxMS with parent-daughter mass transition m/z 414→259 (Figure 4.4). The two peaks marked TPPa and TPPb are C₃₀ TPP 18 α (H), 21R and C₃₀ TPP 18 α (H), 21S (Figure 4.4; Holba et al., 2000). The parent-daughter mass transitions m/z 372→217, 386→217, 400→217, 414→217 were used to detect C₂₇, C₂₈, C₂₉ and C₃₀ steranes, respectively.

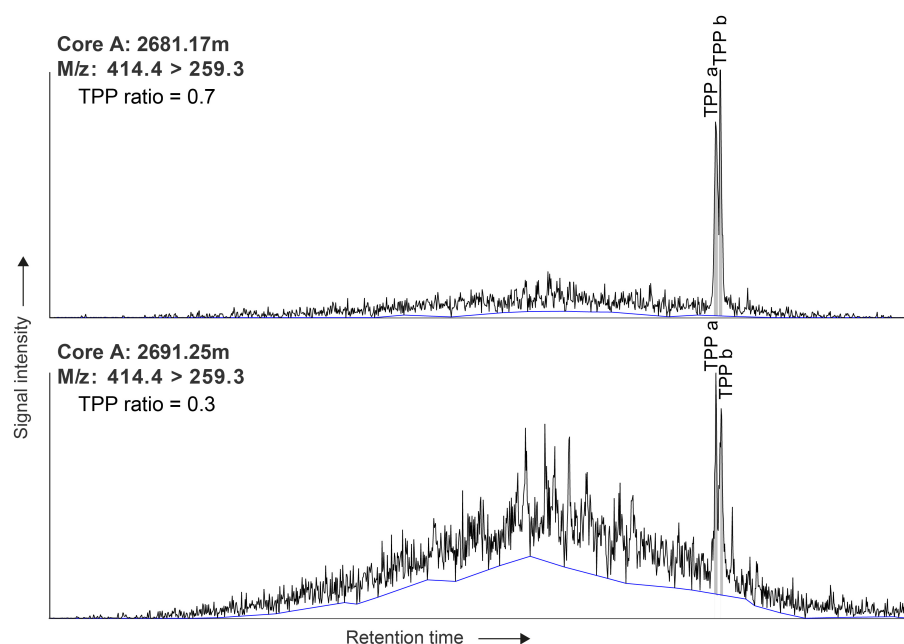


Figure 4.4 Mass chromatograms of TPP biomarker spectra from core depths 2681.17 m and 2691.25 m in Core A. TPP ratios displayed in the figure are calculated based on Holba *et al.* (2000).

Two horizons are selected to illustrate the occurrences of TPP and the distribution of steranes. The sample at 2681.17 m contains no marine palynomorphs but displays a high gammacerane index (Figure 4.2). The sample at 2691.25 m contains ~10% marine palynomorphs (Figure 4.2). TOC of both samples is ~2% and HI values are 301 and 340 mg HC/g TOC, respectively. The sample at 2681.17 m shows a clear presence of TPP (TPP ratio = 0.7), whereas the sample at 2691.25 m shows much lower TPP contents (TPP ratio = 0.3). The sterane distributions are very similar between the two samples (Figure 4.5). C₃₀ steranes (24-*n*-propylcholestanes)

are normally sourced from marine algae. The parent-daughter mass transition m/z 414→217 does not show any clear peaks in either of the samples analysed indicating the near absence of C_{30} steranes in both samples despite one of them containing ~10% marine palynomorphs (Figure 4.5).

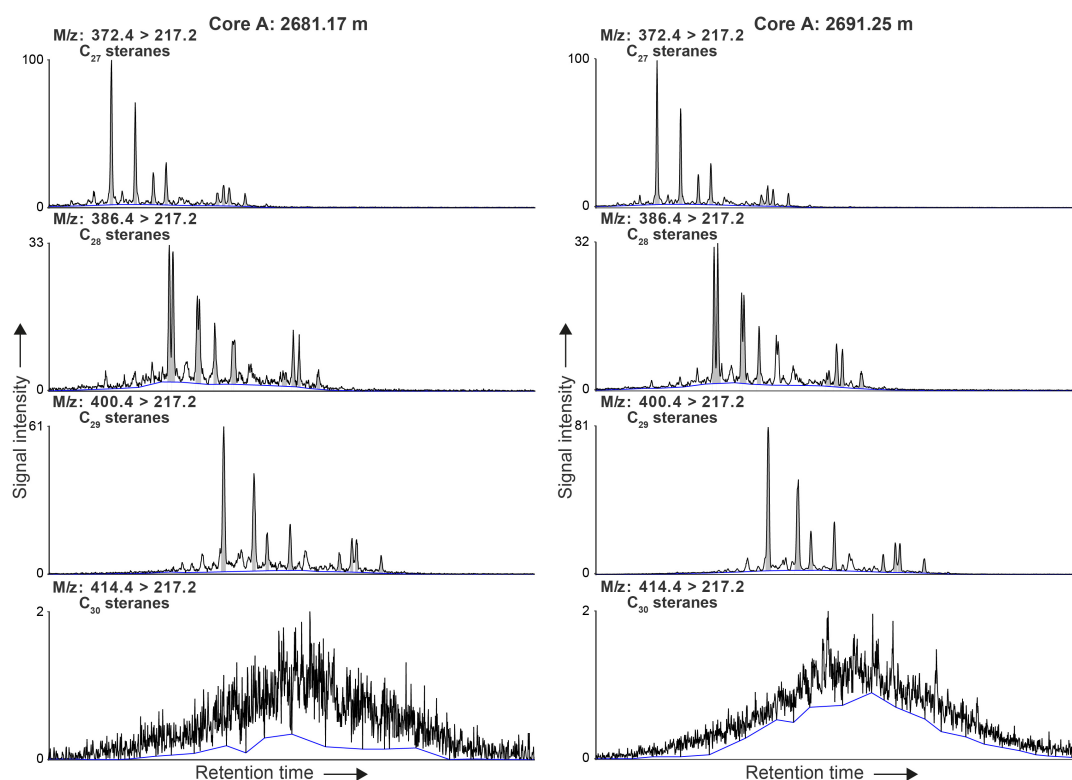


Figure 4.5 Panels of mass chromatograms of C_{27} , C_{28} , C_{29} and C_{30} steranes from GC/MSxMS data from core depths 2681.17 m and 2691.25 m in Core A. The different transitions from the same sample use the same scale for the y-axis.

4.5 Age and stratigraphy

The Da'anzhai Member in both successions exhibits alternating beds of fossiliferous carbonate and a spectrum of mudrocks from clay-rich marl to laminated black shale (Figure 4.2). Diverse freshwater bivalves, ostracods, gastropods and conchostracans in the fossiliferous carbonate beds and mudstone beds confirm these sediments to be lacustrine deposits (Wang et al., 2010). The freshwater ostracod faunal

assemblages, which include *Darwinula* spp. and *Metacypris unibulla*, suggest a late Early Jurassic age (Wei, 1982).

The palynomorph assemblages of the lacustrine Da'anzhai Member (analysed by James Riding in Appendix D), with the superabundance of the pollen *Classopollis* sp. (and the absence of *Callialasporites* spp.), the occurrence of the spore *Ischyosporites variegatus*, the acritarch *Veryhachium collectum*, multi-specimen clumps of the prasinophyte *Halosphaeropsis liassica* and the rare occurrence of the dinoflagellate cyst ?*Skuadinium* sp., are comparable to floras from early Toarcian marine successions in northern Europe and Australia, indicating that the successions studied here are of similar age (see Appendix D). The superabundance of the thermophylic pollen genus *Classopollis* and the occurrence of the opportunistic prasinophyte species *Halosphaeropsis liassica*, thought to have thrived in environmentally stressed conditions and normally occurring in multi-specimen clumps, are especially typical of the T-OAE (see Appendix D) (Wall, 1965, Dybkjær, 1991; Bucefalo Palliani et al., 2002; Riding and Helby, 2001).

Re-Os radiometric dating on 16 samples from two combined intervals of the Da'anzhai lacustrine black shale (Core A) shows a well-constrained single isochron of 180.3 ± 3.2 Ma (Figure 4.7; see Appendix E Figure E.1; data generated by David Selby), constraining the Da'anzhai Member to the Toarcian, following the Jurassic timescale of Ogg and Hinnov (2012). A Re-Os isochron for the organic-rich marine mudrock from the *falciferum* ammonite subzone in Yorkshire (UK) suggests a depositional age of 178.2 ± 5.6 Ma (Cohen et al., 2004). The age obtained here for the lacustrine Da'anzhai Member in the Sichuan Basin is in agreement, within uncertainty, with the marine realm early Toarcian Re-Os isochron-based age (Figure 4.6).

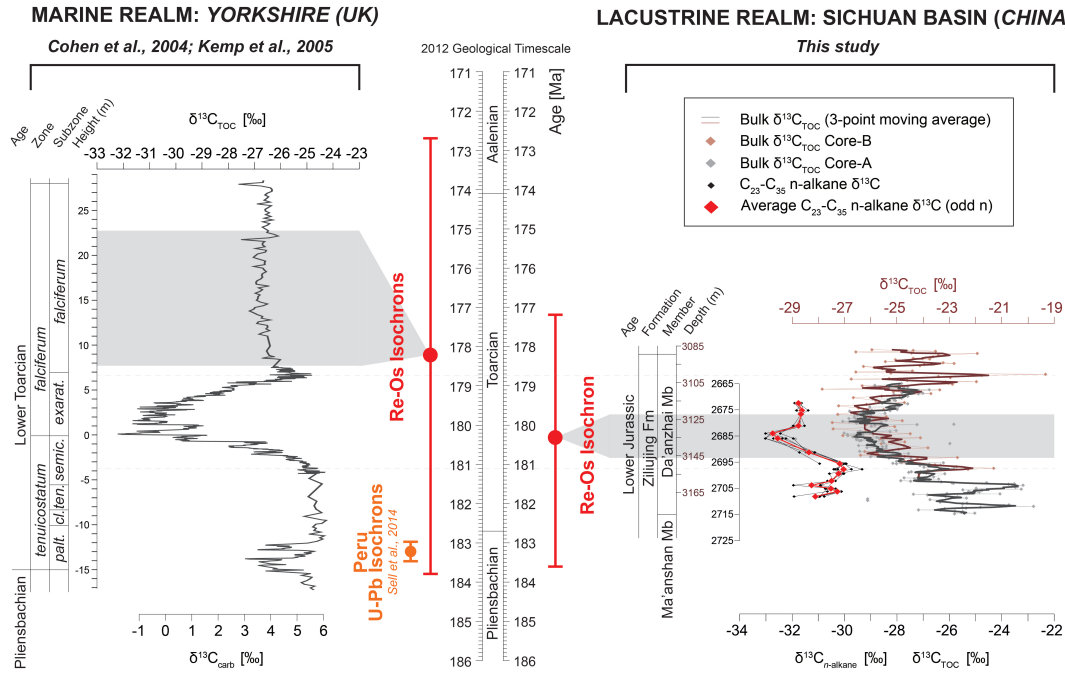


Figure 4.6 Stratigraphic comparison of the Re-Os ages of the marine Jet Rock in Yorkshire (Cohen et al., 2004) and the lacustrine Da'anzhai Member in this study, relative to the 2012 Geological Time-Scale (Ogg and Hinnov, 2012). The two records are aligned with reference to the negative CIE. The light grey shades represent the stratigraphic intervals from which the samples, used for Re-Os dating, were obtained. Also shown is the U-Pb radiometric age (183.22 ± 0.25 Ma) of an ash-bed in a basal Toarcian marine sedimentary succession (in orange) in the Pucara Basin (Peru), which precedes the T-OAE negative CIE (Sell et al., 2014). Although biostratigraphic and chemostratigraphic correlation to the European realm is not straightforward, this basal Toarcian U-Pb radiometric age overlaps, within uncertainty, with the Early Toarcian Re-Os radiometric ages from Yorkshire and the Da'anzhai Member, further constraining the age of the lacustrine Da'anzhai Member.

Furthermore, $\delta^{13}\text{C}_{\text{TOC}}$ analyses of Core A reveal $<3\%$ fluctuations in the basal 15 m of the Da'anzhai Member, followed by a transient $\sim 4\%$ negative excursion (Figure 4.2). The base of Core B is interpreted to be stratigraphically younger than Core A based on carbon-isotope correlation, and similarly shows a $\sim 4\%$ negative excursion in $\delta^{13}\text{C}_{\text{TOC}}$ (Figure 4.2), followed by a full positive return to initial base values. The two cores combined present the complete negative CIE, which is similar in shape and magnitude to that observed in marine records of the T-OAE (Figure 4.7)

(Kemp et al., 2005; Cohen et al., 2004). Compound-specific long-chain *n*-alkane (C_{23} – C_{33}) $\delta^{13}C$ analyses of Core A also show a distinct $\sim 4\text{‰}$ negative excursion, similar in magnitude to the bulk organic-matter $\delta^{13}C_{TOC}$ from the same stratigraphic interval (Figures 4.2 and 4.7). Long-chain *n*-alkanes in sedimentary organic matter are typically sourced from terrestrial higher plants or freshwater algae (Lichtfouse et al., 1994) whose isotopic compositions are commonly indistinguishable because lake-water dissolved inorganic carbon (DIC) is isotopically in equilibrium with the atmosphere (Meyers, 1994). Consequently, the observed shift in $\delta^{13}C_{n\text{-alkanes}}$ directly reflects changes in the carbon isotopic composition of the atmosphere (and lake-water DIC) during the early Toarcian global carbon-cycle perturbation. The odd-over-even predominance in the long-chain (C_{23} – C_{33}) *n*-alkane distribution, typical for terrestrial higher plant leaf waxes or freshwater algal-sourced sedimentary organic matter (Lichtfouse et al., 1994) is, however, not observed from Core A (with a Carbon Preference Index of ~ 1 ; data in Appendix C), probably due to its relatively elevated thermal maturity (T_{max} values mainly of $444\text{--}460^{\circ}\text{C}$) (Meyers and Ishiwatari, 1993). The $\sim 2\text{--}3\text{‰}$ carbon-isotope fluctuations in $\delta^{13}C_{TOC}$ in the lower Da'anzhai Member of Core A (2702–2715m in the core) are, however, not repeated in the $\delta^{13}C_{n\text{-alkane}}$ record. This feature may suggest a shift in the dominant sedimentary organic matter source away from freshwater algae to ^{13}C -enriched terrestrial woody organic matter, with HI values of <100 mg HC/g TOC at 2711.4–2712.3m and 2703.5–2706.6m in the lower Da'anzhai Member of Core A, which are much lower than HI values of the upper Da'anzhai Member, where the degree of maturity is similar (Figure 4.2).

Figure 4.7 Geochemical Comparison between the lacustrine Da'anzhai Member (Sichuan Basin, China) and the lower Toarcian marine succession from Yorkshire (UK). Re-Os (rhenium-osmium) isochrons from both Yorkshire (Cohen et al., 2004) and the Da'anzhai Member (Sichuan Basin; this study) are plotted with short dashed lines on the left of the ages, indicating the depths of samples that produced the Re-Os isochrons. The Re-Os isochron for the upper Lower Jurassic lacustrine Da'anzhai Member (Core A) gives an age of 180.3 ± 3.2 Ma and the lower Toarcian marine Jet Rock (Yorkshire) gives a Re-Os isochron age of 178.2 ± 5.6 Ma (Cohen et al., 2004). The two successions are correlated on the basis of $\delta^{13}\text{C}_{\text{TOC}}$ and $\delta^{13}\text{C}_{n\text{-alkane}}$ from the Da'anzhai Member, and $\delta^{13}\text{C}_{\text{TOC}}$ (Cohen et al., 2004; Kemp et al., 2005), $\delta^{13}\text{C}_{n\text{-alkane}}$ (French et al., 2014) and $\delta^{13}\text{C}_{\text{phytane}}$ (Sælen et al., 2000) from Yorkshire. S and Mo concentrations (from X-ray fluorescence measurements) and TOC (from Rock Eval pyrolysis) on Core A are plotted in orange lines, blue diamonds and black lines with dark grey shades, respectively. S and TOC records from Yorkshire (Kemp et al., 2011) are plotted in orange lines and black lines with dark grey shades, respectively. A conservatively estimated ~460 Gt organic carbon was buried in the palaeo-Sichuan lake system during the T-OAE.

Overall, relatively enriched $\delta^{13}\text{C}_{\text{TOC}}$ values in the more proximal Core B may be explained by the greater woody component of terrestrial residual sedimentary organic matter (the isotopically heavier ligno-cellulose component of a plant) (Hesselbo et al., 2000; van Bergen and Poole, 2002), as suggested indirectly by low HI values (<200 mg HC/g TOC; Figure 4.2) and directly by palynological study (with 26–45% wood). In addition, the more proximal Core B is thermally more mature, with T_{max} values mainly of 453–470°C (T_{max} values of Core A are mainly 444–460°C). Maturation of kerogen can increase its $\delta^{13}\text{C}_{\text{TOC}}$ values by 1–2‰, which may have further contributed to the offset observed between the organic carbon isotope records of cores A and B (Whelan and Thompson-Rizer, 1993). The observed parallel signature in $\delta^{13}\text{C}_{\text{TOC}}$ and $\delta^{13}\text{C}_{n\text{-alkane}}$ in the main phase of the Da'anzhai Member (above 2698 m) therefore likely reflects a true perturbation of the global exogenic carbon cycle. It is similar in shape and magnitude to what is characteristically observed in early Toarcian marine calcite and compound-specific marine and terrestrial organic

matter records from Europe and elsewhere spanning the T-OAE (Sælen et al., 2000; Hermoso et al., 2009a; French et al., 2014; Suan et al., 2015) (Figure 4.7).

The combined macro- and microfossil biostratigraphy, palynostratigraphy, Re-Os chronology and chemostratigraphy uniquely constrain the formation of the Da'anzhai Member to be time-equivalent with the T-OAE.

4.6 $\delta^{13}\text{C}$ vs organic matter source

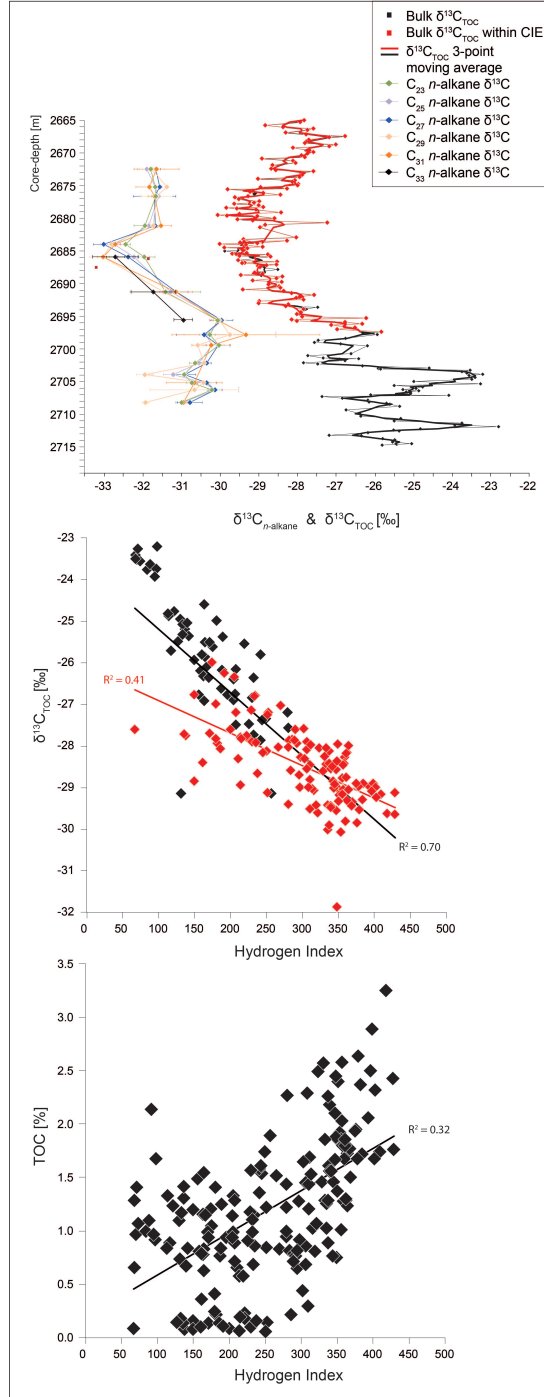
Higher plants and marine or freshwater algae fractionate carbon isotopes differently during photosynthesis, partly also depending on environmental background conditions (e.g. atmospheric and aquatic $p\text{CO}_2$). Hydrogen indices (HI) vary depending on the organic-matter precursors as well as subsequent thermogenic or biogenic degradation. A change in the sedimentary organic-matter source may thus be reflected by a change in HI values and (possibly) result in a change in bulk organic $\delta^{13}\text{C}$. A correlation between HI values and $\delta^{13}\text{C}_{\text{TOC}}$ in a sedimentary record may partly reflect organic-matter source mixing, but such interpretation also deserves caution. Tyson (1995; p412) states: “Cross-plots of hydrogen index and $\delta^{13}\text{C}$ may show a negligible, weak or strong relationship, depending partly upon whether the variation in HI primarily reflects variable preservation of marine material (and thus redox), or terrestrial-marine mixing due to relative fluxes under moderate to good preservational conditions (Arthur et al., 1985; Dean and Arthur, 1987; Dean and Anders, 1991). Where there is no significant variation in $\delta^{13}\text{C}$, one can reasonably hypothesize that there was relatively little change in organic matter source, but where $\delta^{13}\text{C}$ varies with HI (Dean et al., 1984; Dean et al., 1986; Moldowan et al., 1986), it may be unwise to assume that relative terrestrial:phytoplankton ratios are the only factor involved”.

Tyson (1995; p416) also states: “Isotopic analysis of specific biomarker compounds such as porphyrins, which are believed to preserve their original $\delta^{13}\text{C}$ value to within 0.5‰, and comparisons with the bulk TOC $\delta^{13}\text{C}$ values, provides a geochemical methodology for appraising diagenetic alteration and mixing effects (Hayes et al., 1989; Takigiku et al., 1991)”. This methodology has been adopted here, with the bulk $\delta^{13}\text{C}_{\text{TOC}}$ and the $\delta^{13}\text{C}_{n\text{-alkane}}$ records showing a similar $\sim 4\%$ negative carbon isotope excursion (CIE) during the deepest phase of lake development.

$\delta^{13}\text{C}_{\text{TOC}}$ and HI values in cores A and B from the Sichuan Basin may correlate overall, but the correlation breaks down when only the interval of the negative carbon isotope excursion (CIE) is considered, as illustrated in red in Figure 4.8 (with an R^2 value of only 0.41 for Core A and 0.31 for Core B). Correlation is even poorer between $\delta^{13}\text{C}_{\text{TOC}}$ and TOC (Figure 4.8). On the other hand, compound-specific carbon isotope analysis on long-chain *n*-alkanes, sourced from terrestrial higher-plant leaf waxes or freshwater algae, also shows a 3–4‰ negative excursion, similar in magnitude to that observed in the bulk $\delta^{13}\text{C}_{\text{TOC}}$ record of the same core and coeval marine successions (Sælen et al., 2000; French et al., 2014; Suan et al., 2015). Aquatic and terrestrial organic matter (e.g. algae, pollen and spores and waxy leaf material) constitutes high HI values, but woody organic matter results in low HI values. Woody organic matter generally also displays a more positive carbon-isotopic composition. Therefore, sediments showing relatively low HI values (indicating more woody sedimentary organic matter) may also be characterized by more positive carbon-isotope values. Core B shows overall low HI values, suggesting a larger proportion of woody sedimentary organic matter, and possibly explaining the overall more positive signature in bulk $\delta^{13}\text{C}_{\text{TOC}}$. The $\sim 3\%$ fluctuations in bulk $\delta^{13}\text{C}_{\text{TOC}}$ in the lower part of Core A are not reflected in the $\delta^{13}\text{C}_{n\text{-alkane}}$ record and are, therefore, unlikely to reflect

global carbon-cycle changes. They may rather reflect source-mixing, as also suggested by the strong correlation between $\delta^{13}\text{C}_{\text{TOC}}$ and HI values in the interval preceding the CIE, with $R^2 = \sim 0.78$.

Core A



Core B

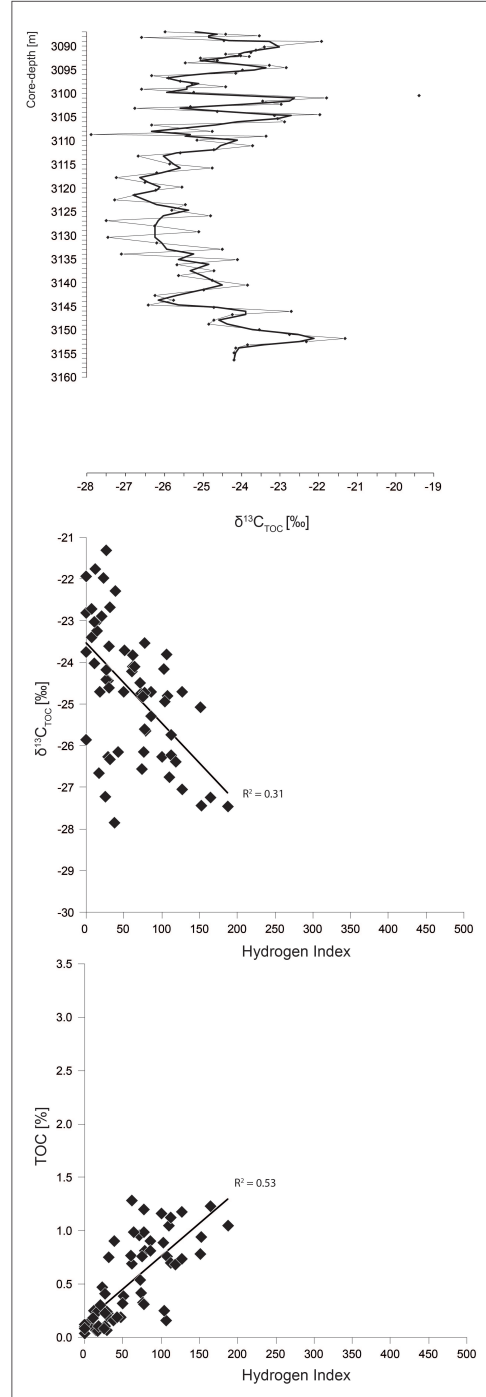


Figure 4.8 The cross-plot relationships between bulk organic $\delta^{13}\text{C}$ and Hydrogen Index (HI), and bulk organic $\delta^{13}\text{C}$ and Total Organic Carbon (TOC). Specifically, bulk organic $\delta^{13}\text{C}$ within the negative CIE from Core A is marked in red.

Correlations between $\delta^{13}\text{C}_{\text{TOC}}$ and HI values are also widely observed in different marine sections of the T-OAE, where $\delta^{13}\text{C}$ of wood or specific compounds already demonstrated the significance of the carbon-cycle perturbation (Hesselbo et al., 2000; French et al., 2014; Suan et al., 2015). Comparison of $\delta^{13}\text{C}_{\text{TOC}}$, $\delta^{13}\text{C}_{\text{compound-specific}}$ and HI from Yorkshire, Dotternhausen, Denkingen with the Sichuan Basin (this study; Hesselbo et al., 2000; Sælen et al., 2000; Schouten et al., 2000; French et al., 2014; Suan et al., 2015), shows that HI values are strongly elevated up to 800 mg HC/g TOC in all marine successions (Figures 4.9 and 4.10). Irrespective of this high value, compound-specific carbon-isotope records in these marine successions still also show a $\sim 3\text{--}4\text{‰}$ negative excursion, suggesting that changes in the composition of organic matter are not the primary cause of the observed negative CIE (Figure 4.9). Changes in HI may, however, potentially have slightly altered the magnitude of the negative CIE in bulk $\delta^{13}\text{C}_{\text{TOC}}$ (Suan et al., 2015). Correction of the bulk $\delta^{13}\text{C}_{\text{TOC}}$ record for changes in the source of the sedimentary organic matter is, however, not straightforward, especially over major global-change events. Changes in carbon-isotopic fractionation in organic matter, under elevated $p\text{CO}_2$, is notoriously poorly constrained, especially in the geological past, and likely differs between major groups of primary producers. As mentioned above, thermal maturity of deeply buried sedimentary rocks can also shift the carbon-isotopic composition of bulk $\delta^{13}\text{C}_{\text{TOC}}$ to 1–2‰ more positive values (Whelan and Thompson-Rizer, 1993), with more labile organic matter changing more easily to more positive values. Furthermore, more labile parts of sedimentary organic matter or compounds are also more easily oxidized depending on the redox state of the depositional environment. This effect means that the $\delta^{13}\text{C}_{\text{TOC}}$ and HI values of the preserved organic matter or compounds may have changed non-linearly relative to their original composition. All these factors make it impossible to calibrate reliably, in

detail, the magnitude of global exogenic carbon- cycle change, especially over major events like the T-OAE, based on simple cross-calibration of bulk $\delta^{13}\text{C}_{\text{TOC}}$ and HI, and especially when this is based on data pre- or succeeding the event. Therefore, although bulk $\delta^{13}\text{C}_{\text{TOC}}$ in sediments can be affected by a change in source mixing, the correlative relationship between $\delta^{13}\text{C}_{\text{TOC}}$ and HI (and its significance, as reflected by R^2) cannot be reliably used to compute the magnitude of change in bulk $\delta^{13}\text{C}_{\text{TOC}}$ due to source mixing. Rather, changes in HI and the carbon-isotopic composition of sedimentary organic matter both are the consequence of the global climatic perturbation at the T-OAE. Major ^{12}C -enriched carbon release into the ocean-atmosphere system, and associated enhanced hydrological cycling and increased nutrient supply to lacustrine and marine basins, resulted in respectively a major shift in global $\delta^{13}\text{C}$ and increased aquatic primary organic productivity with elevated sedimentary HI values.

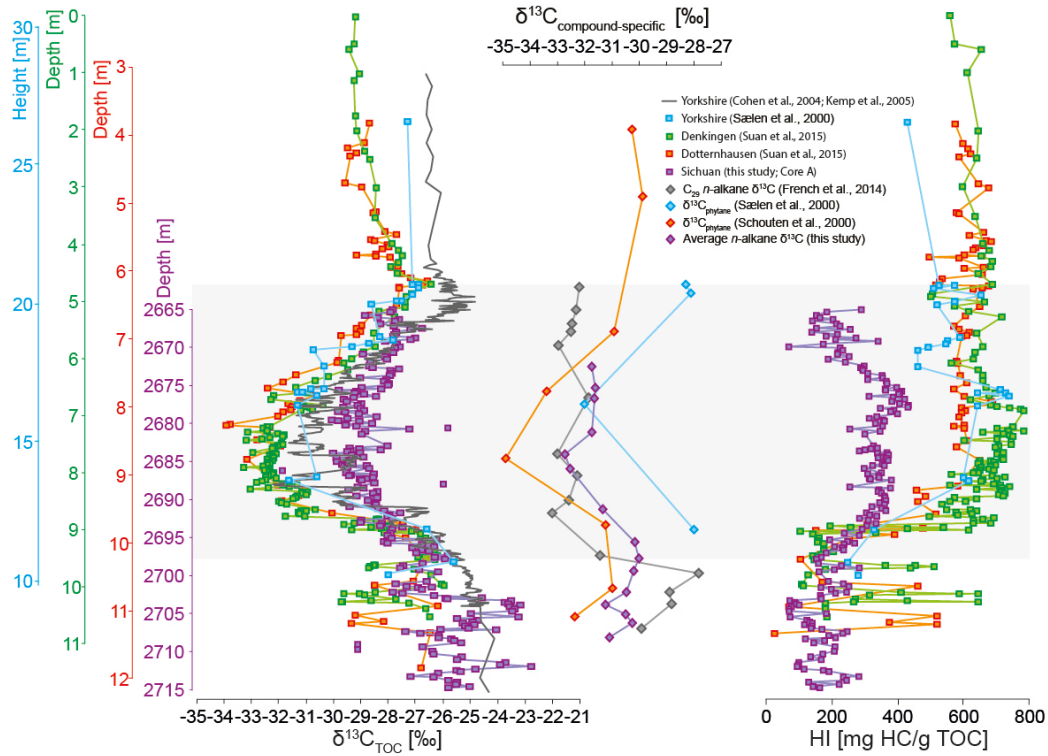


Figure 4.9 Comparison of the $\delta^{13}\text{C}_{\text{TOC}}$, $\delta^{13}\text{C}_{\text{compound-specific}}$, and HI records from Yorkshire, Dotternhausen, Denkingen and the Sichuan Basin (Sælen et al., 2000; Schouten et al., 2000; French et al., 2014; Suan et al., 2015), showing elevated HI values in all marine and lacustrine records, in concert with the T-OAE negative CIE in $\delta^{13}\text{C}_{\text{TOC}}$ and $\delta^{13}\text{C}_{\text{compound-specific}}$, with a ~3–4‰ negative excursion.

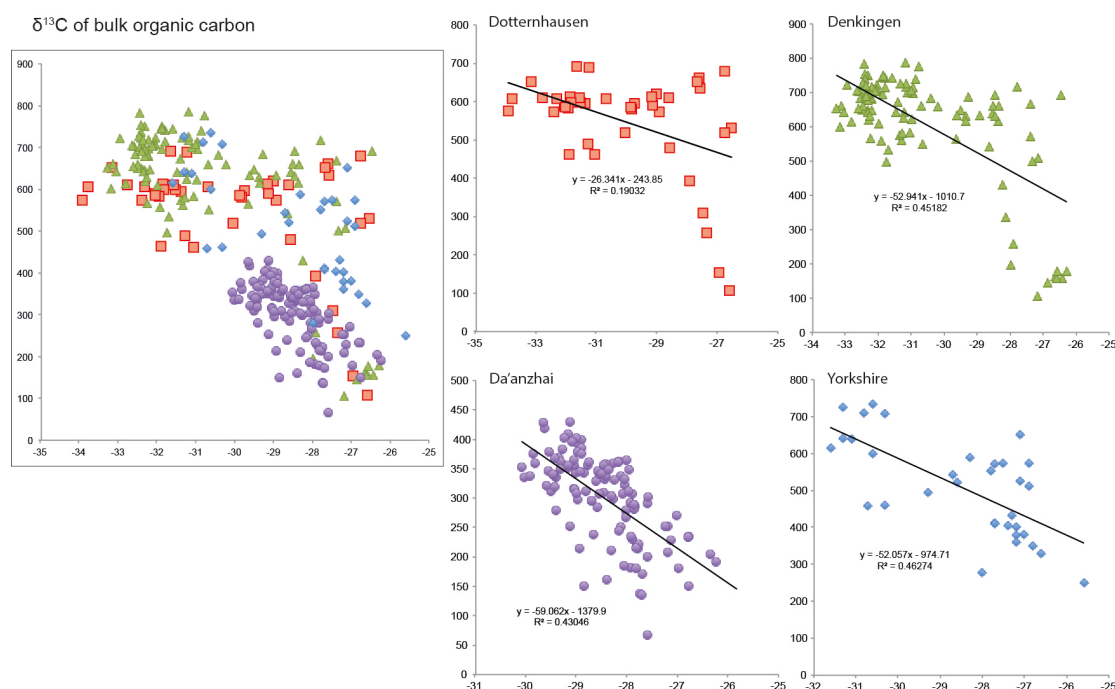


Figure 4.10 The cross-plot relationships between bulk organic $\delta^{13}\text{C}$ and Hydrogen Index (HI) from Yorkshire, Dotternhausen, Denkingen and the Sichuan Basin (Sælen et al., 2000; Schouten et al., 2000; French et al., 2014; Suan et al., 2015), showing correlations between bulk organic $\delta^{13}\text{C}$ and Hydrogen Index for all the marine and lacustrine records during the T-OAE negative CIE intervals, however, with a varying magnitude of correlation between different geological settings.

4.7 Depositional environment of the Da'anzhai Member

Terrestrial (fluvial/deltaic and soil) deposits of the Ma'anshan Member in the Mid- Early Jurassic Sichuan Basin pass up-section into the lacustrine facies of the Da'anzhai Member. Chemostratigraphic correlation between the more distal Core A and the more proximal Core B, based on elevated total organic carbon (TOC) and HI and the observed $\delta^{13}\text{C}_{\text{TOC}}$ negative CIE, suggests a diachronous base of the Da'anzhai Member, as defined by the presence of characteristic lacustrine facies lying

stratigraphically above palaeosols (Figure 4.2). The lower half of the Da'anzhai Member in Core A is marked by abundant fossiliferous limestone, primarily consisting of bivalve and ostracod shell fragments, alternating with more clay-rich sediments. This interval is also marked by generally low TOC (~1%) and HI values (~150 mg C/g TOC), likely suggesting a nearshore depositional environment with low aquatic organic matter productivity and/or preservation. The abrupt transition from palaeosol to fossiliferous limestone at ~2714.85 m, followed by the transition to laminated organic-rich black shale at ~2693.40 m in the more distal Core A, and the coeval transition from palaeosol to laminated organic-rich black shale at ~3156.34 m in Core B (Figure 4.2), suggests the rapid expansion and deepening of the lake, with decreased macrofossil carbonate supply (Figure 4.11). Macrofossils in the regularly occurring limestone beds show variable orientation and degrees of fragmentation and, depending on the stratigraphic horizon, are in life position, or were subjected to local transport and re-deposition. The marl and black shale interbeds are interpreted as representing quieter water sedimentation and/or sedimentation inimical to benthic life.

The fossil assemblages from both cores evidence a predominantly non-marine depositional environment, with the occurrence of the freshwater bivalve genus *Margaritifera* (Wang et al., 2010), lacustrine ostracods, and the freshwater/brackish alga *Botryococcus* (see Appendix D). However, some intervals in Core A (2684.49 m to 2695.80 m and 2702.49 m to 2710.73 m) contain *in situ* marine palynomorphs such as the acritarch *Veryhachium collectum* and the prasinophyte *Halosphaeropsis liassica* (Figure 4.2, see Appendix D). These occurrences suggest marine incursions into the basin. Significantly, the oldest sediments of the lacustrine Da'anzhai Member studied in Core A are devoid of acritarchs (Figure 4.2; see Appendix D), indicating that the lake had already developed before any potential marine incursion took place.

Furthermore, the relative abundance of acritarchs in the samples studied shows no positive correlation with TOC or (pyritic) sulphur abundance, indicating that deposition of the most organic-rich sediments and the supply of sulphate was unrelated to a potential marine connection. Sedimentary facies in Europe and elsewhere indicate that the early Toarcian witnessed a significant marine transgression, culminating in the *falciferum* ammonite biozone (Hallam, 1981; Suan et al., 2011). Although the Early Jurassic Sichuan Basin was surrounded by compressional mountain ranges in the north, east and west, the palaeo-Sichuan lake system likely formed close to sea level and the basin could, therefore, have been temporarily connected to the ocean to the south (Figure 4.1 and references herein, Figure 4.11). Overall, however, the abundance of freshwater fossils and palynomorphs, combined with a highly elevated radiogenic initial $^{187}\text{Os}/^{188}\text{Os}$ composition of ~ 1.29 (Appendix E), significantly higher than Early Jurassic Toarcian open marine $\text{Os}_{\text{initial}}$ values of 0.4–0.8 recorded from Europe (Percival et al., 2016), points to a dominantly lacustrine environment during the deposition of the Da'anzhai Member.

This interpretation is further supported by the presence of tetracyclic polyprenoids (TPP) (typically sourced from freshwater algae; Figure 4.4), the near absence of C_{30} steranes (typically sourced from marine algae; Figure 4.5) and high hopane over sterane biomarker ratios throughout Core A (Moldowan et al., 1985; Holba et al., 2000).

The consistent superabundance in both cores of the thermophylic pollen genus *Classopollis*, which is thought to have derived from gymnosperm conifers dwelling in regions marginal to bodies of water (Vakhrameyev, 1981), suggests high temperature conditions in the continental interior or along the shorelines of the palaeo-Sichuan lake system. Elevated atmospheric and marine temperatures during the T-OAE have also

been suggested from coeval marine records, also with increased abundance of *Classopollis* and the ^{18}O -depleted signature of macrofossil calcite (Vakhrameyev, 1981; Dera et al., 2011a; Jenkyns, 2003). A previous study of a section from Bornholm, Denmark suggested a sharp increase of atmospheric $p\text{CO}_2$ (reconstructed from leaf stomatal density) at the onset of the negative CIE (McElwain et al., 2005). The increased occurrence of *Classopollis* in tetrads (relative to single specimens; Figure 4.2) observed during the negative CIE interval suggests stressed environmental conditions on land during the T-OAE, likely in response to enhanced atmospheric $p\text{CO}_2$ and greenhouse-gas-induced climate warming (Vakhrameyev, 1981; Jenkyns, 2003; McElwain et al., 2005; Dera et al., 2011a; Kürschner et al., 2013).

The Toarcian mid-palaeolatitude setting and geomorphology of the palaeo-Sichuan Basin, with surrounding high mountain ranges (He and Zhu, 2012), may have made the basin susceptible to an enhanced monsoonal system and increased hydrological cycle with high amounts of run-off, particularly when warm shallow transgressive seas approached (cf. the modern South Asian monsoon; Boos and Kuang, 2010). The formation or dramatic expansion of the palaeo-lake system in the early Toarcian Sichuan Basin, with the deposition of the Da'anzhai Member lacustrine black shales with elevated TOC (of up to $\sim 3.3\%$) and HI (of up to 450 mg HC/g TOC) levels, suggests increased aquatic primary productivity, hypothetically due to increased continental weathering and accelerated riverine nutrient supply. Significantly, based on all the stratigraphic data herein (Figure 4.7), the level of maximum TOC enrichment in the Da'anzhai Member developed coevally with the organic-rich black shale in marine sections from Yorkshire, UK (Figure 4.7), consistent with a fundamental global climatic control on the introduction of nutrients into aquatic environments, even

though the quantity and type of organic matter deposited and preserved may have been different.

Elevated sulphur concentrations in the most organic-rich sections of laminated black shale of the Da'anzhai Member in Core A (Figure 4.7), coincide with the occurrence of small (<5 µm diameter) and also larger pyrite framboids (Figure 4.3). The source of sulphur is, however, as yet uncertain, but lake sulphate could originate from the weathering of the Lower–Middle Triassic evaporites in the hinterland (Cai et al., 2003). Although the larger pyrite framboids could have formed diagenetically in sulphide-rich sedimentary pore-waters, the smaller framboids (<5 µm) likely formed by sulphate reduction in the water column, as typically happens under euxinic conditions (Wilkin et al., 1996). The stratigraphic intervals with high (pyritic) sulphur concentrations coincide with levels of elevated sedimentary molybdenum enrichment (with Mo >20 ppm; Figure 4.7). In oxic conditions, Mo exists as soluble molybdate (MoO_4^{2-}) that adsorbs onto Mn-oxides and only slowly precipitates. In sulphidic (euxinic) waters, however, molybdate dissociates into thiomolybdate anions, which are rapidly reduced to highly reactive Mo(IV)-sulphides that precipitate out of solution, leading to sedimentary Mo enrichment (Dahl et al., 2013). Furthermore, water-column stratification, which is a likely prerequisite for sustained euxinia, is also supported by elevated levels of gammacerane in the black-shale interval of Core A (Figure 4.2). Gammacerane is a biomarker derived from tetrahymanol that forms in abundance under conditions of high bacterial productivity within stratified water columns, often in lakes or isolated marine basins (Sinninghe Damsté et al., 1995). The combined geochemical and mineralogical data suggest the development of a physically or chemically stratified water column during laminated black shale formation in the palaeo-Sichuan Lake, even in relatively proximal depositional settings.

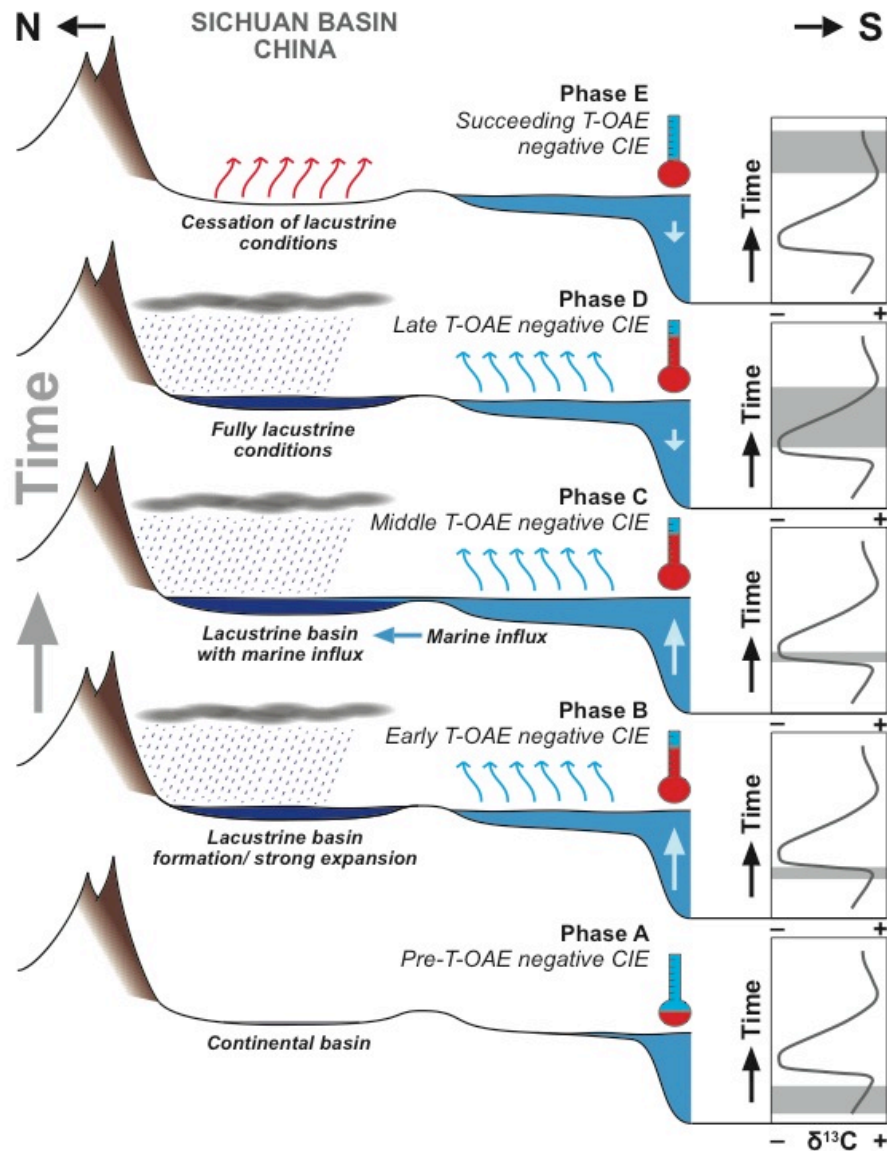


Figure 4.11 Model for the formation of lacustrine conditions in the Sichuan Basin. On the right are idealized $\delta^{13}\text{C}$ records across the T-OAE, with the stratigraphic intervals marked with grey shading representing the different phases in lake evolution. Phase: the continental Sichuan Basin was marked by fluvial and terrestrial sedimentary deposition pre-T-OAE negative CIE, with possibly geographically restricted lacustrine conditions in the central part of the basin. Phase B: early Toarcian temperature and sea-level rise increased evaporation from the approaching marine waters, enhancing the hydrological cycle and promoting precipitation in the continental interior of the Sichuan Basin, which resulted in the formation or strong expansion of the palaeo-Sichuan lake. Phase C: continuing late early Toarcian eustatic sea-level rise allowed for occasional marine incursions into the dominantly lacustrine palaeo-Sichuan Basin. Phase D: eustatic sea-level fall in the latest early Toarcian initiated the return to fully lacustrine conditions and maximum lacustrine organic-carbon burial. Phase E: global recovery from the early Toarcian climatic perturbation, with associated reduction in global temperature and cessation of enhanced hydrological cycling, initiated the return to a terrestrial and fluvial depositional environment in the Sichuan Basin.

4.8 Lacustrine carbon burial and the Toarcian carbon cycle

The early Toarcian negative CIE has been widely attributed to the release of ^{13}C -depleted volcanogenic CO_2 and/or methane from either thermal metamorphism of Gondwanan coals or the dissociation of sub-sea-floor gas hydrates, also resulting in enhanced early Toarcian atmospheric $p\text{CO}_2$ levels (Duncan et al., 1997; Hesselbo et al., 2000; McElwain et al., 2005; Ullmann et al., 2014). The typical early Toarcian $\delta^{13}\text{C}$ pattern, with a stepped negative shift interrupting an overarching positive excursion, has been observed in marine and terrestrial organic matter and shallow-water platform and deep-water pelagic carbonates and manifestly affected the entire ocean–atmosphere system (Hesselbo et al., 2000; Jenkyns et al., 2002; Kemp et al., 2005; Hermoso et al., 2009a). The overall positive shift is attributed to globally accelerated organic-carbon burial whereas the superimposed stepped negative shift suggests that the release of isotopically light carbon took place in pulses that have been attributed to astronomical forcing of the global carbon cycle (Kemp et al., 2005). Astronomical interpretation of periodic fluctuations in chemical and physical proxy records estimate the duration of the early Toarcian negative CIE at 300–900 kyr (Kemp et al., 2005, 2011; Suan et al., 2008; Boulila et al., 2014).

In the early Toarcian Sichuan Basin, the laminated black-shale interval in both cores is marked by elevated HI and TOC values (with HI up to 450 mg HC/g TOC and TOC up to 3.3% in the more distal Core A), likely reflecting increased algal primary productivity, in addition to a background supply of terrestrial organic matter, during the interval with the lowest carbon isotope values of the negative CIE. This chemostratigraphic pattern is very similar to that developed in marine sections from northern Europe, where sedimentary TOC-levels can locally reach ~20%. Box-model studies for the early Toarcian carbon cycle suggest that the release of ~9000 Gt carbon

from methane clathrates (with $\delta^{13}\text{C}$ of $\sim -60\text{‰}$) or $\sim 25,000$ Gt carbon as thermogenic methane (with $\delta^{13}\text{C}$ of $\sim -35\text{‰}$), is required to generate a negative $\delta^{13}\text{C}$ excursion compatible with the mean change in bulk carbonate of 4–6‰, and which would have caused an increase in atmospheric $p\text{CO}_2$ of ~ 1000 ppm (Beerling and Brentnall, 2007; Hesselbo et al., 2007; Hermoso et al., 2009a; Ullmann et al., 2014). Excess atmospheric CO_2 is assumed to have been sequestered both by enhanced weathering of Ca-Mg silicates due to greenhouse warming, and by massive burial of organic carbon in marine dysoxic, anoxic and euxinic depositional environments (Jenkyns, 2010). These combined processes would have dictated the pattern of $\delta^{13}\text{C}$ recovery, but the total amount of ^{13}C -depleted carbon released may have been even larger than modelled because enhanced ^{12}C -enriched carbon burial would have acted as a mechanism to potentially increase ocean-atmosphere $\delta^{13}\text{C}$ during the onset of the T-OAE, even though the resultant summed effect was to move values in the opposite direction.

Sequestration of carbon in marine basins is generally considered to have been a major driver behind $\delta^{13}\text{C}$ recovery. The sheer size of the latest Early Jurassic continental basins, and the expansion of this major lake in response to early Toarcian climatic (and possibly sea-level) change, however, provides an additional, and significant, sink for carbon. The Da'anzhai Member lacustrine black shale formed over $70,000 \text{ km}^2$ in the palaeo-Sichuan Basin, with thicknesses of 60–120 m and TOC contents of 0.8–3.5%; lacustrine marl and carbonate accumulated coevally over large parts of the remaining $160,000 \text{ km}^2$ of the basin (Zou, 2013).

The amount of total organic-carbon burial in the Da'anzhai Member of the Sichuan Basin alone is estimated using equation (1) and with the following parameters: Area1 (Da'anzhai Member black shale deposition) = $70,000 \text{ km}^2$; Thickness1 = 90 m; TOC1 = 2.2%; Density1 (shale) = $2.6 \times 10^3 \text{ kg/m}^3$; Area2 (Da'anzhai Member

limestone dominant) = 160,000 km²; Thickness2 = 50 m; TOC2 = 0.5%; Density2 (limestone) = 2.5×10^3 kg/m³ (Zou, 2013; Li and He, 2014 and this study). Therefore, the total amount of organic-carbon buried in this lake during the T-OAE was estimated to be 460 Gt.

$$(1) M_{\text{Sichuan}} = \text{Area1} * \text{Thickness1} * \text{Density1} * \text{TOC1} + \text{Area2} * \text{Thickness2} * \text{Density2} * \text{TOC2}$$

The amount of total inorganic-carbon burial (M_{IC}) in the Da'anzhai Member of the Sichuan Basin alone is estimated using equation (2), assuming that the Da'anzhai Member over the remaining 160,000 km² is on average ~50 m thick and consists on average of about 50% CaCO₃ (TC = ~6%). Therefore, the total amount of inorganic-carbon buried in this lake during the T-OAE was estimated to be 1200 Gt.

$$(2) M_{\text{IC}} = \text{Area2} * \text{Thickness2} * \text{Density2} * \text{TC}$$

Therefore, ~460 Gt of organic carbon and ~1200 Gt of inorganic carbon was extracted from the global ocean–atmosphere system and sequestered in the palaeo-Sichuan lake during deposition of the early Toarcian Da'anzhai Member black shales alone. This figure is, however, a conservative estimate because original sedimentary TOC values may have been even higher considering the present-day maturity of the rock. Also, TOC values in the deepest, most central part of the basin may have been more elevated than in the more proximal cores studied herein. Enhanced continental inorganic-carbon burial would not affect the isotopic composition of exogenic carbon reservoirs, but the burial of isotopically depleted organic carbon would shift the carbon-isotope composition of the global exogenic carbon cycle to more positive values.

Assuming the (pulsed) release of 9,000 Gt of carbon from methane clathrates (with a $\delta^{13}\text{C}$ of ~ -60‰) or 25,000 Gt as thermogenic methane (with a $\delta^{13}\text{C}$ of ~ -35‰)

to explain the observed step-wise negative shift in $\delta^{13}\text{C}$ (-5‰; from 1‰ to -4‰) during the T-OAE (Beerling and Brentnall, 2007), and assuming carbon sequestration largely by organic-matter burial (with a $\delta^{13}\text{C}$ of -25‰) to explain the observed recovery in global $\delta^{13}\text{C}$, the total (global) amount of organic (marine + terrestrial) carbon burial is estimated with a simple mass-balance calculation:

$$(3) (\delta^{13}\text{C}_{\text{Initial}} * M_{\text{Initial}}) + (\delta^{13}\text{C}_{\text{Add}} * M_{\text{Add}}) - (\delta^{13}\text{C}_{\text{TOC}} * M_{\text{TOC}}) = (\delta^{13}\text{C}_{\text{Initial}} * (M_{\text{Initial}} + M_{\text{Add}} - M_{\text{TOC}}))$$

The initial carbon-isotope ratio of the whole exogenic carbon reservoir is taken as $\delta^{13}\text{C}_{\text{Initial}} = 1\text{‰}$. M_{Add} and $\delta^{13}\text{C}_{\text{Add}}$ represent the amount and isotopic composition of the carbon released from either ocean-floor methane clathrates (with $M_{\text{Add}} = 9,000$ Gt and $\delta^{13}\text{C}_{\text{Add}} = -60\text{‰}$) or as thermogenic methane (with $M_{\text{Add}} = 25,000$ Gt and $\delta^{13}\text{C}_{\text{Add}} = -35\text{‰}$) (Beerling and Brentnall, 2007). Following this and equation (3), the total amount of organic-carbon burial (M_{TOC} , with an assumed $\delta^{13}\text{C}_{\text{TOC}}$ of the buried organic matter of -25‰), is estimated to be between ~21000 Gt (methane clathrates release model) and ~35000 Gt (thermogenic methane release model). The total amount of organic-carbon burial in the palaeo-Sichuan lake alone is therefore estimated to be 1.3–2.2% of the total (global) organic-carbon burial during the T-OAE.

Global organic-carbon burial explains the recovery of the global $\delta^{13}\text{C}$ signal to more positive value after its initial early Toarcian negative shift. Recovery of the global $\delta^{13}\text{C}$ signal would have been delayed if the early Toarcian lacustrine carbon sink in the palaeo-Sichuan Basin had not formed.

$$(4) M_{\text{TOC}} = [(M_{\text{TOC}} - M_{\text{Sichuan}}) / T_0] * T = [(M_{\text{TOC}} - M_{\text{Sichuan}}) / T_0] * [T_0 * (1 + \Delta)] = (M_{\text{TOC}} - M_{\text{Sichuan}}) * (1 + \Delta)$$

T_0 is the duration of the T-OAE; T is the duration of the T-OAE if the palaeo-Sichuan lake was not formed; and Δ is the % of additional time required to return to the pre-excursion values. M_{TOC} has been calculated as either 21,000 Gt (methane clathrate

release model) or 35,000 Gt (thermogenic methane release model); M_{Sichuan} has been estimated as 460 Gt.

Using equation (4) and with the assumption of constant climatic/environmental parameters affecting the rate of carbon drawdown, we compute that the early Toarcian global $\delta^{13}\text{C}$ signal would have taken 1.3–2.2% additional time to return to pre-excursion values (Figure 4.12). With an estimated 300–900 kyr duration for the early Toarcian negative CIE (Kemp et al., 2005, 2011; Suan et al., 2008; Boulila et al., 2014), lacustrine carbon sequestration therefore results in a shortening of the observed negative CIE by ~4–20 kyr. These figures are undoubtedly minima, given that several other latest Early Jurassic lacustrine basins containing organic-rich sediments also developed on both the South and the North China Blocks (Huang et al., 2003; Yang et al., 2005).

The present-day global lake surface area is about ~0.69% of the surface area of the global ocean; lakes, however, account for ~10% of the global carbon drawdown and burial (Dean and Gorham, 1998). The palaeo-Sichuan lake alone covered over ~230,000 km², which is ~10% of the present-day global lake surface, but it was responsible for, at least, 1.3–2.2% of the global organic-carbon burial. The generation of massive sinks of carbon in the early Toarcian continental interiors by the formation and/or expansion of major lakes and subsequent sequestration of carbon, in addition to marine carbon burial, potentially significantly impacts the nature and duration of the observed exogenic carbon-cycle perturbation. If the carbon sink of the Sichuan Basin black shale had not formed, and with the assumption of constant climatic/environmental parameters affecting the rate of carbon drawdown, the recovery from the $\delta^{13}\text{C}$ negative shift would have required an additional ~4,000–20,000 yr of global marine carbon drawdown (Figure 4.12). In addition, massive inorganic-carbon

burial in the Sichuan Basin, extracted from the ocean-atmosphere system, would have significantly lowered atmospheric $p\text{CO}_2$, which likely further shortened the Early Toarcian climatic perturbation. Given that several other lacustrine basins, for example, the Tarim and Ordos basins in northwestern and central northern China (Figure 4.1) also appear to have developed in the late Early Jurassic with the deposition of organic-rich sediments (Huang et al., 2003; Yang et al., 2005), these figures are undoubtedly minima.

These results suggest an as-yet-unexplored, negative feedback in the global exogenic carbon cycle during oceanic anoxic events. Climatic warming induced by addition of greenhouse gases to the atmosphere, and an associated increase in hydrological cycling, allowed for the formation of major lake systems in continental settings, where enhanced fluvial nutrient supply with increased productivity and preservation could have lead to major carbon sequestration. Together with widespread burial of organic matter in the marine realm, the lacustrine carbon sink would have reduced atmospheric $p\text{CO}_2$, allowed rebound of the global $\delta^{13}\text{C}$ signal, and cooled global climate through an inverse greenhouse effect (Jenkyns, 2003).

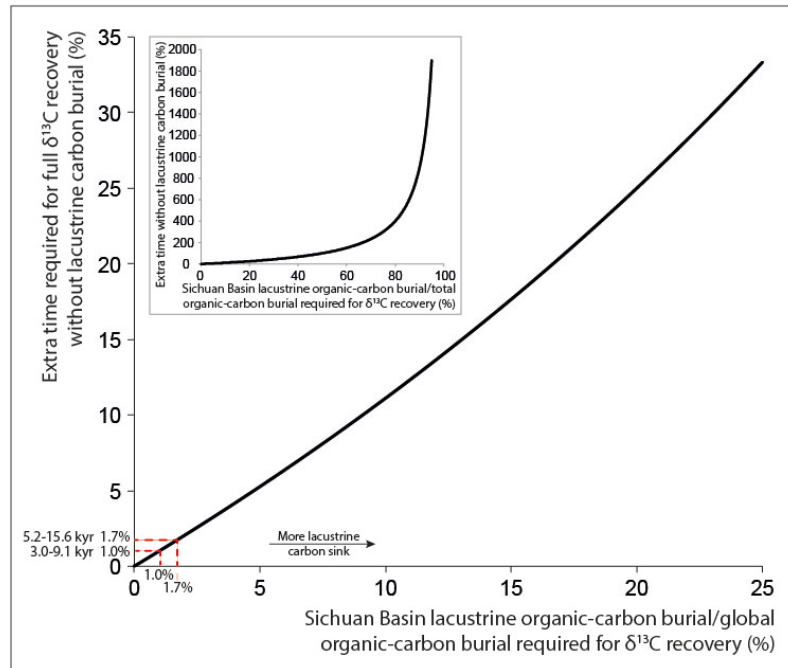


Figure 4.12 Computed % extra time required for the full recovery of the global $\delta^{13}\text{C}$ signal without an Early Toarcian lacustrine carbon sink vs the % size of the lacustrine carbon sink relative to global carbon burial. The additional time needed for full recovery of the $\delta^{13}\text{C}$ to pre-excursion values, if the lacustrine carbon sinks in the palaeo-Sichuan Basin had not formed, correlates exponentially with the size of the lacustrine carbon sink relative to the global carbon sink.

Chapter 5

Organic geochemistry and organic petrography of the Lower Jurassic Toarcian lacustrine Da'anzhai Member, Sichuan Basin, China

This Chapter is modified from **Xu et al.**, Organic geochemistry and organic petrography of the Lower Jurassic Toarcian lacustrine Da'anzhai Member, Sichuan Basin, China. *Organic Geochemistry, in preparation*. Olga Gorbanenko helped with the counting and identification of organic macerals. All other data were generated by myself, including the photos of the organic macerals.

5.1 Introduction

The early Toarcian Oceanic Anoxic Event (T-OAE at ~183 Ma), one of the most intense and geographically extensive events of oceanic redox change and accompanying organic-carbon burial in the Mesozoic Era, is well expressed in both marine and lacustrine environments from both hemispheres (Jenkyns, 1985, 1988, 2010; Al-Suwaidi et al., 2010; Xu et al., 2017). The T-OAE has been described in detail in the introduction section of chapters 2, 3 and 4.

Marine depositional environments and redox conditions during the T-OAE are relatively well constrained, showing enhanced burial of organic matter due to an increased primary productivity and carbon flux to the sea floor, as well as elevated water-column stratification in shallower water semi-restricted marine basins (Farrimond et al., 1989; Jenkyns, 2010; French et al., 2014).

Chapter 4 on the upper Lower Jurassic Da'anzhai Member from the Sichuan Basin, China demonstrated the first stratigraphically well-constrained lacustrine record associated with the early Toarcian Oceanic Anoxic Event (Xu et al., 2017, Chapter 4 of this thesis). A rise in lake level and a more stratified water body have been indicated by sedimentary and biomarker evidence, probably due to enhanced hydrological cycling in response to early Toarcian climatic change. The consequential massive organic-carbon burial in lacustrine systems likely played an important role in the recovery of the global carbon-cycle perturbation (Xu et al., 2017, Chapter 4 of this thesis).

A lacustrine depositional setting for the Jurassic Da'anzhai Member has been previously proposed based on the occurrences of specific assemblages of macro- (bivalve genus *Margaritifera*) (Wang et al., 2010) and micro- (*Botryococcus* alga) fossils, as well as molecular biomarker evidence, such as the high abundance of

tetracyclic polyprenoids (TPP; typical for lacustrine depositional environments) and the near absence of C₃₀ steranes (n-propyl cholestanes; typically sourced from marine algae) (Xu et al., 2017, Chapter 4 of this thesis). Further evidence for lacustrine depositional conditions is provided by the very radiogenic initial ¹⁸⁷Os/¹⁸⁸Os ratios of ~1.29 which are significantly higher than normal Jurassic seawater values of 0.4–0.8 recorded in relatively open-marine environments (Percival et al., 2016) and up to 1.0 in very restricted marine basins (Cohen et al., 2004). Indications for brief incursions of seawater into the palaeo-Sichuan Basin, in the form of occasional acritarchs, prasinophytes and common marine palynomorphs have been proposed to record global marine transgressions during the Toarcian (Xu et al., 2017, Chapter 4 of this thesis). Total organic carbon (TOC) contents and hydrogen indices (HI) are seen to increase significantly during the period of elevated lake levels (Xu et al., 2017; Chapter 4 of this thesis). However, the type and morphology of the organic matter in these sections and the source of the extractable organic matter (lipid content) has not been hitherto examined.

In this study, a comprehensive geochemical and petrographical examination of the extractable and non-extractable sedimentary organic matter is undertaken utilizing multiple techniques (Rock-Eval, molecular biomarker analysis, palynology and organic petrography) to (1) improve understanding of the depositional and redox conditions of the lacustrine Sichuan Basin before and during the T-OAE; and (2) determine the nature of the sedimentary biomass within the studied succession.

5.2 Geological setting

The present-day geographic Sichuan Basin covers a total area of $\sim 230,000 \text{ km}^2$ (Cai et al., 2003), with the Early Jurassic Sichuan Basin (and the palaeo-Sichuan lake system) thought to have been even larger (Guo et al., 2011; Figure 5.1). Detailed geological background of the Early Jurassic Sichuan Basin has been described in Chapter 4 of the thesis. Although recent studies have indicated potential marine incursions into the palaeo-Sichuan lake based on the presence of acritarchs in certain horizons of the Da'anzhai Member (Xu et al., 2017, Chapter 4 of this thesis), the depositional environment of the Da'anzhai Member was still dominantly lacustrine.

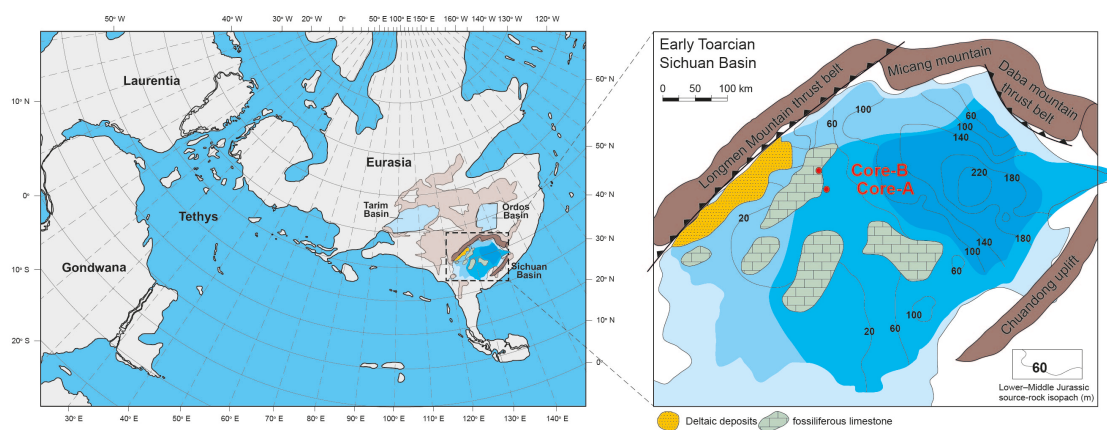


Figure 5.1 Size and location of the palaeo-Sichuan lake at 179 Ma (from Chapter 4 of the thesis). The map on the left shows a regional tectonic plate reconstruction at 179 Ma (edited from a map provided by CGG Robertson and Shell), with positions of the latest Early Jurassic lacustrine Sichuan, Tarim and Ordos Basins marked. The map on the right illustrates the location of the two cores studied within the Sichuan Basin; relative variations in lake depth are illustrated in blue, with the darker shade representing deeper water areas; the green brickwork represents fossiliferous limestone and the yellow dotted ornaments represent deltaic deposits; palaeo-mountain ranges are marked in brown and the Da'anzhai Member isopachs are also indicated.

The two cores studied here are located in the more proximal part of the palaeo-Sichuan lake (Figure 5.1). Core A ($\sim 50 \text{ m}$) and Core B ($\sim 70 \text{ m}$) penetrate almost the complete Da'anzhai Member with less than $\sim 4 \text{ m}$ of palaeosol sediments at the base

(Xu et al., 2017, Chapter 4 of this thesis) (Figure 5.2). The Da'anzhai Member is composed of lacustrine fossiliferous limestone (mainly comprising shell fragments of freshwater bivalves and ostracods), dark mudstone and laminated black shale. The laminated black shale in Core A is mainly in the upper part of the core and is interbedded with fossiliferous limestone at metre-scale over a thickness of ~20 m. The top of Core A is characterized by two thick carbonate beds, each of which is ~3.5 m thick. Core B is richer in carbonate content and the fossiliferous limestone contains bigger shell fragments than that in Core A. The shell fossils in a limestone unit in Core B are commonly more complete than those in Core A and likely dominated by the same species in similar sizes. Black shale in Core B is not obviously laminated and commonly contains fine pieces of shell fragments. The identified macrofossil species in the Da'anzhai Member (Wang et al., 2010), the palynological assemblages, the Re-Os radiometric age of 180.3 ± 3.2 Ma generated from Core A and the distinct negative carbon-isotope excursions in both Core A and Core B together define the age of the Da'anzhai Member in this part of the Sichuan Basin to be time-equivalent to the Toarcian Oceanic Anoxic Event (T-OAE) (Xu et al., 2017, Chapter 4 of this thesis).

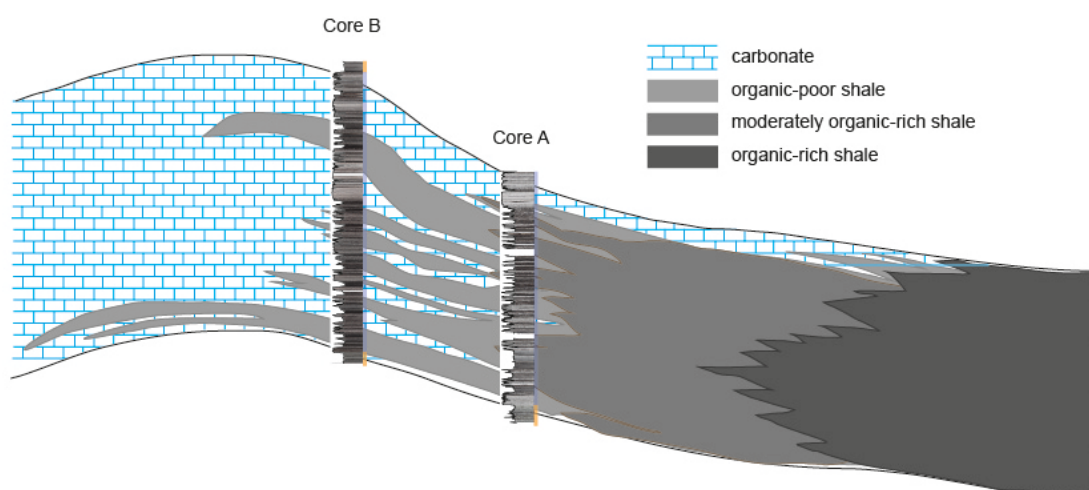


Figure 5.2 Locations of the Core A and Core B in relation to the lithofacies. No cores from the deeper facies are available for study. The schematic facies in the deeper part of the basin is based on Ryder (1991), Guo et al. (2011), He and Zhu (2012), Zou (2013), Li and He (2014).

5.3 Materials and methods

5.3.1 Samples and analytical overview

TOC and Rock Eval data, carbon-isotope profiles (bulk organic matter and the long-chain *n*-alkanes), major- and trace-element concentrations and palynomorph assemblages of the Da'anzhai Member in Core A and B, were previously investigated by Xu et al. (2017, Chapter 4 of this thesis). Based on these results, 6 samples from Core A were selected for organic petrography/maceral analysis, which span the whole interval of the carbon isotope excursion (CIE) from high TOC intervals. Further, 22 samples from Core A and 5 samples from Core B were selected for detailed analyses of extractible fractions. In addition to the bulk sample and selected *n*-alkane compound-specific carbon-isotope analyses previously carried out, carbon-isotope and Rock Eval analyses were also undertaken on residual organic matter after solvent extraction to eliminate any possible effects of contamination by migrated hydrocarbons.

5.3.2 Organic petrology

A total of 6 core samples (diameter of 3 cm) from Core A were cut perpendicular to the bedding plane. Each block sample was embedded in epoxy resin, and subjected to dry polishing to avoid the swelling of the clay minerals. Semi-quantitative and qualitative analyses were carried out using a Leica DMRX microscope. The polished blocks were analyzed in both reflected white light and fluorescence illumination under oil immersion at a magnification of 500x. Vitrinite reflectance is estimated based on the rare occurrence of detrital vitrinite in the samples.

The nomenclature of Taylor et al. (1998) was used for the macerals of the vitrinite and inertinite groups, and that of Hutton (1987) for the liptinite group.

5.3.3 Total lipid extraction

Sample preparation and biomarker analysis were undertaken at the Organic Geochemistry Laboratory facilities at Shell Global Solutions International in Rijswijk (The Netherlands). Total lipid fractions were obtained by extraction using a Dionex ASE® 350 Accelerated Solvent Extractor (ASE). Detailed methodology has been described in section 2.3.7.1 of Chapter 2.

5.3.4 Gas chromatography-flame ionization detector (GC-FID)

The total extract fraction was analyzed using an Agilent 7890A chromatograph with an Agilent 7693 Autosampler to examine the overall distribution of normal, branched and cyclic alkanes and aromatic compounds. Agilent Ultra 1 column (50 m × 0.2 mm internal diameter, 0.11 µm film thickness) was used with the following temperature program for the oven: 35°C (5 min) – 4°C/min – 325°C (15 min). Samples were injected splitless and the injector was set at 325°C. Flow is 25 cm/sec He and Pressure is 31 psi.

5.3.5 Column chromatography

An aliquot of the TLE was separated over AgNO₃-impregnated silica gel columns into saturate, aromatic and resin fractions. After pre-conditioning of the column with cyclohexane and application of the TLE, the saturate fraction was eluted with *n*-hexane, the aromatic fraction with toluene and the resin fraction with acetone (3 column volumes each).

A mixture of known amounts of standard was added to the aromatic fraction at this stage prior to analysis using Gas Chromatography/Mass Selective Detection.

5.3.6 Branched/cyclic fraction separation

The retrieved saturate fraction of each sample was subsequently separated into *n*-alkane and branched/cyclic alkane fractions using zeolite molecular sieve beads (0.5 nm). The molecular sieve beads were activated in an oven for 3 hours at 120°C, added to the saturate fraction (evaporated to dryness first) and left standing overnight in cyclo-hexane to trap the *n*-alkane fraction.

The cyclohexane, containing the branched/cyclic (b/c) fraction, was transferred to a separate vial and beads were rinsed a few times with cyclohexane, which was then added to the b/c fraction. A known amount of standard was added to the b/c fraction at this stage. The b/c fractions were subsequently analyzed using Gas Chromatography/tandem mass spectrometry (GC/MSxMS).

A *n*-pentane:cyclo-hexane mixture (88:12) was added to the molecular sieve beads (containing the entrapped *n*-alkanes) and left overnight to release the *n*-alkanes. The *n*-alkane fraction of each sample, dissolved in the *n*-pentane:cyclo-hexane solution, was concentrated and transferred to an autosampler vial.

5.3.7 B/c and aromatic fractions analysis

B/c fractions were analysed using an Agilent 7890A GC system coupled to an Agilent 7000 Triple Quadrupole Mass Spectrometer. Column and temperature program have been described in section 2.3.7.4 of Chapter 2. A selected set of parent-daughter mass transitions was scanned to monitor the compounds of interest. Compounds were identified in the respective mass transition chromatograms by comparison of their retention times and elution order to standard samples. For selected samples the system was run in full scan GC/MS mode to confirm identifications with full mass spectra.

Aromatic fractions were analyzed using an Agilent 7890B GC system coupled to an Agilent 5973 mass selective detector (MSD). Column and temperature program have been described in section 2.3.7.4 of Chapter 2. It was run in selective ion mode (SIM) scanning for the masses of interest. Compounds were identified in the respective mass chromatograms by comparison of their retention time and elution order with standard samples.

5.3.8 Carbon isotope analysis on ASE-extracted residue

Bulk $\delta^{13}\text{C}$ analyses were performed on one gram of homogenized ASE-extracted residue sample which had been treated with 40 mL cold HCl (3 molar) to dissolve any carbonate. Samples (dissolved in 3 molar HCl) were then placed on a hot plate for 2 hours at 60°C, then rinsed 4 times with distilled water to reach neutral pH. About 1–15 mg (depending on TOC concentrations) of this oven-dried and powdered sample residue was weighed into 8×5 mm tin capsules and prepared for $\delta^{13}\text{C}$ analyses. These analyses were performed on a Sercon Europa EA-GSL sample converter connected to a Sercon 20-22 stable-isotope-ratio mass-spectrometer running in continuous flow mode with a helium carrier gas with a flow rate of 70 ml/min. Carbon-isotope ratios were measured against an internal alanine standard ($\delta^{13}\text{C}_{\text{alanine}} = -26.9\text{‰} \pm 0.2\text{‰}$ V-PDB [Vienna Peedee belemnite]) using a single-point calibration, at the Research Laboratory for Archaeology and History of Art (RLAHA), University of Oxford, UK. The in-house (RLAHA) alanine standard is checked weekly against the certified USGS40, USGS41, and IAEA-CH-6 international reference standards, with a long-term average alanine $\delta^{13}\text{C}$ value of -26.92‰ and a standard deviation of 0.15‰.

5.3.9 Rock-Eval pyrolysis on ASE-extracted residue

Rock-Eval analyses were performed on the ASE-extracted residue samples with a Rock-Eval 6 Standard Analyzer unit from Vinci Technologies, at the Department of Earth Sciences (University of Oxford). These analyses provided direct and derived data for S1, S2, Tmax, S3co/ S3co₂ (New Oxygen Index), S4co/ S4co₂ (Residual Organic Carbon), S5 (Mineral Carbon), to calculate the Total Organic Carbon (TOC, in %), Hydrogen Index (HI, in mg HC/ g TOC) and Oxygen Index (OI, in mg CO₂/g TOC). Laboratory procedures and measurement precisions have been described in section 2.3.1 of Chapter 2.

5.4 Results

5.4.1 Rock-Eval and Carbon-isotope record of the ASE-extracted residue

The pseudo-Van Krevelen diagram (HI vs Tmax) (following Delvaux *et al.*, 1990) shows that the organic matter in the Da'anzhai Member of Core A is primarily composed of type II and type II+III kerogen, with the majority of samples from the interval of the T-OAE negative CIE located in the kerogen type II region. Based on the Tmax values (444–460 °C), the Core A section reached peak oil maturity at a Vitrinite Reflectance equivalent (VR/E) of about 0.8% (Figure 5.3).

Bulk powders of the 22 samples from Core A (where biomarker analyses were afterwards performed) show TOC values of 0.7–3.0%, Hydrogen Indices (HI) of 98–393 mg HC/g TOC and Production Indices (PI) of 0.15–0.34 (Figure 5.4; Xu *et al.*, 2017, Chapter 4 of this thesis). S1 varies between 0.42 mg/g and 3.17 mg/g and S2 varies between 1.57 mg/g and 11.64 mg/g. Rock-Eval analyses were also performed on the 22 ASE-extracted residues from Core A. As expected, these residues show a small decrease in TOC and a significant drop in PI (due to removal of the extractible organic

matter), and a modest residual HI, compared to the original un-extracted samples (Figure 5.4).

The carbon-isotope records generated from this dominantly non-extractable organic matter (ASE-extracted residue) vary between -22.70‰ and -29.02‰ for Core A and -23.49‰ and -26.40‰ for Core B (Figure 5.4) and follow the overall same trends seen in the bulk profiles, although the latter are slightly more enriched in ^{13}C .

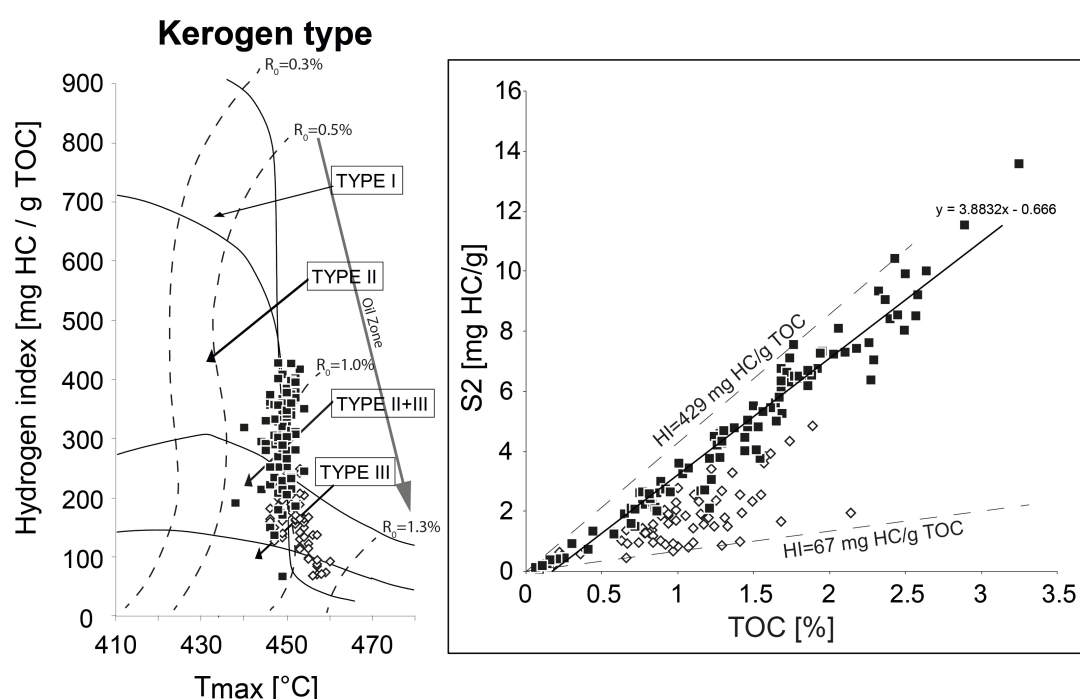


Figure 5.3 Kerogen characterization for Core A. On the left is the pseudo-Van Krevelen diagram (HI vs Tmax) (following Delvaux *et al.*, 1990) and on the right is the S2-TOC cross-plot. The black full squares represent samples from the interval of the negative carbon-isotope excursion; the black open diamonds represent samples from the interval outside of the negative carbon isotope excursion.

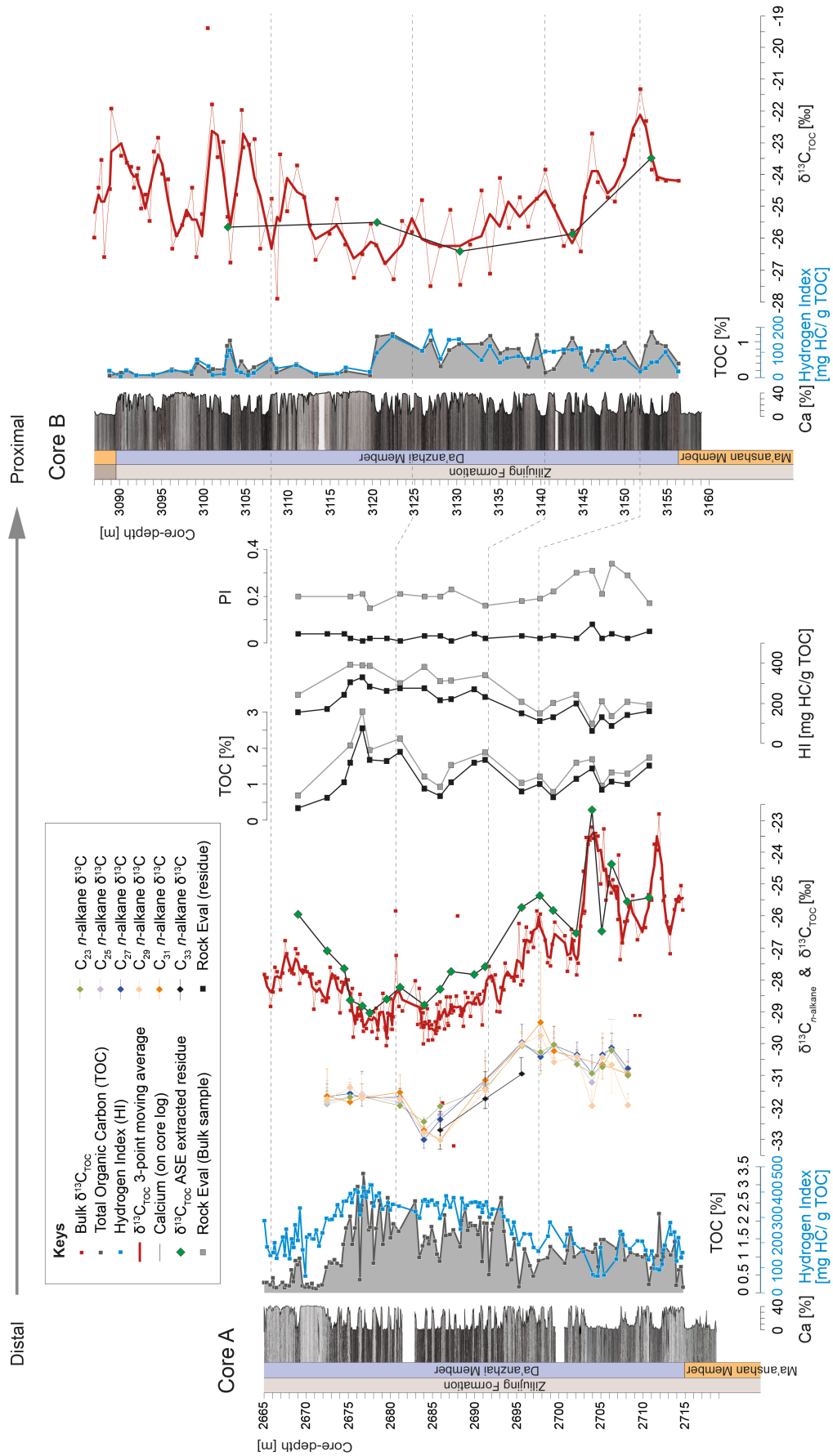


Figure 5.4 Chemostratigraphic (carbon-isotope) correlation between Core A and Core B. Carbon-isotope ratios of the bulk organic matter and the long-chain *n*-alkanes are from Xu et al. (2017, Chapter 4 of this thesis) and carbon-isotope ratios of the ASE-extracted residues from Core A and Core B are from this study. Calcium concentrations are plotted on top of the combined core photos for both cores to illustrate the lithology change, with lighter colours and high Ca% representing limestone and darker colour and lower Ca% representing shale. High-resolution TOC and HI records are plotted in grey shaded area and blue square dots (Xu et al., 2017, Chapter 4 of this thesis). Rock Eval parameters including TOC, HI and PI from the samples that have been processed for biomarker analysis are compared between measurements on the whole rock (black full square symbols) and the ASE-extracted residue (grey full square symbols)

5.4.2 Organic petrology

6 samples from Core A that were analyzed by organic petrography have TOC values ranging from 0.69% to 2.25% and HIs between 194 and 386 mg HC/g TOC. The Tmax ranges from ~449–453°C, indicating peak oil maturity (vitrinite reflectance equivalent: VR/E of about 0.8 to 0.9%).

Preparation of the samples and the semi-quantification of the macerals listed in Table 5.1 were undertaken by Olga Gorbanenko. All major maceral groups are present in the 6 samples, including vitrinite, inertinite and liptinite. Liptinite, the generally more H-rich and fluorescing maceral group, is subdivided into primary and secondary types. Primary liptinite includes sporinite, alginite and liptodetrinite, whereas the secondary liptinite includes migrabitumen and oil droplets (Figure 5.5: Plates 1, 2 and 3).

Macerals of vitrinite and inertinite group are commonly associated with type III and IV kerogen, respectively, whereas liptinite macerals are associated with type I/II kerogen. Qualitative and semi-quantitative characterization of the recognizable organic and mineral matter has been listed in Table 5.1 in vol.%.

Sample	Depth [m]	Rock Eval				Organic matter [vol.%]														Mineral matter [vol.%]		
						Vitrinite (V)		Liptinite (L)							Inertinite (I)							
		S1	S2	TOC	HI	autochthonous	recycled	Spor.	Tel.	Alginite			Liptd.	Migrabitumen	Oil drop.	Fus.	Semifus.	Intd.	Micr.			
										discrete	lamalginate	layered										
30	2669.03	0.42	1.68	0.69	243	0.0	0.1	0.0	0.1	0.4	0.0	0.0	2.0	0.3	0.4	0.6	0.1	0.1	0.0	61.9	4.0	30.0
105	2677.5	1.34	7.45	1.93	386	0.0	0.1	0.0	0.8	0.1	0.1	0.0	0.9	0.1	0.0	0.8	0.2	0.0	0.0	93.9	2.5	0.5
139	2681.17	1.77	6.77	2.25	301	0.0	0.1	0.0	0.4	0.0	0.0	0.0	0.6	0.7	5.0	0.4	0.1	0.0	0.0	68.0	1.7	23.0
221	2691.25	1.21	6.39	1.88	340	0.0	0.0	0.0	0.1	0.0	0.0	0.0	0.4	0.1	0.1	1.0	0.1	0.1	0.0	97.2	0.7	0.2
315	2702.13	1.63	3.83	1.58	242	0.0	0.1	0.0	0.2	0.1	0.0	0.0	0.3	0.2	1.4	1.3	0.2	0.1	0.1	69.5	0.5	26.0
396	2710.73	0.69	3.35	1.73	194	0.0	0.0	0.0	0.1	0.0	0.0	0.0	0.2	0.2	2.0	0.6	0.3	0.1	0.1	84.0	0.4	12.0

Spor. = spores; Tel. = telalginite; fil. = filamentous; Intd. = linopteridinite; Oil drop. = oil droplets; Fus. = fusinite; Semifus. = semifusinite; Intd. = inertopteridinite; Micr. = micrinite.

Spor. - sporinite; Tel. - telalginite; fil. - filamentous; Liptd. - liptodetrinite; Oil drop. - oil droplets; Fus. - fusinite; Semifus. - semifusinite; Intd. - inertodetrinite; Micr. - micrinite.

Table 5.1 Results of qualitative and semi-quantitative characterization of organic and mineral matter in samples from Core A (undertaken by Olga Gorbanenko).

Vitrinite group macerals are rare and are dominated by allochthonous (recycled/oxidized/reworked) particles with a minor amount of autochthonous (indigenous/detrital (transported not far away)) ones. The autochthonous type commonly shows a dark-grey colour under reflected white light and sharp edges, whereas the allochthonous vitrinite is characterized by round edges, absence of fluorescence and high reflectivity. Inertinite includes fusinite, semifusinite, inertodetrinite and secondary micrinite. Among the inertinite group, semifusinite has the darkest colour, followed by fusinite, whereas pyrofurinite has the lightest colour and highest reflectivity under reflected white light. Funginite particles, likely resulting from fungal and microbial degradation, are observed in several samples (Figure 5.5: Plate 3).

Sporinite, exhibiting an orange fluorescing colour, is observed in several samples but not quantified (Figure 5.5: Plate 2). The alginite group is further subdivided into telalginite and lamalginite. The telalginite and lamalginite show yellow to orange fluorescing colours of moderate intensity (lamalginite has slightly lower intensity), indicating oil-window maturity. Telalginite is derived from large, thick-walled unicellular algae, whereas lamalginite is derived from a variety of thin-walled unicellular planktonic or benthic algae (Hutton, 1987). Significantly, a high proportion of telalginites in Core A comprise the green alga *Botryococcus* as well as

other freshwater algae (*Pediastrum*?) and a few acritarchs and prasinophytes (Figure 5.5: Plates 1 and 2). These observations are in agreement with the previous palynological study on the same core (Xu et al., 2017, Chapter 4 of this thesis). Apart from these recognizable primary macerals, there are also varying amounts of bituminite (structureless/amorphous organic matter – SOM/AOM) dispersed in the groundmass, which is commonly very fluorescent and indicative of H-rich material. Oil droplets are observed mainly in the pore space of zooclasts. *Botryococcus*-derived telalginites are often observed close to the oil droplets and some show the transition to a bitumen phase, indicative of incipient conversion to oil (Figure 5.5: Plate 1). It is likely that *Botryococcus* is thus the sources for the oil droplets observed. Whether the oil droplets are indigenous or migrated from far away has been further investigated by comparing the carbon-isotope compositions of the total bulk rock, the *n*-alkanes and the ASE-extracted residues.

Samples from the upper part of Core A (e.g. samples 105 and 139), which have elevated TOC and HI values, also contain *Botryococcus*-derived telalginites that are generally larger in size and with smaller inertinite particles. By contrast, the lower part of the core contains smaller particles of *Botryococcus* and larger and more abundant inertinites, in the form of fusinite, semifusinite and pyrofusinite (likely related to wood or peat fires). Rare filamentous lamalginite, exhibiting moderate fluorescence (lower than that of telalginite), was observed in sample 315 (2702.13 m).

Measurement of the autochthonous vitrinite gave an initial estimate of the vitrinite reflectance (VR) as ~0.82–0.85% R_0 .

Minerals, including varying amounts of mica, quartz, pyrite and calcium carbonate (mainly shell fragments), have been recognized in all the samples. Pyrite in samples 105 and 139 is framboidal and very small in size (diameters commonly <5

µm), likely formed in an anoxic water column, whereas in the samples from the lower part of the core pyrite occurrence is represented by large framboids or as euhedral crystals, and likely formed below the sediment-water interface during early diagenesis due to sulphate reduction in pore water.

Figure 5.5 Photos of different macerals from Core A.

Plate 1: Examples of telalginite (specifically *Botryococcus-derived*) showing an orange-yellow colour of moderate intensity in the UV light and dark grey-brownish colour in the reflected white light (oil immersion).

(A-1) & (A-2) *Botryococcus*-derived telalginite close to oil droplets under UV and reflected white light (139);

(B-1) & (B-2) *Botryococcus*-derived telalginite under UV and reflected white light (139);

(C-1) and (C-2) bitumen originated from *Botryococcus* under UV and reflected white light (221);

(D) *Botryococcus*-derived telalginite under UV light (139);

(E) *Botryococcus*-derived telalginite close to oil droplets under UV light (315);

Plate 2: Examples of liptinite (sporinite, liptodetrinite, telalginite) and zooclast (fish bone) (oil immersion).

(F-1) & (F-2) sporinite and liptodetrinite in orange colour under UV light and dark grey under reflected white light (315);

(G) sporinite showing an orange colour under UV light (396);

(H) oxidized sporinite that is poorly preserved in orange-yellow colour under the UV light (221);

(I) bitumen showing a dark grey colour and low reflectance in reflected white light (315);

(J) telalginite in bright orange colour under UV light (221);

(K-1) & (K-2) a relict of fish bone showing bright orange fluorescence under UV light and dark grey colour in reflected white light (139);

Plate 3: Examples of inertinite particles (fusinite, semifusinite and funginite) (oil immersion).

(L-1) & (L-2) funginite particle showing a light grey colour under reflected white light and dark grey under UV light (396);

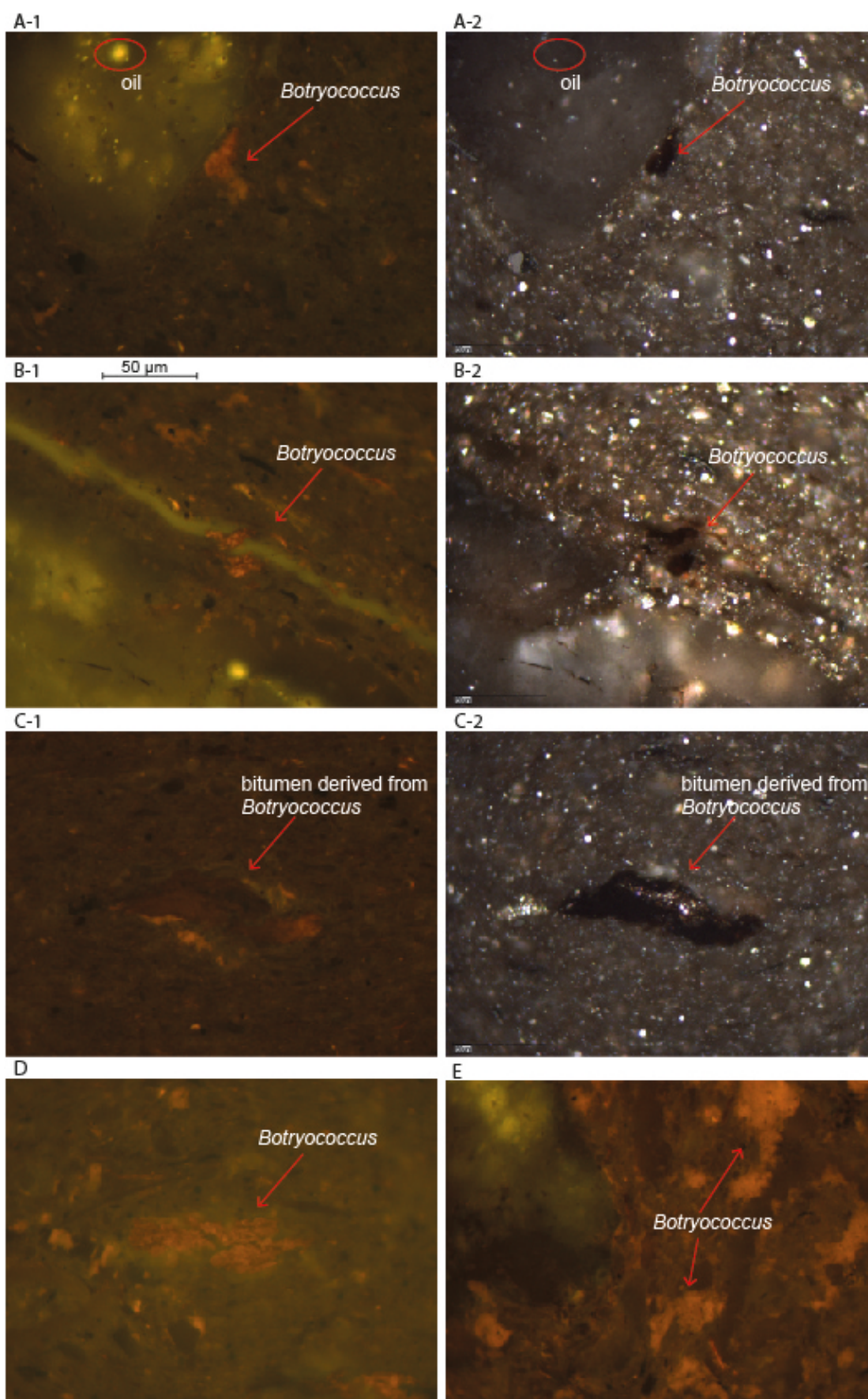
(M-1) & (M-2) fusinite particle showing high-reflecting light grey colour under reflected white light and dark grey under UV light (396);

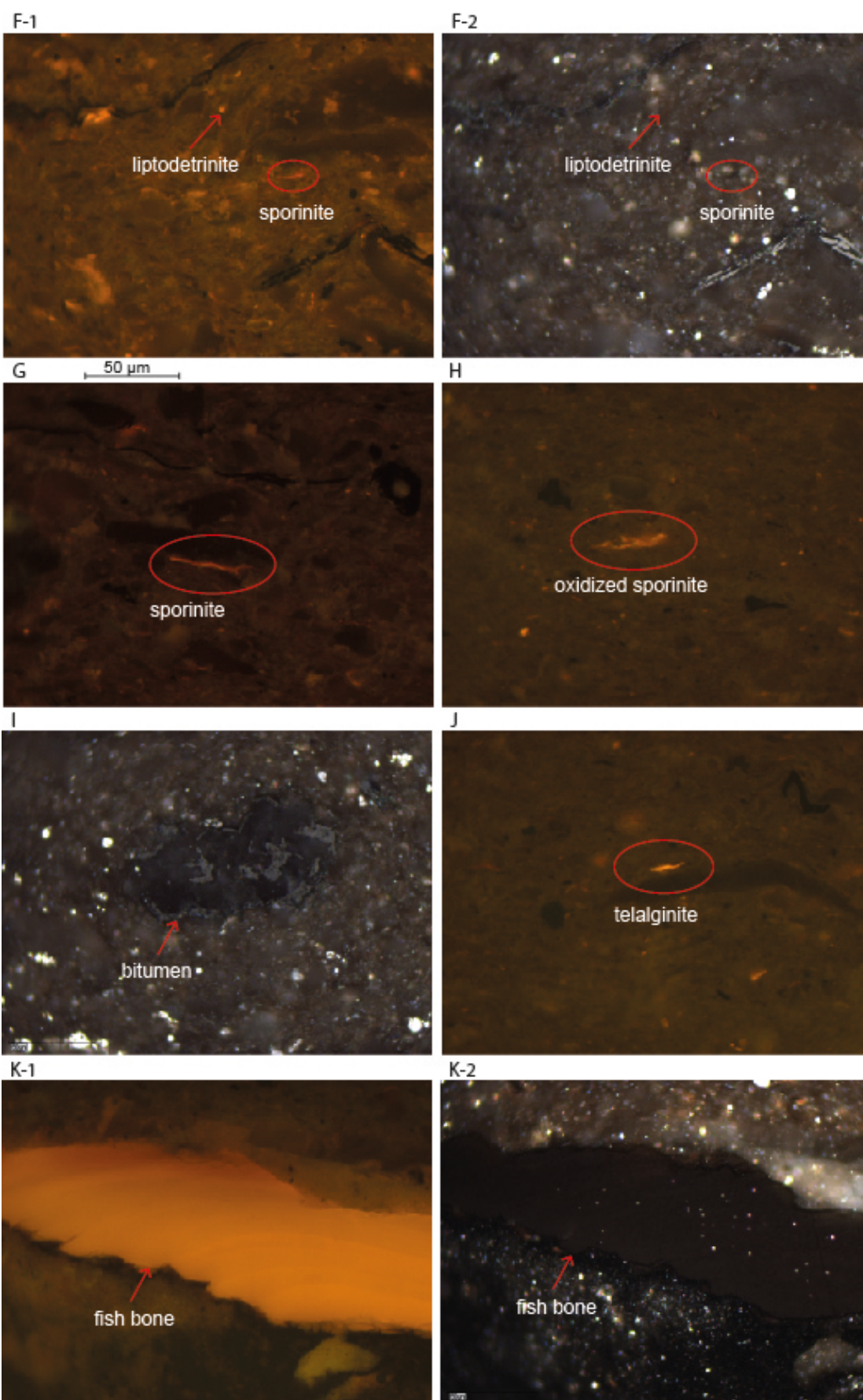
(N) funginite particle showing a light grey colour under reflected white light (221);

(O) fusinite particle exhibiting a high-reflecting light grey colour under reflected white light (221);

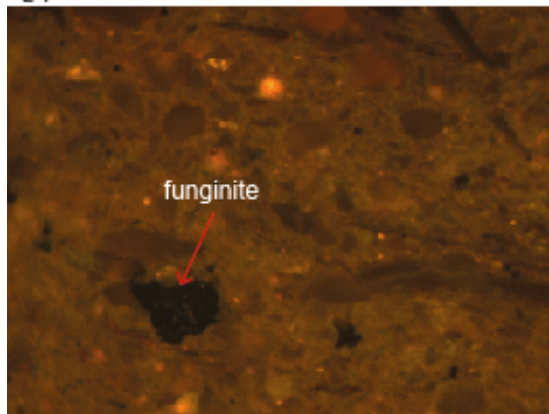
(P) fusinite particle showing high-reflecting light grey colour under reflected white light (396);

(Q) semifusinite particle showing grey colour under reflected white light (396).

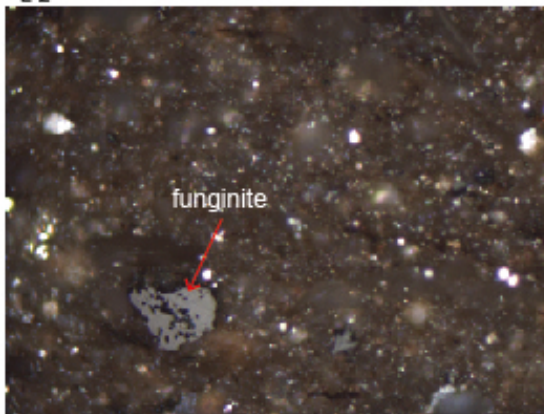




L-1



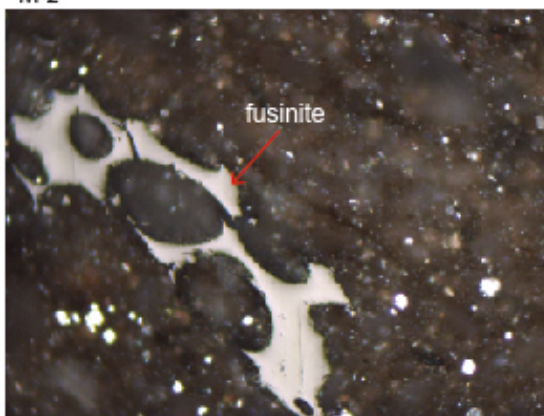
L-2



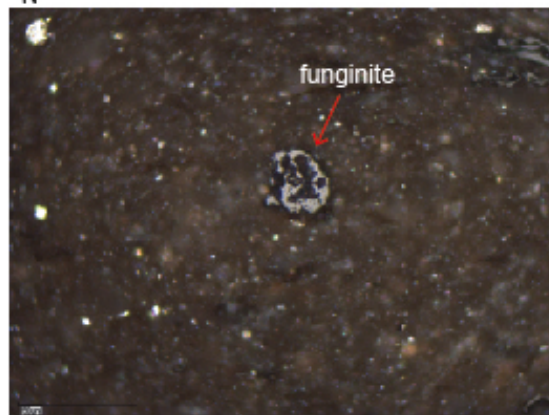
M-1



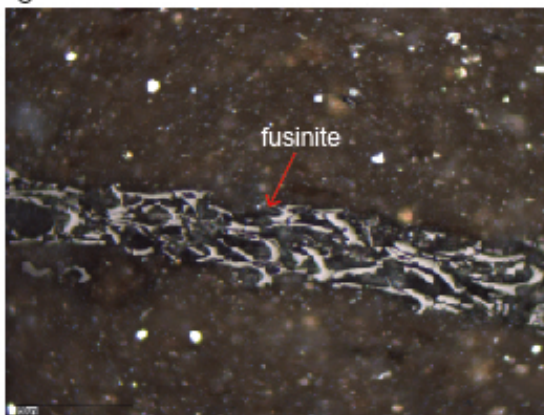
M-2



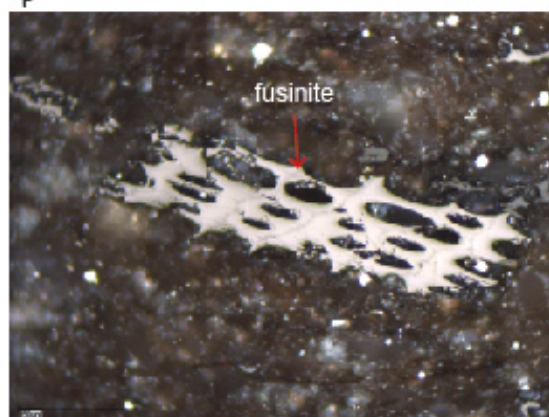
N



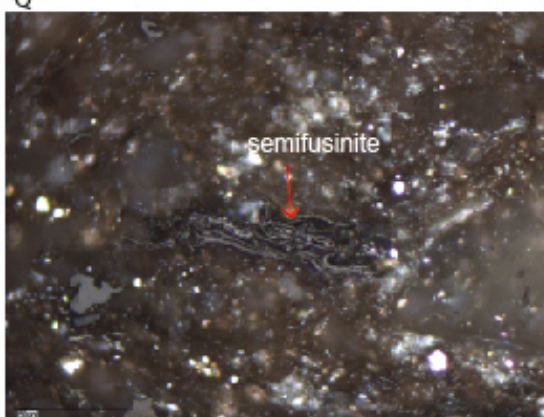
O



P



Q



5.4.3 Extractable Organic Matter

All the samples yielded abundant solvent extracts, particularly samples of the black shale. Detailed results of the straight-chain (*n*-alkanes and acyclic isoprenoids), the branched/cyclic (penta-, tetra- and tricyclic terpanes) and the aromatic fractions are discussed below.

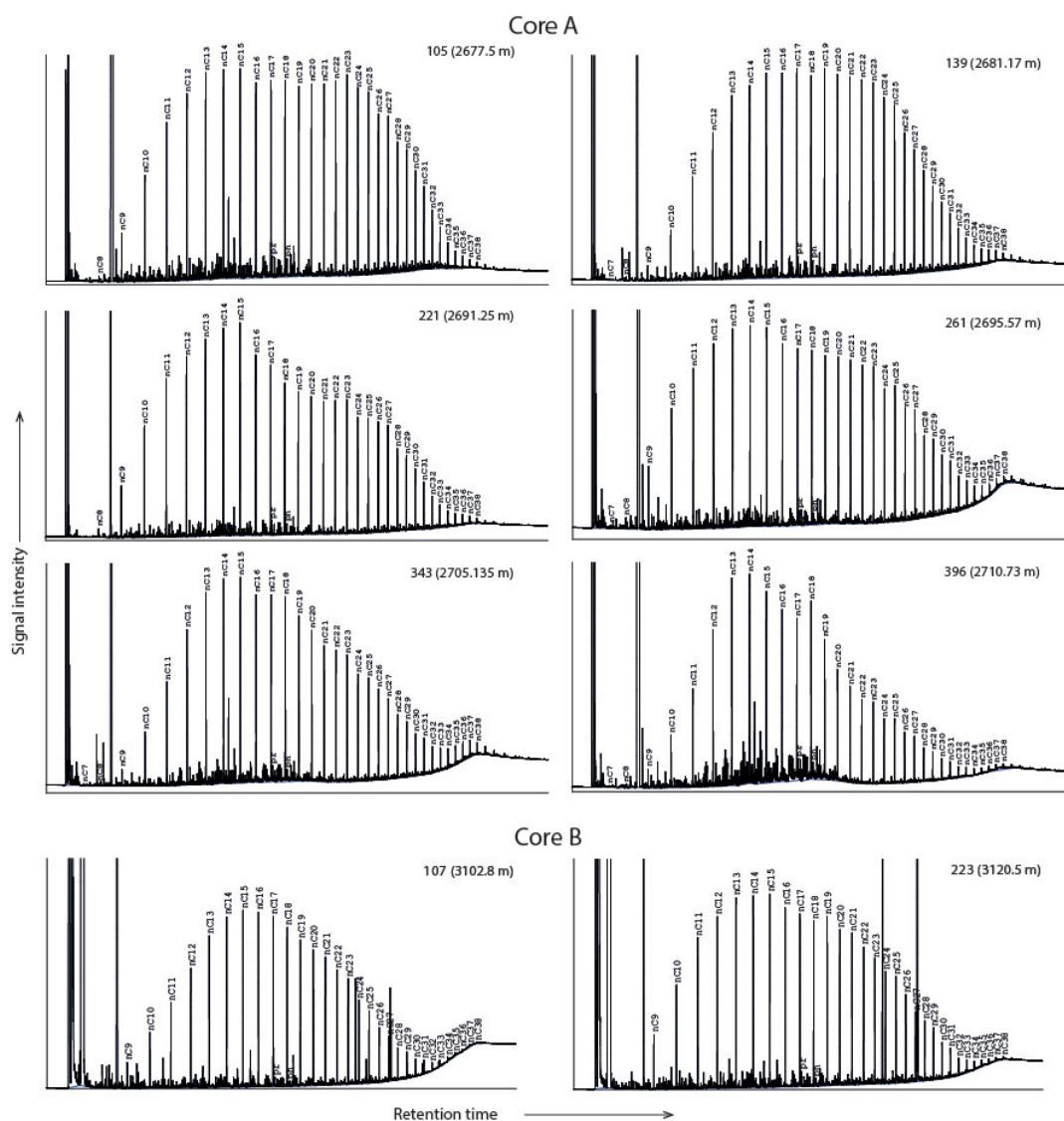


Figure 5.6. GC/FID traces of the total lipid extracts from 6 samples in Core A and 2 samples in Core B. The two high peaks in the Core B samples are likely contaminants.

5.4.3.1 TLE (total lipid extract) analyses

The GC-amenable fractions of the TLE for selected samples from Cores A and B are shown in Figure 5.6. The fractions are clearly dominated by *n*-alkanes, with subordinate amounts of branched, cyclic and aromatics, indicating highly paraffinic extracts and also varying degrees of waxiness, exhibited by the relative amounts of short-, medium- and long-chain *n*-alkanes. The peaks of the *n*-alkanes and the acyclic isoprenoids (pristane (Pr; 2,6,10,14-Tetramethylpentadecane) and phytane (Ph; 2,6,10,14-Tetramethylhexadecane, C₂₀H₄₂)) are integrated in the GC traces of the total lipid extracts by comparing with the internal standard calibrated based on literature data. All the samples have carbon preference index (CPI) values of ~1.0, showing little or no preference of either odd- or even-numbered alkanes, which is probably attributable to the maturity of the samples (Xu et al., 2017, Chapter 4 of this thesis). Some samples do show vestiges of an odd-over-even predominance around C₂₃-C₂₉ (e.g. samples 105 and 261, indicating an initially odd-over-even predominance with subsequent levelling out due to cracking upon increase in maturity) (Figure 5.6).

The *n*-alkane profiles exhibit gradual changes in the relative proportions of the short-, intermediate- and long-chain lengths between the 3 stratigraphic intervals in Core A (Figure 5.6), as illustrated by the two samples in the upper part of the black-shale interval (at 2677.5 m and 2681.17 m), the two samples in the lower part of the black shale interval (at 2691.25 m and 2695.57 m), and the two samples in the carbonate-rich lower part of the core (at 2705.135 m and 2710.73 m). All the samples from the three intervals have relatively high concentrations in the low carbon-number *n*-alkanes (C₁₃–C₁₅). The two samples at the upper part of the black-shale interval both have high concentrations of mid-chain length (C₂₃ or C₂₅) *n*-alkanes, similar in peak height to the low-chain *n*-alkanes (C₁₃ or C₁₅). The concentration of the mid-chain *n*-

alkanes decreases in the extracts from the lower part of the black-shale interval and is minimal in the carbonate-rich interval in the lower part of the core.

The isoprenoids pristane (Pr) and phytane (Ph) are much lower in abundance relative to the *n*-alkanes in all the samples studied, with the Pr/n17 ratios of 0.04–0.26 and the Ph/n18 ratios of 0.08–0.25. The Pr/Ph ratios are between 0.82 and 1.57.

5.4.3.2 Pentacyclic triterpenoids

3 samples, one at depth 2681.17 m (from the laminated black-shale interval in the upper part of Core A), one at depth 2702.13 m (from the carbonate-rich interval in the lower part of Core A) and one at depth 3120.5 m (from Core B), are used as representatives to illustrate the chromatograms of the GC/MS and GC/MSxMS results of the penta-, tetra-, tricyclic terpanes.

Hopane peaks were identified in the saturate fraction using GC/MSxMS mass transitions from 370, 384, 398, 412, 426, 440, 454, 468 and 482 to 191, specific to C₂₇ to C₃₅ hopanes (Figure 5.7). The hopanes in the Da'anzhai Member of both cores show unique features with strikingly high concentrations of rearranged hopanes, including 17 α (*H*)-diahopanes, 18 α (*H*)-neohopanes and the 'early eluting' hopanes (9,15 dimethyl-25,27-bisnorhopanes; Nytoft et al., 2007) (Figure 5.7). The 17 α , 21 β hopane, diahopane and early eluting hopane with carbon numbers C₃₁ to C₃₅ all exhibit the S and R isomer doublets and their concentrations generally decrease as the carbon number increases. The one exception is the anomalous amounts of C₃₂ $\alpha\beta$ hopane S and R isomers in extracts from Core A, whose peak heights are slightly elevated relative to those of the C₃₁ $\alpha\beta$ hopane S and R isomers.

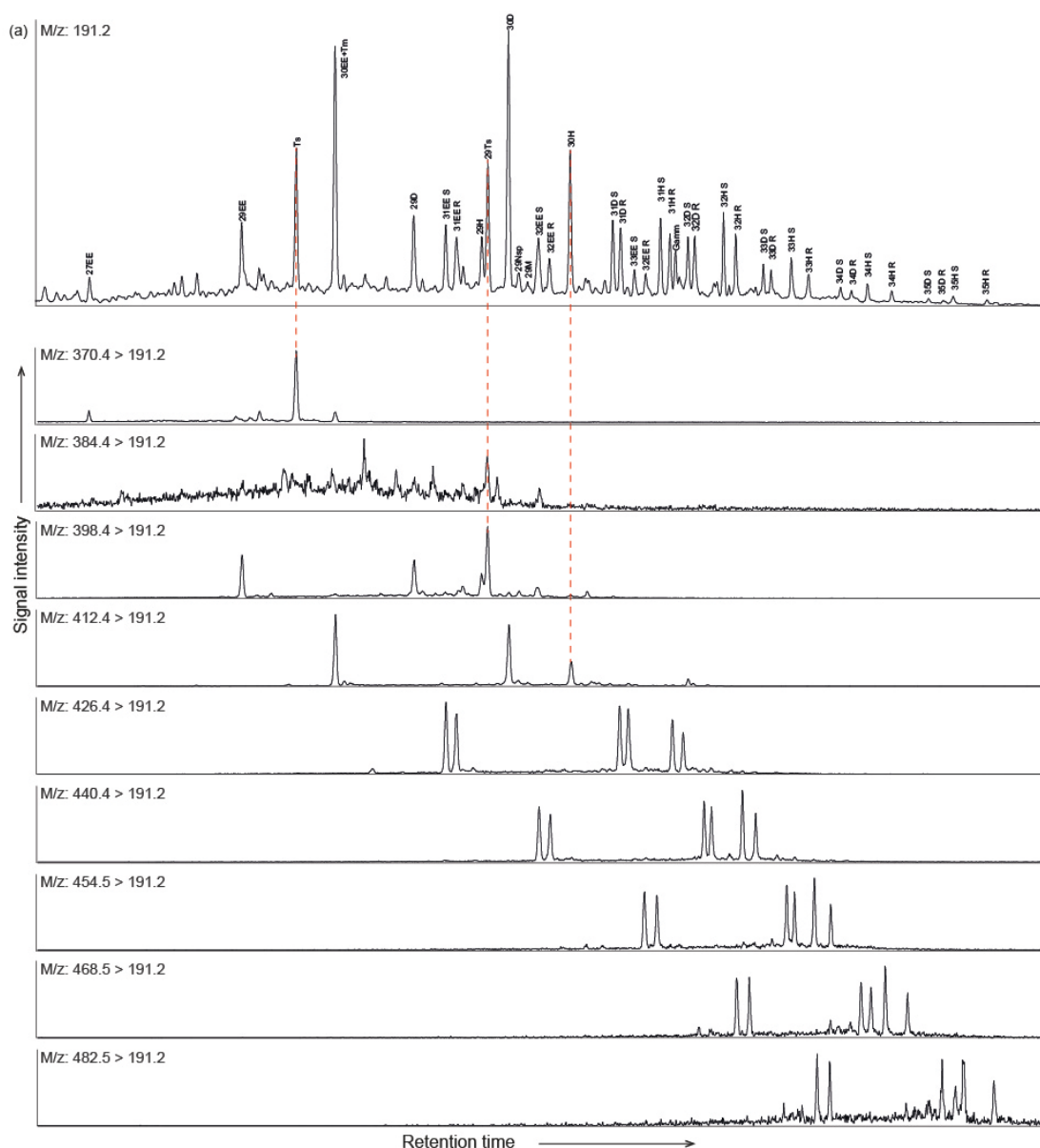
Another rearranged hopane, C₂₉ 28-Nor-spergulananes (29Nsp; mass transition 398→191; Figure 5.7), is also present and has been reported previously as being

abundant in some oils from lacustrine source rocks in South East Asia (Nytoft et al., 2006). C_{29} and C_{30} 17β , 21α hopane (moretane) are also present, although the C_{29} moretane shows stronger signals than the C_{30} moretane (Figure 5.7).

Gammacerane was identified and quantified by GC/MSxMS parent–daughter mass transition m/z $412 \rightarrow 191$, as was the 17α -hopane (C_{30} hopane), in order to calculate the ratios of gammacerane/ C_{30} hopane, commonly used as an index to indicate the degree of water-column stratification.

3β -methylhopane, derived from (mainly) methane-oxidising bacteria and commonly abundant in some lake settings, was identified in the GC/MSxMS parent–daughter mass transition m/z $426 \rightarrow 205$ (Farrimond et al., 2004; Brocks et al., 2005; Welander and Summons, 2012), albeit in low concentrations.

Figure 5.7 Chromatogram of m/z 191 from GC/MS aligned with panels of mass chromatograms of C_{27} – C_{35} hopanes from GC/MSxMS data. (a) depth 2681.17 m (Core A); (b) depth 2702.13 m (Core A); (c) depth 3120.5 m (Core B). In the GC/MSxMS panels, the different transitions all have the same range for the x -axis and are all auto-scaled for the y -axis.



Abbreviations:

27EE: C_{27} 9,15-dimethyl-25,27-dinorhopane (early eluting hopane)

Ts: C_{27} 18a-22,29,30-trisnorneohopane

Tm: C_{27} 17a-22,29,30-trisnorhopane

29EE: C_{29} 9,15-dimethyl-25,27-dinorhopane (early eluting hopane)

29D: C_{29} 15a-methyl-17a-27,30-dinorhopane (diahopane)

29H: C_{29} 17a,21b-30-norhopane

29Ts: C_{29} 18a-30-norneohopane

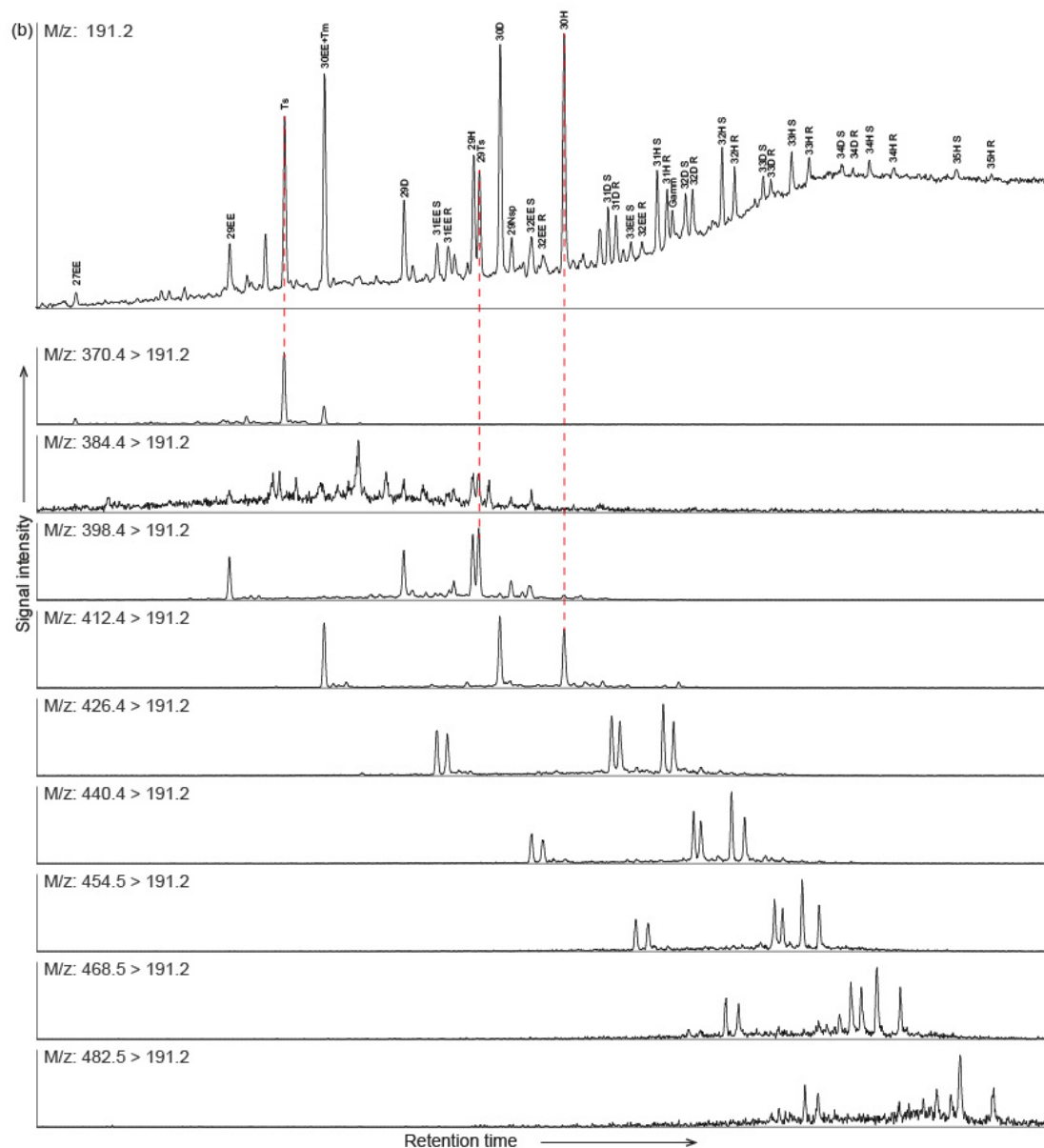
29Nsp: C_{29} 17b,18a-21-methyl-28-nor-spergulane

29M: C_{29} 17b,21a-30-norhopane

30EE: C_{30} 9,15-dimethyl-25,27-dinorhopane (early eluting hopane)

30D: C_{30} 15a-methyl-17a-27-norhopane (diahopane)

30H: C_{30} 17a,21b-hopane



Gamm: Gammacerane

31EE S: C₃₁ 9,15-dimethyl-25,27-dinor,22(S)-hopane (early eluting hopane)

31EE R: C₃₁ 9,15-dimethyl-25,27-dinor,22(R)-hopane (early eluting hopane)

31D S: C₃₁ 15a-methyl-17a,22(S)-27-norhomohopane

31D R: C₃₁ 15a-methyl-17a,22(R)-27-norhomohopane

31H S: C₃₁ 17a,21b,22(S)-homohopane

31H R: C₃₁ 17a,21b,22(R)-homohopane

32EE S: C₃₂ 9,15-dimethyl-25,27-dinor,22(S)-hopane (early eluting hopane)

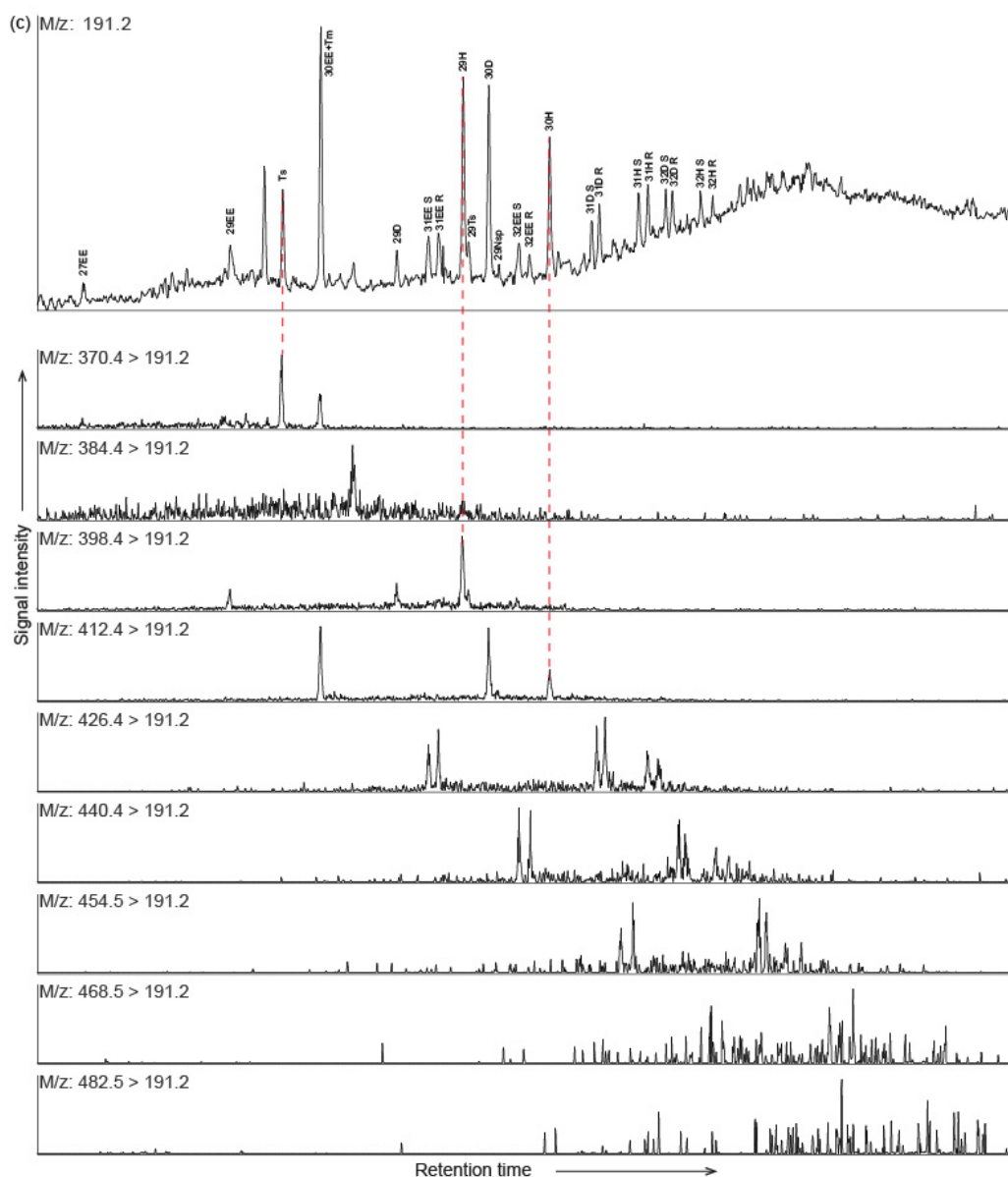
32EE R: C₃₂ 9,15-dimethyl-25,27-dinor,22(R)-hopane (early eluting hopane)

32D S: C₃₂ 15a-methyl-17a,22(S)-27-norhomohopane

32D R: C₃₂ 15a-methyl-17a,22(R)-27-norhomohopane

32H S: C₃₂ 17a,21b,22(S)-homohopane

32H R: C₃₂ 17a,21b,22(R)-homohopane



33D S: C₃₃ 15a-methyl-17a,22(S)-27-norhomohopane

33D R: C₃₃ 15a-methyl-17a,22(R)-27-norhomohopane

33H S: C₃₃ 17a,21b,22(S)-homohopane

33H R: C₃₃ 17a,21b,22(R)-homohopane

34D S: C₃₄ 15a-methyl-17a,22(S)-27-norhomohopane

34D R: C₃₄ 15a-methyl-17a,22(R)-27-norhomohopane

34H S: C₃₄ 17a,21b,22(S)-homohopane

34H R: C₃₄ 17a,21b,22(R)-homohopane

35D S: C₃₅ 15a-methyl-17a,22(S)-27-norhomohopane

35D R: C₃₅ 15a-methyl-17a,22(R)-27-norhomohopane

35H S: C₃₅ 17a,21b,22(S)-homohopane

35H R: C₃₅ 17a,21b,22(R)-homohopane

5.4.3.3 Tetracyclic triterpenoids

The parent–daughter mass transitions m/z 372→217, 386→217, 400→217, 414→217 were used to detect C₂₇, C₂₈, C₂₉ and C₃₀ steranes (the S and R isomers of 14 α ,17 α -cholestane, 14 β ,17 β -cholestane, 13 α ,17 β -diacholestane, 13 β ,17 α -diacholestane), respectively. The parent-daughter mass transition m/z 414→217 does not show obvious peaks in any of the samples analysed, indicating the near absence of C₃₀ steranes (24-*n*-propylcholestanes), normally sourced from marine algae. Dinosteranes, sourced from dinoflagellates, are not present in any of the samples studied.

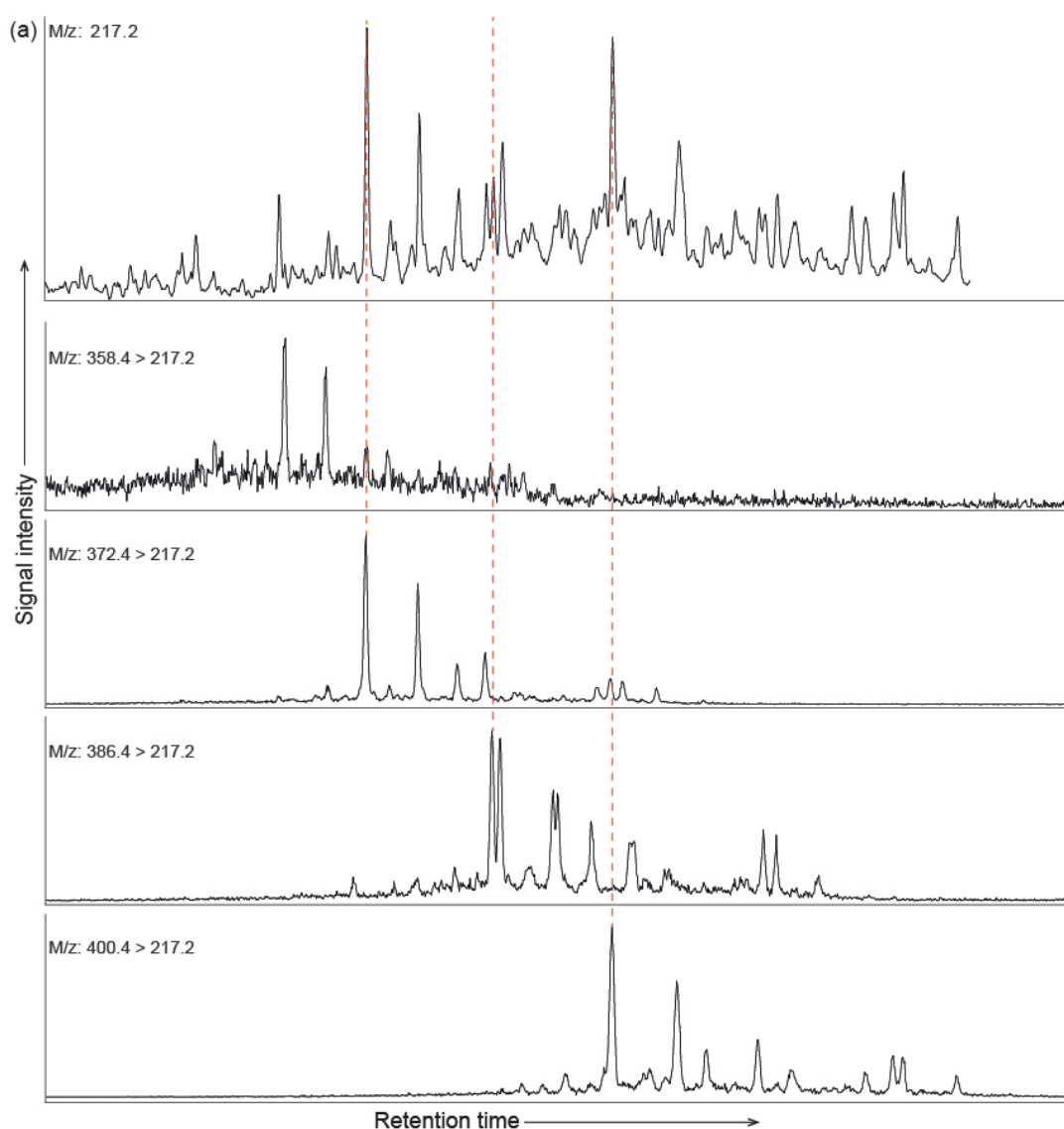
Examples of the m/z 217 mass-chromatogram traces (GC/MS) aligned with the parent–daughter mass transitions m/z 358→217, 372→217, 386→217, 400→217 are illustrated in Figure 5.8. The distributions of C₂₇, C₂₈ and C₂₉ steranes vary slightly among the different samples. All the samples show high concentrations of diasteranes relative to steranes.

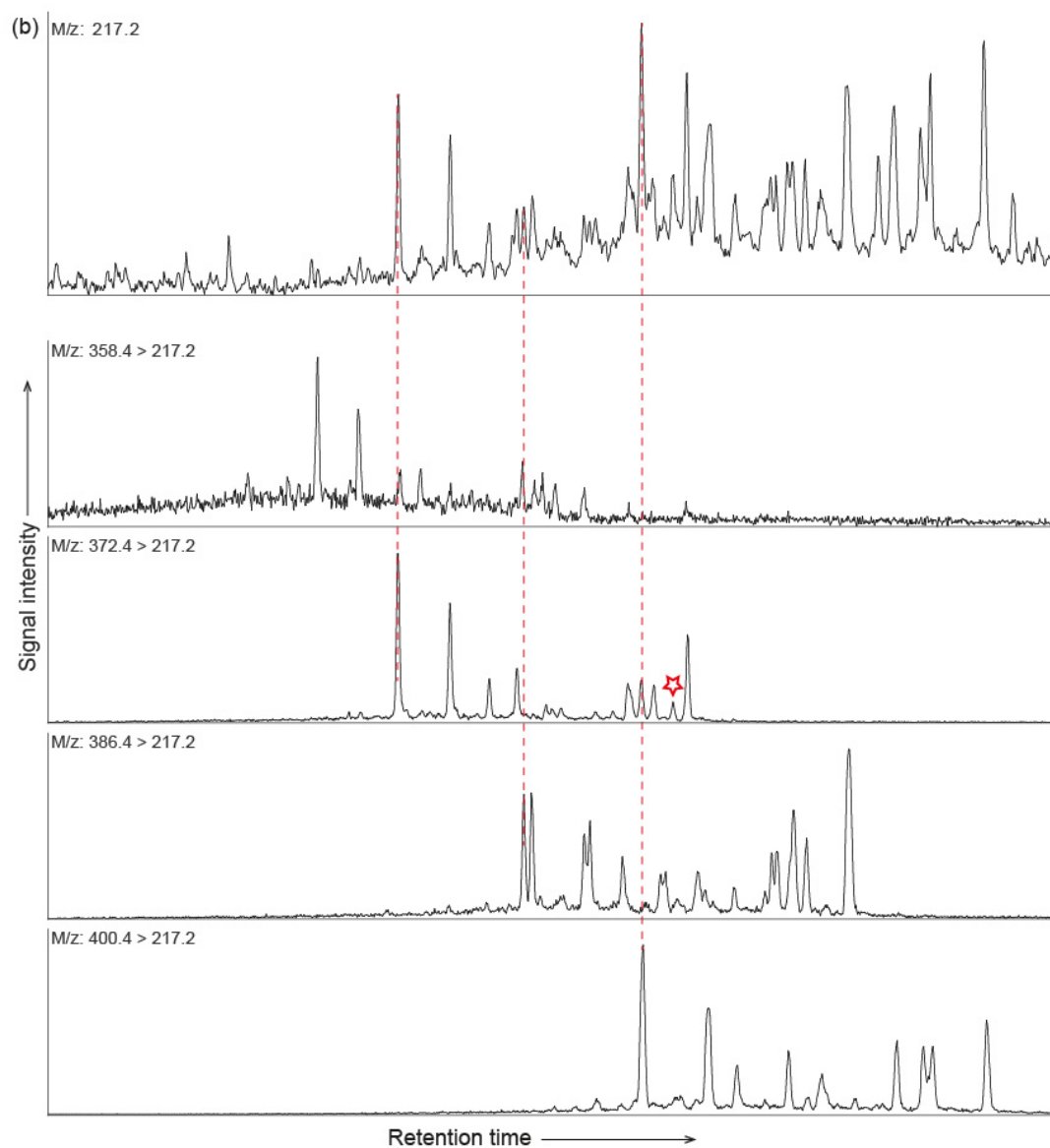
The b/c fractions from the carbonate-rich interval in the lower parts of Core A and in Core B, as illustrated by the two examples in Figure 5.8 (b: 2702.13 m in Core A; c: 3120.5 m in Core B), all show an unknown peak eluting just before C₂₇ $\alpha\alpha\alpha$ R sterane. This compound is not observed in the black-shale interval of Core A (Figure 5.8; a: 2681.17 m in Core A).

Sterane/hopane ratios calculated as regular steranes/17 α -hopanes (Moldowan et al., 1985) range from 0.45 to 1.50.

C₃₀ tetracyclic polyprenoids (TPP) were detected and analyzed by GC/MSxMS with parent–daughter mass transition m/z 414→259, showing the two peaks of TPPa and TPPb (C₃₀ TPP 18 α (H), 21R and C₃₀ TPP 18 α (H), 21S doublet) (Holba et al.,

2000) (Xu et al., 2017, Chapter 4 of this thesis). The TPP ratios based on Holba et al. (2000) are calculated here for all the samples studied.





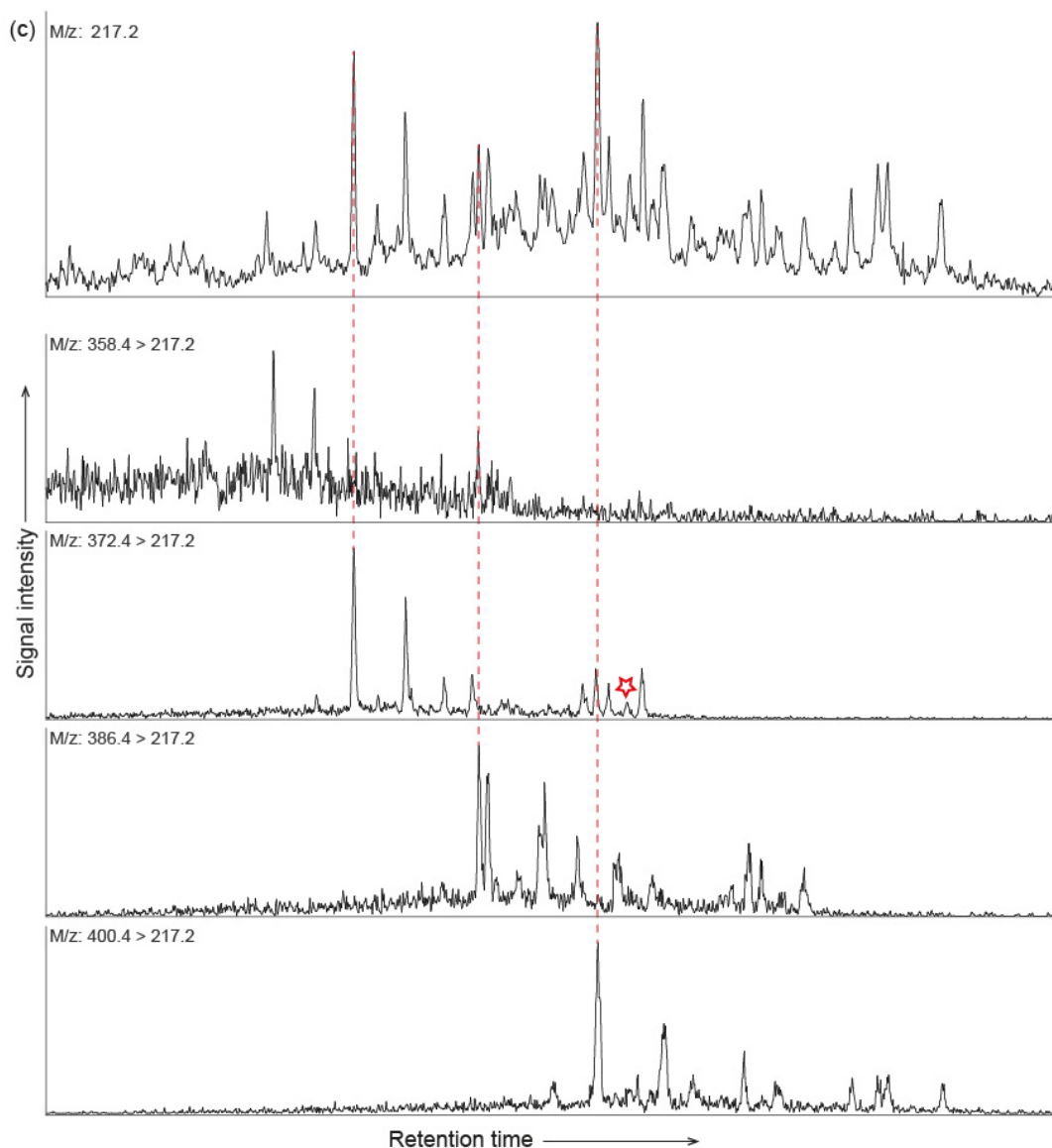


Figure 5.8 Mass chromatogram of m/z 217 from GC/MS aligned with panels of chromatograms of C_{26} – C_{29} steranes from GC/MSxMS data. (a) depth 2681.17 m (Core A); (b) depth 2702.13 m (Core A); (c) depth 3120.5 m (Core B). In the GC/MSxMS panels, the different transitions all have the same range for the x -axis and are all auto-scaled for the y -axis. The red stars marked in the mass transition m/z 372→217 in (b) and (c) indicate the unknown peak.

5.4.3.4 Tricyclic terpanes

Tricyclic terpanes ranging from C₁₉ to C₃₁ were detected in all the samples, although the C₂₉ to C₃₁ tricyclic terpanes are only present in small amounts and are not obvious in the GC/MS mass chromatogram. The C₂₅ to C₃₁ tricyclic terpanes all have S and R isomers. 3 examples of the *m/z* 191 mass chromatogram from GC/MS analyses, including both the tricyclic terpanes and the pentacyclic terpanes, are illustrated (Figure 5.9). All the samples show exceptionally high C₂₁ tricyclic terpanes especially in the sample at 2681.17 m in Core A, where the tricyclic/pentacyclic terpane ratio is the highest. The ratio of C₁₉(tri)/C₂₃(tri), often taken as a proxy of terrestrial input (Peters and Moldowan, 1993), ranges between 0.33 and 2.13.

There is a marked absence of any terrestrial higher plant markers in all of the samples. Peaks of pimarane, rimuane, isopimarane were not found in the GC/MSxMS mass transition *m/z* 276→247, although their nor-versions are present in the mass transition *m/z* 262→233.

5.4.3.5 Botryococcane

Botryococcane (*m/z* 183), a specific biomarker for *Botryococcus* algae, is not present in any of the samples, even with the low EV GCxGC/MS analysis, despite the common occurrence of *Botryococcus*-derived telalginite observed in the organic petrography and palynology analyses.

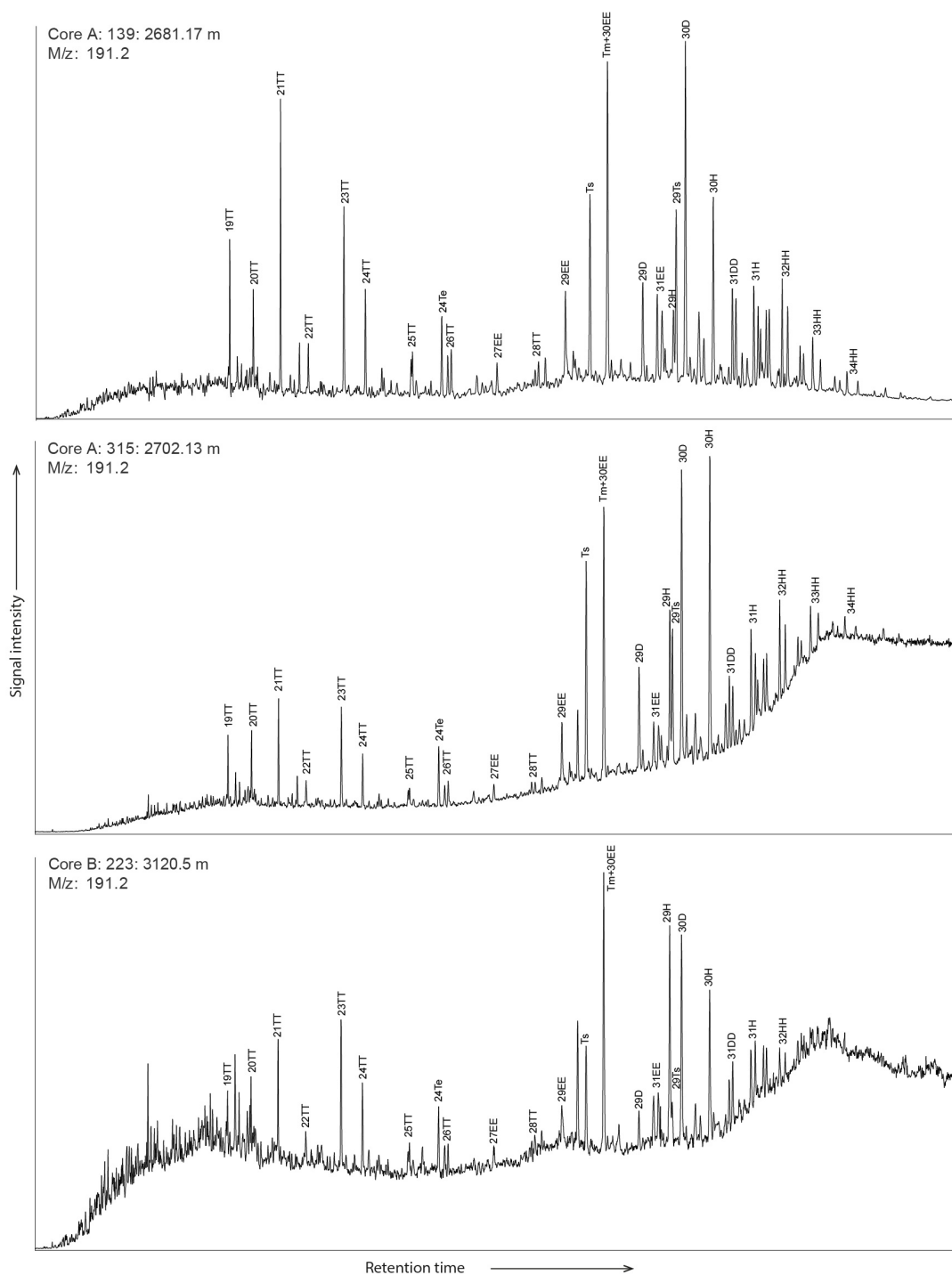


Figure 5.9 GC/MS mass chromatogram of m/z 191 illustrating the tricyclic and pentacyclic terpanes. 19TT to 26TT represent tricyclic terpanes of C_{19} – C_{26} ; 24Te represents C_{24} tetracyclic terpene.

5.4.4 Aromatic fractions

In all the samples analyzed, signals of the aromatic fractions are not very high. Perylene (m/z 252), suggested to be a biomarker for higher plant input (Aizenshtat, 1973), was identified in all the samples studied. Dibenzothiophene (DBT: m/z 184) and Phenanthrene (m/z 178) (Hughes, 1995) are also identified and quantified. The ratios of DBT/Phenanthrene are between 0.004 and 0.061 (Appendix F). 1-Methylphenanthrene (1-MP), 2-Methylphenanthrene (2-MP), 3-Methylphenanthrene (3-MP) and 9-Methylphenanthrene (9-MP) were quantified using the m/z 192 ion chromatogram in order to calculate Methylphenanthrene Indices (MPI-1), commonly used as a maturity parameter. This index, calculated as $1.5 \times (3\text{-MP} + 2\text{-MP}) / (9\text{-MP} + 1\text{-MP})$ (Radke et al., 1982), ranges between 0.46 and 0.68 in the Da'anzhai samples analyzed.

None of the samples studied contained isorenieratane, a pigment of the photosynthetic green sulphur bacteria *Chlorobiaceae*, which thrives in water columns bearing free H_2S , and is indicative of photic zone euxinia (Koopmans et al., 1996).

5.5 Discussion

5.5.1 Syngenicity of the biomarkers

The carbon-isotope records generated from the ASE-extracted residue from both Core A and Core B (Figure 5.4) should record dominantly the composition of the non-extractable organic matter. The trend of the carbon-isotope ratios of the extracted samples is similar to that of the total bulk organic matter, although the absolute values for the ASE-extracted residue are slightly more positive. This feature, whereby the non-extractable residual organic matter is on average isotopically heavier (Figure 5.4) than corresponding extracts, is commonly observed in most systems. The fact that the

trends of the organic carbon-isotope record from the total bulk rock, the non-extractable residue and the long-chain *n*-alkanes are all similar suggests that the extractable organic matter is likely *in situ* and not contaminated by migrated hydrocarbons.

5.5.2 Thermal maturity

The thermal maturity of Core A is estimated to be at peak oil window based on a series of parameters. Tmax ranges between 444 and 460°C (Figure 5.10). These Tmax values, especially in the higher end, are equivalent to vitrinite reflectance (VR) values of around 0.8-0.9%. Production indices (PI; ratio of S1/(S1+S2)) range from 0.15–0.34, indicating that labile kerogen has undergone cracking and has generated hydrocarbons, also in the early to peak oil window.

VR measured on a few reliable vitrinite particles is ~0.82–0.85%. The organic maceral alginite has dark yellow to orange fluorescing colours and the palynomorphs are mid-brown in colour, both indicating that the succession examined has undergone some thermal alteration, consistent with its having been in the oil window.

Biomarker isomerization ratios of the S and R isomers of the extended homohopanes (C₃₁ to C₃₃) reached equilibrium values of 0.55 to 0.60, indicating a minimum maturity of the onset of oil generation (Figure 5.10) (Seifert and Moldowan, 1980).

The MPI-1 has been calibrated against vitrinite reflectance in the range of 0.65 to 1.35% R₀ (Radke and Welte, 1983). The MPI-1 values of 0.46 and 0.68 exhibited by the Da'anzhai sample set indicate a calculated VR range of 0.68–0.81. These calibrations may not be universally applicable and can be affected by other factors such as organofacies and lithology (Cassani et al., 1988).

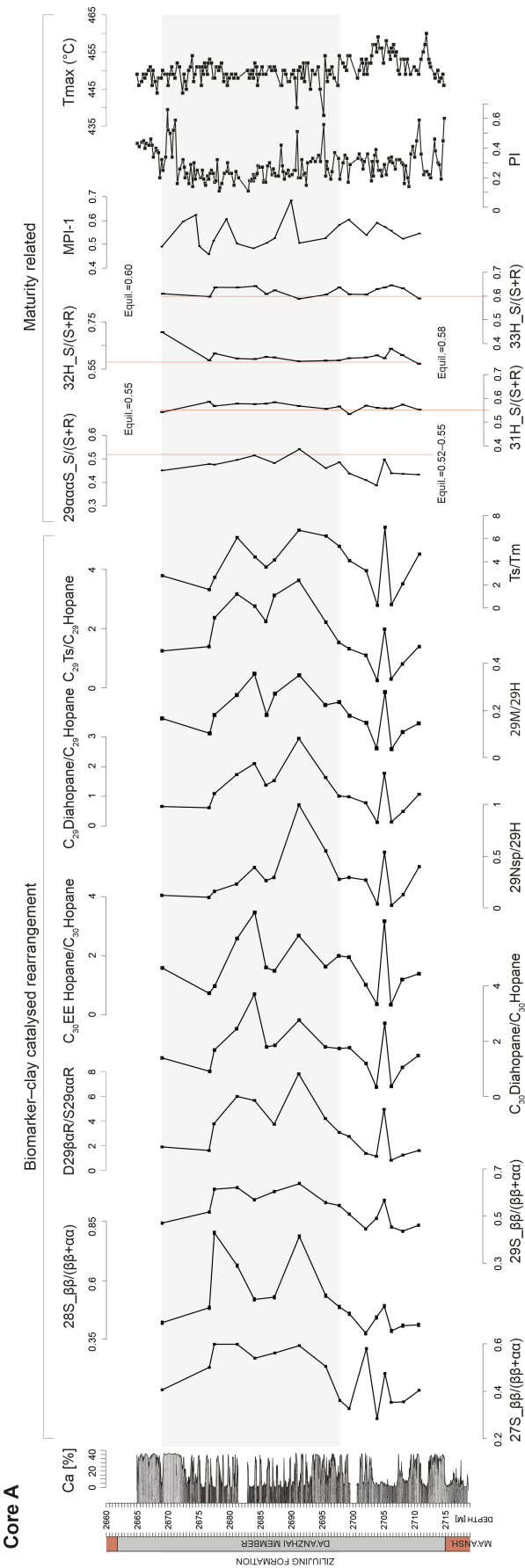


Figure 5.10 Ratios between the different rearranged hopanes and steranes and the normal hopanes and steranes are plotted on the left panel next to the combined core photos with calcium concentration illustrating the lithology change (darker colour—shale; light colour—limestone). On the right are maturity-related biomarker ratios as well as Tmax and PI from Rock Eval pyrolysis. Equilibrium thresholds for the sterane and hopane isomer ratios are marked by red line.

Core B is thermally more mature than Core A with higher Tmax values, mainly between 453 and 470°C (excluding some abnormal values). Palynomorphs are consistently dark brown in colour, an indicator of being at a higher maturity level compared to Core A (Xu et al., 2017, Chapter 4 of this thesis). This conclusion is consistent with the observation that Core B extracts contain significantly lower concentrations of biomarkers than Core A. Therefore, no compound-specific carbon-isotope analysis has been undertaken on Core B extracts and no quantification of biomarker concentrations or ratios have been performed.

Although high concentrations of tricyclic terpane relative to pentacyclic terpane are often taken as an indication of higher maturity, the variation of the tricyclic/pentacyclic ratios in two samples from Core A, where maturity level should be very similar, is more likely related to an overprint of biomass change (Peters, 2000; Moldowan and Seifert, 1983; Tao et al., 2015; Tuo et al., 1999).

5.5.3 Rearrangement of hopanes and steranes

The hopanes in the Da'anzhai Member of Core A show atypical distributions with strikingly high concentrations of rearranged hopanes, including 17 α (H)-diahopanes, 18 α (H)-neohopanes and the early eluting hopanes (9,15 dimethyl-25,27-bisnorhopanes) (Figure 5.7). This situation has been reported previously in Zhu et al. (2007) in oils from the Da'anzhai Member in different wells, and interpreted as related to the high maturity and the enriched clay contents of the source rock. The similarity of the hopane distribution between the Da'anzhai oil in Zhu et al. (2007) and the lipid extracts from the Da'anzhai source rock here suggests the close correlation between the generated hydrocarbons studied in Zhu et al. (2007) and the Da'anzhai as the source rock for these oils. Thermal maturity of all the samples studied in Core A

should be very close as they are all within a 50-metre depth range. Therefore, all the variations in the relative amount of the different rearranged hopanes cannot be simply a reflection of maturity differences. Diahopanes (15Me-27-nor hopanes) are most likely derived from the same precursor molecules as the normal hopanes but have undergone oxidation in the D-ring and rearrangement by clay-mediated acidic catalysis (Peters et al., 2005). Their occurrence is therefore more enhanced in shale (rich in clay) than carbonate source rocks, under oxic to suboxic and slightly acidic environments. Diahopanes are reported to be thermally more stable than neohopanes (Ts and 29Ts), which are themselves more stable than normal hopanes. The three series of rearranged hopanes have also been reported in Toarcian marine sediments from northern Italy (Farrimond and Telnaes, 1996). A similar diagenetic origin of the diahopane and the early eluting hopane has been suggested by Farrimond and Telmaes (1996) because of the covariance of the two molecules. However, different biohopanoid precursors have been indicated, at least partly, as additional contributors to the origin of the neohopanes, as these do not seem to show covariance with the other two rearranged hopane groups (Farrimond and Telnaes, 1996). In Core A, C₃₀EE Hopane/C₃₀Hopane and C₃₀Diahopane/C₃₀hopane have good covariance ($R^2=0.91$); C₂₉Ts/C₂₉Hopane and C₂₉Diahopane/C₂₉Hopane also have good covariance ($R^2=0.84$).

Moretanes (C₂₉ and C₃₀ 17 β , 21 α hopane), the less mature configuration found in oils (Seifert and Moldowan, 1980; Peters et al., 2005), have been identified in all the samples studied in Core A, with higher abundances for the C₂₉ moretane relative to the C₃₀ moretane. The high degree of correlation between C₂₉Moretane/C₂₉Hopane and C₂₉Diahopane/C₂₉Hopane ($R^2=0.88$), suggests a similar diagenetic pathway between the C₂₉Moretane and the C₂₉Diahopane, both likely related to clay-catalyzed rearrangement, with higher abundances in the black-shale interval.

In the Da'anzhai sample set, another rearranged hopane, C_{29} 28-Nor-spergulan-2-one (29Nsp), is also present and has previously been reported in oils generated from lacustrine source rocks in South East Asia (Nytoft et al., 2006). There is a positive correlation between the contents of 29Nsp and the other rearranged C_{29} hopanes (29Ts and 29Dia) in Core A, comparable to the trends of the 29Nsp/29H ratios and the 29Dia/29H ratios ($R^2=0.77$) (Figure 5.10): a feature that has been observed in the Middle Jurassic coal extracts from the Bryne Formation, Danish and Norwegian North Sea (Nytoft et al., 2006). The 29Nsp is thus postulated to have formed by oxidation and rearrangement of precursor hopanes in a similar way as diahopane (Nytoft et al., 2006).

Ratios of C_{27} $\beta\beta/(\beta\beta+\alpha\alpha)$ Sterane, C_{28} $\beta\beta/(\beta\beta+\alpha\alpha)$ Sterane, C_{29} $\beta\beta/(\beta\beta+\alpha\alpha)$ Sterane all show relative elevations in the black-shale interval. The cross-plot of C_{29} $\alpha\alpha\alpha S/(S+R)$ Sterane and C_{29} $\beta\beta/(\beta\beta+\alpha\alpha)$ Sterane shows a good positive correlation with R^2 of 0.64 (based on data in Appendix F). The two ratios are commonly indicators of thermal maturity. However, the fact that maturity level should not vary very much within a 50 m depth interval suggests that something other than maturity might be the controlling factor for the variations of the above ratios. Van Kaam-Peters et al. (1998) discussed the effect of clay minerals on diasterane/sterane ratios as well as C_{29} $\alpha\alpha\alpha S/(S+R)$ Sterane ratios. Both parameters seem to be also affected by the availability of clay minerals relative to TOC, which could explain the elevated ratios of C_{27} $\beta\beta/(\beta\beta+\alpha\alpha)$ Sterane, C_{28} $\beta\beta/(\beta\beta+\alpha\alpha)$ Sterane, C_{29} $\beta\beta/(\beta\beta+\alpha\alpha)$ Sterane in the black shale interval (Figure 5.10).

The strikingly high abundances of rearranged hopanes and steranes in Da'anzhai Member is most likely a result of clay-mediated acidic catalysis rather than a maturity indicator. Such results also suggest that use of these parameters as a

maturity indicator must be applied with caution. C_{29} 28-*Nor*-spergulanes, which seem particularly abundant in some oils from lacustrine source rocks in South East Asia (Nytoft et al., 2006), is likely a diagenetic product, although its more common abundance in oils from South East Asia might still indicate a source overprint.

5.5.4 Origins of *n*-alkanes

The total lipid extractions are very paraffinic (dominance of *n*-alkanes over branched and other compounds), especially within the black-shale interval with the waxy *n*-alkane hump extending to higher C numbers, which is typical of lacustrine source rocks or oils. The amounts of pristane and phytane in all the studied samples are very low compared with *n*-alkanes, due to the relatively high supply of waxy algal material. Long-chain *n*-alkanes (C_{27} , C_{29} , C_{31}) are normally diagenetic products of higher plant leaf waxes or specific freshwater algae (e.g. the A race of *Botryococcus*) (Eglinton and Hamilton, 1967; Derenne et al., 1988; Metzger et al., 1991). Macerals or palynomorphs that are attributed to *Botryococcus braunii* have been identified in a variety of fresh to brackish lacustrine sediments ranging from Precambrian to Recent (Guy-Ohlson, 1992). However, the specific biomarkers that are used to identify the presence of *Botryococcus* vary, depending on the specific races to which it belongs. Botryococcane, the most widely known biomarker derived from *Botryococcus* has only been identified in sediments of Eocene and younger age (e.g. the Eocene Sumatran oils and the Eocene Maoming oil shale) (Moldowan and Seifert, 1980; Brassell et al., 1986; Volkman, 2014). Among the modern races A, B, L and S of the alga *Botryococcus*, only race B appears to produce botryococcane, whereas race A produces long-chain odd-number *n*-alkanes (Metzger et al., 1991). Considering the age of the Da'anzhai Member, the lack of botryococcane does not contradict the presence

of *Botryococcus*. The *Botryococcus* species in these sediments are probably closest to the modern race A and are the likely source of the long-chain *n*-alkanes in the organic-rich black shales in the Da'anzhai Member (Figures 5.5 and 5.6).

The long-chain *n*-alkanes (C₂₇, C₂₉, C₃₁) are present in all the samples. The lack of the odd-over-even predominance has been attributed to the maturity of the samples (Chapter 4 of this thesis). However, the major constituent of the longer-chain *n*-alkanes in many of the samples is not C₂₇, C₂₉, C₃₁ *n*-alkanes, but rather C₂₁, C₂₃, C₂₅. Such mid-chain *n*-alkanes (C₂₁, C₂₃, C₂₅), found in lacustrine source rocks, are thought to be sourced from aquatic macrophytes (submerged and floating plants) (Ficken et al., 2000). The fact that the relative concentration of mid-chain *n*-alkanes (C₂₁, C₂₃, C₂₅) increases from very low in the carbonate-rich lower half of Core A to as high as the short-chain *n*-alkanes in the TOC-rich laminated black-shale interval suggests elevated input and preservation of aquatic macrophytes in the TOC-rich, upper part of Core A, along with other microalgae and bacterial biomass (Cranwell, 1977).

5.5.5 Biomass change in the palaeo-Sichuan lake

Organic matter of the Da'anzhai Member in Core A is mainly composed of type II and type II and III kerogen, based on the pseudo-Van Krevelen diagram (Figure 5.3), with the majority of samples within the CIE containing type II kerogen. Given the maturity of the organic matter in Core A, the original HI and TOC were likely even higher than their current values. Changes of the organic matter from kerogen Type II+III in the interval of the pre-T-OAE negative CIE, to dominantly Type II in the interval within the CIE, indicates changes in the composition of the sedimentary organic matter towards a more hydrogen-rich, algae-derived component during the T-OAE (Figure 5.3).

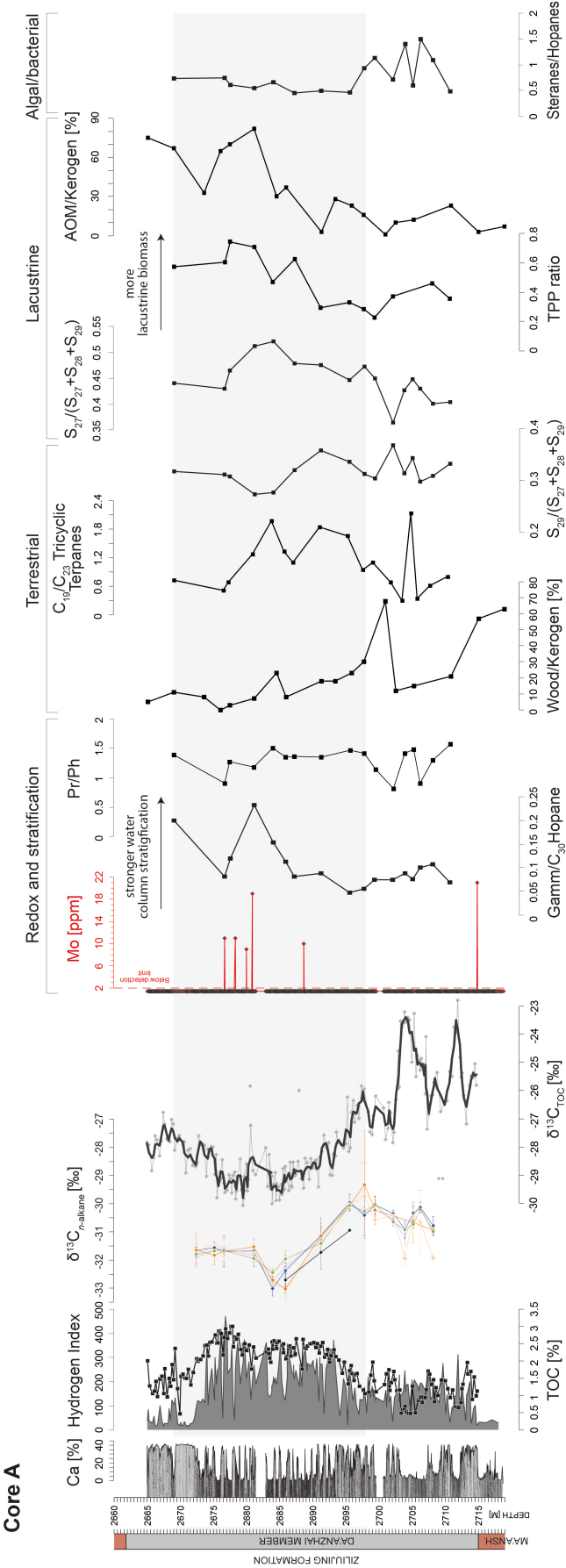


Figure 5.11 Evidence on redox conditions and biomass changes from Rock-Eval, palynological and biomarker study from Core A. Data are divided into redox and stratification, terrestrial and lacustrine biomass and the ratios of products of algal input/bacterial activity.

Based on the palynological study (see Appendix F), the percentage of wood fragments in the total kerogen of the 18 samples studied in Core A varies between 7% and 75% (Figure 5.11; Xu et al., 2017, Chapter 4 of this thesis). The values are on average slightly higher in the lower part of the core, with a few relatively enriched horizons at 2700.90 m, 2714.98 m and 2718.80 m, where wood accounts for 75%, 64% and 70% of the total kerogen, respectively (Figure 5.11). A large amount of inertinite (fusinite, semifusinite, funginite) and a small amount of recycled and indigenous vitrinite is also observed by means of organic petrography, with a larger amount and bigger particles in the lower part of the core (Figure 5.5: Plate 3). By contrast, the percentage of amorphous organic matter (AOM), ranging between 1% and 82%, goes up in the black-shale interval with the peak at 2681.17 m (Figure 5.11).

AOM is the structureless organic component whose origin is varied and difficult to characterize under the microscope. It could be sourced from degraded phytoplankton or bacterially derived sources or derive from higher plant components, or represent the diagenetic products of macrophyte tissues (Tyson, 1995). However, the fact that the AOM (a.k.a. bituminite) is fluorescent indicates a dominantly algal origin. Tetracyclic polyprenoid compounds (TPP), which have been suggested to be typically sourced from freshwater algae, are normally more abundant in oils and associated source rocks deposited under freshwater or brackish-water environments (Holba et al., 2000). The covariance of the AOM percentages and the TPP ratios, further agrees with the suggestion that the AOM is dominantly algae-derived (Figure 5.11). The sterane/hopane ratios are 0.45–1.50 and have higher values in the lower part of the core than in the upper part, where the ratios stay relatively constant (Figure 5.11). Sterane/hopane ratios reflect the ratios between eukaryote and bacterial biomass, with higher values indicating relatively higher algal input (Peters and Moldowan,

1993). The absolute amount of algal input might have increased during deposition of the black-shale interval based on the TPP ratios, but accompanying bacterial activity should also have increased, resulting in a higher relative abundance of bacterially derived components. The elevated input of algae is further supported by the increased percentage of C_{27} steranes, whose primary precursor is predominantly algae (Volkman, 1986), out of the sum of C_{27} , C_{28} and C_{29} steranes (Figure 5.11). On the other hand, the percentage of C_{29} steranes is higher in the lower part of the black-shale interval and decreases towards the upper part of this level (Figure 5.11). C_{29} steranes are normally considered to be associated with terrestrial higher plants, although suggestions have been made that certain algae also produce C_{29} steranes (Volkman et al., 1999). The C_{19} and C_{20} tricyclic terpanes have been suggested previously as having a terrigenous source (Nobel et al., 1986; Peters et al., 2005), although an algal source has also been indicated (Greenwood et al., 2000; Dutta et al., 2006). Therefore, the ratio of C_{19}/C_{23} tricyclic terpanes is not necessarily an indicator for the amount of terrestrial input. Without further evidence for the sources of C_{29} steranes and C_{19} tricyclic terpanes, it is difficult to narrow down what the changes of these parameters in the Da'anzhai samples actually signify.

Relatively high bacterial activity in the Da'anzhai Member has been demonstrated by the high abundance of hopanes relative to steranes and the high concentrations of AOM, especially in the black-shale interval. The presence of 3β -methylhopane, mainly derived from methane-oxidising bacteria and commonly abundant in some lacustrine settings (Farrimond et al., 2004; Brocks et al., 2005; Welander and Summons, 2012), also hints at bacterially promoted methane oxidation when the Da'anzhai Member was deposited.

In addition, the presence of funginite indicates the occurrence of bacterial oxidation of inertinite (Figure 5.5: Plate 3). Funginite is an inertinite maceral derived from fungal spores or fungal remains and has long been recognized in coal (Jeffrey and Chrysler, 1906). Perylene has also been identified in all the samples studied. Perylene is a biomarker commonly used to indicate terrigenous organic matter input, although its occurrence in sediments from Walvis Bay, an area thought to be largely free of terrestrial organic supply, led to the uncertainty of its precursor (Wakeham et al., 1979). Furthermore, Jiang et al. (2000) suggested that fungi may be the major precursor for perylene generated during diagenesis in the Lower–Middle Jurassic rocks from the Northern Carnarvon Basin, Australia. The co-occurrence of funginite macerals and the perylene biomarker in the Da'anzhai Member agrees with this latter hypothesis.

5.5.6 Depositional environment of the Da'anzhai Member

A warm/hot climate in the continental interior or along the palaeo-shore lines of the palaeo-Sichuan lake system is indicated based on the consistent superabundance of the thermophylic pollen genus *Classopollis* in both cores, commonly in tetrads. *Classopollis* is normally thought to have been derived from gymnosperm conifers dwelling in regions marginal to bodies of water (Vakhrameyev, 1981; Xu et al., 2017, Chapter 4 of this thesis). The enhanced atmospheric $p\text{CO}_2$ and greenhouse-gas-induced climatic warming (McElwain et al., 2005) also resulted in the increased occurrence of *Classopollis* in tetrads (relative to single specimens) during the T-OAE negative CIE interval due to stressed environmental conditions on land (Xu et al., 2017, Chapter 4 of this thesis).

Fusinite, semifusinite and pyrofusinite, typically formed from combustion, are more abundant in the lower part of the core (Table 1), suggesting dryer fire-prone climatic conditions pre-T-OAE, compared to elevated hydrological cycling and more humid climate during the event itself. Such a switch in humidity indicated by the abundance of fusinite and semifusinite is further supported by the lake expansion during the T-OAE based on sedimentary observations of lithologies changing from palaeosol to fossiliferous limestone and from limestone to laminated black shale.

The base of the Da'anzhai Member (overlying the terrestrial Ma'anshan Member) is marked by the presence of characteristic lacustrine facies stratigraphically overlying palaeosols. The switch to lacustrine deposits indicates a rise in lake level (Xu et al., 2017, Chapter 4 of this thesis). The lower half of the Da'anzhai Member in Core A is characterized by abundant fossiliferous limestones (primarily consisting of bivalve and ostracod shell fragments) alternating with mudstones that are more enriched in clay (Xu et al., 2017, Chapter 4 of this thesis). This interval has generally low TOC (~1%) and low HI values (~150 mg C/g TOC), and was possibly deposited in a near-shore environment with low aquatic organic-matter productivity and/or preservation. In addition, there are larger amounts of inertinite macerals observed in the lower part of Core A of relatively larger particle size, another indication of a near-shore depositional environment. The transition from fossiliferous limestone to laminated black shale at ~2693 m suggests deepening of the lake and a quieter-water environment. Given the estimated 300–900 kyr duration for the early Toarcian negative CIE (Kemp et al., 2005, 2011, Suan 2008, Boulila et al., 2014, Huang and Hesselbo, 2014), the metre-scale alternation between the laminated black shale and the fossiliferous limestone in the interval of ~2673–2693 m was likely caused by astronomically controlled lake level fluctuations. The top of Core A is composed of

two thick (~4 m each) fossiliferous limestones separated by a thin shale layer indicating a drop in lake level around the end of the T-OAE.

The large-scale expansion and deepening of the palaeo-lake system in the Sichuan Basin during the T-OAE is further suggested by the presence of filamentous algae (lamalginate), a shallow-water dweller (Valiela et al., 1997; Scheffer et al., 1997), in the sample at 2702.13 m in Core A, compared with the more abundant *Botryococcus* in the black-shale interval.

In response to rising lake level, physical and/or chemical stratification likely developed in the water column of the palaeo-Sichuan Lake, promoting algal productivity in near-surface environments, low-oxygen bottom-water conditions and the formation of black shale, even in relatively proximal depositional settings. The geochemical indicators of such stratification and reduced oxygen levels are seen in elevated levels of the gammacerane index, which have been observed in coeval marine basins (Farrimond et al., 1989; French et al., 2014), and increased Mo concentration (with Mo > 20ppm) (Xu et al., 2017, Chapter 4 of this thesis).

Tiny pyrite framboids (<5µm), observed under scanning electron microscopy (SEM) and in organic petrographical study, are present in the black-shale interval, whereas bigger pyrite framboids or single crystals are observed in the carbonate-rich intervals, suggesting a transition from oxic conditions for the deposition of the fossiliferous limestone to euxinic water-column conditions during the time when the black shale was deposited (Wilkin et al., 1996). However, the absence of isorenieratane in all the samples studied suggests that euxinia did not rise into the photic zone (Koopmans et al., 1996). The Pr/Ph ratio throughout Core A ranges between 0.8 and 1.6 (Figure 5.11), which is in a range typical of anoxic to suboxic

conditions, when the Da'anzhai Member was deposited (Didyk et al., 1978; ten Haven et al., 1987).

The DBT/Phenanthrene ratios, which reflect the amount of sulphur in the organic matter (Hughes et al., 1995), are extremely low in all the samples studied, supporting the freshwater nature of the lake. However, they are consistently slightly higher in the lower half of the core, where TOC is low (Appendix F). One explanation could be that the increased hydrological cycling during the T-OAE, which not only caused the lake to be more expanded and deeper, also diluted the sulphate concentration in the system even further, with limited incorporation into the organic matter. The low DBT/Phenanthrene ratios in the black-shale interval could also be related to elevated sulphate reduction in the more reducing environment with more sulphur removed from the system through pyrite burial, limiting availability for uptake by the organic matter. The two mechanisms together could explain why there is elevated sulphur concentration in the bulk rock of the black-shale interval, reflecting the amount of pyrite burial, yet organically bound sulphur, indicated by the DBT/Phenanthrene ratios, is limited.

In summary, the greenhouse-gas-induced warm/humid climate during the T-OAE caused an enhanced hydrological cycle with concomitant expansion of lake systems on land. Accelerated continental weathering brought more nutrients into the lake, causing increased aquatic organic productivity. The amount of terrestrial organic matter transported into the lake was lower in abundance relative to aquatic organic matter, and also of smaller grain size due to its further distance of transportation. The transition from oxic/suboxic conditions to more stratified or even euxinic conditions in the lake body during the T-OAE promoted the preservation of the organic matter that was deposited in the lake bottom with bacterial reworking forming abundant AOM.

Eventually, the high productivity and high preservation of organic matter in the palaeo-Sichuan lake system led to the formation of organic-rich laminated black shale dominated by the presence of algal biomass.

5.6 Conclusions

Climate around the palaeo-Sichuan lake was relatively dry with frequent forest fires before the T-OAE, followed by increased rainfall and more humid conditions during the event itself, likely resulting from enhanced hydrological cycling during greenhouse-gas-induced global warming. Organic matter in the laminated black-shale interval of the Da'anzhai Member was largely derived from bacterially modified algae (e.g. *Botryococcus*), deposited when lake level was relatively high and lake area extensive. The organic enrichment in the Da'anzhai Member mainly results from enhanced organic-matter productivity linked to elevated nutrient supply during periods of rapid hydrological cycling and enhanced continental weathering. The reducing/stratified conditions in the lake body and/or pore space facilitated the preservation of the organic matter. Such a depositional environment, with an overriding global climatic control during the super-greenhouse conditions of the early Toarcian, eventually led to the widespread synchronous deposition of organic-rich black shales in many marine and lacustrine basins across the globe.

Chapter 6

Orbital pacing of the Early Jurassic carbon cycle, black shale formation and seabed methane seepage

This chapter is modified from **Xu, W.**, Ruhl, M., Hesselbo, S.P., Riding, J.B., Jenkyns, H.C., 2017. Orbital pacing of the Early Jurassic carbon cycle, black shale formation and seabed methane seepage. *Sedimentology*, 64, 127–149. Micha Ruhl performed the time series analysis and Jim Riding performed the palynology study.

6.1 Introduction

The Early Jurassic (~201–174 Ma) was punctuated by several major and minor fluctuations in climate, palaeoenvironment, and global geochemical cycles (Jenkyns et al., 2002; Dera et al., 2011; Korte and Hesselbo, 2011; Ullmann et al., 2014; Brazier et al., 2015). The most significant of these perturbations, the Early Toarcian Oceanic Anoxic Event (T-OAE, at ~183Ma) (Jenkyns, 1985, 1988), has been discussed in Chapters 2–5. The T-OAE has now been extensively studied and has been recognized in both hemispheres (Jenkyns, 1988; Jenkyns et al., 2002; Hesselbo et al., 2007; Al-Suwaidi et al., 2010, 2016). However, several recent studies have demonstrated that the T-OAE was preceded by smaller-magnitude global carbon-cycle changes, during the Early Jurassic, in the Late Sinemurian (*Asteroceras obtusum* to *Oxynoticeras oxynotum* ammonite biozones), and at the Sinemurian–Pliensbachian and the Pliensbachian–Toarcian stage boundaries (Hesselbo et al., 2007; Littler et al., 2010; Korte and Hesselbo, 2011; Jenkyns and Weedon, 2013; Riding et al., 2013; Duarte et al., 2014; Porter et al., 2014).

A 2–3‰ negative CIE in bulk organic matter was previously observed for the Early Sinemurian *Arietites bucklandi* ammonite Biozone (*Coroniceras rotiforme* ammonite Subbiozone) at East Quantoxhead (Somerset, UK) (Ruhl et al., 2010; Hüsing et al., 2014). This negative excursion in $\delta^{13}\text{C}_{\text{TOC}}$ is associated with an interval of laminated black shale, with elevated total organic carbon (TOC) values of up to ~8%, suggesting at least local/basinal changes in the depositional environment. The nature of this environmental change and its relation to the global carbon cycle have, however, not been investigated previously. Furthermore, the *A. bucklandi* ammonite Zone at Kilve, Somerset, is also marked by methane seepage and the associated formation of large (~1.5 m) conical mounds or mud volcanoes (Cornford, 2003;

Allison et al., 2008; Price et al., 2008). The present contribution addresses (1) a potential Early Sinemurian global carbon-cycle perturbation and palaeoenvironmental change leading to black-shale deposition in the Bristol Channel Basin; (2) its link to the orbital pacing of Early Jurassic climate; and (3) the subsequent genesis of the Early Jurassic seabed methane seepage. We also include new observations on recently reported methane seep carbonates from the Lower Jurassic (Toarcian) of Yorkshire, which serve as a comparison example.

6.2 Geological background

6.2.1 Origin of sedimentary rhythms and TOC-enrichment in the Blue Lias

Formation of Somerset

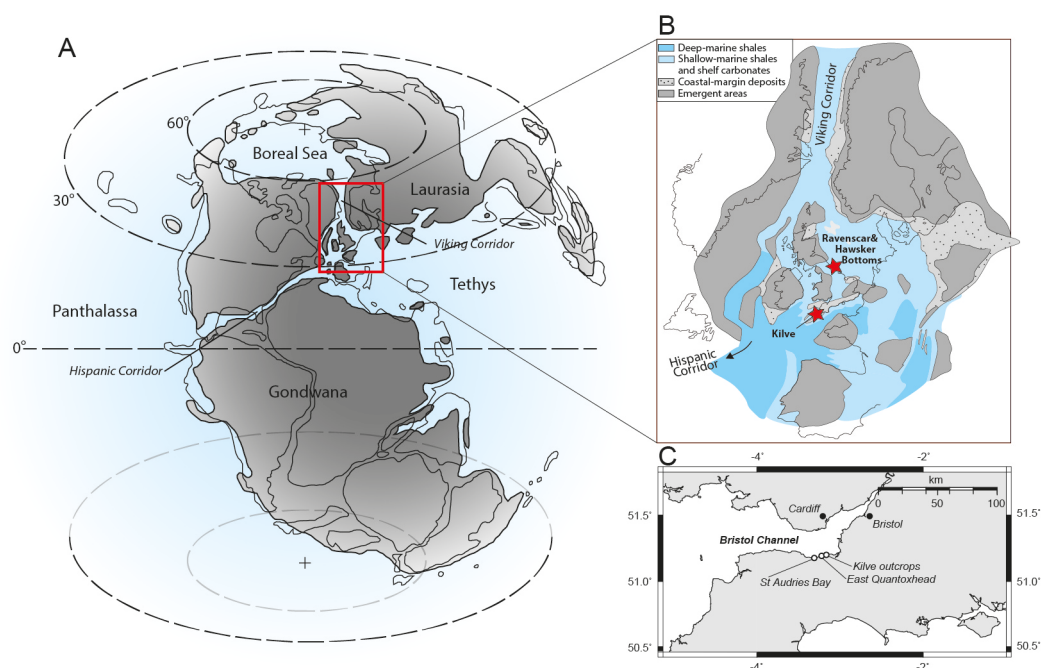


Figure 6.1 Geographical maps. (A) Early Jurassic global palaeogeography, modified after Dera et al. (2011) and Korte et al. (2015). (B) Zoom-in map of the red-square-marked area in map A, showing the palaeogeographic position (red stars) of the Bristol Channel Basin (with the Kilve section) and the Cleveland Basin (with the Ravenscar, Hawsker Bottoms and Staithes sections) at the northwestern end of the Tethys Ocean; (C) Modern map of the Bristol Channel with sample localities marked (modified after Ruhl et al., 2010).

The Early Jurassic Bristol Channel Basin was part of the Laurasian Seaway, and was marked by a generally progressive marine transgression, including a terrestrial to marine transition, during the latest Triassic (Figure 6.1; Hesselbo, 2008). The Lower Jurassic Blue Lias Formation formed during a phase of rapid flooding, and resulted in the periodic development of organic-rich laminated black shales (Hallam, 1995, 1997; Warrington et al., 2008). The relatively deeper marine (shelf) sediments of the Hettangian and Sinemurian Blue Lias Formation overlie the shallow-marine Lillstock Formation which is Rhaetian (latest Triassic) in age (Richardson, 1911; Whittaker and Green, 1983; Cox et al., 1999; Warrington et al., 2008). The *A. bucklandi* ammonite Zone may be marked by a relative sea-level fall, reaching a lowstand in the *C. rotiforme* ammonite Subzone (Hesselbo and Jenkyns, 1998; Hesselbo and Coe, 2000; Hesselbo, 2008).

The Blue Lias Formation has been subject to extensive stratigraphical studies (e.g. Hallam, 1964, 1987; Smith, 1989; McRoberts and Newton, 1995; Weedon et al., 1999; Hesselbo et al., 2002; Deconinck et al., 2003; Hounslow et al., 2004; Mander and Twitchett, 2008; Korte et al., 2009; Bonis et al., 2010; Clémence et al., 2010; Ruhl et al., 2010; Bonis and Kürchner, 2012; Hüsing et al., 2014). Locally, on the North Somerset coast, the Blue Lias Formation defined in Cox et al. (1999) has been subdivided into Aldergrove Beds, St. Audrie's Shales, Blue Lias, Kilve Shales, Quantocks Beds, Doniford Shales and Helwell Marls (Palmer, 1972). This Blue Lias Formation with a regional extent comprises alternations of limestone and marl/shale beds on the Somerset coast (Ruhl et al., 2010). Limestone beds (10–20 cm thick, locally up to 50 cm thick) are mostly micritic mudstone to wackestone. The limestone beds are fine-grained, containing varying proportions of clay minerals and micrite (Paul et al., 2008), which probably settled from suspension (Weedon, 1986). Some

limestone beds are also concretionary (Hallam, 1986; Weedon, 1986). The limestone beds of the Blue Lias Formation alternate with beds of grey marl and organic-rich laminated black shale (Hallam, 1964, 1986; Campos and Hallam, 1979; Hallam, 1986; Paul et al., 2008), which variably contain terrigenous clay minerals and marine- and terrestrially-derived organic matter (Weedon 1986; Clémence et al., 2010). The sedimentary rhythms in the Blue Lias Formation consist of laminated black shale grading into dark or pale grey marl, commonly with concretionary to tabular micritic limestone, which has been suggested to be diagenetic in origin (Hallam, 1964; Paul et al., 2008). These sedimentary rhythms are not always complete because organic-rich shale or marl/limestone beds are not always developed, or because the carbonate-rich sediments were diagenetically altered (Ruhl et al., 2010). The origin of cyclic sedimentation in the Blue Lias Formation has been much discussed in the literature, and has been mostly attributed to astronomical forcing (Hallam, 1964, 1986; Campos and Hallam, 1979; Weedon, 1986; Bottrell and Raiswell, 1989; Smith, 1989; Waterhouse, 1999; Paul et al., 2008).

The geographical extent of the limestone-shale couplets indicates chronostratigraphical significance and hence a stable allogenic forcing mechanism likely to be high-frequency climate control (Weedon, 1986; Smith, 1989). Integrated stratigraphical and palaeomagnetic studies on the Blue Lias Formation of Somerset demonstrate that the sedimentary rhythms, with the periodic formation of laminated organic-rich black shale, directly reflect orbitally controlled changes in the depositional environment at ~20 kyr precession periodicities, modulated by the short and long eccentricity cycles (Bonis et al., 2010; Ruhl et al., 2010; Hüsing et al., 2014). Periodically enhanced TOC values in the Hettangian and the lowermost Sinemurian Blue Lias Formation, with values of up to 10%, are especially high at the base of the *P.*

planorbis ammonite Zone, the middle of the *A. liasicus* ammonite Zone and the *S. angulata*–*A. bucklandi* ammonite zone boundary, probably in response to 405 kyr (and potentially ~2 Myr) modulated, precession-controlled changes in the palaeo-depositional environment (Ruhl et al., 2010; Hüsing et al., 2014; Sha et al., 2015).

Black shales from the *A. bucklandi* ammonite Zone at Kilve have previously been categorized as oil shale, albeit of rather low quality (Gallois, 1979). A 2-m-thick black-shale interval, with TOC >10%, in the *A. bucklandi* ammonite Zone in East Quantoxhead is marked by a ~2.5‰ negative excursion in $\delta^{13}\text{C}_{\text{TOC}}$ (Ruhl et al., 2010). Lower in the stratigraphy, 1–2‰ fluctuations in $\delta^{13}\text{C}_{\text{TOC}}$ in the Hettangian and the Sinemurian succession of St Audrie's Bay and East Quantoxhead in Somerset potentially reflect changes in the global exogenic carbon cycle, on Milankovitch periodicities (Clémence et al., 2010; Ruhl et al., 2010; Hüsing et al., 2014). Alternatively, these periodic alternations in $\delta^{13}\text{C}$ may express changes in sedimentary organic-matter source, changes in the magnitude of marine and/or terrestrial fractionation for ^{12}C , and/or changes in the basinal isotopic composition of the dissolved inorganic carbon (DIC) pool in response to changes in basin hydrography. The orbitally paced deposition of laminated black shale at this time was probably in response to changes in both productivity and preservation, likely due to enhanced nutrient (and terrestrial organic-matter) supply and water-column stratification resulting from precession-controlled changes in the hydrological cycle modulated by eccentricity (Bonis et al., 2010; Clémence et al., 2010; Ruhl et al., 2010).

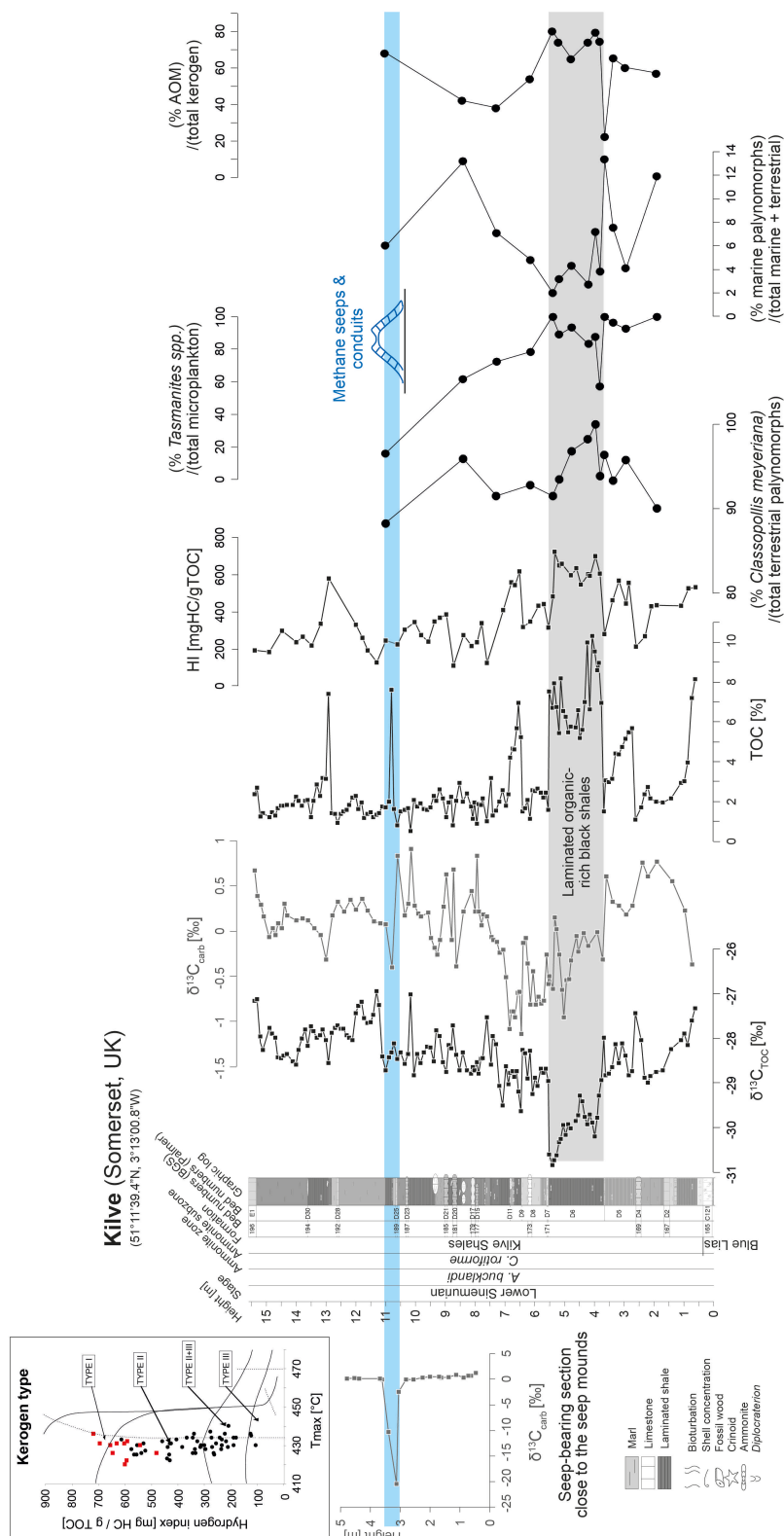


Figure 6.3 Sedimentary description and geochemical and palynological results from the *A. bucklandi* ammonite zone of Kilve, Somerset, UK. Geochemical data, including $\delta^{13}\text{C}_{\text{TOC}}$, $\delta^{13}\text{C}_{\text{carb}}$, TOC and HI are in black and grey squares. Palynological results including (% *Classopollis meyeriana*) / (total terrestrial palynomorphs), (% *Tasmanites* spp.) / (total microplankton), (% marine palynomorphs) / (total marine + terrestrial) and (% AOM) / (total kerogen) are in black circles (AOM = amorphous organic matter). Levels of methane seepage and organic-rich black-shale occurrence are marked by, respectively, blue and grey bands. A pseudo-Van Krevelen diagram (with HI vs Tmax) is given on the left (following Delvaux et al., 1990), with red squares representing samples from the level of the negative carbon-isotope excursion (CIE).

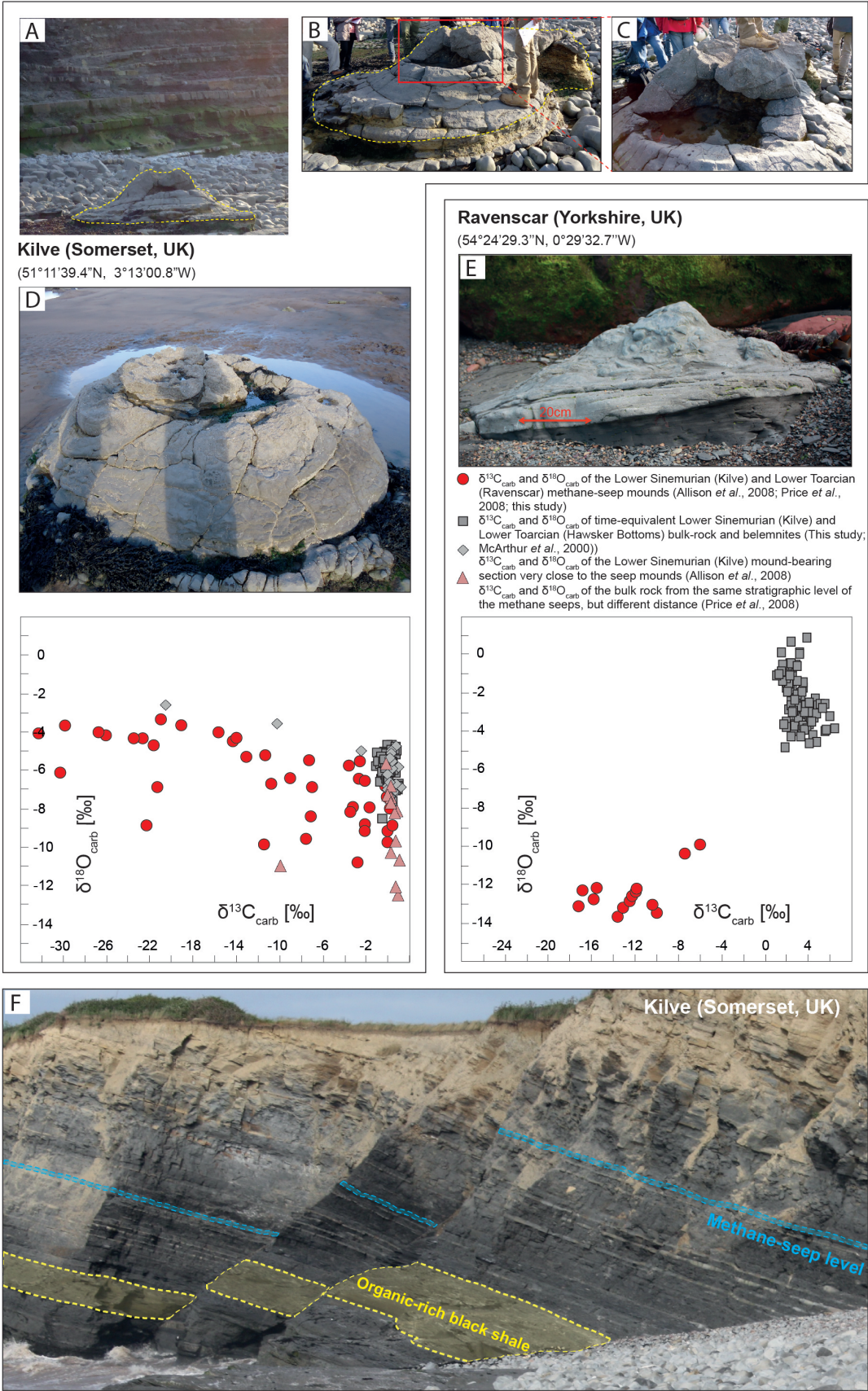


Figure 6.4 Outcrop and methane seep-mound images and associated geochemical data from Kilve (Somerset, UK) and Ravenscar (Yorkshire, UK). Photographs (A), (B), (C) and (D) show methane seep-mounds from Kilve. Photograph (E) shows a methane seep-mound from Ravenscar. In the cross-plots between $\delta^{13}\text{C}_{\text{carb}}$ and $\delta^{18}\text{O}_{\text{carb}}$, red circles represent values from the Early Sinemurian methane seep-mounds at Kilve (Allison et al., 2008; Price et al., 2008) and the Early Toarcian methane seep-mounds at Ravenscar (this study); dark grey squares represent values for the Lower Sinemurian mudrocks in the Kilve cliff-section, ~50 m away from the nearest visible seep-mound (this study); dark grey squares also represent values of Lower Toarcian belemnites from Yorkshire (McArthur et al., 2000); light grey diamonds represent values from Lower Sinemurian mudrocks at Kilve, which formed stratigraphically above and below the methane seep-mounds (Allison et al., 2008); pink triangles represent values from mudrock samples from the mound-bearing bed, in close proximity (1–20 m) to the seep-mounds (Price et al., 2008). Photograph (F) illustrates the sampled outcrop succession with black-shale interval and methane-seep level marked in yellow and blue.

The Kilve coastal cliff section studied here is located west of Bridgwater and the River Parrett on the Somerset coast, UK, ~500 m east of Kilve Beach and ~1 km north of Kilve village (Figure 6.1). The exposure at Kilve covers the stratigraphical interval of the *A. bucklandi* ammonite Zone with laminated black shale (with TOC up to ~10%), similar to as previously observed at East Quantoxhead (Figure 6.2; Ruhl et al., 2010). The foreshore outcrop is also marked by conical seep-mounds (mud volcanoes) occurring at a single stratigraphical level that overlies this high-TOC black-shale interval by ~5 m (Figures 6.2, 6.3 and 6.4) (Whittaker and Green, 1983; Cornford, 2003; Allison et al., 2008; Price et al., 2008). The cliff section sampled herein is ~50 m west of the nearest visible seep-mound on the foreshore.

6.2.2 Early Jurassic chronostratigraphy

The age of the Triassic–Jurassic boundary is radiometrically constrained at 201.36 ± 0.17 Ma in the Pucara Basin, Peru (Schaltegger et al., 2008; Schoene et al., 2010; Wotzlaw et al., 2014), and astrochronologically constrained at 201.42 ± 0.022 Ma in the Newark/Hartford Basins, USA (Blackburn et al., 2013). The duration of the

Hettangian Stage has previously been estimated using cyclostratigraphy at $> \sim 1.29$ Myr, from the relatively incomplete marine Blue Lias Formation succession in Dorset and Devon, Southwest England, or at ~ 2.86 Myr based on an assumed constant linear Early Jurassic decrease in seawater $^{87}\text{Sr}/^{86}\text{Sr}$ ratios (Weedon et al., 1999). More recent estimates suggest a duration of $\sim 1.7\text{--}1.9$ Myr, based on the astronomical interpretation of periodically occurring laminated black shales and systematic fluctuations in organic and inorganic geochemical proxy records in the relatively expanded Blue Lias Formation in Somerset (Ruhl et al., 2010; Hüsing et al., 2014). This duration is further supported by palaeomagnetic correlation to the Geomagnetic Polarity Time Scale (GPTS) of the Newark Basin, USA (Hüsing et al., 2014), and a $199.43 (\pm 0.10)$ Ma $^{238}\text{U}/^{206}\text{Pb}$ age for the base Sinemurian in the Pucara Basin of Peru (Schaltegger et al., 2008; Guex et al., 2012). The integrated bio-, cyclo- and magnetostratigraphic framework for the Blue Lias Formation, combined with radiometric dating, directly constrains the age and duration of changes in the depositional environment in the Early Jurassic Bristol Channel Basin.

6.2.3 Early Sinemurian methane seeps

Several large, conical mounds, interpreted as mud volcanoes, have been observed in a foreshore outcrop east of Kilve Beach in western Somerset, occurring at a discrete level within the Kilve Shales (division of Palmer, 1972) in the *C. rotiforme* ammonite Subzone of the *A. bucklandi* ammonite Zone (Whittaker and Green, 1983; Cornford, 2003; Allison et al., 2008; Price et al., 2008). These mounds are up to 1 m high and up to 3 m in diameter, and their flanks are formed by a limestone shell, which is composed of micritic carbonate and includes pods and sheets of bioclasts and intraclasts (Allison et al., 2008). The shape of ammonites and intraclasts on the flanks

of the mounds suggests cementation close to the sediment–water interface, prior to compaction (Allison et al., 2008). This mound-forming level is interpreted as being largely oxygen-deficient because of the scarcity of benthic biota, except for one of the mounds, where benthic foraminifera (*Involutina liassica*), bivalves, crinoidal fragments and gastropods, are present (Allison et al., 2008; Price et al., 2008). The abundance of the benthic foraminifer *Involutina liassica* in one mound indicates at least brief episodes of oxygenation (Allison et al., 2008; Price et al., 2008). The mound-forming authigenic carbonate (cf. Liang et al., 2016) has depleted carbon-isotope signatures of -11.5‰ to -32.3‰ and such ^{12}C -enriched signatures have been interpreted to originate from anaerobic methane oxidation, and mixing of the liberated carbon with seawater DIC (Allison et al., 2008; Price et al., 2008).

Early Jurassic seep mounds have previously been observed in several localities in Europe, including an Upper Pliensbachian outcrop in southern France (van de Schootbrugge et al., 2010), and a Lower Toarcian coastal Jet Rock outcrop at Ravenscar, Yorkshire, UK (Figure 6.4; Hesselbo et al., 2013). The shape and lithological composition of the conical mounds at Ravenscar are similar to the ones on the foreshore of the Kilve coast.

6.3 Materials and methods

6.3.1 Materials

6.3.1.1 The Early Sinemurian *A. bucklandi* ammonite Zone at Kilve

In this study, 15.6 m of mudstone and laminated black shale of the Early Sinemurian *A. bucklandi* ammonite Zone (*C. rotiforme* ammonite Subzone) was sampled at 10–11 cm resolution at the coastal cliff outcrop east of Kilve Beach (Figures 6.3 and 6.4; $51^{\circ}11'39.4''\text{N}$, $3^{\circ}13'00.8''\text{W}$). The logged and sampled interval covers the

sedimentary sequence between and including beds C121 and E1 (division of Palmer, 1972), in the Blue Lias Formation (Cox et al., 1999). The interval sampled is stratigraphically coeval with the 2–3‰ negative CIE as observed in the middle of the *A. bucklandi* ammonite Zone at East Quantoxhead and it also spans the stratigraphic horizon with methane seep occurrence, ~5 m above the top of the laminated black shale (Figure 6.2; Ruhl et al., 2010). In the cliff section, samples were only collected from the grey mudstones and the laminated black shales but not from the locally developed concretionary limestone beds.

The base of the sampled outcrop is marked by alternations of limestones and marly mudstones containing complete and fragmentary macrofossils, including ammonites, bivalves and crinoids (Figures 6.3 and 6.4). There is a ~2 m thick (Figures 6.3 and 6.4), laminated black shale with little bioturbation and sparse ammonite fossils at a stratigraphical height of 3.7–5.5 m. The trace fossil *Diplocraterion* appears close to the top of the black-shale interval (Figures 6.3 and 6.4). Strata overlying the laminated black-shale interval consist of alternating marl and shale beds, with a few discrete nodular limestone beds. This interval has yielded ammonites, bivalves and crinoids. Coalified wood fragments of up to 10 cm in length occur throughout, especially in the black shale beds (Figures 6.3 and 6.4).

6.3.1.2 Early Toarcian conical seep mounds at Ravenscar

Conical seep mounds in the Lower Toarcian Upper Jet Rock at Ravenscar (Yorkshire; 54°24'29.3''N, 0°29'32.7''W) occur stratigraphically above the high TOC (~15%) Lower Jet Rock in the *H. exaratum* ammonite Subzone by ~3 m (Hesselbo et al., 2013). 14 Samples were collected from several carbonate mounds on the foreshore for carbon- and oxygen-isotope analysis in order to test the origin of the seep

formation during sub-seafloor gas venting (Figure 6.4).

6.3.2 Methods

Total Carbon (TC) and Total Inorganic Carbon (TIC) were determined for all the studied samples using a Strohlein Coulomat 702 Analyser (manufactured by Firma Ströhlein GmbH, Kaarst, Germany) at the Department of Earth Sciences, University of Oxford. For TIC analyses, ~120 mg of powdered sample was roasted overnight at 420 °C to remove the organic matter. Total carbon (~80 mg of powdered sample) and TIC were measured, respectively, on the unroasted and roasted samples, and TOC was the difference between the two. Reproducibility of sample analyses with this method is generally better than 0.1% (Jenkyns 1988). The in-house standard (SAB134; Blue Lias organic-rich marl) was regularly measured. The long-term average value and standard deviation of TOC measurements on the in-house SAB134 standard is 2.95% and 0.069%, respectively.

Organic matter was further characterized by Rock-Eval pyrolysis on a Rock-Eval VI standard instrument (Vinci Technologies, Nanterre, France). Detailed methodology and measurement precisions have been described in section 2.3.1 of Chapter 2.

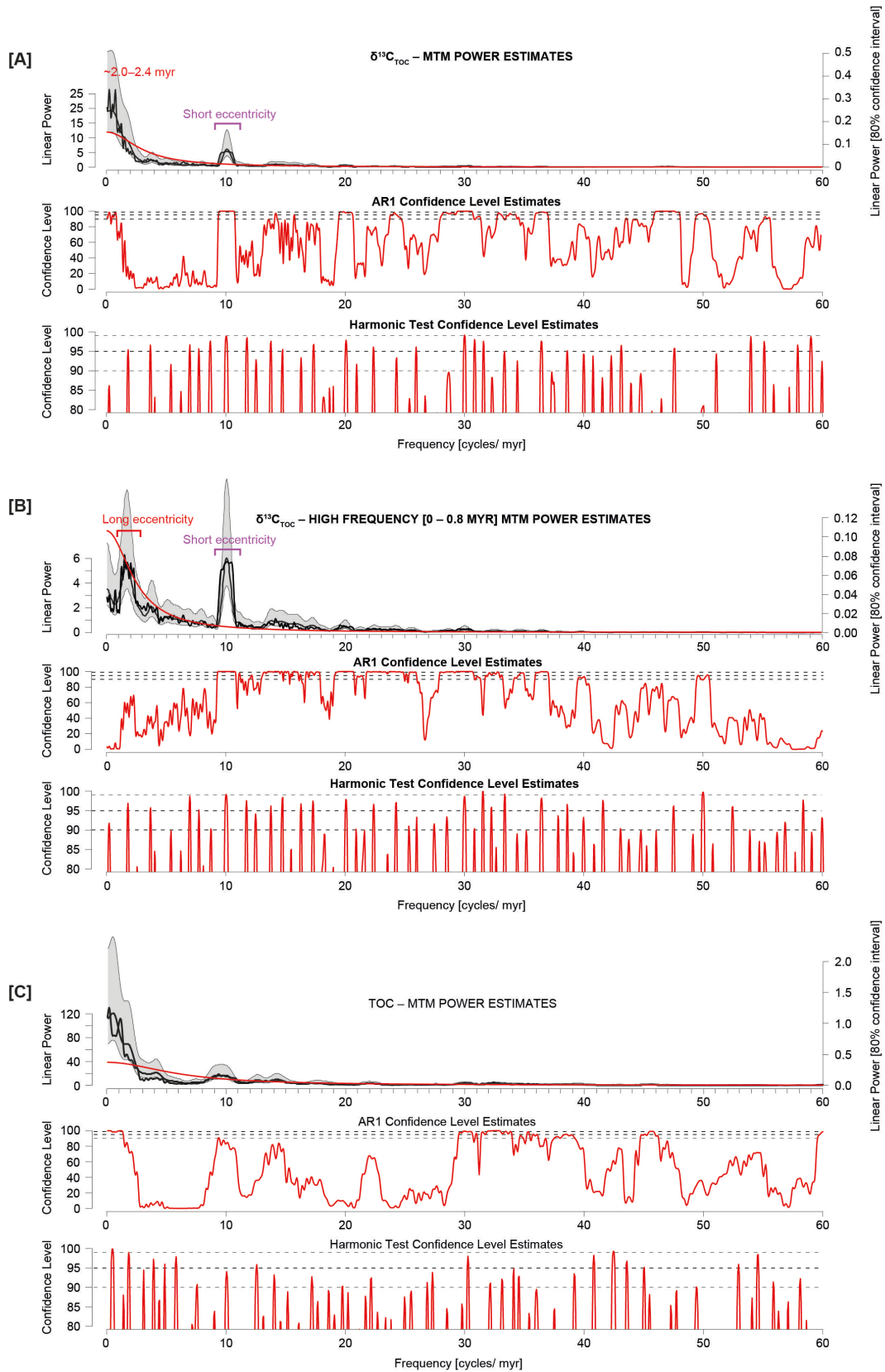
Analyses of $\delta^{13}\text{C}_{\text{TOC}}$ were performed on one gram of homogenized sample. Sample preparation, measurement methodology and precision have been described in section 5.3.8 of Chapter 5.

Analyses of carbonate $\delta^{13}\text{C}$ were performed at the Stable Isotope Laboratory at the Open University, Milton Keynes, UK. Bulk samples were dissolved in phosphoric acid on a Thermo Gas Bench II, and C and O isotope analysis was performed on a Thermo Finnegan Delta+ Advantage mass spectrometer (Thermo Fisher Scientific,

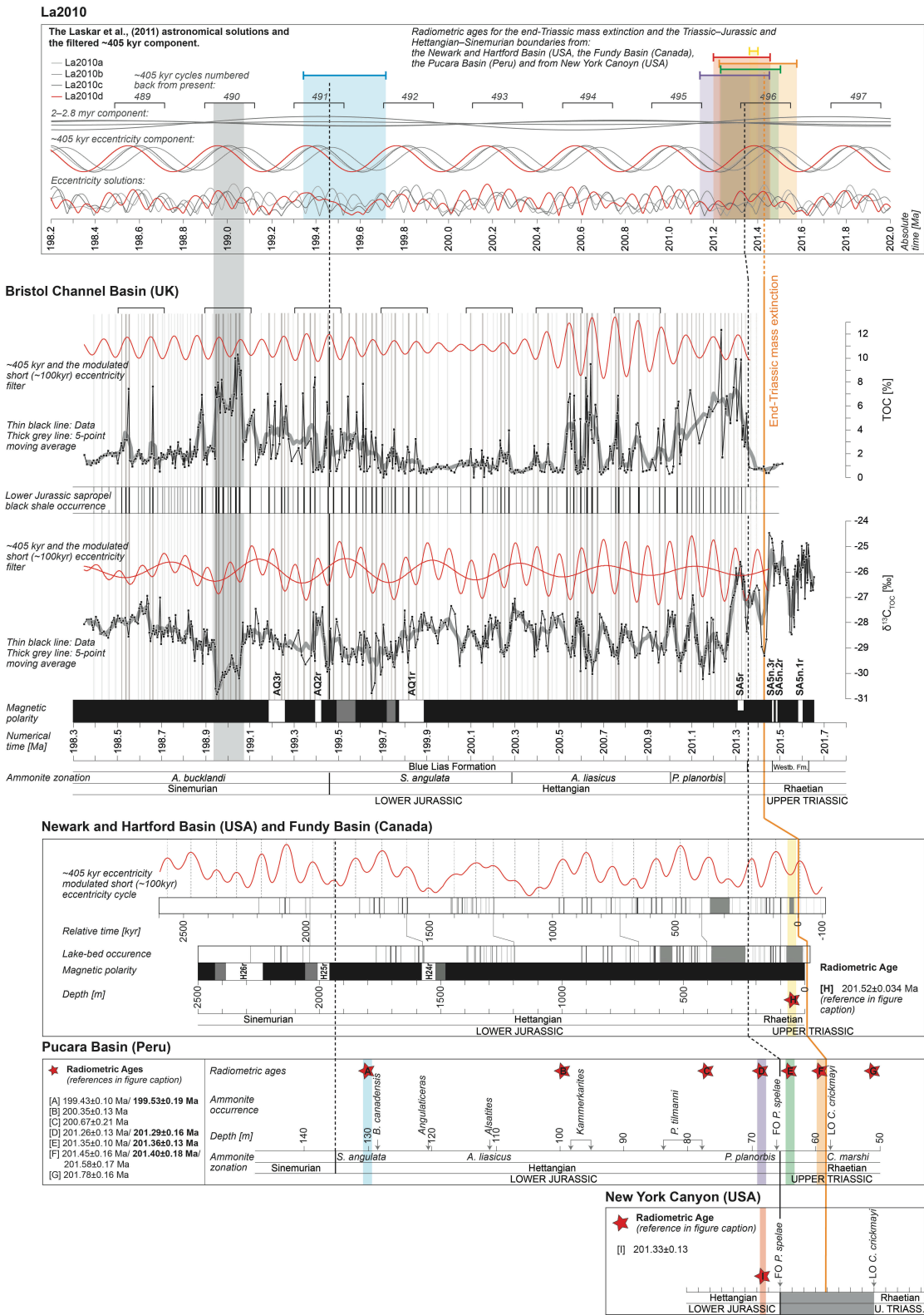
Waltham, MA, USA). Carbon- and oxygen-isotope compositions were expressed relative to VPDB by reference to in-house carbonate standards calibrated to NBS-19. Reproducibility is $\pm 0.1\text{‰}$ for $\delta^{18}\text{O}$, and $< 0.1\text{‰}$ for $\delta^{13}\text{C}$.

Standard palynological techniques (Wood et al., 1996) were used, and sample preparation was carried out by John Marshall at the National Oceanographic Centre, University of Southampton, UK. The samples were rough-crushed and then subjected to successive treatments in 30% HCl and 60% HF, with both treatments being followed by rinsing of the sample with deionized water to neutral pH. Following the HF treatment, the samples were sieved at 15 μm . This process was followed by a short treatment in hot concentrated HCl to solubilize any neoformed fluorides. The samples were then diluted with 500 ml of water and sieved again at 15 μm . The resulting kerogen concentrate was stored in vials, and strew-slides were mounted in Elvacite 2044.

Multi-taper (MTM: multi-taper method; 3π) spectral analyses, with robust red noise models (Mann and Lees, 1996), of the obtained integrated Lower Jurassic (Uppermost Rhaetian to Lower Pliensbachian at St. Audries Bay, East Quantoxhead and Kilve) $\delta^{13}\text{C}_{\text{TOC}}$ and TOC record in the time-domain (Figure 6.5), was performed by Micha Ruhl using the Astrochron (R (3.1.2) Package for astrochronology, version 0.3.1) toolkit (Meyers, 2014), following the short and long eccentricity interpretations as presented in Ruhl et al. (2010) and Hüsing et al. (2014). Dominant spectral components (Figure 6.5) were subsequently filtered from the data series and compared to the data in the time-domain, and the interpreted short- and long-eccentricity periodicities (Figure 6.6).



(Figure 6.5)



(Figure 6.6)

Figure 6.5 Multi-taper (MTM; 3π) power spectra of the obtained $\delta^{13}\text{C}_{\text{TOC}}$ and TOC time series (after Ruhl et al. (2010) and Hüsing et al. (2014)) using the Astrochron (R (3.1.2) Package for astrochronology, version 0.3.1) toolkit (Meyers, 2014), with robust red-noise models (Mann and Lees, 1996). A) $\delta^{13}\text{C}_{\text{TOC}}$ time-series multi-taper power spectrum of the complete data-set as in Figure 6, showing dominant short ~ 100 kyr eccentricity and long 2–2.4 myr astronomical forcing. B) Multi-taper power spectrum of the high-frequency (0–0.8 Myr) band-pass filter of the $\delta^{13}\text{C}_{\text{TOC}}$ time-series, showing dominant short (~ 100 kyr) and long (~ 405 kyr) eccentricity. C) TOC time-series multi-taper power spectrum of the complete dataset (as presented in Figure 6), showing dominant short (~ 100 kyr) eccentricity and long 405 kyr to 2–2.4 myr astronomical forcing. $\delta^{13}\text{C}_{\text{TOC}}$ and TOC time-series data were first manipulated to give uniform sample spacing using linear interpolation. MTM power estimates, AR1 confidence-level estimates and harmonic test confidence-level estimates are performed with the Astrochron (R (3.1.2) Package for astrochronology, version 0.3.1) toolkit (Meyers, 2014). An independent check of the dominant spectral components has been performed with AnalySeries 2.0.8 (Paillard et al., 1996), giving an 80% confidence interval (grey).

Figure 6.6 Upper Triassic to Lower Jurassic (Uppermost Rhaetian to Lower Sinemurian) $\delta^{13}\text{C}_{\text{TOC}}$ and total organic carbon (TOC) composite from the Westbury, Lillstock and Blue Lias Formation at St Audrie's Bay (Hesselbo et al., 2002; Ruhl et al., 2010), East Quantoxhead (Ruhl et al., 2010; Hüsing et al., 2014) and Kilve (Somerset, UK) (this study), plotted against numerical (absolute) time following bio-, magneto- and cyclostratigraphic and radiometric correlation between the Bristol Channel Basin (UK; this study; Hesselbo et al., 2002; Hounslow et al., 2004; Ruhl et al., 2010; Hüsing et al., 2014), the Newark and Hartford Basins (USA; Kent and Olsen, 2008; Blackburn et al., 2013), the Fundy Basin (Canada; Schoene et al., 2010), the Pucara Basin (Peru; Sell et al., 2014), New York Canyon (Nevada, USA; Schoene et al., 2010) and the La2010^{a/b/c/d} astronomical solutions (Laskar et al., 2011). Radiometric age-constraints are from [A: Schaltegger et al., 2008; Guex et al., 2012], [B: Guex et al., 2012], [C: Guex et al., 2012], [D: Schoene et al., 2010; Guex et al., 2012], [E: Schoene et al., 2010; Guex et al., 2012], [F: Schaltegger et al., 2008; Schoene et al., 2010; Guex et al., 2012], [G: Guex et al., 2012], [H: Blackburn et al., 2013] and [I: Schoene et al., 2010].

6.4 Results

6.4.1 Early Sinemurian $\delta^{13}\text{C}$ and kerogen characterization at Kilve

The TOC content in the studied succession is generally between 1–3%, but increases up to 10.3% in the organic-rich laminated black-shale interval in the lower part of the succession. High TOC values of up to 7.6% are also observed at discrete horizons at ~ 2.7 , ~ 6.5 , ~ 10.8 and ~ 12.9 m in the cliff section at Kilve (Figure 6.3).

High-resolution carbon-isotope analyses of bulk-rock samples, from ~4 m below the black-shale interval up to 4.5 m above the methane seep horizon, exhibit a distinct 3‰ negative excursion in $\delta^{13}\text{C}_{\text{TOC}}$ and a 2‰ negative excursion in $\delta^{13}\text{C}_{\text{carb}}$ (Figure 6.3). The $\delta^{13}\text{C}_{\text{TOC}}$ negative shift is similar in magnitude to that previously observed in coeval strata of nearby East Quantoxhead (Ruhl et al., 2010). The low $\delta^{13}\text{C}_{\text{TOC}}$ values directly coincide with elevated TOC values in the laminated black shale; $\delta^{13}\text{C}_{\text{carb}}$ values remain, however, low for another ~1.5 m, with TOC concentrations already restored to background values (Figure 6.3). Hydrogen Indices from Rock Eval pyrolysis vary between 108 and 720 mg HC/g TOC, with consistently elevated values in the laminated black-shale interval (Figure 6.3). Elevated HI values closely match high TOC in the lower part of the section (up to 7 m), but this relationship breaks down in the upper part of the studied interval (Figure 6.3). Tmax values of 428–440°C suggest an immature to early mature kerogen in the studied succession (Appendix G). The characterization of kerogen type, defined by both HI and Tmax values of the studied samples, suggests a gradual transition of kerogen Type II, to Type I and back to Type II/III up-section (Figure 6.3). These transitions suggest distinct changes in the composition of the sedimentary organic matter in terms of the relative proportions of marine phytoplankton and terrestrial higher-plant organic matter. The bulk-rock $\delta^{13}\text{C}_{\text{carb}}$ record of the Lower Sinemurian at Kilve, geographically ~50 m away from the nearest visible conical seep-mound (although mounds may be hidden in the cliff near the sampled section), also exhibits a shift to relatively depleted values at the level of the seep-mounds (Figure 6.3).

6.4.2 $\delta^{13}\text{C}$ analyses of Early Toarcian conical seep mounds at Ravenscar

The isotopic analyses of bulk-rock samples of the Lower Toarcian seep mounds at Ravenscar (Yorkshire, UK) reported here show relatively depleted values for both carbon and oxygen ($\delta^{13}\text{C}_{\text{carb}}$: -6 to -18‰ ; $\delta^{18}\text{O}_{\text{carb}}$: -10 to -14‰ ; Figure 6.4).

6.4.3 Palynomorph and kerogen assemblages

The palynology study has been contributed by James Riding as a collaborative study in Xu et al. (2017). Samples studied for palynomorphs and kerogen are generally strongly enriched in amorphous organic matter (AOM), which is typical for black shales, and the palynomorph diversity is relatively low (Figure 6.3). The percentage AOM relative to total kerogen (% AOM/total kerogen) is especially high (up to 80%) in the black-shale interval, where wood accounts for as low as 8% of the total kerogen (Figure 6.3, Appendix G). Fern spores are generally low in abundance, whereas the gymnosperm pollen species *Classopollis meyeriana* is consistently superabundant, accounting for more than 88% of the total terrestrial palynomorph composition (Figure 6.3). The *Classopollis meyeriana* abundance increases to almost 100% of the terrestrial palynomorph fraction in the laminated black-shale interval (Figure 6.3). A subsequent change in palynofacies is observed from 6.15 m upwards, where the palynomorph composition becomes more diverse, with the presence of acritarch genus *Micrhystridium*; the amount of wood fragments also increases (Figure 6.3; Appendix G). By contrast, palynomorph diversity is much lower, AOM content is higher, and the prasinophyte (green algae) genus *Tasmanites* dominates the microplankton in the laminated black shale with depleted $\delta^{13}\text{C}$ values (Figure 6.3; Appendix G).

The relative abundance of *Tasmanites*, relative to the total microplankton assemblage, gradually decreases from 100% at the top of the laminated black-shale interval to ~16% at the top of the studied section (Figure 6.3). The percentage of

marine palynomorphs relative to the total palynomorph assemblage (marine + terrestrial palynomorphs) is generally low ($< 13.4\%$), and is especially low in the laminated black-shale interval (Figure 6.3).

6.5 Discussion

6.5.1 The Early Sinemurian $\delta^{13}\text{C}$ record, orbital pacing of palaeoclimate and palaeoenvironment

The observed $\sim 3\%$ negative excursion in $\delta^{13}\text{C}_{\text{TOC}}$ at Kilve (Figure 6.3) stratigraphically coincides with a similarly sized negative CIE at East Quantoxhead (Figure 6.2; Ruhl et al., 2010). The contemporaneous $\sim 2\%$ negative excursion in $\delta^{13}\text{C}_{\text{carb}}$ at Kilve (Figure 6.3) may reflect changes in the carbon-isotope composition of Early Sinemurian seawater DIC in the Bristol Channel Basin, at a time of basin restriction during sea level lowstand. Combined, these data may suggest a change in the isotopic composition of the globally exchangeable carbon pools. Similarly, the observed sedimentary carbon-isotope fluctuations throughout the earliest Jurassic (Hettangian) in the marine sediments of the Bristol Channel Basin (Hesselbo et al., 2002; Clémence et al., 2010; Ruhl et al., 2010), may also have reflected true changes in the global exogenic carbon cycle because carbon-isotope fluctuations equal in magnitude and spacing are also present in the sedimentary organic matter of the continental Newark and Hartford Basin in the eastern USA (Whiteside et al., 2010). Alternatively, periodic changes in the source of the sedimentary organic matter (explaining varying $\delta^{13}\text{C}_{\text{TOC}}$) and/or periodic changes in the water-column redox state may have taken place, with the oxidation of sedimentary organic matter and the release and subsequent biomineralization of ^{12}C during phases of re-oxygenation (explaining varying $\delta^{13}\text{C}_{\text{carb}}$) (Clémence et al., 2010; Ruhl et al., 2010).

The $\delta^{13}\text{C}_{\text{carb}}$ record at Kilve remains low (for another ~ 1.5 m) following the recovery of the $\delta^{13}\text{C}_{\text{TOC}}$ signal (Figure 6.3). Sedimentary organic-matter content in limestone and mudstone stratigraphically overlying the organic-rich black shales is likely to have been partly reworked and of a mixed marine/terrestrial origin, resulting in somewhat elevated HI values (Figure 6.3). The organic-rich laminated black shale was probably deposited under anoxic (or euxinic) conditions, given the distinct lack of bioturbation. By contrast, the underlying and overlying mudrock beds are strongly bioturbated, and the trace fossil *Diplocraterion* reappears at the top of the black-shale interval (Figure 6.3). The re-establishment of oxygenated conditions following the deposition of the organic-rich black shale, may have oxidized and remobilized the ^{12}C enriched organic carbon (Clémence et al., 2010). Degradation of the sedimentary organic matter, following the deposition of organic-rich black shale, and the subsequent release of isotopically light (^{12}C -enriched) carbon into the pore-space and overlying seawater DIC pools allowed for the precipitation of isotopically depleted (diagenetic) carbonate. Alternatively, anaerobic oxidation of methane under anoxic/euxinic conditions in the sedimentary pore space during deposition of the organic-rich black shale may have significantly decreased the carbon-isotope composition of interstitial fluids and the overlying water column. Such a process may also have allowed cementation at the seabed or in the shallow subsurface during deposition of the organic-lean mudrocks, following the formation of the organic-rich black shale.

Irrespective of the true cause of carbon-isotope changes in the Lower Jurassic sedimentary records of the Bristol Channel Basin, the observed fluctuations in biota, lithology, sedimentary organic matter, TOC and $\delta^{13}\text{C}$ are periodic in nature and probably reflect high-frequency climatic and environmental change at Milankovitch

periodicities (Bonis et al., 2010; Clémence et al., 2010; Ruhl et al., 2010; Whiteside et al., 2010; Hüsing et al., 2014; Sha et al., 2015). The Lower Sinemurian *C. rotiforme* ammonite Subzone was previously suggested to coincide with a sea-level lowstand (Hesselbo and Jenkyns, 1998). The laminated black shales in the Bristol Channel Basin of *C. rotiforme* ammonite Subzone age, however, formed directly in line with eccentricity modulated, precession-controlled laminated black shales throughout the Hettangian and the Lower Sinemurian, suggesting astronomical control as the dominant factor on the depositional environment rather than sea-level change, although the two mechanisms may not be mutually exclusive (Ruhl et al., 2010; Hüsing et al., 2014). The laminated black shale of the *C. rotiforme* Subzone studied here, is, however, arguably more expanded and more organic-rich compared to the underlying Upper Hettangian and Lower Sinemurian strata (Figure 6.2).

Possible analogues are the TOC-rich Pliocene–Pleistocene sapropels in the Eastern Mediterranean, the periodic development of which was strongly paced by eccentricity modulated precession forcing with the development of anoxic bottom-water conditions in response to regional changes in runoff (Hilgen, 1991; Calvert and Fontugne, 2001; Lourens et al., 2004; Becker et al., 2005; Bosmans et al., 2015). In addition, Palaeocene and Eocene hyperthermal events were marked by distinct changes in the global carbon cycle, with major implications for global palaeoclimate and palaeoenvironment, and they, also, were paced at orbital timescales (Lourens et al., 2005; Zachos et al., 2010). The Eocene Thermal Maxima 2 and 3 (ETM2 and ETM3) occurred during short- and long-term eccentricity maxima and possibly even at longer (~1.2 Myr) periodicity maxima, whereas the pacing of ETM1 (at the Palaeocene–Eocene boundary) is slightly out of phase, possibly due to non-orbital internal forcing of the Earth system (Zachos et al., 2010).

The observed Early Jurassic Hettangian and Sinemurian periodic formation of laminated black shales and coeval fluctuations in $\delta^{13}\text{C}$ and palaeoenvironmental proxies (e.g. biological proxies, CaCO_3 , magnetic susceptibility, TOC) in the Bristol Channel Basin are also paced at orbital time-scales (Figures 6.2, 6.5 and 6.6; Bonis et al., 2010; Clémence et al., 2010; Ruhl et al., 2010; Hüsing et al., 2014). They likely reflect intensified, regional to global, palaeoenvironmental change on short astronomical (precession) timescales, modulated by short- (~100 kyr) and long-term (~405 kyr) (and possibly even longer ~2 Myr) eccentricity (Figures 6.2 and 6.6; Ruhl et al., 2010; Hüsing et al., 2014; Sha et al., 2015), coeval with eccentricity modulated precession and obliquity forcing in the continental Newark (eastern USA) and Jungar (northwestern China) Basins (Kent and Olsen, 2008; Sha et al., 2015).

Periodic palaeoenvironmental and palaeoceanographic changes in the Hettangian and Sinemurian of the Bristol Channel Basin are relatively minor compared with the Triassic–Jurassic boundary and the Early Toarcian oceanographic changes which are both more intense and longer in duration (Suan et al., 2008; Deenen et al., 2010; Ruhl et al., 2010; Kemp et al., 2011; Huang and Hesselbo, 2014; Boulila et al., 2014). Similar to the ETM1 (at the Palaeocene–Eocene boundary), these events were suggested to have resulted from internal (i.e. volcanic) forcing of the Earth system (e.g. Hesselbo et al., 2002; Deenen et al., 2010; Jenkyns, 2003, 2010; Ruhl et al., 2011; Sell et al., 2014; Percival et al., 2015). Studying the time-periods between such major events allows for better constraints on the background sensitivity of the Earth system, and our data suggest that major changes in the palaeoenvironment and basin oceanography manifestly occurred on orbital timescales, in a warm, largely ice-free, world.

6.5.2 Early Sinemurian climatic and environmental change

Elevated TOC contents of up to 10% in the Lower Sinemurian laminated black-shale interval studied here coincide with Type I/II kerogen (high HI values of > 700 mg HC/g TOC) (Figure 6.3) and increased amounts of AOM. This Type I kerogen may have been sourced by bacterially degraded marine algal organic matter (Figure 6.3). Alternatively, lipid remains of leaf waxes may have been the source of this type of kerogen with high HI values (Wignall, 1994; Tyson, 1995; Killops and Killops, 2005). Similarly, the end-Triassic mass-extinction interval in the Eiberg Basin of Austria is marked by strongly enhanced HI values, coinciding with a shift to almost 100% *Classopollis meyeriana* in terms of the total terrestrial palynomorph assemblage (Ruhl et al., 2010; Figure 6.3).

The superabundance of the *Classopollis* pollen, inferred to be a thermophilic taxon during this interval, suggests a shift to even warmer climatic conditions from an already greenhouse state in the Hettangian (Bonis et al., 2010; Bonis and Kurschner, 2012; Riding et al., 2013). Possible astronomically controlled changes in the hydrological cycle during this warm phase in the Hettangian, potentially influencing the supply of terrestrial organic matter to the basin, may have significantly affected the marine palaeoenvironment (Bonis et al., 2010). Alternatively, the enhanced supply of terrestrial organic matter may have resulted from an approaching palaeocoastline during an Early Sinemurian sea-level lowstand (Hesselbo and Jenkyns, 1998). The bloom of the *Tasmanites* green algae (a “disaster index”) during the Early Sinemurian negative perturbation in $\delta^{13}\text{C}$, similar to that following the end-Triassic mass extinction in the Bristol Channel and the west Germanic basins (van de Schootbrugge et al., 2007; Richoz et al., 2012), suggests a salinity- and/or temperature-stressed environment in the marine realm at this time (Vigran et al., 2008). The change in the

sedimentary organic-matter type, combined with the change in apparent redox state of waters in the Bristol Channel Basin during the studied time-interval, could potentially explain the observed changes in the organic and inorganic $\delta^{13}\text{C}$ values. Whether the negative CIE is a local (kerogen source-related or diagenetic) phenomenon or represents global carbon-cycle change remains to be tested in other basins or by the sampling of specific carbon pools. The changes in sedimentary geochemistry and organic matter do, however, suggest changes in global climate and the terrestrial and marine palaeoenvironment at orbital timescales.

6.5.3 Methane seepage linked to organic-rich shale formation

Marine methane seepage and the formation of authigenic carbonates in/on the seabed have occurred before and throughout the Phanerozoic, in a wide variety of environments and with many different (shallow and deep) sources for the biogenic/thermogenic methane (Tryon et al., 2002; Jiang et al., 2003; Niemann et al., 2006; Walter Anthony et al., 2012; Kiel et al., 2013; Nesbitt et al., 2013; Skarke et al., 2014). One of the best-studied Jurassic methane seeps formed in the Oxfordian time (~160 Ma) at Beauvoisin, southeast France (Peckmann et al., 1999). Very low $\delta^{13}\text{C}_{\text{carb}}$ values of down to -30‰ in calcite nodules within the Oxfordian section likely result from hydrocarbon-sourced methane seepage (Louis-Schmid et al., 2007).

The conical seep-mounds described here now occur ~5 m stratigraphically above the top of the laminated black-shale interval and crop out on the foreshore at Kilve. Previous analyses of these conical mounds indicated that they were likely formed as seafloor mud volcanoes associated with methane seepage (Allison et al., 2008; Price et al., 2008). Micritic carbonate on the flanks of the mounds typically show a wide range of $\delta^{13}\text{C}_{\text{carb}}$ values of 0 to -32‰ ($\delta^{18}\text{O}_{\text{carb}}$: -3 to -11‰ ; Figure 6.4),

which likely resulted from microbial anaerobic methanotrophy and subsurface methanogenesis (Allison et al., 2008; Price et al., 2008). The isotopic compositions of coeval mudrocks adjacent to the seep-mounds are generally less depleted in ^{13}C , but still display values down to -20‰ (Allison et al., 2008). The coeval stratigraphic level in the cliff section studied here, ~ 50 m away from the nearest visible mound on the foreshore, also shows an abrupt shift towards more depleted $\delta^{13}\text{C}_{\text{carb}}$ values (from $+1$ to -0.5‰), suggesting that methane-seepage from the mud-mounds actively altered the isotopic composition of the nearby DIC pool during oxidation of methane at or just below the seabed (Figure 6.3; cf. Mediterranean analogue from Aloisi et al., 2000). Alternatively, these values may come from methane diffusion through the sedimentary column and (authigenic) carbonate formation in the sedimentary pore space or at the seabed. The $\delta^{13}\text{C}_{\text{TOC}}$ record from the same cliff section, however, does not show a coeval shift to more depleted values, and sedimentary organic matter at this stratigraphic interval is terrestrially dominated (with low HI values of 200 mg HC/g TOC) and relatively sparse (6%) in marine palynomorphs (Figure 6.3). Therefore, methane seepage from the seafloor was likely localized and concentrated at the seep-mounds, with its oxidation mostly at and around the mounds and with limited dispersion into the surrounding water-column and atmosphere.

The nature and source of fluids released through the early Sinemurian seafloor seeps was previously suggested as resulting from compaction of Triassic pore water (Cornford, 2003), or as biogenic methane from the directly underlying organic-rich shale (Allison et al., 2008); alternatively the methane may have had a thermogenic origin, being derived from Palaeozoic rocks in the deep subsurface (Price et al., 2008). The latter model would suggest a migration of methane gas along deep fault systems to

the surface (Cornford, 2003). The seep-mounds are, however, randomly located on the foreshore and do not show any clear alignment along the observable fault systems.

Here, we propose a model (Figure 6.7) suggesting that biogenic methane was sourced from the underlying Lower Sinemurian laminated organic-rich black shale of the *A. bucklandi* ammonite Zone. In this model, organic-lean mudstones from the Lower Sinemurian *A. bucklandi* ammonite Zone formed under oxygenated seafloor conditions, due to limited supply of marine and terrestrial organic matter (Phase 1, Figure 6.7). Oxygenated conditions in the pore water and minor microbial methanogenesis generated only a minor flux (if any at all) of methane gas across the sediment–water interface and into the overlying water column. Palaeoenvironmental and palaeoceanographic changes in response to orbitally paced changes in climate and palaeoenvironment may have enhanced the hydrological cycle, leading to an increased flux of terrestrial organic matter into the basin (Phase 2, Figure 6.7; Figure 6.3). Enhanced nutrient supply possibly also initiated increased marine primary productivity. This larger flux of carbon to the sedimentary organic matter pool, in concert with possible density stratification of the water column resulting from increased run-off (Weedon, 1986; Waterhouse, 1999), likely initiated a switch to anoxic conditions in the sedimentary pore water and possibly also the overlying water column. The increased flux of organic carbon, combined with enhanced preservation under anoxic conditions, ultimately resulted in the formation of the laminated organic-rich black shale, with TOC > 10% (Figure 6.3). Anoxic conditions in the sedimentary pore space may have initiated microbial methanogenesis (Niemann et al., 2006) with a strongly enhanced flux of methane to the sediment–water interface, similar to modern-day anoxic/organic-rich lakebeds or in the modern-day Black Sea (Mazzini et al., 2004). Transition back to earlier climatic and environmental conditions returned the

system to organic-lean mudrock deposition (Phase 3, Figure 6.7; Figure 6.3). An elevated flux of biogenic methane from the underlying organic-rich laminated shale, however, still reached the sediment–water interface under conditions of elevated methane pore pressure and an (non-compacted/non-cemented) open pore space in the overlying organic-lean mudrock. Continued burial of the laminated organic-rich shale, possibly with the initiation of compaction and/or cementation of the host rock, may have prohibited biogenic methane from reaching the sediment–water interface via random dispersion through the pore spaces of the overlying mudrock (Phase 4, Figure 6.7).

Over-pressured free methane in the organic-rich host rock may have migrated upwards by diffusion, possibly along faults that were initiated, for example, due to compaction-related failure (Cornford, 2013; Talukder, 2012). Alternatively, the channelling of free biogenic methane from the organic-rich black shale to the sediment-water interface may have occurred through pipe-conduits, likely resulting in highly localized methane release from the seabed into the overlying water-column, allowing seep mounds to form. Such a model directly explains the observations made within the Lower Sinemurian succession at Kilve.

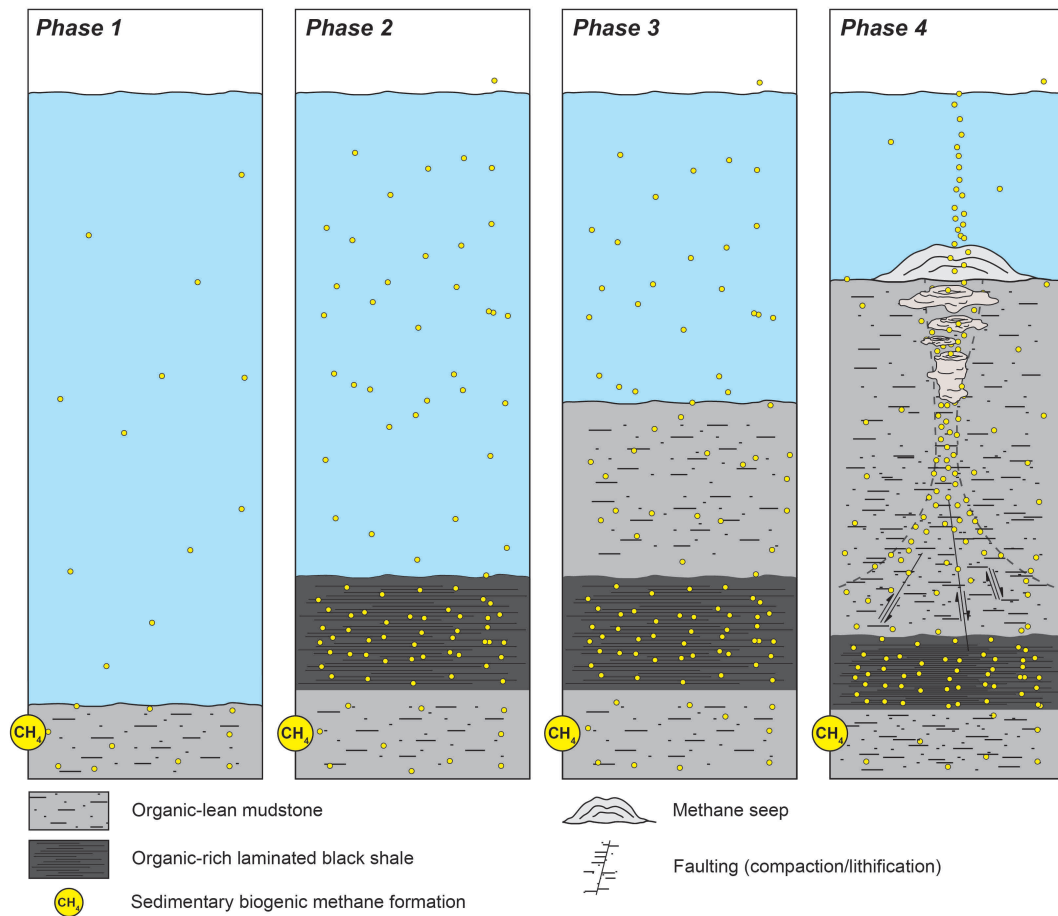


Figure 6.7 A suggested model explaining subsequent phases of change in the environmental and depositional environment leading to methane seep-mound formation, sourced by shallow-subsurface biogenic methane. Phase 1: the formation of organic-lean mudstones under oxygenated seafloor conditions with minor microbial methanogenesis generated only a minor flux (if any at all) of methane gas across the sediment–water interface and into the overlying water column; Phase 2: organic-rich laminated black shale deposited under anoxic conditions with microbial methanogenesis causing a strongly enhanced flux of methane to the sediment–water interface; Phase 3: transition back to organic-lean mudstone deposition under oxic conditions with still elevated flux of biogenic methane from the underlying organic-rich laminated shale reaching the sediment–water interface under conditions of elevated methane pore pressure and a (non-compacted/non-cemented) open pore space in the overlying organic-lean mudrock; Phase 4: continued burial of the laminated organic-rich shale, possibly with the initiation of compaction and/or cementation of the host rock, potentially prohibited biogenic methane from reaching the sediment–water interface via random dispersion through the pore spaces of the overlying mudrock. Channeling of methane resulted in the localized transfer of methane across the sediment–water interface and the formation/deposition of (authigenic) carbonates and carbonaceous methane seeps.

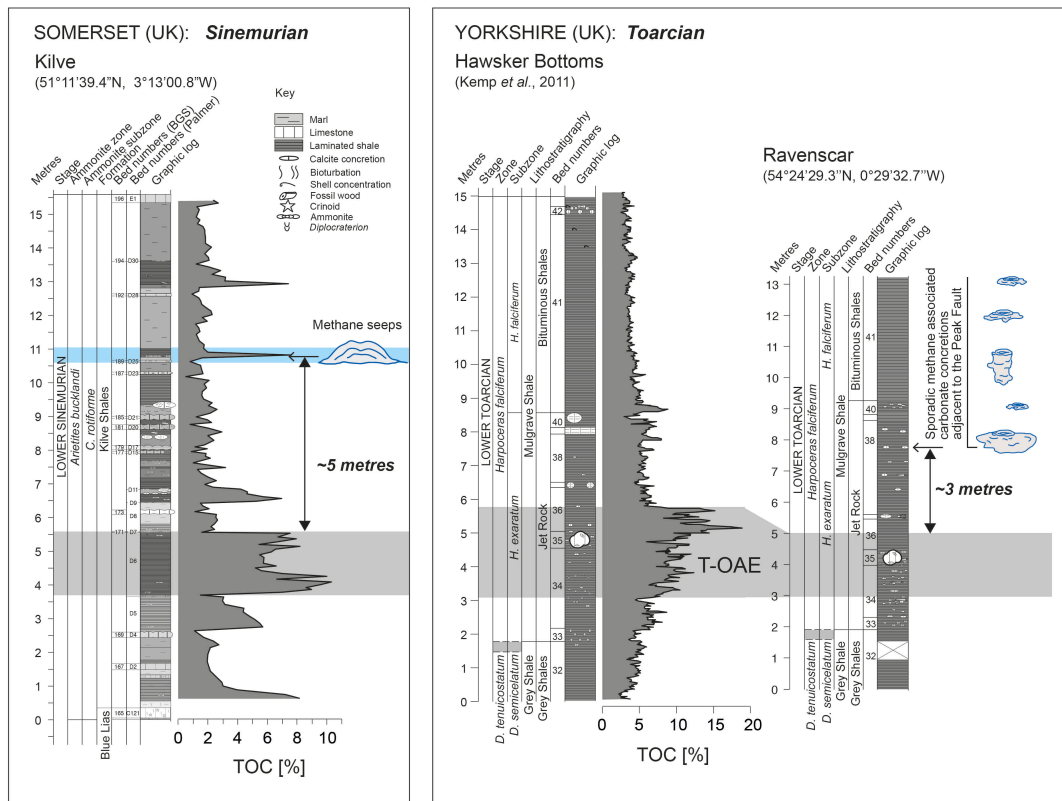


Figure 6.8 Lithostratigraphy of the Lower Sinemurian in the Bristol Channel Basin at the Kilve section (Somerset, UK) and the Lower Toarcian in the Cleveland Basin at the Ravenscar section (Yorkshire, UK). The methane seeps at Kilve appear at one horizon marked by the blue coloured band; methane associated carbonate concretions and conduits at Ravenscar occurred sporadically throughout the marked interval adjacent to the Peak Fault. In both localities, the seeps and conduits occur stratigraphically above the intervals of laminated organic-rich black shale marked by the grey band. TOC records are from this study (Kilve) and Kemp et al. (2011) (Yorkshire).

Interestingly, similar observations were made for the Lower Toarcian succession at Ravenscar, Yorkshire, UK (Hesselbo et al., 2013 and herein). Methane-seep carbonates, similarly with low $\delta^{13}\text{C}_{\text{carb}}$ values of -6 to -18% , occur ~ 3 m stratigraphically above the most organic-rich interval (up to 19% TOC) in the Lower Toarcian organic-rich Jet Rock (Mulgrave Shale Member; Figures 6.4 and 6.8; Hesselbo et al., 2013; Kemp et al., 2011). There, the seep occurrences are roughly aligned along the nearby Peak Fault. The sedimentary organic matter in the Jet Rock at Port Mulgrave was dominantly sourced by marine algae deposited under anoxic to

euxinic conditions (Salen et al., 2000, French et al., 2014). Differences in the stratigraphical distance between the top of the organic-rich black-shale interval and the subsequent occurrence of methane seep-mounds in the Lower Sinemurian of Somerset (~5 m) and the Lower Toarcian of Yorkshire (~3 m), may reflect differences in lithology and original pore space and thus different compaction rates or differences in water depth and/or sedimentary TOC content, potentially leading to differences in the build-up of over-pressure in the sediment pile. Interestingly, conduit like sedimentary carbonate structures do occur in the studied succession, directly preceding the methane seeps, suggesting a direct channelling of free methane from the TOC-rich Jet Rock upwards. With the model proposed here, formation of seabed methane seep-mounds would probably occur in a limited stratigraphical window after the deposition of an organic-rich black shale: after sufficient compaction and the formation of subsurface structures (i.e. faults) for the channelling of free methane, but before complete closure (by compaction or cementation) of the interstitial pore-space.

6.6 Conclusions

Changes in the isotopic composition of organic and inorganic sedimentary carbon from the Lower Sinemurian (*A. bucklandi* ammonite Zone) sedimentary record at Kilve, Somerset, UK (Bristol Channel Basin) coincided with changes in the depositional environment and palaeoclimate. The 3‰ negative excursion in the $\delta^{13}\text{C}_{\text{TOC}}$ and the 2‰ negative excursion in the $\delta^{13}\text{C}_{\text{carb}}$, in concert with a mass bloom of *Tasmanites* (green algae) and an apparent shift to anoxic/euxinic water-column conditions, coincided with the deposition of organic-rich laminated black shales. These phenomena, combined with a change in the terrestrial vegetation assemblage, occurred over a period of ~100 kyr. This perturbation of the palaeoenvironment was in phase

with a long-term (~405 kyr) eccentricity maximum and succeeds similar, but less intense, events throughout the Early Jurassic Hettangian Stage in the Bristol Channel Basin.

The formation of methane seep-mounds on the Early Sinemurian (*A. bucklandi* ammonite Zone) seabed in the Kilve area followed the deposition of organic-rich laminated black shale deposition by ~200 kyr (~5 m). Seep formation possibly resulted from biogenic methane production (by microbial methanogenesis) in the organic-rich shale and the channelling of this gas, which was likely over-pressured in the pore spaces of the source-rock, along fractures and faults to the sediment–water interface. Similar observations, with methane seep-mounds forming stratigraphically closely above the Lower Toarcian organic-rich Jet Rock at Ravenscar, Yorkshire, UK, suggests that seabed seep-mound formation could be a common phenomenon in the stratigraphical record, following local, regional or global black-shale deposition.

Chapter 7

Key Findings and Research Outlook

The studies presented in this thesis aim to improve our understanding of the Early Jurassic Toarcian Oceanic Anoxic Event (T-OAE; ~183 Ma), an extreme oceanographic and global climatic change event of the Phanerozoic, but also to provide insight on the causal mechanisms behind other carbon-cycle perturbations in the Early Jurassic.

(1) In this work, I identified the first lacustrine record of the T-OAE, in the Da'anzhai Member of the Sichuan Basin (China), and demonstrate that a major lake system developed contemporaneously with the T-OAE, likely due to enhanced hydrological cycling under elevated atmospheric $p\text{CO}_2$. Increased lacustrine organic productivity from elevated fluvial nutrient supply resulted in ~460 Gt of organic carbon burial in the palaeo-Sichuan lake alone, representing a major, but hitherto overlooked, carbon sink and negative feedback mechanism in the T-OAE global carbon cycle. It also provides a model for hydrocarbon source-rock prediction and exploration in continental basins during major global change events. Together with widespread burial of organic matter in the marine realm, the lacustrine carbon sink, involving the massive burial of organic (and also inorganic) carbon, possibly reduced atmospheric $p\text{CO}_2$, allowed the rebound of the global $\delta^{13}\text{C}$ signal, and cooled global climate through an inverse greenhouse effect. Future work on other lacustrine records that are associated with the T-OAE and other similar events will enable better quantification of the magnitude and significance of lacustrine carbon burial during major carbon-cycle perturbations in Earth history, and improve constraints on the continental palaeoenvironmental response at these times.

(2) Accurate and precise definition of the age of the lacustrine Da'anzhai Member and correlation to the marine stratigraphic record is challenging due to a lack of volcanoclastic deposits for high-precision radio-isotopic dating and the only limited

availability of reliable biostratigraphic proxies spanning both realms. Exceptional results from Re-Os radio-isotopic dating of mudrocks, palynostratigraphy and the observed distinct carbon-isotope excursion in both bulk organic matter and compound specific *n*-alkanes have constrained the lacustrine Da'anzhai Member black shales in the Sichuan Basin to be time-equivalent to the T-OAE. However, an improved stratigraphic framework and reference record for stratigraphic correlation between marine–marine and marine–terrestrial successions is still highly desirable. In this work, I present the first integrated (marine) stratigraphic reference framework, combining bio-, magneto- and chemostratigraphy for the complete Toarcian Stage from the Llanbedr (Mochras farm) Borehole (Cardigan Bay Basin, UK). This shows a (tentative) precise correlation between the Pliensbachian–Toarcian and T-OAE events and Karoo Large Igneous Province volcanism. Future work on high-precision U-Pb radio-isotopic dating of volcanoclastic deposits in biostratigraphically well constrained sedimentary records, together with high-precision radio-isotopic dating of emplaced basalt sequences will confirm the exact temporal (and causal) relationships between large igneous province volcanism and the T-OAE. This will significantly improve the mechanistic understanding of processes of climatic and environmental change at this time, and at other major global change events.

(3) Elevated atmospheric $p\text{CO}_2$ -induced accelerated hydrological cycling during the T-OAE not only resulted in lake expansion and major lacustrine carbon drawdown, but likely also caused enhanced continental weathering and the subsequent coeval change in early Toarcian seawater $^{87}\text{Sr}/^{86}\text{Sr}$, $^{187}\text{Os}/^{188}\text{Os}$, $\delta^{44/40}\text{Ca}$, increase in relative abundance of kaolinite, and the broadly synchronous occurrence of coarser-grained turbiditic/ mass-transport deposits in geographically widespread, shallow- and deeper marine basins. Similarly, elevated iron (Fe) supply from continental weathering

and relatively low oceanic sulphate concentrations due to abundant global pyrite fixation in organic-rich sediments during the T-OAE caused the formation of diagenetic siderite minerals in the relatively open-marine Cardigan Bay Basin.

(4) Blooms of aquatic primary producers and the elevated flux of (organic) matter to the lake- and seabed during the T-OAE negative carbon isotope excursion likely occurred due to elevated riverine nutrient supply under accelerated hydrological cycling. Together with enhanced organic-matter preservation because of water-column stratification and anoxia/euxinia, this led to the large-scale deposition of hydrogen-rich organic matter in many marine basins as well as in large inland lakes (e.g. the palaeo-Sichuan Lake). Deposition and preservation of hydrogen-rich organic matter could potentially generate high-quality hydrocarbon source-rocks in these basins at these times. Deposition of algal-dominated biomass under a stratified water column during lake level rise in the palaeo-Sichuan Basin marks the Da'anzhai Member studied here, as a potentially successful hydrocarbon source rock. These findings predict that good quality source-rocks may form in continental (lacustrine) basins during major global change events. This may aid targeted exploration by hydrocarbon industries, for conventional and unconventional source-rocks in sedimentary basins that formed under specific environmental conditions during temporally restricted time-intervals, such as the T-OAE.

(5) Periodic carbon-isotope fluctuations in Hettangian and Sinemurian marine sedimentary archives may reflect astronomical forcing of the global carbon cycle and the formation of organic-rich laminated black shales in the Bristol Channel Basin (UK), possibly in phase with short (~100kyr) and long (~405kyr) eccentricity and similar to Mediterranean sapropel formation during the Pleistocene. These findings suggest astronomically modulated mechanistic environmental processes that

control recent Mediterranean sapropel deposition, were likely also at play in the Early Jurassic and possibly throughout Earth history. This finding is especially relevant to unconventional hydrocarbon source-rock exploration as it provides direct and predictable constraints on the (changes in) quality and stratigraphic position of unconventional source-rocks in (marine) sedimentary basins.

(6) The formation of methane seep-mounds on the Early Sinemurian (*A. bucklandi* ammonite Zone) seabed in the palaeo Bristol Channel Basin (Kilve, Somerset, UK), followed the deposition of organic-rich laminated black shales by ~200 kyr. Seep formation possibly resulted from biogenic methane production, by microbial methanogenesis, in the organic-rich shale in the shallow subsurface, and the subsequent channeling of this biogenic methane from the over-pressured pore spaces towards the sediment–water interface. Similar observations, with methane seep-mounds forming stratigraphically closely above the Lower Toarcian organic-rich Jet Rock at Ravenscar (Yorkshire, UK), suggest that seabed seep-mound formation could be a common phenomenon in the stratigraphic record, following local, regional or global black-shale deposition. It also shows that processes leading to palaeoenvironmental perturbations and the deposition of organic-rich sediments, can continue to perturb (at least the local) environment for 100s of kyrs after the initial perturbation ceased. Future work on the source and geographic extend of methane seep-mound occurrence may allow further constraints on regional to global seafloor methane fluxes. This work is particularly important as hydrocarbon exploration companies consider (palaeo) methane-seepage as indicator for methane leakage from possible gas-reservoirs in the deep subsurface, while the actual source of the seeped methane may only lie a few (tens of) meters below the seabed.

Wider implications:

The major findings presented in this thesis have several wider implications. (a) Increased hydrological cycle and the accompanying intensified continental weathering resulted in the enhanced aquatic organic productivity in both the marine and continental realms (Chapters 2, 4 and 5 of this thesis), which subsequently buried significant amount of organic matter in geographically widespread localities. An accelerated hydrological cycle under high atmospheric CO₂ conditions has also been indicated in other global greenhouse events, e.g. the Late Cretaceous oceanic anoxic event (OAE2) and the Palaeocene/Eocene thermal maximum (PETM) (van Helmond et al., 2014; Pagani et al., 2006), which is likely to be the mechanism for organic carbon burial at these times; (b) lacustrine carbon burial potentially functions as an important carbon-sink that accelerates the recovery of the global carbon cycle perturbation, possibly not only at the T-OAE (Chapter 4 of this thesis), but potentially also at other major greenhouse events throughout the Phanerozoic. Such implication is supported by the recently identified lacustrine records associated with the OAE1a, the OAE2 and the PETM (Suarez et al., 2013; Chen et al., 2014; Zhang et al., 2016); (c) continental carbon burial in response to major environmental change events and associated enhanced hydrological cycling might not only have resulted in carbon burial in lacustrine settings (chapters 4 and 5 of this thesis). Abundant Lower to Middle Jurassic coal is present in the south Junggar, north Tarim, and Turpan basins (Hendrix et al., 1992), which, given a better age linkage to the T-OAE, would also dramatically drawdown organic carbon from the ocean-atmosphere system at that time. Such hypothesis has been given to the Early Cretaceous Valanginian event, where increased carbon storage of organic matter on the continent has been suggested as an additional mechanism for the observed carbon cycle perturbation (Westermann et al., 2010).

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Appendix A — Data from Chapter 2

Depth (ft)	Depth (m)	$\delta^{13}\text{C}$ ‰ VPDB	Tmax (°C)	TOC (%)	HI	MINC (%)
2832'4"	863.30	-26.8	438	1.19	121	1.05
2831'7"	863.07	-27.3				
2830'7"	862.76	-26.6				
2829'7"	862.46	-26.5				
2828'3"	862.05	-26.6	429	0.86	119	1.22
2827'5"	861.80	-26.2				
2826'5"	861.49	-26.4	436	1.01	108	1.41
2824'7"	860.93	-26.7	431	0.68	115	1.15
2822'2"	860.20	-25.1				
2820'	859.54	-25.2	438	1.3	66	1.31
2817'8"	858.82	-25.3	436	0.95	79	1.17
2815'8"	858.22	-24.6				
2813'10"	857.66	-24.5	436	1.21	51	1.08
2811'	856.79	-24.5				
2808'2"	855.93	-24.7	432	0.83	67	0.96
2805'11"	855.24	-24.7	440	0.8	59	1.25
2798'8"	853.03	-25.0				
2796'7"	852.40	-24.9	433	0.46	41	6.25
2794'6"	851.76	-24.8	438	0.92	63	2.25
2792'5"	851.13	-25.4				
2790'1"	850.42	-24.9	431	1.29	126	2.32
2788'2"	849.83	-24.6	438	1.14	44	
2785'9"	849.10	-24.7	436	0.67	54	0.82
2783'5"	848.39	-24.7				
2781'11"	847.93	-24.5	438	0.85	56	1.43
2779'11"	847.32	-24.7				
2778'4"	846.84	-24.2	432	0.83	63	1.99
2776'3"	846.20	-24.7	436	1.24	94	2.03
2774'6"	845.67	-24.4	431	0.63	71	3.88
2772'2"	844.96	-24.2				
2770'	844.30	-24.1	441	1	70	2.24
2768'9"	843.92	-24.0				
2766'6"	843.23	-24.2	432	0.8	78	1.31
2765'4"	842.87	-24.4	436	1.02	50	0.87
2763'9"	842.39	-23.9	431	0.62	71	2.77
2762'2"	841.91	-24.3				
2761'1"	841.58	-24.0	438	0.87	61	1.91
2760'5"	841.38	-23.8	433	0.75	73	2.02
2759'2"	840.99	-23.8				
2758'	840.64	-24.1	437	0.89	58	1.49
2756'7"	840.21	-24.0	435	0.9	80	1.46
2755'2"	839.77	-23.8				
2754'1"	839.44	-23.7	436	3.48	16	2.98
2752'7"	838.99	-24.0	432	0.82	71	1.16
2751'6"	838.66	-24.2				
2750'7"	838.38	-24.2	437	0.78	51	1.05
2749'3"	837.97	-24.4	433	0.71	70	1.46
2748'1"	837.62	-24.5				
2746'10"	837.23	-24.7	436	0.66	48	0.9
2743'6"	836.22	-24.9	429	0.56	77	0.81
2742'1"	835.79	-24.6				
2740'10"	835.41	-24.3	437	0.77	69	1.25
2739'11"	835.13	-24.6	432	0.65	72	0.94
2738'9"	834.77	-25.3				

Depth (ft)	Depth (m)	$\delta^{13}\text{C}$ ‰ VPDB	Tmax (°C)	TOC (%)	HI	MINC (%)
2737'5"	834.36	-25.5	436	0.53	81	1.22
2736'6"	834.09	-25.0	430	0.59	98	1.18
2735'3"	833.70	-25.2				
2734'3"	833.40	-27.4	434	0.45	62	0.78
2732'11"	832.99	-27.4	430	0.43	77	0.54
2731'8"	832.61	-27.2				
2730'4"	832.21	-27.1	436	0.46	76	0.89
2729'2"	831.85	-26.8				
2728'4"	831.60	-26.7				
2727'	831.19		428	0.13	31	0.07
2725'8	830.78	-29.8	429	0.38	100	0.48
2724'5.5"	830.41	-28.5				
2723'2.5"	830.03	-30.2	434	0.42	95	0.29
2722'	829.67	-29.9	430	0.43	114	0.35
2721'3"	829.44	-29.2				
2719'11"	829.03	-28.8	438	0.6	113	0.44
2719	828.75	-28.9				
2717'8	828.75	-28.6	430	0.83	146	0.67
2716'7"	828.34	-28.2	437	0.9	123	0.53
2716'1	828.01	-28.2				
2714'8	827.86	-27.9	435	0.89	148	0.54
2710'4	827.43	-29.6				
2713'6"	827.07	-27.7	435	0.93	129	0.67
2711'10"	826.57	-27.7				
2709'	826.11	-29.5	435	1.07	157	0.38
2706'8"	824.99	-29.1	436	1.4	162	0.52
2704'7"	824.36	-30.5	413	1.66	51	0.17
2703'8"	824.08	-30.0	437	1.03	118	0.2
2701'6"	823.42	-30.0	423	1.51	74	0.21
2699'10"	822.91	-30.6	428	1.65	260	0.42
2698'8"	822.55	-30.0	434	1.61	169	0.3
2697'1"	822.07	-30.1				
2696'	821.74		431	2.05	166	0.28
2694'6"	821.28	-30.0	434	1.76	203	0.8
2693'3	820.90	-31.1				
2692'1	820.55	-30.1	428	0.97	181	0.52
2690'8"	820.12	-30.0	434	1.31	203	0.35
2689'7	819.79	-30.2				
2688'3	819.38	-30.1	427	2.09	283	1.34
2687'4"	819.10	-31.2	430	2.43	279	0.74
2686'2	818.74	-29.5	436	1.05	172	0.88
2685	818.39	-29.6	432	1.16	185	1.15
2683'9"	818.01	-29.5	434	1.72	248	1.98
2682'3	817.55	-30.2	425	2.3	284	2.45
2681'3	817.25	-30.6				
2679'10"	816.81	-30.2	430	1.69	202	0.49
2678'8"	816.46	-29.7	429	1.13	142	0.19
2677'3	816.03	-29.9	432	1.49	246	0.28
2676'4"	815.75	-30.0	432	2.09	258	0.44
2675'6	815.49	-28.4	437	0.13	100	0.28
2672'8	814.63		426	0.11	73	0.4
2671'	814.12		422	0.1	10	0.2
2670	813.82	-28.9	418	0.19	58	0.18
2667'8	813.10	-30.2	425	1.53	250	0.5

Depth (ft)	Depth (m)	$\delta^{13}\text{C}$ ‰ VPDB	Tmax (°C)	TOC (%)	HI	MINC (%)
2666'6"	812.75	-29.9	430	1.72	233	0.47
2665'1"	812.32	-28.7	432	1.12	202	0.74
2664'2"	812.04	-29.3	429	2.01	290	0.92
2662'11"	811.66	-29.4	428	2.67	339	1.46
2661'8"	811.28	-29.2				
2660'10"	811.02	-28.3	435	0.65	137	0.85
2659'2"	810.51	-27.7	433	0.81	154	1.51
2658	810.16	-27.4				
2656'11"	809.83	-28.5	431	1.15	187	1.61
2655'3"	809.3	-27.3	433	0.95	152	0.74
2653'3"	808.7	-27.0				
2651'7"	808.2	-27.0	435	1.03	149	1.57
2648'4"	807.2	-28.9				
2646'9"	806.7	-26.3	434	0.68	69	1.18
2644'8"	806.1	-26.6				
2642'8"	805.5	-26.4	431	0.77	142	2.07
2640'8"	804.9	-25.8				
2638'10"	804.3	-25.5	437	0.92	115	2.27
2636'11"	803.7	-26.0				
2634'3"	802.9	-25.8	433	1.44	220	1.88
2632'6"	802.4	-25.0				
2629'7"	801.5	-24.6	434	0.71	107	2.05
2627'9"	800.9	-24.0				
2626'3"	800.5	-27.0	436	0.96	107	1.77
2623'11"	799.8	-24.6	436	0.72	101	2.54
2621'8"	799.1	-25.0				
2619'4"	798.4	-24.8	434	0.5	60	3.95
2617'5"	797.8	-25.7				
2615'1"	797.1	-25.3	435	0.62	95	2.85
2611'9"	796.1	-25.3	434	0.92	130	2.12
2610'2"	795.6	-24.9				
2607'8"	794.8	-25.0	434	0.84	131	2.91
2605'10"	794.3	-24.5				
2604'	793.7	-24.7	435	0.65	103	2.03
2601'	792.8	-24.3				
2598'7"	792	-24.4	436	1.01	127	2.96
2596'9"	791.5	-24.5				
2594'6"	790.8	-24.7	435	0.71	103	2.32
2592'7"	790.2	-24.6				
2590'7"	789.6	-25.2	435	0.68	81	1.81
2588'4"	788.9	-24.8				
2586'9"	788.4	-25.2	434	1.1	149	1.86
2584'7"	787.8	-25.1				
2582'8"	787.2	-25.2	435	0.84	93	2.24
2580'11"	786.7	-25.4				
2578'7"	786	-25.0	433	0.76	72	2.22
2576'6"	785.3	-25.1				
2574'8"	784.8	-24.9	434	0.71	79	3.07
2572'6"	784.1	-25.2				
2570'9"	783.6	-25.0	434	0.85	106	2.51
2568'6"	782.9	-25.5				
2566'5"	782.2	-25.2	436	0.64	73	3.11
2564'6"	781.7	-24.9				
2562'5"	781	-25.5	435	0.45	62	3.31
2560'3"	780.4	-25.4				
2558'4"	779.8	-25.2	438	0.68	88	4.76

Depth (ft)	Depth (m)	$\delta^{13}\text{C}$ ‰ VPDB	Tmax (°C)	TOC (%)	HI	MINC (%)
2556'4"	779.2	-25.4				
2554'4"	778.6	-25.4	435	0.73	108	2.86
2552'3"	777.9	-25.5				
2550'7"	777.4	-25.5	436	0.57	68	3.63
2548'3"	776.7	-25.8				
2546'3"	776.1	-25.2	433	0.71	77	3.93
2543'11"	775.4	-25.6				
2540'11"	774.5	-25.9	430	0.67	112	5.09
2538'10"	773.8	-25.9				
2536'10"	773.2	-26.0	430	0.84	120	2.35
2534'3"	772.4	-26.1				
2532'10"	772	-26.1	432	0.94	111	2.54
2529'10"	771.1	-26.4				
2528'6"	770.7	-26.4	434	0.82	140	2.88
2526'7"	770.1	-26.3				
2524'4"	769.4	-26.7	427	0.7	160	3.36
2522'4"	768.8	-26.4				
2520'3"	768.2	-25.9	431	0.79	118	3.81
2517'8"	767.4	-26.5				
2515'5"	766.7	-26.7	430	0.87	154	4
2513'10"	766.2	-26.6				
2511'1"	765.4	-26.9	431	0.68	84	3.4
2509'1"	764.8	-26.6				
2507'1"	764.2	-26.1	431	0.72	101	3.96
2503'11"	763.2	-26.2				
2502'1"	762.6	-26.6	430	0.61	131	4.99
2500'1"	762	-26.3				
2497'11"	761.4	-26.5	429	0.91	189	4.45
2495'10"	760.7	-26.2	429	0.87	141	5.27
2493'	759.9	-26.7	427	1.14	225	3.76
2490'3"	759	-26.6	427	0.85	156	3.86
2488'1"	758.4	-26.6	429	1.08	150	4
2486'	757.7	-26.7	429	0.96	148	5.14
2483'9"	757	-26.6	429	0.86	169	5.58
2481'10"	756.5	-26.6	429	0.86	153	5.45
2479'9"	755.8	-26.7	426	1.06	205	4.58
2477'1"	755	-27.0	425	1.51	273	3.04
2474'9"	754.3	-27.1	431	1.64	244	3.81
2473'2"	753.8	-27.2	429	0.99	180	4.87
2470'7"	753	-27.2	427	0.92	246	5.21
2467'10"	752.2	-27.2	426	1.27	243	4.11
2465'7"	751.5	-27.0	428	1.16	214	4.41
2463'4"	750.8	-26.8	430	1.09	150	4.17
2461'2"	750.2	-26.7	429	1.15	150	3.48
2459'2"	749.6	-28.4	426	1.32	225	4.88
2456'9"	748.8	-27.8	428	1.16	222	5.6
2454'10"	748.2	-27.7	426	0.95	204	5.32
2453'2"	747.7	-27.7	429	1.24	238	4.45
2450'11"	747	-27.9	429	1.21	247	5.35
2447'10"	746.1	-28.5	426	1.64	237	3.77
2445'7"	745.4	-28.3	429	1.6	269	4.47
2443'4"	744.7	-28.5	428	1.66	287	4.84
2440'5"	743.8	-28.3	428	1.41	233	5.24
2438'9"	743.3	-27.9	427	1.44	217	4.57
2436'10"	742.7	-28.7	427	1.95	296	5.69
2434'1"	741.9	-28.0	429	1.26	236	4.91

Depth (ft)	Depth (m)	δ13C ‰ VPDB	Tmax (°C)	TOC (%)	HI	MINC (%)
2432'1"	741.3	-28.0	429	1.54	255	5.09
2429'8"	740.6	-28.1	428	1.46	232	4.68
2427'7"	739.9	-28.0	429	1.59	231	4.46
2425'8"	739.3	-27.3	431	0.98	238	4.34
2422'6"	738.4	-26.8	428	1.32	158	3.4
2420'1"	737.6	-28.1	425	1.61	209	4.04
2418'	737	-28.4	429	1.24	250	5.52
2416'5"	736.5	-27.8	427	1.15	217	4.58
2414'	735.8	-27.5	429	0.92	225	5.12
2411'8"	735.1	-27.5	427	1.39	200	4.15
2410'1"	734.6	-27.8	432	1.27	193	5.23
2407'8"	733.9	-28.0				
2405'7"	733.2	-28.1	426	1.47	231	4.71
2402'10"	732.4	-27.9				
2401'1"	731.9	-27.9	430	1.16	205	4.7
2399'7"	731.4	-28.3				
2396'11"	730.6	-28.3	427	1.4	239	5.21
2394'10"	729.9	-27.8				
2393'3"	729.5	-27.3	430	0.78	150	5.96
2390'7"	728.6	-27.4				
2388'7"	728	-27.3	432	0.9	137	4.88
2386'8"	727.5	-27.5				
2384'6"	726.8	-28.6	427	1.51	281	5.3
2382'5"	726.2	-28.1				
2380'4"	725.5	-28.6	428	1.28	260	6.14
2377'2"	724.6	-28.3				
2375'6"	724.1	-27.4	429	0.93	181	4.51
2373'8"	723.5	-27.2				
2372'	723	-27.4	429	0.97	162	4.23
2369'6"	722.2	-27.5				
2367'9"	721.7	-27.2	428	0.91	159	4.28
2364'7"	720.7	-27.6				
2362'4"	720	-27.4				
2360'6"	719.5	-27.4				
2358'10"	719	-27.1	430	0.83	99	3.68
2356'6"	718.3	-27.6				
2354'3"	717.6	-28.0	427	1.53	232	5.17
2351'11"	716.9	-28.6				
2350'3"	716.4	-28.5	426	1.75	290	4.22
2348'	715.7	-28.0				
2345'11"	715	-28.6	429	1.47	231	5.28
2344'5"	714.6	-28.4				
2342'3"	713.9	-28.3	430	0.98	237	3.85
2339'11"	713.2	-27.5				
2337'9"	712.5	-27.3	431	1.03	117	3.72
2335'5"	711.8	-27.6				
2333'2"	711.1	-27.7	430	1	153	4.21
2331'9"	710.7	-28.5				
2330'1"	710.2	-28.0	429	1.17	182	5.22
2327'7"	709.4	-28.3				
2325'8"	708.9	-27.5	430	1.17	125	3.9
2323'7"	708.2	-28.0				
2321'5"	707.6	-28.3	431	1.5	194	5.46
2319'1"	706.9	-28.4				
2317'3"	706.3	-28.3	430	1.12	177	5.14
2315'	705.6	-28.4				

Depth (ft)	Depth (m)	δ13C ‰ VPDB	Tmax (°C)	TOC (%)	HI	MINC (%)
2312'7"	704.9	-27.7	429	1.12	204	4.67
2310'9"	704.3	-28.1				
2308'5"	703.6	-27.8	429	1.27	187	3.41
2306'4"	703	-27.8				
2304'5"	702.4	-28.4	431	1.46	232	4.63
2302'4"	701.8	-28.1				
2300'4"	701.1	-28.5	429	1.79	263	4.37
2298'2"	700.5	-27.8				
2296'	699.8	-27.7	427	1.3	175	3.75
2293'9"	699.1	-27.6				
2291'9"	698.5	-27.9	429	1.37	165	3.65
2289'7"	697.9	-27.4				
2287'7"	697.3	-27.4	429	0.98	158	4.57
2285'2	696.5	-28.7				
2283'1	695.9	-28.7	426	0.95	196	3.96
2281'	695.2	-28.7				
2279'2	694.7	-29.0	426	1.65	224	3.86
2277'1"	694.1	-28.3				
2275'	693.4	-28.2				
2272'10"	692.8	-27.0	428	0.67	122	2.28
2270'10	692.2	-27.6				
2268'8"	691.5	-27.6	428	1.16	174	2.94
2266'11"	691	-27.8				
2264'10	690.3	-27.8	428	1.02	225	4.74
2262'5"	689.6	-27.4				
2260'0.5"	688.9	-28.6				
2258'7"	688.4	-27.9				
2255'11	687.6	-28.0	428	1.38	235	5.06
2254'2.5"	687.1	-28.8				
2252'3"	686.5	-28.2	426	1.46	273	5.31
2250'6"	686	-28.4				
2247'6"	685.04	-28.0				
2245'10"	684.5	-28.5				
2243'5"	683.8	-28.0	427	1.35	249	3.42
2241'5"	683.2	-28.1				
2239'3.5	682.5	-28.1	428	1.61	204	4.15
2237'2"	681.9	-27.7				
2235'0.5"	681.2	-28.7	427	2.21	265	3.93
2232'9.5"	680.3	-27.8				
2230'10"	680	-27.6	429	0.8	151	3.49
2229'4"	679.5	-27.9				
2226'5.5"	678.6	-27.5	430	0.7	150	5.61
2224'10"	678.1	-27.4				
2222'5"	677.4	-27.3	430	1	132	3.94
2220'5"	676.8	-26.6				
2218'11"	676.3	-27.0				
2216'10"	675.7	-27.2	429	0.94	110	3.96
2214'10.5	675.1	-27.5				
2213'7"	674.7	-27.6	429	0.96	134	4.45
2210'6	673.8	-27.6				
2208'4"	673.1	-27.9	430	1.02	105	2.84
2206'1"	672.4	-27.9				
2204'2"	671.8	-28.4	428	1.25	168	3.74
2202'3"	671.2	-27.4				
2200'6"	670.7	-26.9	429	0.74	77	3.58
2197'11"	669.9	-27.5				

Depth (ft)	Depth (m)	$\delta^{13}\text{C}$ ‰ VPDB	Tmax (°C)	TOC (%)	HI	MINC (%)
2195'8"	669.2	-27.6	430	0.4	122	7.17
2193'7"	668.6	-28.0				
2190'10"	667.8	-27.9	428	1.03	134	2.76
2189	667.2	-27.7				
2187'2"	666.6	-27.1	427	0.98	91	2.31
2185'3"	666.1	-27.7				
2182'10"	665.3	-27.9	431	0.86	116	3.11
2181'2"	664.8	-28.0				
2178'11	664.1	-28.1	428	1.03	161	3.75
2177	663.5	-28.0				
2174'10"	662.9	-27.8	431	1	113	2.99
2172'7"	662.2	-27.6				
2170'4"	661.5	-27.6	430	0.9	99	2.23
2168'4"	660.9	-27.5				
2166	660.20	-27.0				
2163'10"	659.5	-27.3	429	0.81	111	2.3
2163'0"	659.3	-27.1				
2161'1"	658.7					
2159'1"	658.1	-27.0	428	0.84	99	2.32
2156'8"	657.4	-27.0				
2154'6"	656.7	-26.9				
2152'6"	656.1	-27.4				
2150'5"	655.4	-27.7	428	0.92	129	3.54
2148'8"	654.9	-27.2				
2146'5"	654.2	-27.3	430	0.81	107	4.11
2144'11"	653.8	-27.7				
2142'3"	653	-27.8	427	1.04	118	2.79
2140'8"	652.5	-27.5				
2138'7"	651.8	-27.1	433	0.69	107	4.19
2135'11"	651	-27.5				
2133'7.5"	650.3	-27.6				
2131'9"	649.8	-27.5	430	0.81	162	3.79
2129'4"	649	-27.3				
2127'5"	648.4	-27.4	430	0.77	135	4.47
2124'10.5	647.7	-27.5				
2122'11	647.1	-27.5	430	1	137	4.4
2120'7"	646.4	-27.5				
2118'5"	645.7	-27.5	430	1.06	137	3.97
2116'1"	645	-27.9				
2113'9"	644.3	-27.9	428	0.99	152	4.23
2112'0.5"	643.8	-27.7				
2109'8"	643	-28.1	428	1.03	170	3.97
2107'5"	642.3	-27.8				
2105'5"	641.7	-27.8	425	1.1	217	4.01
2103'4"	641.1	-27.7				
2101'3"	640.5	-27.9	429	1.23	201	4.83
2099'2"	639.8	-27.5				
2096'2.5"	638.9	-27.1	429	1.02	163	3.46
2093'11"	638	-27.0				
2091'8"	637.5	-27.2	429	1.03	197	3.44

Depth (ft)	Depth (m)	$\delta^{13}\text{C}$ ‰ VPDB	Tmax (°C)	TOC (%)	HI	MINC (%)
2090	637	-27.4				
2087'9"	636.3	-27.2	426	1.06	181	3.87
2084'11.5	635.5	-27.1				
2082'9"	634.8	-26.7	430	0.85	131	3.01
2080'5.5"	634.1	-27.1				
2078'5"	633.5	-27.2	431	0.93	189	3.72
2076'5"	632.9	-27.4				
2073'11	632.1	-27.1	426	0.98	208	3.84
2072'2"	631.6	-27.4				
2068'8"	630.5	-27.7	429	1.04	222	4.57
2067'4"	630.1	-27.5				
2065'3"	629.5	-27.8				
2063'10"	629.1	-27.2	430	0.92	149	5.1
2061'11	628.5	-27.1				
2060'4"	628	-26.9				
2058'6"	627.4	-27.4	430	0.75	213	4.76
2053'1"	625.8	-26.9				
2051'7"	625.3	-27.4	430	1.02	170	5.19
2049	624.5	-27.3				
2046'10"	623.9	-26.9	430	0.86	172	5.44
2044'9"	623.2	-26.9				
2042'1"	622.4	-26.6				
2040'1"	621.8	-26.7	431	0.85	144	3.59
2037'10"	621.1	-26.7				
2035'8"	620.5	-26.5	427	0.85	148	5.3
2033'3"	619.7	-26.8				
2031'7"	619.2	-26.5				
2029'2"	618.5	-26.7	429	0.84	163	4.7
2027'2"	617.9	-27.2				
2025'5"	617.3	-27.3				
2023'4"	616.7	-26.6	429	0.76	151	4.8
2020'8"	615.9	-26.6				
2018'3"	615.2	-26.8				
2015'10"	614.4	-27.1	430	0.99	198	3.93
2013'5"	613.7	-26.7				
2012'	613.3	-27.0				
2009'8"	612.5	-26.7	430	1.1	173	4.04
2007'7"	611.9	-27.1				
2006'	611.4	-26.4				
2003'10"	610.8	-26.8	431	1.13	148	4.01
2001'5"	610	-26.9				
1999'6"	609.4	-27.3				
1997'1"	608.7	-26.9	431	1.07	158	3.97
1995'3"	608.2	-27.0				
1992'4"	607.3	-26.3				
1990'10"	606.8	-26.8	431	0.98	187	4.66
1981'1"	603.8	-26.9	430	0.87	208	5.59
1979'3"	603.3	-27.0				
1977'9"	602.8	-26.9				
1975'3"	602.1	-27.1	406	1.73	42	0.2

Table A-1. Bulk organic carbon isotope data and Rock Eval data from the Toarcian interval of the Mochras core.

Depth [m]	Al	Al +/-	Si	Si +/-	S	S +/-	Ca	Ca +/-	Ti	Ti +/-	Fe	Fe +/-	Rb	Rb +/-	Zr	Zr +/-
602.06	7.06	0.06	29.98	0.08	2.47	0.009		0.049	0.471	0.0072	3.57	0.011	0.011	0.0001	0.0243	0.0001
602.82	6.42	0.06	22.15	0.07	1.17	0.006	12.03	0.032	0.405	0.0077	2.859	0.0105	0.0088	0.0001	0.0176	0.0001
603.28	5.85	0.06	19	0.06	1.03	0.006	15.22	0.042	0.355	0.0076	2.949	0.0113	0.0079	0.0001	0.0154	0.0001
603.83	5.48	0.06	16.93	0.06	0.7	0.005	18.68	0.05	0.359	0.0078	2.358	0.0098	0.0069	0.0001	0.0143	0.0001
606.81	6.49	0.06	19.06	0.06	1.36	0.007	16.73	0.044	0.384	0.0077	2.943	0.0108	0.0075	0.0001	0.0143	0.0001
607.26	6.26	0.06	18.78	0.06	2.93	0.011	12.05	0.033	0.387	0.0075	2.897	0.0107	0.0092	0.0001	0.0159	0.0001
608.15	6.01	0.06	18.68	0.06	1.48	0.007	14.77	0.041	0.339	0.0074	2.912	0.011	0.008	0.0001	0.0145	0.0001
608.71	6.04	0.06	22.26	0.07	1	0.006	13.63	0.036	0.389	0.0076	2.564	0.0097	0.0088	0.0001	0.0167	0.0001
609.45	5.69	0.06	19.88	0.06	1.09	0.006	16.21	0.043	0.359	0.0076	2.767	0.0105	0.0083	0.0001	0.0143	0.0001
610.03	5.15	0.06	19.73	0.06	0.92	0.006	15.75	0.044	0.352	0.0077	2.581	0.0103	0.0079	0.0001	0.0135	0.0001
610.77	5.57	0.06	15.64	0.06	2.18	0.01	15.12	0.047	0.335	0.0079	2.547	0.011	0.0086	0.0001	0.0132	0.0001
611.43	5.18	0.06	15.98	0.06	2.82	0.011	16.36	0.047	0.344	0.0075	2.635	0.0105	0.0074	0.0001	0.0142	0.0001
611.91	6.83	0.06	20.36	0.07	1.15	0.006	12.49	0.035	0.434	0.0083	3.036	0.0114	0.0097	0.0001	0.0162	0.0001
612.55	5.5	0.06	20.97	0.07	0.91	0.006	14.72	0.04	0.379	0.0079	2.678	0.0103	0.0082	0.0001	0.0155	0.0001
613.26	5.65	0.06	21.58	0.06	0.99	0.006	14.33	0.038	0.347	0.0074	2.582	0.0097	0.0078	0.0001	0.0158	0.0001
613.69	5.18	0.06	19.66	0.06	0.94	0.006	17.82	0.048	0.34	0.0076	2.509	0.0099	0.007	0.0001	0.0143	0.0001
614.43	5.13	0.07	16.49	0.08	0.89	0.007	10.71	0.043	0.438	0.01	2.813	0.0143	0.0086	0.0001	0.0171	0.0002
615.16	5.26	0.06	19.79	0.06	1.35	0.007	15.21	0.041	0.355	0.0076	2.467	0.0097	0.0067	0.0001	0.0157	0.0001
615.90	5.94	0.06	21	0.07	0.91	0.006	13.37	0.036	0.383	0.0078	2.568	0.0099	0.0085	0.0001	0.0178	0.0001
616.71	4.23	0.05	17.64	0.06	1.48	0.007	18.46	0.05	0.294	0.0075	3.591	0.0134	0.0057	0.0001	0.0138	0.0001
617.35	3.55	0.05	19.46	0.06	0.87	0.005	20.1	0.05	0.25	0.007	2.304	0.0094	0.0044	0.0001	0.0138	0.0001
617.88	4.06	0.05	23.1	0.07	0.98	0.006	12.88	0.035	0.328	0.0075	2.376	0.0095	0.0062	0.0001	0.015	0.0001
618.49	4.91	0.06	18.84	0.06	0.86	0.006	15.65	0.045	0.347	0.0079	2.631	0.0107	0.0076	0.0001	0.0161	0.0002
619.23	5.78	0.06	18.46	0.07	1.71	0.008	13.16	0.04	0.378	0.0083	2.552	0.0107	0.0073	0.0001	0.0156	0.0002
619.73	4.34	0.05	15.37	0.06	1.38	0.007	20.54	0.06	0.303	0.0075	2.082	0.0091	0.0059	0.0001	0.0119	0.0001
620.47	5.4	0.06	18.61	0.06	0.55	0.004	17.64	0.049	0.36	0.0079	2.38	0.0097	0.0072	0.0001	0.0127	0.0001
621.13	5	0.06	16.78	0.06	1.44	0.007	17.82	0.05	0.327	0.0076	2.3	0.0096	0.007	0.0001	0.0118	0.0001
621.82	6.91	0.06	22.09	0.06	1.1	0.006	12.39	0.032	0.425	0.0079	2.635	0.0097	0.0089	0.0001	0.0152	0.0001
622.43	5.91	0.06	21.74	0.07	1.05	0.006	14.17	0.038	0.353	0.0076	2.855	0.0106	0.008	0.0001	0.0142	0.0001
623.24	5.19	0.06	17.15	0.06	0.99	0.006	18.25	0.05	0.286	0.0073	2.569	0.0103	0.007	0.0001	0.0124	0.0001
623.87	5.53	0.06	18.17	0.06	1.88	0.008	16.53	0.045	0.352	0.0076	2.437	0.0096	0.0065	0.0001	0.0116	0.0001
624.54	5.27	0.06	21.67	0.07	1.15	0.006	13.67	0.037	0.33	0.0074	2.74	0.0104	0.0076	0.0001	0.0138	0.0001
625.32	4.81	0.06	17.38	0.06	0.92	0.006	18.56	0.05	0.284	0.0074	2.716	0.0109	0.0067	0.0001	0.0111	0.0001
625.78	7.03	0.06	22.11	0.07	0.98	0.006	11.34	0.03	0.428	0.008	2.742	0.0101	0.0093	0.0001	0.016	0.0001
627.43	5.65	0.06	18.5	0.06	0.73	0.005	17.17	0.047	0.368	0.0078	2.666	0.0103	0.0076	0.0001	0.0139	0.0001
627.99	4.68	0.05	14.45	0.05	6.95	0.021	13.54	0.036	0.336	0.007	2.515	0.0094	0.0089	0.0001	0.0137	0.0001
628.47	5.87	0.06	19.66	0.06	2.76	0.01	12.58	0.034	0.383	0.0076	2.641	0.0099	0.0089	0.0001	0.0154	0.0001
629.06	4.73	0.06	18.5	0.06	0.84	0.005	18.63	0.05	0.305	0.0075	2.681	0.0106	0.0068	0.0001	0.0124	0.0001
629.49	4.56	0.05	18.46	0.06	0.96	0.006	17.36	0.049	0.317	0.0076	2.513	0.0102	0.007	0.0001	0.0138	0.0001
630.12	4.8	0.05	15.87	0.05	5.37	0.017	13.37	0.038	0.344	0.0073	2.692	0.0103	0.0082	0.0001	0.0148	0.0001
630.53	5.37	0.06	18.99	0.06	0.86	0.005	15.75	0.044	0.366	0.0079	2.507	0.0101	0.0082	0.0001	0.013	0.0001
631.60	3.69	0.05	10.76	0.04	8.77	0.027	14.46	0.043	0.292	0.0068	2.851	0.011	0.0075	0.0001	0.0136	0.0001
632.13	6.27	0.06	21.6	0.07	1.02	0.006	13.64	0.037	0.42	0.0081	2.676	0.0102	0.0088	0.0001	0.0148	0.0001
632.89	6.64	0.06	18.11	0.06	2.36	0.009	12.4	0.035	0.382	0.0078	2.438	0.0097	0.0094	0.0001	0.0137	0.0001
633.50	6.05	0.07	17.69	0.07	1.81	0.009	12.03	0.039	0.4	0.0088	2.93	0.0126	0.0086	0.0001	0.015	0.0002
634.12	6.18	0.06	20.59	0.06	1.18	0.006	12.91	0.035	0.402	0.0079	2.932	0.0109	0.0091	0.0001	0.0139	0.0001
634.82	7.61	0.06	22.12	0.06	2.25	0.009	9.83	0.026	0.46	0.008	2.497	0.0093	0.0098	0.0001	0.0153	0.0001
635.50	5.68	0.06	21.94	0.07	1.15	0.006	14.11	0.038	0.36	0.0076	2.981	0.0109	0.008	0.0001	0.0154	0.0001
636.35	6.19	0.06	23.19	0.07	1.08	0.006	11.94	0.032	0.387	0.0078	2.778	0.0103	0.0086	0.0001	0.0163	0.0001
637.03	4.53	0.05	20.88	0.06	0.86	0.005	15.49	0.042	0.324	0.0074	2.707	0.0103	0.0067	0.0001	0.0146	0.0001
637.54	5.64	0.06	21.55	0.07	1.36	0.007	12.55	0.034	0.37	0.0077	2.698	0.0102	0.0078	0.0001	0.0152	0.0001
638.23	5.79	0.06	21.15	0.07	1	0.006	13.12	0.036	0.347	0.0076	2.75	0.0104	0.0084	0.0001	0.0143	0.0001
638.92	5.86	0.06	21.52	0.07	1.38	0.007	12.28	0.033	0.373	0.0076	3.161	0.0114	0.0079	0.0001	0.0144	0.0001
639.83	5.13	0.05	21.65	0.07	1.02	0.006	14.38	0.039	0.376	0.0077	2.599	0.01	0.0074	0.0001	0.0152	0.0001
640.46	4.8	0.06	17.77	0.06	1.18	0.006	17.16	0.049	0.286	0.0073	3.011	0.0116	0.0067	0.0001	0.0118	0.0001
641.10	5.03	0.05	22.88	0.07	1.62	0.007	12.77	0.034	0.34	0.0074	3.266	0.0116	0.0068	0.0001	0.0148	0.0001
641.73	5.39	0.06	22.71	0.07	0.97	0.006	13.18	0.036	0.372	0.0078	2.634	0.0101	0.0073	0.0001	0.0145	0.0001
642.34	5.56	0.06	21.39	0.07	1.05	0.006	14.14	0.039	0.385	0.0079	2.834	0.0107	0.007	0.0001	0.0155	0.0001
642.68	5.72	0.06	21.48	0.07	0.97	0.006	12.54	0.034	0.344	0.0074	2.462	0.0096	0.008	0.0001	0.0169	0.0001
643.03	4.59	0.05	20.38	0.06	0.81	0.005	15.62	0.043	0.303	0.0073	2.59	0.0101	0.0066	0.0001	0.0143	0.0001
643.47	6.39	0.06	22.47	0.07	1.17	0.006	11.78	0.031	0.393	0.0076	3.038	0.0109	0.008	0.0001	0.0158	0.0001
643.75	5.3	0.06	20.47	0.07	1.01	0.006	15.18	0.042	0.351	0.0077	2.638	0.0103	0.0072	0.0001	0.0132	0.0001
644.07	5.76	0.06	21.31	0.07	1.05	0.006	13.13	0.036	0.359	0.0075	2.982	0.011	0.0077	0.0001	0.0152	0.0001
644.27	5.45	0.06	20.28	0.06	0.9	0.006	15.64	0.043	0.327	0.0075	2.699	0.0104	0.0067	0.0001	0.0138	0.0001
644.82	5.56	0.06	21.91	0.07	0.92	0.006	14.27	0.038	0.349	0.0075	2.558	0.0098	0.0073	0.0001	0.0162	0.0001
644.98	5.18	0.06	19.6	0.06	1.06	0.006	16.6	0.045	0.342	0.0075	2.941	0.0111	0.0071	0.0001	0.0142	0.0001
645.69	6.15	0.06	20.58	0.06	1.13	0.006	14.26	0.038	0.36	0.0074	3.239	0.0115	0.0084	0.0001	0.0144	0.0001
646.35	6.34	0.06	22.05	0.07	0.99	0.006	11.93	0.033	0.406	0.0079	3.04	0.0111	0.0088	0.0001	0.0158	0.0001
647.07	5.49	0.06	19.33	0.06	0.98	0.006	15.57	0.043	0.327	0.0074	3.24	0.0119	0.0078	0.0001	0.013	0.0001

Depth [m]	Al	Al +/-	Si	Si +/-	S	S +/-	Ca	Ca +/-	Ti	Ti +/-	Fe	Fe +/-	Rb	Rb +/-	Zr	Zr +/-
647.66	6.56	0.06	24.01	0.07	1.13	0.006	10.64	0.028	0.397	0.0077	3.109	0.0111	0.0096	0.0001	0.0157	0.0001
648.44	5.46	0.06	20.69	0.06	0.99	0.006	15.63	0.041	0.372	0.0077	2.947	0.0108	0.0079	0.0001	0.0138	0.0001
649.02	5.37	0.06	20.87	0.07	0.8	0.005	12.87	0.036	0.359	0.0077	2.856	0.0109	0.0085	0.0001	0.0154	0.0001
649.76	5.75	0.06	18.92	0.06	1.56	0.007	14.08	0.04	0.346	0.0075	3.283	0.0122	0.0079	0.0001	0.0132	0.0001
650.33	6.48	0.06	21.99	0.07	0.97	0.006	13.38	0.035	0.444	0.008	3.231	0.0115	0.0086	0.0001	0.0167	0.0001
651.03	5.82	0.06	19.12	0.06	1.18	0.006	15.52	0.043	0.37	0.0078	3.543	0.0128	0.0081	0.0001	0.0144	0.0001
651.84	6.21	0.06	20.13	0.06	0.51	0.004	14.59	0.04	0.401	0.0079	2.56	0.0099	0.0085	0.0001	0.0155	0.0001
652.48	6.66	0.06	20.88	0.07	1.13	0.006	13.01	0.036	0.411	0.008	3.442	0.0124	0.0091	0.0001	0.0156	0.0001
652.96	7.68	0.06	22.87	0.07	1.65	0.008	8.892	0.024	0.443	0.008	2.914	0.0106	0.0102	0.0001	0.016	0.0001
653.77	7.16	0.06	21.16	0.07	1.25	0.006	10.63	0.029	0.383	0.0076	3.326	0.0118	0.0095	0.0001	0.0145	0.0001
654.23	5.24	0.05	20.5	0.06	0.73	0.005	14.65	0.039	0.354	0.0075	2.638	0.0101	0.0081	0.0001	0.0135	0.0001
654.91	7.06	0.06	20.46	0.07	1.54	0.007	9.134	0.027	0.431	0.0082	2.859	0.011	0.0102	0.0001	0.0152	0.0001
655.45	6.53	0.06	20.36	0.06	1.19	0.006	13.42	0.037	0.394	0.0079	3.67	0.0129	0.0089	0.0001	0.0136	0.0001
656.08	7.62	0.06	24.15	0.07	0.91	0.005	9.454	0.025	0.454	0.008	3.399	0.0115	0.0106	0.0001	0.0173	0.0001
656.69	7.27	0.06	23.83	0.07	0.75	0.005	9.753	0.026	0.427	0.0077	3.014	0.0106	0.0097	0.0001	0.018	0.0001
657.35	7	0.06	21.67	0.07	0.72	0.005	11.19	0.03	0.417	0.0079	3.234	0.0115	0.0093	0.0001	0.0174	0.0001
658.09	6.98	0.06	22.03	0.07	2.19	0.009	7.86	0.022	0.409	0.0076	3.228	0.0115	0.0093	0.0001	0.0185	0.0002
658.70	6.21	0.06	20.23	0.07	1.12	0.006	8.272	0.025	0.449	0.0082	2.986	0.0117	0.0103	0.0001	0.0183	0.0002
659.28	6.75	0.06	21.36	0.07	0.71	0.005	12.23	0.033	0.404	0.0077	2.855	0.0105	0.0094	0.0001	0.0154	0.0001
659.54	6.88	0.07	20.96	0.07	1.41	0.008	6.91	0.022	0.434	0.0084	3.012	0.0121	0.01	0.0001	0.0171	0.0002
660.20	7.73	0.06	26.09	0.07	0.53	0.004	6.819	0.018	0.476	0.008	2.899	0.0101	0.0115	0.0001	0.0173	0.0001
661.52	7.89	0.06	23.1	0.06	3	0.01	7.762	0.02	0.426	0.0074	4.113	0.0129	0.0105	0.0001	0.0172	0.0001
662.20	6.74	0.06	20.78	0.06	1.34	0.007	10.06	0.028	0.409	0.0078	3.475	0.0122	0.0099	0.0001	0.0148	0.0001
662.89	6.59	0.06	22.55	0.07	0.97	0.006	11.57	0.031	0.368	0.0074	3.197	0.0113	0.0094	0.0001	0.0153	0.0001
663.55	5.5	0.06	17.49	0.06	2.36	0.01	11.86	0.036	0.376	0.0081	3.375	0.0132	0.0086	0.0001	0.0142	0.0002
664.13	6.02	0.06	17.96	0.06	2.91	0.011	12.48	0.035	0.374	0.0076	3.479	0.0125	0.0088	0.0001	0.0139	0.0001
664.82	6.37	0.06	21.96	0.07	0.96	0.006	12.04	0.032	0.395	0.0077	3.265	0.0115	0.0089	0.0001	0.0161	0.0002
665.33	7.23	0.06	21.24	0.06	2.35	0.009	10.09	0.027	0.42	0.0076	2.95	0.0105	0.0093	0.0001	0.0168	0.0001
666.06	6.71	0.06	21.13	0.07	2.28	0.009	9.649	0.027	0.401	0.0077	4.988	0.0162	0.0097	0.0001	0.0159	0.0001
666.65	7.45	0.06	21.51	0.07	1.07	0.006	7.178	0.022	0.455	0.0083	3.466	0.0128	0.0101	0.0001	0.017	0.0002
667.21	6.84	0.06	21.38	0.07	1.25	0.007	11.05	0.031	0.42	0.0079	3.739	0.013	0.0098	0.0001	0.0148	0.0001
667.77	6.78	0.06	22	0.07	1.16	0.006	10.37	0.028	0.412	0.0078	3.725	0.0127	0.0098	0.0001	0.0167	0.0001
668.60	6.85	0.06	20.85	0.06	0.91	0.005	12.32	0.033	0.401	0.0077	3.348	0.0117	0.0085	0.0001	0.0154	0.0001
669.24	4.36	0.06	12.96	0.05	1.92	0.009	24.67	0.07	0.255	0.0073	3.123	0.0124	0.0051	0.0001	0.0076	0.0001
669.93	7.14	0.06	21.5	0.07	1.11	0.006	11.77	0.032	0.466	0.0083	3.436	0.0123	0.0102	0.0001	0.0155	0.0001
670.71	6.36	0.06	20.24	0.06	0.75	0.005	13.18	0.037	0.43	0.0081	3.185	0.0117	0.0097	0.0001	0.0148	0.0001
671.25	7.04	0.06	22.1	0.07	0.84	0.005	12.48	0.033	0.431	0.008	3.267	0.0115	0.0092	0.0001	0.0158	0.0001
671.83	6.34	0.06	20.94	0.06	1.26	0.006	12.49	0.034	0.388	0.0076	3.258	0.0116	0.0093	0.0001	0.014	0.0001
672.41	5.86	0.06	20.26	0.06	1.12	0.006	14.4	0.04	0.383	0.0079	3.354	0.0123	0.0079	0.0001	0.0143	0.0001
673.10	7.25	0.06	22.92	0.07	0.83	0.005	10.23	0.028	0.448	0.0081	3.023	0.0109	0.0098	0.0001	0.0164	0.0001
673.76	7.11	0.06	23.2	0.07	0.81	0.005	9.766	0.026	0.446	0.008	2.97	0.0107	0.01	0.0001	0.0171	0.0001
674.70	5.67	0.06	19.2	0.06	0.97	0.006	16.21	0.045	0.348	0.0077	2.991	0.0113	0.0077	0.0001	0.012	0.0001
675.09	6.78	0.06	23.66	0.07	0.66	0.005	10.43	0.028	0.422	0.008	2.701	0.0101	0.0096	0.0001	0.0162	0.0001
675.69	6.13	0.06	21.72	0.07	0.7	0.005	12.78	0.035	0.395	0.0079	2.69	0.0103	0.0085	0.0001	0.014	0.0001
676.33	6.05	0.06	20.42	0.06	0.94	0.006	15.02	0.041	0.362	0.0078	2.846	0.0108	0.0081	0.0001	0.0134	0.0001
676.78	6.91	0.06	23.2	0.07	0.66	0.005	10.83	0.03	0.408	0.0079	2.945	0.0108	0.0095	0.0001	0.0147	0.0001
677.39	6.55	0.06	21.02	0.07	0.68	0.005	12.81	0.036	0.404	0.0081	3.051	0.0116	0.009	0.0001	0.013	0.0001
678.13	5.52	0.06	21.66	0.07	0.69	0.005	14.86	0.04	0.343	0.0075	2.743	0.0103	0.0076	0.0001	0.0118	0.0001
678.62	4.33	0.05	16.46	0.06	1.11	0.006	20.59	0.06	0.282	0.0074	2.711	0.0109	0.0059	0.0001	0.0097	0.0001
679.50	6.53	0.06	20.57	0.06	0.9	0.005	14.09	0.038	0.377	0.0078	3.222	0.0117	0.0085	0.0001	0.0124	0.0001
679.96	6.6	0.06	21.52	0.07	0.87	0.005	13.18	0.036	0.417	0.0081	3.175	0.0115	0.0085	0.0001	0.0132	0.0001
680.55	6.29	0.06	21.72	0.07	1.06	0.006	11.96	0.033	0.395	0.0078	3.401	0.0121	0.0088	0.0001	0.0144	0.0001
681.24	5.64	0.06	19.69	0.06	1.81	0.008	12.71	0.036	0.345	0.0076	4.209	0.0147	0.008	0.0001	0.0124	0.0001
681.89	5.54	0.06	20.18	0.06	0.99	0.006	13.37	0.037	0.375	0.0077	3.065	0.0113	0.0086	0.0001	0.0134	0.0001
682.54	5.57	0.06	20.21	0.06	0.99	0.006	16.35	0.044	0.34	0.0076	2.85	0.0108	0.007	0.0001	0.011	0.0001
683.18	6.61	0.06	22.46	0.07	1.79	0.008	9.782	0.026	0.374	0.0075	3.213	0.0113	0.0085	0.0001	0.0135	0.0001
683.79	5.45	0.06	23.35	0.07	1	0.006	12.7	0.034	0.343	0.0074	3.053	0.011	0.0078	0.0001	0.0122	0.0001
684.53	4.82	0.05	20.15	0.06	1.25	0.006	16.61	0.044	0.303	0.0071	2.719	0.0101	0.0067	0.0001	0.0108	0.0001
685.04	5.46	0.06	21.38	0.07	0.78	0.005	13.06	0.036	0.331	0.0074	2.934	0.011	0.0078	0.0001	0.0121	0.0001
685.95	4.79	0.05	21.74	0.07	1.38	0.007	14.86	0.04	0.323	0.0073	2.413	0.0095	0.0071	0.0001	0.0128	0.0001
686.49	4.23	0.05	18.28	0.06	0.99	0.006	19.39	0.05	0.296	0.0074	2.312	0.0096	0.006	0.0001	0.0099	0.0001
687.08	4.34	0.05	19.61	0.06	0.9	0.005	16.99	0.047	0.308	0.0074	2.66	0.0105	0.0061	0.0001	0.0108	0.0001
687.60	4.65	0.05	19.19	0.06	1.01	0.006	17.57	0.048	0.291	0.0072	2.825	0.0108	0.0064	0.0001	0.0099	0.0001
688.42	5.42	0.06	20.84	0.07	0.8	0.005	14.63	0.041	0.346	0.0078	2.849	0.0111	0.0074	0.0001	0.0127	0.0001
689.01	4.58	0.06	16.99	0.06	0.68	0.005	19.07	0.05	0.316	0.0076	2.596	0.0105	0.0069	0.0001	0.0101	0.0001
689.58	5.32	0.06	18.49	0.06	0.9	0.006	15.54	0.046	0.342	0.0078	3.33	0.0127	0.008	0.0001	0.0112	0.0001
690.32	5.73	0.06	19.47	0.06	1.73	0.008	15.18	0.041	0.354	0.0076	2.965	0.0111	0.0075	0.0001	0.0131	0.0001
690.96	5.84	0.06	19.96	0.06	1.01	0.006	15.9	0.044	0.363	0.0078	3.245	0.0119	0.0076	0.0001	0.012	0.0001
691.49	6.37	0.06	22.42	0.07	0.81	0.005	10.2	0.028	0.403	0.0077	2.982	0.0108	0.009	0.0001	0.0145	0.0001

Depth [m]	Al	Al +/-	Si	Si +/-	S	S +/-	Ca	Ca +/-	Ti	Ti +/-	Fe	Fe +/-	Rb	Rb +/-	Zr	Zr +/-
692.15	6.73	0.06	20.69	0.06	0.85	0.005	13.68	0.037	0.384	0.0078	3.459	0.0123	0.0086	0.0001	0.0134	0.0001
692.76	7.16	0.06	24.7	0.07	0.97	0.006	8.155	0.022	0.483	0.0081	3.586	0.0121	0.0097	0.0001	0.018	0.0001
693.42	7.24	0.06	23.33	0.07	1.05	0.006	10.24	0.027	0.445	0.008	3.624	0.0123	0.0095	0.0001	0.0145	0.0001
694.06	5.7	0.06	23.19	0.07	0.9	0.006	13.25	0.035	0.384	0.0079	3.184	0.0115	0.0069	0.0001	0.0147	0.0001
694.69	4.31	0.05	21.13	0.07	0.89	0.006	15.35	0.043	0.334	0.0077	2.834	0.011	0.0058	0.0001	0.0177	0.0002
695.25	5.14	0.06	20.28	0.06	0.83	0.005	15.85	0.043	0.343	0.0076	2.692	0.0104	0.0058	0.0001	0.0135	0.0001
695.88	6.35	0.06	21.1	0.07	1.4	0.007	13.38	0.037	0.432	0.0082	3.441	0.0124	0.0072	0.0001	0.0172	0.0002
696.52	7.49	0.06	19.92	0.06	5.76	0.018	4.95	0.015	0.536	0.0084	1.766	0.0074	0.012	0.0001	0.0203	0.0001
696.93	5.55	0.06	18.01	0.06	1.11	0.006	18.57	0.05	0.321	0.0076	3.3	0.0122	0.007	0.0001	0.0112	0.0001
697.26	5.33	0.07	17.06	0.07	0.93	0.006	14.56	0.05	0.363	0.0087	2.905	0.0131	0.0078	0.0001	0.0121	0.0002
697.53	6.69	0.06	21.6	0.06	1.16	0.006	13.74	0.036	0.383	0.0078	3.779	0.0129	0.0089	0.0001	0.0134	0.0001
697.87	7.23	0.06	19.47	0.07	0.94	0.006	11.86	0.034	0.404	0.0079	3.277	0.0122	0.009	0.0001	0.0145	0.0001
698.22	5.92	0.06	20.72	0.06	0.94	0.006	12.97	0.036	0.402	0.0079	3.236	0.0118	0.0085	0.0001	0.0152	0.0001
698.53	7.1	0.06	21.27	0.07	1.37	0.007	11.34	0.032	0.4	0.0079	3.267	0.012	0.0097	0.0001	0.0146	0.0002
698.83	6.17	0.06	21.56	0.07	1.39	0.007	12.75	0.034	0.412	0.0079	3.562	0.0125	0.0089	0.0001	0.0155	0.0002
699.14	7.04	0.06	22.29	0.07	1.06	0.006	10.98	0.03	0.419	0.0079	2.79	0.0103	0.009	0.0001	0.0146	0.0001
699.54	6.1	0.06	23.22	0.07	0.89	0.005	12.21	0.032	0.366	0.0075	2.863	0.0104	0.0089	0.0001	0.0142	0.0001
699.82	6.01	0.06	23.06	0.07	0.94	0.006	13.57	0.036	0.359	0.0076	2.754	0.0102	0.0083	0.0001	0.0128	0.0001
700.18	5.33	0.06	19.16	0.06	0.98	0.006	15.49	0.042	0.309	0.0073	2.738	0.0104	0.0078	0.0001	0.0118	0.0001
700.48	6.05	0.06	22.99	0.07	0.79	0.005	11.52	0.032	0.386	0.0077	2.677	0.0102	0.0083	0.0001	0.0143	0.0001
700.63	5.85	0.06	21.98	0.07	0.97	0.006	11.44	0.031	0.399	0.0077	3.21	0.0115	0.0085	0.0001	0.0151	0.0001
701.14	5.38	0.06	19.12	0.06	2.44	0.01	15.17	0.042	0.309	0.0073	2.475	0.0098	0.0066	0.0001	0.0111	0.0001
701.42	4.51	0.05	20.12	0.07	1.08	0.006	14.89	0.043	0.295	0.0074	3.033	0.0118	0.0071	0.0001	0.0116	0.0001
701.75	6.53	0.06	22.76	0.07	0.96	0.006	12.19	0.032	0.349	0.0074	2.489	0.0094	0.0085	0.0001	0.0126	0.0001
702.11	5.02	0.06	21.94	0.07	1.04	0.006	13.67	0.038	0.334	0.0077	2.83	0.011	0.0068	0.0001	0.0125	0.0001
702.39	5.53	0.06	19.45	0.06	1.76	0.008	15.42	0.043	0.307	0.0074	2.605	0.0103	0.0067	0.0001	0.0106	0.0001
702.61	5.21	0.06	17.93	0.06	1.79	0.008	14.41	0.043	0.315	0.0076	2.579	0.0107	0.0075	0.0001	0.0119	0.0002
702.97	7.39	0.06	22.99	0.07	1.71	0.008	11.73	0.031	0.464	0.0082	2.397	0.0091	0.0086	0.0001	0.015	0.0001
703.28	6.53	0.06	21.2	0.07	1.29	0.007	9.396	0.027	0.427	0.0081	3.155	0.0118	0.0089	0.0001	0.0158	0.0002
703.61	6.43	0.06	20.57	0.07	2.06	0.009	10.36	0.03	0.337	0.0074	4.487	0.0154	0.0079	0.0001	0.0132	0.0002
703.94	5.45	0.06	17.48	0.06	2.39	0.01	15.35	0.044	0.337	0.0078	3.067	0.012	0.0072	0.0001	0.0117	0.0002
704.32	6.38	0.06	20.54	0.07	1.09	0.006	13.25	0.038	0.366	0.0078	2.636	0.0104	0.0077	0.0001	0.0147	0.0002
704.52	5.07	0.05	18.01	0.06	1.33	0.007	16.26	0.045	0.335	0.0075	2.419	0.0096	0.0072	0.0001	0.0131	0.0001
704.88	5.5	0.06	21.25	0.07	0.85	0.005	15.43	0.043	0.338	0.0076	2.648	0.0103	0.0069	0.0001	0.0127	0.0001
705.31	4.59	0.06	15.65	0.06	1.62	0.008	18.32	0.05	0.311	0.0076	2.711	0.0111	0.0053	0.0001	0.0096	0.0002
705.61	5.68	0.06	17.09	0.06	1.95	0.008	17.06	0.048	0.321	0.0074	2.488	0.01	0.0073	0.0001	0.012	0.0001
705.92	4.88	0.06	20.42	0.07	0.58	0.005	15.97	0.044	0.322	0.0076	2.327	0.0096	0.0068	0.0001	0.0116	0.0001
706.30	4.64	0.06	17.8	0.06	1.71	0.008	17.01	0.049	0.319	0.0075	2.597	0.0105	0.0069	0.0001	0.0116	0.0001
706.55	5.01	0.06	17.62	0.06	1.01	0.006	17.11	0.047	0.301	0.0073	2.783	0.0107	0.0069	0.0001	0.0114	0.0001
706.86	4.5	0.06	16.43	0.06	1.8	0.008	18.65	0.06	0.279	0.0072	2.501	0.0104	0.0062	0.0001	0.0103	0.0001
707.29	4.86	0.05	18.05	0.06	1.66	0.007	16.1	0.044	0.312	0.0073	3.042	0.0114	0.0071	0.0001	0.012	0.0001
707.57	4.46	0.06	16.37	0.06	1.61	0.008	18.01	0.05	0.29	0.0073	2.66	0.0109	0.0064	0.0001	0.0102	0.0001
707.92	5.34	0.06	19.23	0.06	0.79	0.005	15.1	0.041	0.341	0.0075	2.917	0.0109	0.0078	0.0001	0.0123	0.0001
708.23	5.71	0.06	20.89	0.07	1.15	0.006	15.55	0.043	0.345	0.0077	2.939	0.0112	0.0074	0.0001	0.0126	0.0001
708.48	5.57	0.06	17.46	0.06	1.36	0.007	15.85	0.045	0.333	0.0077	3.091	0.0119	0.0075	0.0001	0.0114	0.0002
708.86	5.58	0.06	21.31	0.07	1.12	0.006	15.58	0.042	0.328	0.0075	2.948	0.0111	0.0069	0.0001	0.0137	0.0001
709.17	6.11	0.06	20.41	0.06	1.09	0.006	14.06	0.037	0.369	0.0075	2.996	0.0108	0.0079	0.0001	0.0126	0.0001
709.45	4.66	0.06	19.06	0.06	1.05	0.006	19.18	0.05	0.274	0.0072	2.877	0.0112	0.0058	0.0001	0.0109	0.0001
709.85	4.3	0.05	18.05	0.06	0.69	0.005	17.73	0.05	0.31	0.0077	2.592	0.0107	0.0062	0.0001	0.0109	0.0001
710.21	4.3	0.06	17.8	0.06	1.33	0.007	18.47	0.05	0.288	0.0073	2.565	0.0105	0.006	0.0001	0.0117	0.0001
710.39	4.39	0.05	18.22	0.06	1.76	0.008	16.98	0.046	0.279	0.007	2.637	0.0102	0.0063	0.0001	0.0121	0.0001
710.72	5.71	0.06	18.39	0.06	0.96	0.006	16.11	0.047	0.328	0.0077	2.907	0.0114	0.007	0.0001	0.0111	0.0001
711.00	4.38	0.05	17.2	0.06	2.26	0.009	16.54	0.046	0.308	0.0073	2.358	0.0096	0.007	0.0001	0.0129	0.0001
711.15	4.7	0.06	16.6	0.06	2.96	0.012	13.27	0.042	0.327	0.0078	2.507	0.0108	0.0071	0.0001	0.0137	0.0002
711.50	4.88	0.06	18.85	0.06	0.87	0.005	18.71	0.05	0.3	0.0074	2.982	0.0114	0.0063	0.0001	0.0105	0.0001
711.84	5.87	0.06	21.87	0.07	0.63	0.005	16	0.043	0.342	0.0076	2.605	0.0101	0.0076	0.0001	0.0121	0.0001
712.01	5.48	0.06	20.38	0.06	1.08	0.006	12.77	0.035	0.373	0.0077	2.972	0.0111	0.0087	0.0001	0.0145	0.0001
712.55	4.61	0.05	14.55	0.05	5.86	0.019	15.24	0.044	0.277	0.007	2.412	0.0098	0.0077	0.0001	0.0121	0.0001
712.83	5.64	0.06	20.14	0.06	2.3	0.009	11.54	0.031	0.353	0.0073	2.817	0.0104	0.0087	0.0001	0.0142	0.0001
713.21	6.17	0.06	23.16	0.07	0.68	0.005	12.74	0.036	0.374	0.0077	2.792	0.0106	0.0084	0.0001	0.0141	0.0001
713.59	4.43	0.05	18.12	0.06	0.69	0.005	19.94	0.06	0.291	0.0075	2.656	0.0107	0.0056	0.0001	0.0099	0.0001
713.92	3.28	0.05	12.77	0.05	1.87	0.009	20.31	0.06	0.251	0.0072	2.845	0.0119	0.0052	0.0001	0.0118	0.0001
714.17	4.26	0.05	19.25	0.06	2.05	0.009	14.38	0.039	0.318	0.0073	2.622	0.0101	0.0068	0.0001	0.0119	0.0001
714.58	5.17	0.06	22.14	0.07	0.68	0.005	15.41	0.042	0.344	0.0077	2.257	0.0092	0.0052	0.0001	0.0136	0.0001
714.81	3.96	0.05	16.64	0.06	2.29	0.009	17.31	0.048	0.295	0.0072	2.235	0.0093	0.0061	0.0001	0.0125	0.0001
715.04	3.1	0.05	15.57	0.06	3.5	0.013	17.71	0.05	0.25	0.0069	1.873	0.0085	0.0053	0.0001	0.0107	0.0001
715.42	4.33	0.05	21.33	0.06	0.69	0.005	17.81	0.047	0.299	0.0074	2.482	0.0098	0.0057	0.0001	0.0105	0.0001
715.67	4.88	0.05	22.83	0.07	0.65	0.005	16.71	0.044	0.311	0.0074	2.321	0.0092	0.0061	0.0001	0.0112	0.0001
715.98	3.07	0.05	13.96	0.05	3.16	0.012	19.98	0.06	0.263	0.007	2.299	0.0096	0.0053	0.0001	0.0093	0.0001

Depth [m]	Al	Al +/-	Si	Si +/-	S	S +/-	Ca	Ca +/-	Ti	Ti +/-	Fe	Fe +/-	Rb	Rb +/-	Zr	Zr +/-
716.36	4.95	0.05	22.9	0.07	0.85	0.005	15.08	0.04	0.315	0.0074	2.434	0.0096	0.0065	0.0001	0.012	0.0001
716.66	3.52	0.05	16.98	0.06	2.24	0.009	17.61	0.049	0.249	0.0068	2.179	0.0091	0.0058	0.0001	0.0111	0.0001
716.86	5.1	0.05	23.89	0.07	0.76	0.005	13.36	0.035	0.329	0.0073	2.536	0.0096	0.0073	0.0001	0.0124	0.0001
717.19	4.99	0.05	22.7	0.07	0.8	0.005	14.79	0.039	0.319	0.0075	2.52	0.0098	0.0068	0.0001	0.0111	0.0001
717.58	5.2	0.06	20.47	0.07	0.8	0.005	17.44	0.048	0.336	0.0076	2.505	0.0101	0.0069	0.0001	0.0124	0.0002
717.98	5.62	0.05	25.07	0.07	0.91	0.006	10.2	0.027	0.377	0.0076	2.756	0.0101	0.0082	0.0001	0.0138	0.0001
718.72	4.96	0.05	20.5	0.06	1.66	0.007	13.39	0.036	0.346	0.0074	2.62	0.01	0.0074	0.0001	0.0148	0.0001
718.97	6.13	0.06	21.94	0.07	0.9	0.005	13.57	0.036	0.385	0.0077	2.635	0.01	0.009	0.0001	0.0141	0.0001
719.23	5.61	0.06	20.97	0.06	1	0.006	13.65	0.037	0.37	0.0076	2.45	0.0095	0.0079	0.0001	0.0143	0.0001
719.48	6.03	0.06	22.67	0.07	0.9	0.005	13.77	0.036	0.363	0.0075	3.031	0.0108	0.008	0.0001	0.0125	0.0001
719.71	5.85	0.06	21.11	0.06	1.55	0.007	11.78	0.031	0.386	0.0076	2.946	0.0107	0.0086	0.0001	0.0143	0.0001
720.04	5.55	0.05	24.14	0.07	0.67	0.005	12.61	0.033	0.366	0.0075	2.442	0.0093	0.0077	0.0001	0.0138	0.0001
721.28	4.78	0.05	19.58	0.06	0.9	0.005	17.01	0.046	0.32	0.0074	2.854	0.0108	0.0064	0.0001	0.0111	0.0001
721.69	5.02	0.05	20.66	0.06	0.95	0.006	17.96	0.047	0.297	0.0071	2.883	0.0106	0.0065	0.0001	0.0108	0.0001
721.79	5.44	0.05	18.78	0.06	2.43	0.009	13.51	0.036	0.34	0.0073	3.007	0.0109	0.0073	0.0001	0.013	0.0001
722.22	5.49	0.06	21.46	0.07	0.84	0.005	13.8	0.037	0.351	0.0074	2.673	0.0101	0.0073	0.0001	0.0138	0.0001
722.63	4.6	0.05	17.74	0.06	1.78	0.008	16.6	0.046	0.323	0.0074	2.885	0.011	0.0069	0.0001	0.0122	0.0001
722.99	4.77	0.05	18.1	0.06	1.94	0.008	15.45	0.044	0.331	0.0074	2.61	0.0103	0.0075	0.0001	0.0123	0.0001
723.29	4.36	0.05	15.5	0.05	2.87	0.011	17.6	0.05	0.309	0.0074	2.983	0.0115	0.0068	0.0001	0.0103	0.0001
723.49	5.79	0.06	21.68	0.07	1.02	0.006	14.13	0.038	0.335	0.0075	3.155	0.0116	0.008	0.0001	0.0129	0.0001
723.80	4.96	0.06	21.55	0.07	0.97	0.006	13.05	0.037	0.355	0.0078	2.79	0.0109	0.0077	0.0001	0.0142	0.0001
724.05	5.19	0.06	20.75	0.07	1.17	0.006	16.03	0.044	0.328	0.0074	3.261	0.012	0.0069	0.0001	0.0124	0.0001
724.43	5.09	0.05	21.73	0.07	1.13	0.006	12.99	0.035	0.335	0.0074	3.109	0.0113	0.0073	0.0001	0.0122	0.0001
724.56	2.95	0.05	17.4	0.06	0.9	0.005	20.89	0.06	0.24	0.0068	2.268	0.0095	0.0043	0.0001	0.0094	0.0001
725.12	3.59	0.05	21.32	0.07	0.63	0.005	18.36	0.049	0.274	0.0072	2.09	0.0088	0.0046	0.0001	0.01	0.0001
725.53	3.63	0.05	19.18	0.06	0.7	0.005	21.59	0.06	0.239	0.0069	2.281	0.0094	0.0044	0.0001	0.0091	0.0001
725.81	4.03	0.05	19.98	0.06	0.66	0.005	18.42	0.049	0.293	0.0073	2.468	0.0098	0.0052	0.0001	0.0102	0.0001
726.16	3.37	0.05	16.28	0.06	1.22	0.006	21.87	0.06	0.248	0.007	1.908	0.0085	0.0046	0.0001	0.0102	0.0001
726.49	3.67	0.05	17.66	0.06	2.02	0.008	17.18	0.047	0.276	0.007	2.438	0.0097	0.0059	0.0001	0.0101	0.0001
726.80	4.15	0.05	20.85	0.06	0.87	0.005	18.04	0.049	0.27	0.007	2.779	0.0106	0.0053	0.0001	0.0103	0.0001
727.08	4.98	0.06	20.38	0.06	1.05	0.006	15.82	0.043	0.317	0.0076	3.155	0.0118	0.0072	0.0001	0.0113	0.0001
727.46	5.4	0.06	21.8	0.07	0.75	0.005	16.59	0.044	0.317	0.0073	2.413	0.0095	0.0072	0.0001	0.0126	0.0001
727.71	6.03	0.06	19.15	0.06	1.39	0.007	14.2	0.04	0.347	0.0077	3.278	0.0123	0.0076	0.0001	0.0122	0.0002
728.04	4.89	0.06	19.21	0.06	0.73	0.005	18.36	0.05	0.309	0.0074	2.601	0.0103	0.0068	0.0001	0.0111	0.0001
728.50	3.07	0.05	10.64	0.04	6.88	0.022	17.19	0.05	0.238	0.0065	2.346	0.0097	0.0065	0.0001	0.0108	0.0001
728.65	5.72	0.06	19.49	0.06	0.86	0.005	16.03	0.045	0.339	0.0075	2.951	0.0112	0.0077	0.0001	0.0124	0.0001
728.98	2.9	0.05	12.21	0.05	5.98	0.02	19.01	0.06	0.227	0.0067	2.49	0.0103	0.0059	0.0001	0.0115	0.0001
729.46	2.53	0.05	10.32	0.04	6.06	0.02	21.96	0.07	0.19	0.0063	2.266	0.0097	0.0049	0.0001	0.0078	0.0001
729.67	4.46	0.05	17.78	0.06	1.96	0.008	16.86	0.047	0.313	0.0074	3.005	0.0114	0.007	0.0001	0.0113	0.0001
729.95	5.43	0.06	21.84	0.07	1.02	0.006	14.23	0.042	0.33	0.0077	2.853	0.0114	0.0067	0.0001	0.0117	0.0001
730.43	3.48	0.05	17.67	0.06	1.28	0.006	19.83	0.05	0.262	0.007	1.958	0.0084	0.0053	0.0001	0.0094	0.0001
730.58	3.43	0.05	15.91	0.06	2.57	0.011	16.28	0.05	0.26	0.0071	1.846	0.0086	0.0062	0.0001	0.0105	0.0001
730.99	3.56	0.05	18.29	0.06	0.52	0.004	21.58	0.06	0.252	0.0071	2.061	0.0089	0.0049	0.0001	0.0088	0.0001
731.39	4.08	0.05	17.25	0.06	1.48	0.007	18.09	0.05	0.242	0.0066	2.188	0.009	0.0057	0.0001	0.0109	0.0001
731.60	4.47	0.05	20.11	0.06	0.74	0.005	17.64	0.049	0.286	0.0074	2.423	0.01	0.0062	0.0001	0.0106	0.0001
731.85	4.91	0.06	19.05	0.07	1.58	0.008	15.14	0.047	0.342	0.008	2.416	0.0105	0.0067	0.0001	0.0115	0.0001
732.18	3.87	0.05	18.34	0.06	0.59	0.005	21.05	0.06	0.277	0.0073	2.236	0.0093	0.0053	0.0001	0.0089	0.0001
732.38	3.58	0.05	16.09	0.05	2.89	0.011	19.02	0.05	0.274	0.0069	2.089	0.0088	0.0058	0.0001	0.0127	0.0001
732.74	4.96	0.05	21.43	0.07	0.88	0.005	16.38	0.043	0.332	0.0075	2.602	0.01	0.0068	0.0001	0.012	0.0001
733.22	4.75	0.05	21.42	0.07	0.92	0.006	17.56	0.048	0.303	0.0073	2.501	0.0099	0.0062	0.0001	0.0114	0.0001
733.53	3.65	0.05	15.31	0.05	2.87	0.011	19.02	0.05	0.259	0.007	2.232	0.0093	0.0056	0.0001	0.0107	0.0001
733.86	4.83	0.05	22.02	0.07	0.68	0.005	16.59	0.044	0.293	0.007	2.201	0.0088	0.0066	0.0001	0.0125	0.0001
734.36	4.64	0.05	21.56	0.07	0.79	0.005	16	0.042	0.311	0.0073	2.65	0.0101	0.0064	0.0001	0.0127	0.0001
734.59	6.57	0.06	22.94	0.07	0.7	0.005	8.882	0.025	0.409	0.0077	3.368	0.012	0.0089	0.0001	0.0166	0.0001
734.85	5.3	0.05	22.14	0.07	0.93	0.006	14.76	0.039	0.348	0.0076	2.903	0.0108	0.0075	0.0001	0.0128	0.0001
735.08	5.22	0.06	18.3	0.06	2.83	0.011	15.9	0.045	0.302	0.0072	2.449	0.0098	0.0069	0.0001	0.0122	0.0002
735.43	4.03	0.05	16.53	0.06	1.75	0.008	19.05	0.05	0.3	0.0074	2.548	0.0103	0.0058	0.0001	0.0113	0.0001
735.79	5.91	0.06	19.22	0.07	2.52	0.01	11.94	0.035	0.384	0.0079	3.321	0.0126	0.0075	0.0001	0.0143	0.0001
736.17	5.03	0.06	20.67	0.07	0.69	0.005	16.08	0.044	0.331	0.0077	2.414	0.0098	0.0064	0.0001	0.013	0.0002
736.52	4.77	0.06	16.73	0.06	2.19	0.009	16.53	0.048	0.329	0.0075	2.385	0.0099	0.0064	0.0001	0.0119	0.0001
736.78	3.96	0.05	18.74	0.07	0.68	0.005	16.89	0.05	0.323	0.0079	2.668	0.0111	0.0065	0.0001	0.012	0.0002
737.01	4.61	0.05	19.67	0.06	0.7	0.005	19.56	0.05	0.294	0.0073	2.442	0.0098	0.0061	0.0001	0.0104	0.0001
737.34	5.46	0.05	23.38	0.07	0.99	0.006	13.14	0.034	0.352	0.0075	2.833	0.0103	0.0081	0.0001	0.0128	0.0001
737.64	5.2	0.05	19.9	0.06	1.01	0.006	15.03	0.04	0.312	0.007	2.606	0.0098	0.0071	0.0001	0.0125	0.0001
738.00	4.65	0.05	19.07	0.06	1.71	0.008	15.83	0.043	0.319	0.0074	2.45	0.0097	0.0072	0.0001	0.0113	0.0001
738.38	5.41	0.06	20.15	0.06	2.24	0.009	12.49	0.034	0.36	0.0074	2.849	0.0106	0.0083	0.0001	0.0145	0.0001
738.91	4.19	0.05	19.97	0.06	0.59	0.005	18.34	0.049	0.304	0.0073	2.297	0.0093	0.0063	0.0001	0.011	0.0001
739.34	4.53	0.05	18.16	0.06	2.67	0.01	15.72	0.043	0.313	0.0071	2.417	0.0095	0.007	0.0001	0.0139	0.0001
739.67	4.52	0.05	18.53	0.06	1.49	0.007	16.67	0.045	0.329	0.0074	2.564	0.01	0.007	0.0001	0.0122	0.0001

Depth [m]	Al	Al +/-	Si	Si +/-	S	S +/-	Ca	Ca +/-	Ti	Ti +/-	Fe	Fe +/-	Rb	Rb +/-	Zr	Zr +/-
739.93	5.75	0.06	18.71	0.06	0.88	0.005	17.81	0.05	0.316	0.0073	2.654	0.0104	0.0067	0.0001	0.013	0.0001
740.56	5.04	0.06	20.33	0.07	1.02	0.006	17.17	0.049	0.32	0.0075	2.804	0.0111	0.0068	0.0001	0.0127	0.0002
740.82	4.48	0.05	18.85	0.06	1.47	0.007	15.5	0.043	0.314	0.0073	3.125	0.0116	0.0068	0.0001	0.0116	0.0001
741.30	5.02	0.06	19.09	0.06	2.01	0.009	16.64	0.048	0.311	0.0074	2.2	0.0093	0.0063	0.0001	0.0105	0.0001
741.65	4.37	0.05	19.27	0.06	1.9	0.008	16.53	0.044	0.305	0.0072	2.47	0.0097	0.0063	0.0001	0.0109	0.0001
741.91	4.72	0.06	18.35	0.06	1.16	0.006	18.46	0.05	0.31	0.0072	2.341	0.0096	0.0064	0.0001	0.0114	0.0001
742.29	2.6	0.05	13.11	0.05	4.24	0.015	21.01	0.06	0.218	0.0066	1.876	0.0084	0.0047	0.0001	0.0105	0.0001
742.75	4.46	0.05	19.69	0.06	0.69	0.005	19.13	0.05	0.3	0.0072	2.082	0.0087	0.006	0.0001	0.0122	0.0001
743.03	4.36	0.05	22.33	0.07	0.88	0.005	15.67	0.042	0.31	0.0073	2.477	0.0097	0.006	0.0001	0.0126	0.0001
743.33	4.72	0.05	22.16	0.07	0.88	0.005	15.41	0.041	0.322	0.0073	2.382	0.0093	0.0073	0.0001	0.0114	0.0001
743.51	4.36	0.05	21.64	0.07	0.8	0.005	15.93	0.043	0.313	0.0075	2.396	0.0097	0.0064	0.0001	0.0116	0.0001
743.84	5.09	0.05	19.64	0.06	0.89	0.005	16.55	0.044	0.316	0.0072	2.39	0.0094	0.0067	0.0001	0.0109	0.0001
744.65	4.1	0.05	21.69	0.07	0.75	0.005	17.09	0.045	0.283	0.0072	2.23	0.0091	0.0058	0.0001	0.01	0.0001
744.73	4.2	0.06	21.43	0.07	0.58	0.005	17.85	0.05	0.284	0.0074	2.132	0.0093	0.0056	0.0001	0.0095	0.0001
745.13	3.39	0.05	15.04	0.05	4.63	0.016	16.38	0.046	0.248	0.0067	2.191	0.0091	0.0057	0.0001	0.0101	0.0001
745.41	4.86	0.05	19.1	0.06	3.77	0.012	14.9	0.038	0.276	0.0066	2.426	0.009	0.0063	0.0001	0.0109	0.0001
745.59	3.29	0.05	15.83	0.05	4.57	0.015	16.36	0.046	0.247	0.0067	2.301	0.0094	0.0063	0.0001	0.0105	0.0001
746.10	4.7	0.05	21.88	0.07	0.89	0.005	14.7	0.039	0.339	0.0073	2.638	0.0099	0.0068	0.0001	0.0119	0.0001
746.66	3.45	0.05	16.1	0.06	1.57	0.007	20.33	0.06	0.272	0.0072	2.083	0.009	0.0053	0.0001	0.0116	0.0001
747.04	3.63	0.05	20.62	0.06	0.55	0.004	19.18	0.05	0.264	0.007	1.79	0.0079	0.0049	0.0001	0.0087	0.0001
747.34	3.18	0.05	15.71	0.05	2.08	0.009	20.47	0.06	0.272	0.0072	2.069	0.0089	0.0048	0.0001	0.0098	0.0001
747.73	2.19	0.05	10.43	0.05	6.43	0.023	17.72	0.06	0.232	0.0069	1.733	0.0085	0.0048	0.0001	0.0094	0.0001
747.98	3.47	0.05	22.51	0.07	0.62	0.005	16.9	0.044	0.253	0.0069	2.011	0.0084	0.0051	0.0001	0.0102	0.0001
748.23	4.09	0.05	21.22	0.07	0.84	0.005	17.94	0.049	0.284	0.0071	2.482	0.0099	0.0053	0.0001	0.0105	0.0001
748.61	3.21	0.05	16.38	0.06	2.94	0.011	18.61	0.05	0.241	0.0068	2.132	0.009	0.0053	0.0001	0.0095	0.0001
748.82	4.07	0.05	19.27	0.06	0.63	0.005	21.62	0.06	0.243	0.007	2.149	0.0093	0.0048	0.0001	0.0095	0.0001
749.22	4.79	0.05	22.01	0.07	0.89	0.005	15.81	0.042	0.309	0.0074	3.037	0.0112	0.0064	0.0001	0.0113	0.0001
749.55	4.93	0.05	22.33	0.07	0.69	0.005	14.62	0.038	0.342	0.0073	2.464	0.0094	0.0058	0.0001	0.0123	0.0001
749.99	4.68	0.05	19.45	0.06	1.87	0.008	14.91	0.041	0.317	0.0074	3.052	0.0114	0.007	0.0001	0.0118	0.0001
750.16	3.67	0.05	13.91	0.05	6.25	0.02	13.96	0.04	0.275	0.0066	2.566	0.01	0.008	0.0001	0.0121	0.0001
750.44	3.51	0.05	15.03	0.05	4.98	0.017	16.2	0.046	0.271	0.0069	2.311	0.0094	0.0063	0.0001	0.0126	0.0001
750.82	3.71	0.05	14.68	0.05	5.56	0.019	14.96	0.044	0.256	0.0068	2.174	0.0093	0.0063	0.0001	0.011	0.0001
751.05	4.61	0.05	17.95	0.06	2.15	0.009	14.34	0.042	0.287	0.0073	2.378	0.0099	0.0069	0.0001	0.0115	0.0001
751.51	5.08	0.06	19.32	0.06	2.2	0.009	13.2	0.038	0.331	0.0075	2.434	0.0099	0.0075	0.0001	0.0117	0.0002
751.87	3.19	0.05	14.63	0.05	5.05	0.017	17.07	0.048	0.256	0.0067	2.252	0.0092	0.0062	0.0001	0.0103	0.0001
752.20	4.43	0.05	22.36	0.07	0.94	0.006	15.32	0.042	0.281	0.0072	2.528	0.0101	0.0062	0.0001	0.0107	0.0001
752.50	4.21	0.05	21.21	0.06	1.06	0.006	17.39	0.046	0.268	0.0071	2.734	0.0104	0.0056	0.0001	0.0098	0.0001
753.03	3.06	0.05	13.84	0.05	4.45	0.016	19.75	0.06	0.229	0.0067	2.219	0.0096	0.0052	0.0001	0.01	0.0001
753.47	3.95	0.05	20.12	0.06	1.38	0.007	16.37	0.045	0.32	0.0074	2.69	0.0104	0.0058	0.0001	0.0113	0.0001
753.82	5.69	0.06	22.03	0.07	1.48	0.007	10.83	0.03	0.398	0.0077	3.275	0.0118	0.0083	0.0001	0.0159	0.0001
754.10	4.55	0.05	20.78	0.06	0.62	0.005	16.93	0.045	0.329	0.0075	2.312	0.0093	0.0068	0.0001	0.0118	0.0001
754.30	5.32	0.06	22.98	0.07	1.01	0.006	15.16	0.04	0.321	0.0073	2.62	0.01	0.0071	0.0001	0.0124	0.0002
754.84	4.63	0.05	18.92	0.06	1.36	0.007	15.71	0.044	0.33	0.0075	2.973	0.0113	0.007	0.0001	0.0116	0.0001
755.02	6	0.06	21.9	0.07	2.42	0.009	10.39	0.028	0.386	0.0074	3.242	0.0114	0.0079	0.0001	0.0143	0.0001
755.40	5.8	0.06	19.11	0.06	3.94	0.014	11.8	0.033	0.376	0.0077	3.291	0.012	0.0076	0.0001	0.0129	0.0001
755.83	4.64	0.06	20.85	0.07	0.68	0.005	18.57	0.05	0.297	0.0074	2.397	0.0098	0.0057	0.0001	0.0113	0.0001
756.13	4.99	0.05	22.47	0.07	1.25	0.006	14.29	0.038	0.315	0.0073	3.058	0.0111	0.007	0.0001	0.0121	0.0001
756.79	5.44	0.05	24.47	0.07	1.24	0.006	12.18	0.032	0.354	0.0075	3.056	0.011	0.0078	0.0001	0.0144	0.0001
757.05	3.76	0.05	14.98	0.05	4.07	0.015	18.32	0.05	0.269	0.007	2.38	0.01	0.0064	0.0001	0.0104	0.0001
757.43	3.74	0.05	16.33	0.06	4.47	0.015	15.35	0.043	0.301	0.0071	2.318	0.0094	0.0066	0.0001	0.0132	0.0001
757.73	4.43	0.05	19.26	0.06	0.74	0.005	18.84	0.05	0.281	0.0071	2.461	0.0099	0.0061	0.0001	0.0106	0.0001
758.01	4.98	0.05	21.36	0.07	1.59	0.007	13.88	0.037	0.343	0.0074	2.969	0.0109	0.0073	0.0001	0.0134	0.0001
758.70	4.56	0.05	22.42	0.07	0.93	0.006	15.65	0.041	0.295	0.0072	2.785	0.0105	0.007	0.0001	0.0109	0.0001
759.36	5.18	0.05	24.64	0.07	0.88	0.005	12.61	0.033	0.349	0.0075	2.513	0.0096	0.0072	0.0001	0.0136	0.0001
759.87	3.66	0.05	16.99	0.06	3.95	0.014	15.23	0.042	0.285	0.0068	2.215	0.009	0.0069	0.0001	0.0115	0.0001
760.73	4.47	0.05	19.87	0.06	0.56	0.005	20.13	0.05	0.278	0.0071	2.274	0.0093	0.006	0.0001	0.0105	0.0001
761.11	3.66	0.05	15.35	0.05	4.68	0.016	15.36	0.044	0.316	0.0072	2.232	0.0092	0.0074	0.0001	0.0132	0.0001
761.37	6.8	0.06	22.01	0.07	0.2	0.004	12.6	0.036	0.387	0.008	2.624	0.0104	0.0079	0.0001	0.0153	0.0001
761.72	5.74	0.05	25.74	0.07	1.29	0.007	10.29	0.027	0.371	0.0075	3.162	0.0111	0.0085	0.0001	0.0155	0.0001
762.03	4.68	0.05	20.14	0.06	0.42	0.004	18.66	0.05	0.299	0.0072	2.189	0.009	0.0067	0.0001	0.011	0.0001
762.28	4.47	0.05	20.74	0.06	2.5	0.01	13.09	0.036	0.329	0.0073	2.758	0.0104	0.0073	0.0001	0.0134	0.0001
762.64	5.15	0.06	21.29	0.07	0.86	0.005	15.93	0.042	0.343	0.0075	2.758	0.0104	0.0076	0.0001	0.0122	0.0001
763.02	3.27	0.05	13.37	0.05	4.75	0.016	18.21	0.05	0.266	0.0069	2.402	0.0099	0.0066	0.0001	0.0121	0.0001
763.19	7.75	0.07	23.8	0.08	0.67	0.005	6.175	0.019	0.456	0.0082	3.669	0.0133	0.0106	0.0001	0.0182	0.0002
763.68	5.03	0.06	21.74	0.07	0.81	0.005	15.07	0.041	0.351	0.0077	2.825	0.0108	0.0074	0.0001	0.0143	0.0001
764.16	5.4	0.06	22.1	0.07	0.9	0.006	14.6	0.04	0.339	0.0075	2.978	0.0111	0.0073	0.0001	0.0147	0.0001
764.44	6.71	0.06	26.4	0.07	0.56	0.005	8.071	0.022	0.418	0.0078	3.47	0.0119	0.0095	0.0001	0.016	0.0001
764.77	4.93	0.06	22.27	0.07	0.82	0.005	15.73	0.043	0.317	0.0074	2.734	0.0105	0.0066	0.0001	0.0131	0.0001
765.12	6.76	0.06	22.27	0.07	1.18	0.006	9.328	0.027	0.429	0.0081	3.03	0.0114	0.0088	0.0001	0.0155	0.0002

Depth [m]	Al	Al +/-	Si	Si +/-	S	S +/-	Ca	Ca +/-	Ti	Ti +/-	Fe	Fe +/-	Rb	Rb +/-	Zr	Zr +/-
765.38	9.49	0.07	22.12	0.07	3.91	0.014	2.443	0.009	0.617	0.0085	5.102	0.0162	0.0142	0.0001	0.0195	0.0001
766.04	6.67	0.06	21.03	0.07	2.39	0.01	8.709	0.025	0.42	0.0078	3.512	0.0124	0.009	0.0001	0.0172	0.0002
766.22	4.46	0.05	16.92	0.06	2.88	0.011	16.58	0.047	0.301	0.0071	2.936	0.0113	0.0071	0.0001	0.0117	0.0001
766.52	5.57	0.06	20.61	0.06	1.69	0.008	13.78	0.038	0.363	0.0076	3.151	0.0115	0.0078	0.0001	0.0132	0.0001
766.70	5.53	0.06	23.55	0.07	0.83	0.005	14.28	0.037	0.384	0.0077	2.934	0.0106	0.0078	0.0001	0.014	0.0001
767.18	5.69	0.06	18.32	0.06	4.05	0.014	10.34	0.029	0.346	0.0071	2.998	0.0109	0.009	0.0001	0.016	0.0001
767.38	5.02	0.05	21.37	0.07	1.05	0.006	15.14	0.041	0.347	0.0075	3.418	0.0122	0.0072	0.0001	0.0148	0.0001
767.79	6.55	0.06	21.03	0.07	2.37	0.01	8.053	0.024	0.416	0.0079	3.458	0.0126	0.0098	0.0001	0.0155	0.0001
768.17	3.24	0.05	12.73	0.05	6.81	0.023	15.78	0.048	0.261	0.0068	2.332	0.0098	0.0067	0.0001	0.0123	0.0001
768.43	4.16	0.05	16.21	0.06	4.39	0.015	14.74	0.042	0.326	0.0072	2.734	0.0106	0.0074	0.0001	0.0137	0.0001
768.81	5.14	0.06	19.43	0.06	3.06	0.011	12.88	0.036	0.335	0.0073	2.861	0.0109	0.0081	0.0001	0.0144	0.0001
769.11	4.19	0.05	16.32	0.06	4.03	0.014	15.61	0.044	0.34	0.0075	2.981	0.0114	0.0072	0.0001	0.0138	0.0001
769.42	2.13	0.05	10.72	0.04	5.91	0.021	22.07	0.07	0.193	0.0065	2.257	0.0099	0.0042	0.0001	0.0091	0.0001
770.10	5.27	0.06	18.59	0.06	3.28	0.012	13.29	0.038	0.352	0.0074	2.856	0.0108	0.0081	0.0001	0.0138	0.0001
770.33	4.85	0.06	20.4	0.06	0.76	0.005	18.14	0.049	0.337	0.0076	2.815	0.0108	0.0063	0.0001	0.0122	0.0001
770.69	5.27	0.05	19.8	0.06	3.53	0.012	12.31	0.032	0.344	0.007	2.761	0.0099	0.0081	0.0001	0.0162	0.0001
771.04	3.63	0.05	14.05	0.05	5.13	0.017	17.43	0.05	0.3	0.0071	2.172	0.0091	0.0064	0.0001	0.0138	0.0001
771.09	2.5	0.05	9.72	0.04	7.31	0.024	19.37	0.06	0.233	0.0065	2.166	0.0093	0.0058	0.0001	0.0116	0.0001
771.65	6.17	0.06	19.92	0.07	2.69	0.011	7.885	0.025	0.387	0.0078	3.854	0.0144	0.0088	0.0001	0.0152	0.0002
772.01	4.69	0.06	18.51	0.06	0.7	0.005	17.74	0.05	0.323	0.0075	2.505	0.0101	0.0068	0.0001	0.0124	0.0001
772.08	6.86	0.06	23.74	0.07	1.36	0.007	8.496	0.023	0.42	0.0076	3.703	0.0122	0.0094	0.0001	0.0172	0.0001
772.44	5.97	0.06	22.06	0.07	1.65	0.008	9.594	0.029	0.353	0.0078	3.385	0.0129	0.0069	0.0001	0.0154	0.0001
772.80	5.8	0.06	20	0.07	2.02	0.009	10.23	0.03	0.381	0.0078	3.049	0.0116	0.0081	0.0001	0.0149	0.0002
773.23	6.2	0.06	19.71	0.06	2.46	0.009	8.367	0.023	0.423	0.0075	3.572	0.0123	0.0096	0.0001	0.0168	0.0001
773.53	6.34	0.06	19.62	0.07	2.16	0.009	9.024	0.027	0.419	0.0082	3.466	0.0131	0.009	0.0001	0.0163	0.0002
773.84	6.67	0.06	20.01	0.06	3.29	0.012	8.357	0.023	0.438	0.0077	3.577	0.0123	0.01	0.0001	0.0163	0.0001
774.14	5.96	0.06	20.25	0.06	1.1	0.006	13.08	0.036	0.397	0.0079	3.389	0.0123	0.0087	0.0001	0.0164	0.0002
774.47	4.99	0.06	19.81	0.06	0.62	0.005	18.52	0.049	0.334	0.0076	2.895	0.0109	0.0069	0.0001	0.0121	0.0001
775.11	6.5	0.06	23.64	0.07	0.9	0.006	12.08	0.032	0.403	0.0079	3.372	0.0118	0.0093	0.0001	0.0159	0.0001
775.39	5.38	0.06	16.75	0.06	2.57	0.01	15.43	0.042	0.359	0.0074	2.813	0.0105	0.0081	0.0001	0.0146	0.0001
775.72	5.76	0.06	22.23	0.07	0.45	0.004	14.46	0.038	0.394	0.0079	2.785	0.0104	0.0082	0.0001	0.0149	0.0001
776.10	5.07	0.05	16.79	0.05	3.39	0.012	14.52	0.039	0.382	0.0074	2.783	0.0103	0.0084	0.0001	0.0154	0.0001
776.40	6.09	0.06	21.7	0.07	0.99	0.006	14.17	0.038	0.375	0.0079	3.605	0.0128	0.0085	0.0001	0.0141	0.0001
776.71	6.36	0.06	19.95	0.06	2.65	0.01	9.966	0.028	0.411	0.0077	3.385	0.0121	0.0096	0.0001	0.0165	0.0001
777.09	6.23	0.06	17.67	0.06	2.12	0.009	9.766	0.03	0.435	0.0083	3.781	0.0142	0.0096	0.0001	0.0173	0.0002
777.42	6.49	0.06	18.4	0.06	1.48	0.007	11.47	0.035	0.416	0.0083	3.166	0.0124	0.0087	0.0001	0.0161	0.0002
777.85	5.9	0.06	20.15	0.06	0.33	0.004	14.56	0.041	0.388	0.008	3.53	0.0129	0.0084	0.0001	0.0141	0.0001
777.93	7.35	0.06	19.74	0.06	3.31	0.012	10.03	0.027	0.415	0.0076	3.291	0.0115	0.009	0.0001	0.0173	0.0001
778.56	7.14	0.06	24.72	0.07	0.29	0.004	9.563	0.025	0.442	0.0079	3.433	0.0118	0.0098	0.0001	0.0173	0.0001
778.84	5.82	0.06	19.11	0.06	3.05	0.011	12	0.033	0.391	0.0075	3.483	0.0122	0.0089	0.0001	0.016	0.0001
779.17	7.67	0.06	19.56	0.06	3.27	0.012	8.783	0.024	0.45	0.0078	3.585	0.0122	0.0102	0.0001	0.0191	0.0001
779.50	5.96	0.06	18.31	0.06	1.82	0.008	13.26	0.037	0.377	0.0076	3.299	0.0119	0.0084	0.0001	0.0177	0.0002
779.78	5.26	0.06	18.77	0.06	0.54	0.004	17.54	0.049	0.344	0.0077	3.241	0.0121	0.0071	0.0001	0.014	0.0001
780.36	7.1	0.06	24.71	0.07	0.66	0.005	9.686	0.026	0.443	0.0079	3.564	0.012	0.0097	0.0001	0.0181	0.0001
780.59	5.31	0.06	17.6	0.06	2.81	0.011	12.17	0.035	0.377	0.0077	3.156	0.012	0.0079	0.0001	0.017	0.0001
781.02	7.78	0.06	20.39	0.06	2.31	0.009	10.53	0.029	0.462	0.0081	3.704	0.0127	0.0096	0.0001	0.0163	0.0001
781.33	5.67	0.06	16.44	0.05	5.12	0.016	11.46	0.032	0.381	0.0074	3.009	0.011	0.0087	0.0001	0.0176	0.0001
781.66	6.2	0.06	19.1	0.06	2.27	0.009	11.76	0.032	0.393	0.0075	2.966	0.0107	0.0086	0.0001	0.0176	0.0001
781.91	6.61	0.06	19.01	0.06	3.56	0.013	9.708	0.027	0.42	0.0078	3.718	0.013	0.01	0.0001	0.0177	0.0001
782.24	6.78	0.06	18.58	0.06	1.75	0.008	10.47	0.029	0.45	0.0079	3.323	0.0118	0.0087	0.0001	0.0178	0.0001
782.52	6.04	0.06	16.89	0.06	4.5	0.015	9.869	0.028	0.412	0.0076	3.612	0.0128	0.0079	0.0001	0.0198	0.0001
782.88	6.82	0.06	22.7	0.07	0.38	0.004	11.89	0.032	0.411	0.0078	3.903	0.0132	0.0087	0.0001	0.016	0.0001
783.26	6.57	0.06	23.54	0.07	0.46	0.004	8.604	0.025	0.478	0.0084	3.629	0.0129	0.0099	0.0001	0.0198	0.0002
783.82	6.31	0.06	23.69	0.07	0.24	0.004	9.793	0.028	0.46	0.0083	3.701	0.0131	0.0089	0.0001	0.0185	0.0002
784.10	7.59	0.06	18.82	0.06	4.26	0.014	6.86	0.019	0.444	0.0075	4.251	0.0139	0.0109	0.0001	0.0182	0.0001
784.40	6.9	0.06	22.52	0.07	0.61	0.005	11.39	0.031	0.447	0.0082	3.986	0.0136	0.0098	0.0001	0.017	0.0002
784.76	5.71	0.06	18.93	0.06	3.05	0.011	12.13	0.033	0.406	0.0076	3.161	0.0113	0.0088	0.0001	0.0183	0.0001
785.09	6.03	0.06	22.49	0.07	0.94	0.006	12.96	0.035	0.412	0.008	3.982	0.0136	0.0081	0.0001	0.0172	0.0002
785.32	6.82	0.06	17.96	0.06	1.94	0.008	13.11	0.037	0.417	0.008	3.722	0.0134	0.0085	0.0001	0.0164	0.0001
785.77	3.97	0.05	11.68	0.04	9.03	0.028	12.05	0.035	0.323	0.0069	3.103	0.0116	0.009	0.0001	0.0171	0.0001
785.95	7.66	0.06	25.61	0.07	0.84	0.005	7.537	0.02	0.497	0.0082	4.05	0.0133	0.0109	0.0001	0.0189	0.0002
786.26	6.96	0.06	24.37	0.07	0.92	0.006	7.31	0.021	0.486	0.0083	4.149	0.014	0.0104	0.0001	0.0196	0.0002
786.66	7.23	0.06	24.46	0.07	0.48	0.004	9.331	0.025	0.481	0.0081	3.681	0.0123	0.0094	0.0001	0.0184	0.0001
786.97	7.86	0.06	24.41	0.07	0.91	0.006	7.374	0.021	0.484	0.0083	4.294	0.0144	0.0108	0.0001	0.0192	0.0002
787.20	6.54	0.06	17.87	0.06	5.24	0.016	10.55	0.028	0.411	0.0073	3.445	0.0116	0.01	0.0001	0.0194	0.0001
787.58	7.08	0.06	20.52	0.06	2.68	0.01	9.232	0.025	0.431	0.0077	3.507	0.0121	0.0095	0.0001	0.0182	0.0001
787.78	8.07	0.06	25.55	0.07	0.4	0.004	7.716	0.021	0.475	0.0081	3.713	0.0124	0.0101	0.0001	0.0201	0.0002
788.06	6.09	0.06	17.41	0.06	2.39	0.01	14.41	0.04	0.398	0.0079	3.346	0.0123	0.0085	0.0001	0.0152	0.0001
788.44	4.68	0.05	11.59	0.04	9.56	0.028	11.93	0.033	0.325	0.0066	3.87	0.013	0.0092	0.0001	0.0184	0.0001

Depth [m]	Al	Al +/-	Si	Si +/-	S	S +/-	Ca	Ca +/-	Ti	Ti +/-	Fe	Fe +/-	Rb	Rb +/-	Zr	Zr +/-
788.72	7.87	0.06	19.68	0.06	4.61	0.015	6.172	0.018	0.474	0.0078	4.177	0.0139	0.0107	0.0001	0.0191	0.0001
788.92	4.4	0.05	12.4	0.05	8.13	0.025	11.47	0.033	0.352	0.0071	3.09	0.0114	0.009	0.0001	0.0182	0.0001
789.36	6.29	0.06	19.3	0.06	3.34	0.012	9.329	0.026	0.425	0.0077	3.772	0.0131	0.0101	0.0001	0.0172	0.0001
789.61	5.98	0.06	16.46	0.06	6.22	0.019	9.768	0.028	0.422	0.0076	4.181	0.0141	0.0101	0.0001	0.0169	0.0001
790.22	6.56	0.06	18.95	0.06	3.8	0.013	10.37	0.028	0.399	0.0073	3.961	0.0131	0.0092	0.0001	0.0181	0.0001
790.58	4.82	0.05	15.15	0.05	4.79	0.016	13.73	0.04	0.368	0.0075	3.305	0.0123	0.008	0.0001	0.016	0.0001
790.80	7.04	0.06	20.01	0.06	3.07	0.011	8.978	0.024	0.439	0.0076	4.098	0.0135	0.01	0.0001	0.0186	0.0001
791.18	6.61	0.06	18.74	0.06	3.95	0.013	9.25	0.026	0.422	0.0076	4.362	0.0145	0.0098	0.0001	0.0179	0.0001
791.49	7.42	0.06	23.27	0.07	0.74	0.005	10.41	0.028	0.464	0.0081	4.026	0.0133	0.0092	0.0001	0.0175	0.0001
791.79	6.23	0.06	17.69	0.06	3.46	0.012	12.09	0.034	0.415	0.0078	3.878	0.0136	0.009	0.0001	0.017	0.0001
792.33	6.05	0.06	21.01	0.07	0.72	0.005	13.85	0.038	0.393	0.0079	3.522	0.0127	0.0079	0.0001	0.0171	0.0002
792.78	6.9	0.06	21.37	0.07	0.75	0.005	12.95	0.035	0.431	0.008	3.474	0.0122	0.0081	0.0001	0.017	0.0001
793.70	8.11	0.06	25.3	0.07	0.38	0.004	7.046	0.019	0.497	0.0081	4.164	0.0134	0.0111	0.0001	0.0194	0.0001
793.80	7.89	0.06	25.62	0.07	0.59	0.005	6.979	0.02	0.509	0.0082	4.468	0.0145	0.0107	0.0001	0.0196	0.0002
794.26	6.71	0.06	22.74	0.07	0.75	0.005	10.93	0.029	0.443	0.008	3.665	0.0126	0.0085	0.0001	0.0182	0.0001
794.56	7.04	0.06	21.43	0.07	0.99	0.006	9.097	0.026	0.455	0.008	4.288	0.0145	0.0089	0.0001	0.0196	0.0002
794.82	6.19	0.06	17.42	0.06	3.56	0.013	11.69	0.033	0.401	0.0077	3.73	0.0131	0.0085	0.0001	0.0173	0.0001
795.15	6.38	0.06	17.06	0.06	2.88	0.011	13.24	0.038	0.415	0.0079	3.855	0.0137	0.0087	0.0001	0.0161	0.0001
795.58	6.12	0.06	15.8	0.05	4.64	0.015	10.83	0.031	0.41	0.0076	3.916	0.0135	0.0098	0.0001	0.0169	0.0001
795.83	5.41	0.06	15.12	0.05	5.66	0.019	11.06	0.032	0.401	0.0076	3.819	0.0137	0.0092	0.0001	0.0168	0.0001
796.06	7.54	0.06	21.21	0.06	2.49	0.01	8.06	0.022	0.475	0.0079	4.697	0.015	0.0105	0.0001	0.018	0.0001
796.42	7.26	0.06	23.77	0.07	0.71	0.005	9.855	0.027	0.453	0.008	4.521	0.0147	0.009	0.0001	0.0165	0.0001
797.08	7.08	0.06	24.85	0.07	0.39	0.004	9.995	0.027	0.446	0.0079	4.133	0.0136	0.0086	0.0001	0.0196	0.0002
797.36	5.83	0.06	18.5	0.06	5.29	0.017	7.975	0.023	0.429	0.0075	3.803	0.013	0.0092	0.0001	0.0206	0.0001
797.79	5.32	0.05	14.39	0.05	7.31	0.022	10.2	0.028	0.38	0.007	3.883	0.013	0.0088	0.0001	0.0178	0.0001
798.04	7.49	0.06	25.1	0.07	0.17	0.003	8.034	0.022	0.482	0.0081	4.281	0.014	0.0092	0.0001	0.0187	0.0001
798.37	6.49	0.06	21.16	0.07	0.21	0.003	12.97	0.036	0.416	0.0079	5.983	0.019	0.0074	0.0001	0.0174	0.0002
798.65	7.4	0.06	22.91	0.07	1.78	0.008	5.968	0.017	0.509	0.008	5.152	0.0164	0.0098	0.0001	0.0209	0.0002
799.08	5.3	0.06	16.32	0.06	4.49	0.015	12.17	0.034	0.378	0.0074	3.961	0.0138	0.0076	0.0001	0.018	0.0002
799.49	6.91	0.06	22.06	0.07	0.44	0.004	11.16	0.031	0.447	0.0081	3.715	0.0131	0.0084	0.0001	0.018	0.0002
799.77	6.49	0.06	21.84	0.07	0.31	0.004	8.309	0.025	0.483	0.0085	3.971	0.0144	0.0092	0.0001	0.0203	0.0002
800.48	7.58	0.06	24.34	0.07	1.73	0.008	6.083	0.017	0.513	0.0081	4.751	0.0151	0.0088	0.0001	0.0232	0.0002
800.71	6.94	0.06	24.81	0.07	0.68	0.005	8.102	0.023	0.468	0.0081	3.914	0.0134	0.0084	0.0001	0.0227	0.0002
800.94	6.66	0.06	24.18	0.07	0.4	0.004	10.66	0.028	0.444	0.0079	3.296	0.0114	0.0081	0.0001	0.0211	0.0002
801.22	6.54	0.06	20.82	0.07	1.46	0.007	9.808	0.028	0.459	0.008	3.602	0.0128	0.0085	0.0001	0.0176	0.0001
801.50	7.24	0.06	23.25	0.07	1.71	0.007	7.315	0.019	0.482	0.0077	3.456	0.0114	0.0093	0.0001	0.0203	0.0001
801.62	5.97	0.06	17.2	0.06	4.27	0.015	11.84	0.033	0.401	0.0076	3.629	0.0129	0.0088	0.0001	0.0175	0.0001
802.03	5.94	0.06	21.46	0.07	0.4	0.004	11.59	0.034	0.427	0.0083	3.502	0.0131	0.0071	0.0001	0.0195	0.0002
802.39	6.74	0.06	23.11	0.07	0.38	0.004	11.68	0.031	0.436	0.008	3.321	0.0116	0.0078	0.0001	0.0181	0.0001
802.59	7.24	0.06	26.07	0.08	0.24	0.004	6.595	0.019	0.521	0.0084	3.288	0.0116	0.0092	0.0001	0.0214	0.0002
803.28	7.37	0.06	24.79	0.08	0.61	0.005	5.236	0.016	0.527	0.0083	5.098	0.0169	0.0077	0.0001	0.0184	0.0001
803.73	9.34	0.06	28.16	0.08	0.65	0.005	2.65	0.009	0.574	0.0082	4.903	0.0148	0.0128	0.0001	0.0204	0.0001
803.99	8.15	0.06	20.77	0.06	3.87	0.013	5.955	0.017	0.457	0.0076	5.555	0.0173	0.0099	0.0001	0.0199	0.0001
804.32	7	0.06	25.92	0.07	0.55	0.004	7.645	0.02	0.484	0.008	3.308	0.0112	0.0088	0.0001	0.0226	0.0002
804.52	7.17	0.06	23.6	0.07	1.63	0.008	8.65	0.025	0.471	0.0082	4.601	0.0154	0.009	0.0001	0.0203	0.0002
804.88	7.66	0.06	25.79	0.08	1.01	0.006	7.687	0.021	0.462	0.008	4.049	0.0135	0.0093	0.0001	0.0211	0.0002
805.48	7.77	0.06	25.42	0.07	0.51	0.004	7.052	0.02	0.49	0.0081	4.178	0.0137	0.0086	0.0001	0.0189	0.0001
805.69	7.21	0.06	22.18	0.07	1.72	0.008	7.112	0.021	0.486	0.008	4.233	0.0143	0.009	0.0001	0.0208	0.0001
806.09	8.27	0.06	27.82	0.08	0.49	0.004	5.713	0.016	0.513	0.0081	4.512	0.014	0.0104	0.0001	0.02	0.0001
806.37	8.28	0.07	23.6	0.07	2.55	0.01	3.833	0.012	0.506	0.0079	5.644	0.0177	0.0105	0.0001	0.0208	0.0001
806.73	8.17	0.06	25.84	0.07	1.38	0.007	4.403	0.013	0.5	0.0079	5.152	0.0159	0.0099	0.0001	0.022	0.0002
806.96	8.93	0.07	25.37	0.08	0.83	0.006	4.587	0.014	0.584	0.0085	4.797	0.0156	0.0108	0.0001	0.0217	0.0002
807.21	6.66	0.06	20.44	0.06	2.67	0.01	11.81	0.031	0.44	0.0078	3.869	0.013	0.0065	0.0001	0.018	0.0001
807.80	8.77	0.07	24.85	0.07	0.98	0.006	4.575	0.014	0.554	0.0083	4.508	0.0148	0.011	0.0001	0.0221	0.0002
808.20	8.37	0.06	23.28	0.07	1.98	0.008	7.008	0.019	0.502	0.0078	4.771	0.0144	0.009	0.0001	0.021	0.0001
808.38	9.19	0.07	21.73	0.07	1.45	0.008	4.087	0.014	0.56	0.0086	4.384	0.0155	0.0123	0.0001	0.0207	0.0002
808.71	10.2	0.07	26.46	0.07	0.89	0.006	2.931	0.01	0.589	0.0082	5.425	0.0162	0.0112	0.0001	0.0206	0.0001
809.04	10.7	0.07	26.32	0.07	0.98	0.006	2.703	0.009	0.577	0.0082	4.453	0.014	0.013	0.0001	0.022	0.0001
809.32	9.02	0.06	21.22	0.06	3.44	0.012	3.967	0.012	0.548	0.0079	4.288	0.0135	0.0134	0.0001	0.0207	0.0001
809.68	8.05	0.06	20.58	0.06	3.21	0.011	6.643	0.018	0.492	0.0077	4.921	0.0153	0.0107	0.0001	0.0188	0.0001
809.83	7.69	0.07	18.96	0.07	2.27	0.01	5.919	0.019	0.493	0.0084	4.035	0.0149	0.0106	0.0001	0.0198	0.0002
810.16	8.62	0.07	20.85	0.07	1.79	0.008	6.363	0.019	0.539	0.0083	4.207	0.0142	0.0108	0.0001	0.0192	0.0002
810.34	9.1	0.06	21.49	0.06	1.94	0.008	4.867	0.014	0.553	0.0081	4.047	0.0132	0.0123	0.0001	0.0204	0.0001
810.51	11	0.07	25.89	0.07	0.59	0.005	1.732	0.007	0.62	0.0084	4.186	0.0132	0.0147	0.0001	0.0224	0.0001
810.72	9.84	0.07	24.9	0.07	2.02	0.008	2.185	0.008	0.609	0.0083	5.039	0.0152	0.0123	0.0001	0.0224	0.0002
810.79	7.69	0.06	21.62	0.07	0.16	0.003	3.529	0.011	0.393	0.0064	14.11	0.0388	0.0095	0.0001	0.0163	0.0001
810.84	5.36	0.06	17.09	0.06	0.26	0.003	5.132	0.016	0.213	0.0057	24.79	0.07	0.0055	0.0001	0.0112	0.0002
811.02	8.21	0.07	18.83	0.06	2.75	0.011	8.396	0.024	0.493	0.0081	4.288	0.0145	0.0102	0.0001	0.0208	0.0002
811.15	9.86	0.07	24.08	0.07	3.05	0.011	2.888	0.009	0.573	0.0081	5.23	0.0157	0.0136	0.0001	0.02	0.0001

Depth [m]	Al	Al +/-	Si	Si +/-	S	S +/-	Ca	Ca +/-	Ti	Ti +/-	Fe	Fe +/-	Rb	Rb +/-	Zr	Zr +/-
811.28	6.64	0.06	19.45	0.06	4.66	0.015	7.152	0.02	0.439	0.0076	3.719	0.0127	0.0096	0.0001	0.0203	0.0001
811.43	9.03	0.07	20.24	0.06	3.16	0.012	5.733	0.017	0.475	0.0078	4.719	0.0153	0.0102	0.0001	0.0178	0.0001
811.86	8.64	0.07	19.12	0.06	2.47	0.01	3.984	0.013	0.534	0.0083	4.528	0.0156	0.0131	0.0001	0.0189	0.0001
812.17	10.1	0.07	23.86	0.07	3.21	0.011	2.433	0.009	0.558	0.008	5.499	0.0164	0.0129	0.0001	0.0178	0.0001
812.55	7.49	0.06	16.12	0.05	6.34	0.02	5.15	0.016	0.484	0.0077	4.896	0.0161	0.0135	0.0001	0.017	0.0001
812.98	9.21	0.07	20.19	0.06	4.15	0.014	3.1	0.01	0.546	0.008	5.48	0.0172	0.0131	0.0001	0.0207	0.0002
813.10	8.09	0.06	22.67	0.06	4.18	0.013	4.105	0.012	0.532	0.0077	5.1	0.0152	0.0101	0.0001	0.0237	0.0001
813.28	7.72	0.06	15.2	0.05	6.02	0.018	5.165	0.015	0.403	0.0069	4.844	0.0153	0.015	0.0001	0.0177	0.0001
813.82	11.1	0.07	21.63	0.07	1.6	0.007	0.877	0.005	0.555	0.0079	5.346	0.0166	0.0155	0.0001	0.0192	0.0001
813.89	13.1	0.07	25.83	0.07	0.39	0.004		0.066	0.672	0.0085	3.271	0.0104	0.0159	0.0001	0.0199	0.0001
814.12	13.8	0.07	26.03	0.07	0.91	0.006	0.022	0.005	0.662	0.0087	2.98	0.0099	0.0167	0.0001	0.019	0.0001
814.35	11.7	0.07	25.7	0.07	1.56	0.007	0.511	0.005	0.61	0.0081	4.788	0.0142	0.0155	0.0001	0.0254	0.0002
814.63	9.22	0.07	18.28	0.06	4.41	0.014	2.856	0.009	0.448	0.007	7.61	0.022	0.0142	0.0001	0.0174	0.0001
815.49	10.5	0.07	23.78	0.07	1.88	0.008	1.118	0.006	0.56	0.0077	9.983	0.0279	0.013	0.0001	0.0202	0.0002
815.59	10.1	0.07	23.06	0.07	2.5	0.01	1.845	0.007	0.584	0.0081	5.308	0.0162	0.0137	0.0001	0.0221	0.0001
815.59	12	0.07	24.88	0.06	1.52	0.007	0.673	0.005	0.663	0.0078	6.999	0.0183	0.0143	0.0001	0.0232	0.0001
815.82	10.1	0.07	22.4	0.07	1.8	0.008	2.594	0.009	0.566	0.0082	4.965	0.0158	0.0138	0.0001	0.0215	0.0002
816.28	10.3	0.07	22.26	0.07	1.78	0.008	1.403	0.006	0.608	0.0083	5.21	0.0164	0.0152	0.0001	0.0195	0.0001
817.17	9.82	0.07	22.79	0.07	2.41	0.01	2.459	0.009	0.58	0.0085	4.48	0.0148	0.0133	0.0001	0.0201	0.0002
817.25	8.23	0.07	22.12	0.07	1.49	0.008	2.938	0.01	0.579	0.0086	4.059	0.0143	0.0118	0.0001	0.0228	0.0002
817.47	7.9	0.06	17.73	0.06	4.9	0.016	8.133	0.023	0.462	0.0077	3.92	0.0131	0.0105	0.0001	0.0196	0.0001
817.55	7.8	0.07	19.2	0.07	4.43	0.016	4.437	0.015	0.509	0.0085	5.715	0.0199	0.0108	0.0001	0.019	0.0002
817.85	8.77	0.07	19.9	0.06	2.47	0.01	6.115	0.018	0.524	0.0082	4.076	0.0139	0.0121	0.0001	0.0203	0.0002
818.18	9.34	0.07	22.02	0.07	2.04	0.009	4.536	0.014	0.5	0.008	4.926	0.0158	0.0125	0.0001	0.0188	0.0002
818.52	9.6	0.07	21.59	0.07	2.78	0.01	3.684	0.012	0.544	0.008	4.965	0.0156	0.0132	0.0001	0.0211	0.0001
818.97	8.43	0.06	21.31	0.06	3.73	0.013	4.817	0.014	0.519	0.0078	4.85	0.0152	0.0107	0.0001	0.024	0.0002
819.23	9.09	0.07	21.18	0.07	1.52	0.008	3.704	0.012	0.572	0.0087	4.353	0.0152	0.0139	0.0001	0.0198	0.0002
819.38	9.87	0.07	23.13	0.07	2.23	0.009	5.139	0.015	0.542	0.0083	5.196	0.0166	0.0112	0.0001	0.0201	0.0002
819.61	10.2	0.07	23.72	0.07	1.13	0.006	1.863	0.007	0.563	0.0082	4.626	0.0149	0.0127	0.0001	0.0206	0.0001
819.79	8.34	0.07	19.41	0.07	3.45	0.013	4.042	0.013	0.504	0.0081	4.96	0.0168	0.0112	0.0001	0.0201	0.0002
819.94	8.52	0.07	20.15	0.07	2.84	0.011	2.496	0.009	0.519	0.0082	4.476	0.0157	0.0135	0.0001	0.0207	0.0002
820.27	9.24	0.07	21.29	0.07	2.03	0.009	1.893	0.008	0.564	0.0084	4.654	0.016	0.0145	0.0001	0.0196	0.0002
820.55	6.9	0.06	15.26	0.05	3.43	0.012	10.32	0.03	0.432	0.0078	4.173	0.0146	0.0124	0.0001	0.0179	0.0001
820.72	9.91	0.07	22.7	0.07	2.61	0.01	2.076	0.008	0.554	0.0082	4.592	0.0149	0.0142	0.0001	0.0201	0.0002
820.90	10.5	0.07	24.4	0.07	1.92	0.008	1.491	0.007	0.585	0.0081	5.079	0.0157	0.014	0.0001	0.0202	0.0001
821.51	7.63	0.07	17.86	0.07	3.48	0.014	4.407	0.015	0.478	0.0082	5.445	0.0195	0.0107	0.0001	0.0212	0.0002
821.94	7.79	0.07	18.11	0.07	3.17	0.014	2.888	0.011	0.529	0.0088	4.344	0.0168	0.0133	0.0001	0.0205	0.0002
822.07	11.8	0.07	26.84	0.07	1.28	0.006	1.331	0.006	0.605	0.0079	4.418	0.0129	0.0135	0.0001	0.0234	0.0001
822.25	10.1	0.07	23.13	0.07	1.77	0.008	1.975	0.008	0.575	0.0082	5.19	0.0162	0.0128	0.0001	0.0221	0.0002
822.81	9.92	0.07	20.86	0.06	3.05	0.011	3.136	0.01	0.529	0.0079	5.191	0.0162	0.0141	0.0001	0.0209	0.0001
823.11	10.6	0.07	24.58	0.07	1.49	0.007	2.026	0.008	0.572	0.008	6.266	0.0185	0.0122	0.0001	0.022	0.0002
823.80	6.48	0.06	13.46	0.05	8.79	0.028	5.945	0.019	0.396	0.0073	7.294	0.0239	0.0095	0.0001	0.0179	0.0002
824.26	10	0.07	21.72	0.06	3.51	0.012	1.869	0.007	0.548	0.0078	5.199	0.0158	0.0135	0.0001	0.0211	0.0001
824.41	11.4	0.06	24.18	0.06	2.74	0.01	1.152	0.006	0.561	0.0075	5.265	0.0146	0.0156	0.0001	0.0189	0.0001
825.17	7.54	0.07	17.26	0.06	0.37	0.004	2.774	0.01	0.267	0.0058	22.11	0.07	0.0083	0.0001	0.0108	0.0002
825.40	11.2	0.07	24.3	0.07	0.82	0.005	0.826	0.005	0.605	0.0082	4.955	0.0151	0.0154	0.0001	0.0208	0.0001
825.91	9.27	0.07	19.84	0.06	3.86	0.014	2.611	0.009	0.514	0.0079	4.727	0.0155	0.0141	0.0001	0.0204	0.0001
826.11	11.3	0.07	25.72	0.07	0.96	0.006	1.126	0.006	0.6	0.0083	4.719	0.0146	0.0136	0.0001	0.0261	0.0002
826.34	11.5	0.07	26.17	0.07	1.72	0.008	0.665	0.005	0.625	0.0084	5.891	0.0174	0.0137	0.0001	0.0206	0.0002
826.57	11.1	0.07	25.37	0.07	1.1	0.006	2.908	0.01	0.586	0.0082	3.936	0.0126	0.0139	0.0001	0.0205	0.0001
826.74	10	0.06	21.11	0.06	4.93	0.014	4.941	0.013	0.523	0.0075	4.087	0.0122	0.0131	0.0001	0.0204	0.0001
827.25	9.93	0.07	22.57	0.07	2.54	0.01	2.951	0.01	0.553	0.008	4.387	0.0138	0.013	0.0001	0.0215	0.0001
827.43	11	0.07	26.06	0.07	1.3	0.007	2.241	0.008	0.584	0.0081	4.834	0.0143	0.0132	0.0001	0.023	0.0001
827.66	9.32	0.07	21.51	0.07	1.78	0.009	2.344	0.009	0.558	0.0087	4.073	0.0149	0.0137	0.0001	0.0208	0.0002
827.86	10.4	0.07	24.8	0.07	1.31	0.006	1.618	0.007	0.605	0.0081	4.706	0.0142	0.0134	0.0001	0.0233	0.0001
828.14	12.2	0.07	28.16	0.07	1.55	0.007	2.091	0.008	0.582	0.0079	4.319	0.0124	0.0138	0.0001	0.0244	0.0001
828.34	11.4	0.07	26.31	0.08	2	0.009	1.621	0.007	0.623	0.0089	5.184	0.0166	0.0147	0.0001	0.0208	0.0002
828.57	10.6	0.07	24.72	0.07	1.36	0.007	1.354	0.006	0.59	0.0083	5.036	0.0156	0.0132	0.0001	0.024	0.0002
828.75	10.6	0.07	23.03	0.07	2.7	0.01	2.166	0.008	0.558	0.008	4.878	0.015	0.015	0.0001	0.0192	0.0001
828.85	9.37	0.06	22.69	0.07	2.64	0.01	2.325	0.008	0.573	0.0079	4.913	0.0151	0.0135	0.0001	0.0224	0.0001
829.23	12.7	0.07	27.61	0.07	0.47	0.004	0.55	0.005	0.636	0.008	4.807	0.0134	0.0156	0.0001	0.022	0.0001
829.36	5.85	0.06	14.52	0.06	0.24	0.003	3.698	0.013	0.206	0.0056	28.47	0.09	0.006	0.0001	0.0084	0.0002
829.44	10.7	0.07	24.26	0.07	2.65	0.01	1.785	0.007	0.542	0.0074	5.209	0.0149	0.0131	0.0001	0.0206	0.0001
829.56	11.8	0.07	26.67	0.07	0.76	0.005	0.873	0.006	0.612	0.0082	6.332	0.0182	0.0154	0.0001	0.0205	0.0001
829.82	12.4	0.07	27.16	0.07	0.39	0.004	0.331	0.005	0.664	0.0084	4.483	0.0132	0.0157	0.0001	0.0217	0.0001
830.41	11.3	0.07	25.67	0.07	1.78	0.008	1.405	0.006	0.614	0.0084	4.727	0.0144	0.0149	0.0001	0.0216	0.0001
830.62	11.6	0.07	25.92	0.07	1.9	0.008	1.174	0.006	0.627	0.008	4.742	0.0135	0.0155	0.0001	0.0205	0.0001
830.78	11.8	0.07	26.07	0.07	1.92	0.008	0.693	0.005	0.83	0.0097	2.062	0.0078	0.013	0.0001	0.0289	0.0002
830.99	13.9	0.07	29.86	0.07	1.17	0.006		0.06	0.828	0.0093	2.162	0.0075	0.0157	0.0001	0.0273	0.0001

Depth [m]	Al	Al +/-	Si	Si +/-	S	S +/-	Ca	Ca +/-	Ti	Ti +/-	Fe	Fe +/-	Rb	Rb +/-	Zr	Zr +/-
831.19	9.68	0.07	22.62	0.07	1.93	0.009	2.622	0.009	0.583	0.0087	4.052	0.0139	0.0137	0.0001	0.0222	0.0002
831.39	9.79	0.07	22.23	0.06	2.28	0.009	7.121	0.019	0.551	0.0082	3.843	0.0124	0.011	0.0001	0.0193	0.0001
831.60	5.27	0.06	14.09	0.05	5.51	0.019	13.62	0.041	0.38	0.0076	3.407	0.0128	0.009	0.0001	0.0166	0.0001
831.77	7.93	0.06	21.81	0.06	0.18	0.003	9.966	0.026	0.504	0.0079	4.248	0.0134	0.0108	0.0001	0.0181	0.0001
832.02	10.3	0.07	23.99	0.08	4.22	0.015	2.551	0.01	0.51	0.0083	12.69	0.0372	0.0106	0.0001	0.0177	0.0002
832.21	7.99	0.06	19.03	0.06	5.36	0.016	5.242	0.015	0.55	0.0079	4.041	0.0129	0.0126	0.0001	0.0219	0.0001
832.41	10.6	0.07	24.71	0.07	1.38	0.007	1.626	0.007	0.599	0.0081	4.408	0.0135	0.0146	0.0001	0.021	0.0001
832.61	10.9	0.07	25.48	0.07	2.3	0.009	2.235	0.008	0.579	0.0082	4.708	0.0143	0.0139	0.0001	0.0216	0.0001
832.71	7.52	0.06	18.15	0.06	5.73	0.018	3.801	0.012	0.546	0.0077	4.261	0.0138	0.0136	0.0001	0.0213	0.0001
833.20	8.16	0.07	19.75	0.08	1.54	0.008	2.077	0.009	0.589	0.0092	3.976	0.0158	0.0148	0.0001	0.021	0.0002
833.40	10.1	0.07	23.19	0.07	2.21	0.009	2.724	0.009	0.604	0.0083	5.24	0.0161	0.0147	0.0001	0.0203	0.0001
833.53	10.1	0.06	22.7	0.06	3.35	0.011	3.291	0.01	0.599	0.0081	3.499	0.0111	0.0153	0.0001	0.0207	0.0001
833.70	8.89	0.07	21.49	0.07	2.54	0.01	4.329	0.014	0.531	0.0082	4.42	0.0148	0.0115	0.0001	0.0209	0.0002
833.93	7.36	0.06	17.25	0.06	4.8	0.017	6.225	0.019	0.475	0.0081	3.991	0.0143	0.0109	0.0001	0.0214	0.0002
834.09	8.11	0.07	19.68	0.07	3.19	0.012	4.908	0.016	0.539	0.0085	3.992	0.0143	0.0123	0.0001	0.0209	0.0002
834.24	9.09	0.07	22.01	0.07	2.16	0.009	3.951	0.012	0.559	0.0083	3.872	0.013	0.0124	0.0001	0.0214	0.0002
834.36	12	0.07	28.27	0.07	0.43	0.004	3.149	0.009	0.61	0.0081	4.654	0.013	0.0128	0.0001	0.0217	0.0001
834.59	9.95	0.06	23.78	0.07	1.79	0.008	2.277	0.008	0.579	0.008	4.526	0.0138	0.0137	0.0001	0.021	0.0001
835.13	9.84	0.07	24.02	0.07	1	0.006	2.902	0.01	0.588	0.0084	3.835	0.0129	0.0129	0.0001	0.0221	0.0001
835.63	8.01	0.06	19.97	0.06	3.9	0.013	5.368	0.016	0.503	0.0078	3.876	0.0128	0.0122	0.0001	0.0202	0.0002
835.79	6.94	0.06	16.75	0.05	6.21	0.019	7.402	0.021	0.45	0.0073	3.832	0.0127	0.0114	0.0001	0.0202	0.0001
835.99	7.83	0.07	18.52	0.06	3.8	0.014	4.19	0.014	0.523	0.0082	4.731	0.0163	0.0122	0.0001	0.0211	0.0002
836.22	9.83	0.07	23.77	0.07	2.08	0.009	3.188	0.01	0.574	0.0082	4.168	0.0132	0.0134	0.0001	0.0207	0.0001
836.45	8.84	0.07	22.08	0.07	1.84	0.008	2.462	0.009	0.564	0.0084	4.238	0.0145	0.0135	0.0001	0.0206	0.0002
837.23	11	0.07	26.5	0.07	1.08	0.006	2.762	0.009	0.559	0.0079	4.148	0.0126	0.0132	0.0001	0.0206	0.0001
837.44	10.3	0.07	23.97	0.07	0.87	0.005	2.804	0.009	0.592	0.0081	4.164	0.013	0.0136	0.0001	0.022	0.0001
837.77	7.37	0.06	20.41	0.06	2.78	0.01	8.48	0.023	0.456	0.0077	3.571	0.0121	0.0093	0.0001	0.0213	0.0001
837.97	9.37	0.06	22.66	0.06	2.91	0.01	5.907	0.016	0.507	0.0075	3.835	0.0119	0.0108	0.0001	0.0216	0.0001
838.30	2.43	0.05	7.869	0.04	0.12	0.003	8.94	0.032	0.09	0.0053	32.64	0.11	0.0029	0.0001	0.0047	0.0002
838.38	10.1	0.07	24.62	0.07	1.82	0.008	2.866	0.009	0.552	0.0081	4.326	0.0136	0.0125	0.0001	0.0207	0.0001
838.78	5.72	0.06	15.75	0.06	0.17	0.003	11.11	0.034	0.224	0.0063	18.72	0.06	0.0053	0.0001	0.0102	0.0001
838.81	9.1	0.06	22.01	0.07	1.67	0.008	4.485	0.013	0.545	0.0081	3.736	0.0125	0.0119	0.0001	0.0214	0.0001
838.99	9.41	0.06	23.03	0.07	2.13	0.009	4.6	0.013	0.561	0.008	3.971	0.0126	0.0114	0.0001	0.0197	0.0001
839.24	8.93	0.07	22.18	0.07	1.58	0.007	4.531	0.014	0.529	0.0082	3.975	0.0134	0.0114	0.0001	0.0216	0.0002
839.44	9.09	0.07	21.21	0.06	2.89	0.011	5.985	0.017	0.533	0.008	3.891	0.0127	0.0121	0.0001	0.0206	0.0001
839.77	7.1	0.06	17.9	0.06	4.28	0.015	7.306	0.022	0.459	0.0078	3.824	0.0135	0.0106	0.0001	0.0187	0.0001
840.03	9.22	0.06	24.06	0.07	1.07	0.006	5.95	0.016	0.504	0.0078	3.786	0.0122	0.0108	0.0001	0.0198	0.0001
840.21	9.24	0.07	23.04	0.07	1.05	0.006	4.631	0.014	0.546	0.0081	4.073	0.0134	0.0115	0.0001	0.0217	0.0002
840.46	8.38	0.07	21	0.07	1.82	0.008	4.753	0.015	0.512	0.0081	4.734	0.0158	0.0121	0.0001	0.0204	0.0002
840.82	8.71	0.07	21.34	0.07	1.31	0.007	4.785	0.015	0.542	0.0083	3.956	0.0136	0.0119	0.0001	0.0209	0.0002
840.99	6.46	0.06	16.33	0.06	5.07	0.017	10.57	0.03	0.416	0.0074	3.653	0.0128	0.01	0.0001	0.0176	0.0001
841.25	8.38	0.06	21.24	0.06	2.86	0.01	10.46	0.027	0.428	0.0076	3.777	0.0124	0.0089	0.0001	0.0163	0.0001
841.38	8.04	0.06	20.28	0.06	3.25	0.012	6.754	0.02	0.496	0.0081	3.773	0.0129	0.0101	0.0001	0.0204	0.0001
841.53	8.81	0.06	21.93	0.06	2.06	0.008	5.993	0.017	0.494	0.0078	3.919	0.0127	0.0108	0.0001	0.0215	0.0002
841.73	8.32	0.07	21.59	0.07	1.36	0.007	4.434	0.014	0.52	0.0084	4.223	0.0149	0.0114	0.0001	0.0204	0.0002
841.91	9.19	0.07	24.21	0.08	0.16	0.003	2.416	0.009	0.574	0.0083	4.254	0.0143	0.0132	0.0001	0.022	0.0002
842.04	8.66	0.06	21.93	0.06	1.77	0.008	4.309	0.013	0.507	0.0076	4.745	0.0147	0.0116	0.0001	0.0215	0.0001
842.09	10.4	0.07	24.52	0.07	1.11	0.006	3.1	0.01	0.561	0.008	4.316	0.0134	0.0125	0.0001	0.0199	0.0001
842.39	8.75	0.07	22.53	0.07	0.23	0.003	8.412	0.023	0.533	0.0082	4.325	0.0139	0.0101	0.0001	0.0197	0.0001
843.10	9.26	0.07	22.8	0.07	1.01	0.006	3.843	0.012	0.542	0.0082	4.257	0.014	0.0125	0.0001	0.0206	0.0001
843.61									0.332	0.0067	2.69	0.0127	0.0092	0.0001	0.0194	0.0002
843.92	6.92	0.06	18.33	0.06	4.33	0.014	8.055	0.023	0.454	0.0075	3.652	0.0124	0.011	0.0001	0.0206	0.0001
844.65	4.68	0.05	12.09	0.04	8.41	0.026	10.9	0.031	0.365	0.0071	4.241	0.0145	0.0099	0.0001	0.0173	0.0001
844.96	8.02	0.06	22.55	0.07	2.28	0.009	5.27	0.015	0.518	0.0079	4.168	0.0135	0.0119	0.0001	0.0201	0.0001
845.21	6.5	0.06	18.38	0.06	4.61	0.015	7.301	0.021	0.467	0.0077	3.636	0.0124	0.0109	0.0001	0.0209	0.0001
845.67	5.6	0.06	15.93	0.06	0.71	0.005	17.65	0.05	0.36	0.0077	3.747	0.0138	0.0074	0.0001	0.0126	0.0001
845.92	6.91	0.06	18.91	0.06	1.67	0.008	12.21	0.033	0.43	0.0079	4.031	0.0137	0.0095	0.0001	0.0171	0.0001
846.84	7.88	0.06	21.98	0.07	2.49	0.01	7.449	0.02	0.479	0.0078	4.088	0.0133	0.0109	0.0001	0.02	0.0001
847.09	9.1	0.06	22.63	0.07	1.51	0.007	5.299	0.015	0.5	0.008	4.421	0.0141	0.011	0.0001	0.0197	0.0001
847.32	7.93	0.06	19.15	0.06	3.9	0.014	5.135	0.016	0.519	0.008	4.248	0.0144	0.0122	0.0001	0.02	0.0001
847.50	5.08	0.05	14.61	0.05	6.1	0.02	8.96	0.026	0.393	0.0073	4.139	0.0143	0.0106	0.0001	0.0185	0.0001
848.16	7.06	0.06	16.83	0.05	5.42	0.017	7.209	0.02	0.453	0.0075	4.2	0.0138	0.0117	0.0001	0.0201	0.0001
848.39	7.39	0.06	18.61	0.06	4.47	0.016	5.341	0.017	0.481	0.0078	4.294	0.0148	0.0115	0.0001	0.0197	0.0002
848.82	8.51	0.06	20.69	0.06	2.77	0.01	2.672	0.009	0.553	0.0079	5.098	0.0159	0.0139	0.0001	0.0215	0.0002
849.10	5.16	0.06	16.37	0.06	0.39	0.004	13.15	0.037	0.275	0.0065	12.68	0.0369	0.0061	0.0001	0.0125	0.0001
849.48	8.31	0.06	22.34	0.07	2.24	0.009	5.346	0.015	0.52	0.008	4.165	0.0135	0.0123	0.0001	0.0204	0.0001
850.11	7.77	0.06	20	0.06	2.5	0.01	8.254	0.023	0.481	0.0079	4.27	0.0139	0.0111	0.0001	0.0191	0.0001
850.42	8.12	0.06	24.99	0.07	0.3	0.004	8.374	0.023	0.496	0.0081	3.635	0.0122	0.0103	0.0001	0.0218	0.0002
850.80	6.46	0.06	16.01	0.05	5.68	0.018	9.012	0.025	0.432	0.0075	3.695	0.0126	0.0109	0.0001	0.0191	0.0001

Depth [m]	Al	Al +/-	Si	Si +/-	S	S +/-	Ca	Ca +/-	Ti	Ti +/-	Fe	Fe +/-	Rb	Rb +/-	Zr	Zr +/-
851.13	8.62	0.06	20.36	0.06	1.51	0.007	5.079	0.015	0.509	0.0078	4.693	0.0151	0.0119	0.0001	0.0213	0.0002
852.12	7.7	0.06	19.62	0.06	2.04	0.009	8.967	0.025	0.443	0.0078	6.119	0.0191	0.0105	0.0001	0.017	0.0001
852.40	4.79	0.05	14.57	0.05	0.08	0.003	21.79	0.06	0.309	0.0072	3.249	0.0118	0.007	0.0001	0.0125	0.0001
852.40	6	0.06	16.05	0.06	0.12	0.003	21.14	0.06	0.347	0.0079	3.638	0.0137	0.0066	0.0001	0.0129	0.0001
852.81	7.69	0.07	19.09	0.07	1.35	0.008	2.691	0.011	0.532	0.0086	5.904	0.0214	0.0123	0.0001	0.0215	0.0002
853.03	8.75	0.07	19.96	0.07	0.81	0.006	3.58	0.013	0.433	0.0074	10.28	0.0329	0.0106	0.0001	0.0172	0.0002
853.03	8.28	0.06	22.52	0.07	0.35	0.004	3.426	0.01	0.468	0.007	7.758	0.0219	0.0109	0.0001	0.0198	0.0001
853.39	8.3	0.06	21.23	0.06	2.76	0.01	4.948	0.014	0.519	0.0079	4.333	0.0138	0.0122	0.0001	0.02	0.0001
855.24	8.9	0.07	20.52	0.06	2.87	0.011	4.434	0.013	0.538	0.008	3.985	0.0132	0.0129	0.0001	0.0191	0.0001
855.93	8.64	0.07	21.02	0.07	2.19	0.009	3.694	0.012	0.527	0.0083	4.033	0.0142	0.0123	0.0001	0.0207	0.0002
856.54	9.08	0.07	23.05	0.07	1.06	0.006	2.904	0.01	0.539	0.0083	4.523	0.015	0.0125	0.0001	0.021	0.0002
856.79	8.89	0.06	20.59	0.06	2.87	0.011	3.805	0.012	0.525	0.0078	3.906	0.0128	0.0132	0.0001	0.021	0.0001
857.02	8.49	0.07	20.58	0.07	1.48	0.007	4.171	0.013	0.519	0.008	5.856	0.0188	0.0114	0.0001	0.0212	0.0002
857.94	8.91	0.06	27.74	0.07	0.32	0.004	4.087	0.012	0.539	0.0081	4.231	0.0131	0.0122	0.0001	0.0217	0.0001
858.22	7.72	0.06	19.26	0.06	3.16	0.011	7.797	0.022	0.454	0.0076	3.988	0.0133	0.011	0.0001	0.0186	0.0001
858.55	8.18	0.06	21.5	0.06	1.71	0.008	6.747	0.019	0.503	0.008	4.185	0.0137	0.0113	0.0001	0.0203	0.0001
858.82	8.44	0.06	20.33	0.06	2.91	0.011	5.3	0.015	0.494	0.0078	3.773	0.0126	0.0122	0.0001	0.02	0.0001
859.92	8.78	0.06	26.28	0.07	0.28	0.003	5.065	0.015	0.541	0.0083	4.131	0.0133	0.0125	0.0001	0.0197	0.0001
860.20	10.6	0.07	24.98	0.07	2.13	0.009	7.027	0.02	0.599	0.0089	5.88	0.0179	0.0118	0.0001	0.0197	0.0002
860.63	8.58	0.06	26.22	0.07	0.27	0.004	5.605	0.015	0.522	0.0081	4.069	0.0129	0.0116	0.0001	0.0201	0.0001
860.93	9.44	0.07	27.44	0.08	0.22	0.004	3.11	0.01	0.577	0.0083	4.108	0.0131	0.0139	0.0001	0.0201	0.0001
861.21	7.49	0.06	20.48	0.06	0.41	0.004	6.92	0.02	0.453	0.0073	7.986	0.0234	0.0111	0.0001	0.0171	0.0001
861.80	9.58	0.07	23.86	0.07	1.44	0.007	4.705	0.014	0.568	0.0083	3.944	0.0127	0.0132	0.0001	0.0204	0.0001
862.05	9.95	0.07	23.33	0.07	1.03	0.006	3.856	0.012	0.57	0.0082	3.828	0.0125	0.0136	0.0001	0.0211	0.0001
862.23	9.38	0.06	24.16	0.06	1.1	0.006	2.981	0.009	0.55	0.0075	4.578	0.0134	0.0142	0.0001	0.0199	0.0001
862.46	9.26	0.06	20.67	0.06	3.75	0.012	4.779	0.014	0.555	0.0081	3.467	0.0115	0.0144	0.0001	0.0202	0.0001
862.76	9.24	0.07	21.75	0.07	1.58	0.008	4.517	0.014	0.536	0.0084	4.053	0.0142	0.0132	0.0001	0.02	0.0002

Table A-2. XRF data measured by hand-held XRF (the Delta Premium model) under the Geochem mode.

Depth (m)	illite & mica	illite-rich illite- smectite	kaolinite	chlorite	quartz	K feldspar	plagio- clase	calcite	siderite	Fe dolomite	pyrite	gypsum
762.64	21%	6%	0.00%	6%	20%	1%	1%	42%	0%	2%	1%	0%
766.70	29%	9%	0.00%	7%	17%	2%	2%	30%	0%	3%	1%	0%
770.69	27%	10%	0.24%	11%	21%	1%	2%	24%	0%	3%	1%	0%
774.47	22%	11%	0.00%	9%	14%	1%	2%	37%	1%	2%	2%	0%
777.42	29%	9%	1.34%	14%	16%	2%	2%	25%	1%	1%	1%	0%
781.02	25%	8%	1.17%	17%	17%	2%	3%	23%	1%	3%		0%
784.76	26%	10%	1.19%	11%	23%	1%	2%	22%		3%		0%
788.44	27%	9%	0.66%	16%	21%	2%	1%	18%	2%	2%	1%	0%
792.05	28%	8%	0.81%	14%	21%	2%	2%	22%	1%	1%	1%	0%
794.82	26%	9%	0.97%	16%	19%	2%	2%	21%	0%	3%	1%	0%
798.37	23%	9%	1.16%	15%	19%	1%	2%	28%	0%	2%		0%
801.50	28%	9%	1.68%	17%	23%	1%	4%	13%		4%		0%
805.48	26%	7%	1.31%	16%	25%	1%	2%	16%	0%	4%	1%	0%
808.20	29%	10%	2.42%	20%	20%	2%	2%	12%		1%		0%
811.66	28%	9%	1.56%	16%	22%	3%	2%	12%		1%	1%	4%
815.75	33%	11%	2.23%	23%	20%	2%	2%	4%		1%	1%	1%
818.01	36%	7%	2.30%	10%	22%	2%	1%	15%	1%	2%	2%	0%
821.28	34%	12%	2.85%	18%	20%	2%	2%	7%		1%	1%	0%
825.17	24%	7%	0.00%	14%	15%	1%	1%	4%	31%	2%	1%	0%
826.57	32%	10%	1.91%	18%	23%	1%	2%	9%		2%	1%	0%
829.36	18%	8%	0.00%	12%	14%	1%	1%	5%	42%	0%	0%	0%
829.44	32%	8%	1.53%	24%	23%	3%	3%		1%	2%	1%	0%
831.60	24%	8%	1.43%	14%	18%	1%	1%	30%	1%	1%		0%
834.36	34%	11%	4.85%	12%	25%	2%	2%	8%	0%	0%		0%
838.30	20%	4%	0.00%	5%	6%	0%	0%	18%	43%	1%	2%	0%
838.38	30%	11%	1.71%	21%	21%	2%	4%	6%	0%	2%		0%
838.78	23%	7%	0.00%	10%	15%	1%	1%	24%	19%	0%	1%	0%
840.99	26%	9%	1.09%	15%	21%	2%	1%	19%	1%	4%	1%	0%
843.92	31%	11%	1.06%	14%	23%	2%	2%	13%	1%	2%	1%	0%
847.32	29%	8%	0.99%	19%	24%	2%	2%	11%	1%	3%	1%	0%
849.83	31%	9%	0.83%	14%	26%	2%	1%	13%	1%	1%	1%	
852.40	23%	4%	0.00%	8%	11%	1%	1%	52%	0%	1%		0%
853.03	31%	9%	0.00%	21%	24%	2%	2%	9%	0%	1%		0%
856.79	35%	9%	0.48%	19%	24%	3%	2%	7%	1%	0%		0%
859.54	31%	8%	0.50%	17%	25%	2%	2%	11%	1%	2%	1%	0%
862.76	34%	9%	1.13%	17%	23%	2%	2%	11%	1%	0%	1%	0%

Table A-3. XRD data from the Mochras core.

Penta		Depth (m)	863.30	840.64	824.08	819.10	811.66	792.05
Peak name	Ion	Area	Area	Area	Area	Area	Area	Area
standard-DC		374.4 > 219.2	1450535	1.75E+07	9503519	2.38E+07	1.01E+07	1.86E+07
30EE	9,15-dimethyl-25,27-dinorhopane (early eluting hopane)	412.4 > 191.2	930.817	12700.85	6693.808	10629.566	6994.614	22300.98
30H	17a,21b-hopane	412.4 > 191.2	70853.1	508808.4	296279.1	1940152.1	544164.9	1030771
30norHH	30-norhomohopane	412.4 > 191.2		12594.25	6153.132		10187.13	
30Ts	18a-neohopane	412.4 > 191.2		10378.64	13624.75	103748.6	29056.64	50393.61
30aaH	17a,21a-hopane	412.4 > 191.2	2004.26	11389.46	11321.4	102792.23	27674.9	31059.98
30Mba	17b,21a-hopane (moretane)	412.4 > 191.2	15717.2	87159.37	47212.44	511406.28	151423.7	181044.3
Gamm	Gammacerane	412.4 > 191.2		4985.6	4575.279	49517.3	14160.19	20436.91
30bbH	17b,21b-hopane	412.4 > 191.2	34833.2	72909.15	57290.28	937236.2	217155.8	259422.2
bb/(bb+ab+ba)			0.28692	0.109002	0.142946	0.2765692	0.237915	0.176329
Gamm/C30H				0.009799	0.015442	0.0255224	0.026022	0.019827
30bbH/30H			0.49163	0.143294	0.193366	0.4830736	0.399062	0.251678
Tetra		Ion	Area	Area	Area	Area	Area	Area
Standard-DC		374.4 > 219.2	2048943	17852116	9011054	25561250	8884318	12155527
D27baS	20S-13b, 17a-diacholestane	372.4 > 217.2	31938.86	333193.88	292049.44	1359582.00	684176.10	531211.20
D27baR	20R-13b, 17a-diacholestane	372.4 > 217.2	24472.32	192879.14	207829.90	1200128.80	493044.28	328696.47
D27abS	20S-13a, 17b-diacholestane	372.4 > 217.2	9418.91	68476.09	83590.28	512645.40	202051.98	125377.95
D27abR	20R-13a, 17b-diacholestane	372.4 > 217.2	9137.12	83799.43	87968.47	492135.72	215671.70	142691.11
S27bba		372.4 > 217.2	7196.93	128718.45	52633.61	380841.62	153019.66	121164.56
S27aaS	20S-5a, 14a, 17a-cholestane	372.4 > 217.2	14879.95		64031.76	894079.00	329302.22	106673.59
S27bbR	20R-5a, 14b, 17b-cholestane	372.4 > 217.2	16532.44	106077.76	88212.59	960348.56	487433.78	178895.39
S27bbS	20S-5a, 14b, 17b-cholestane	372.4 > 217.2	12408.01	83686.30	72819.39	751450.94	391848.75	144687.05
S27aaR	20R-5a, 14a, 17a-cholestane	372.4 > 217.2	50230.72	236556.44	186165.06	2602029.20	748663.00	358029.20
D28baSR	(20S,24R)-24-Methyl-13b, 17a-diacholestane	386.4 > 217.2	9119.46	94011.25	97038.98	432062.62	177193.61	151827.11
D28baSS	(20S,24S)-24-Methyl-13b, 17a-diacholestane	386.4 > 217.2		91204.10	98210.66	467552.40	186649.25	152464.69
D28baRS	(20R,24S)-24-Methyl-13b, 17a-diacholestane	386.4 > 217.2	6177.03	54925.71	63821.09	361932.25	127486.62	70774.97
D28baRR	(20R,24R)-24-Methyl-13b, 17a-diacholestane	386.4 > 217.2	8253.01	82672.90	85321.84	442487.97	159130.19	140333.72
S28aaSS	(20S, 24S)-24-Methyl-5a, 14a, 17a-cholestane	386.4 > 217.2	4242.77	21002.85	13246.57	61449.48	21377.44	27983.23
S28aaSR	(20S, 24R)-24-Methyl-5a, 14a, 17a-cholestane	386.4 > 217.2	2845.28	30291.83	28558.16	215819.27	65987.68	44366.78
S28bba		386.4 > 217.2	14241.85	78038.41	77496.84	768070.56	262921.47	148487.45
S28bbS	(20S)-24-Methyl-5a, 14b, 17b-cholestane	386.4 > 217.2	7522.59	53229.25	53136.59	560113.56	162708.75	92080.45
S28aaR	(20R)-24-Methyl-5a, 14a, 17a-cholestane	386.4 > 217.2	16061.11	68100.16	88032.15	1118908.80	262907.78	160116.88
D29baS	20S-24-Ethyl-13b, 17a-diacholestane	400.4 > 217.2	19458.44	177213.53	236863.33	1118956.60	366228.78	260073.19
D29baR	20R-24-Ethyl-13b, 17a-diacholestane	400.4 > 217.2	20823.24	144999.47	223512.42	1126211.50	342752.60	230477.12
D29abS	20S-24-Ethyl-13a, 17b-diacholestane	400.4 > 217.2	7444.81	50087.15	82024.59	425580.75	122105.95	73754.31
D29abR	20R-24-Ethyl-13a, 17b-diacholestane	400.4 > 217.2	8983.66	59242.73	99088.70	467732.97	126148.80	94481.41
S29aaS	20S-24-Ethyl-5a, 14a, 17a-cholestane	400.4 > 217.2	7773.65	54441.36	46676.89	281114.22	87908.92	96275.02
S29bbR	20R-24-Ethyl-5a, 14b, 17b-cholestane	400.4 > 217.2	17603.45	68662.96	110039.88	1198626.60	333708.72	121556.05
S29bbS	20S-24-Ethyl-5a, 14b, 17b-cholestane	400.4 > 217.2	26563.11	132587.90	160369.45	1921566.10	496095.56	251553.34
S29aaR	20R-24-Ethyl-5a, 14a, 17a-cholestane	400.4 > 217.2	49712.73	165930.78	201409.12	2874760.00	573151.60	295198.16
D30nPbaS(A+B)	20S-24-n-Propyl-13b, 17a-diacholestane	414.4 > 217.2	1504.84	11257.90	21433.60	106120.71	31553.09	34924.55
D30nPbaR	20R-24-n-Propyl-13b, 17a-diacholestane	414.4 > 217.2	2053.51	8591.90	18149.42	111540.75	26705.26	22565.86
D30nPabS	20S-24-n-Propyl-13a, 17b-diacholestane	414.4 > 217.2				22451.28		
D30nPabR	20R-24-n-Propyl-13a, 17b-diacholestane	414.4 > 217.2		3105.05	8545.75	38962.73	11296.02	14083.04
S30nPaaS	20S-24-n-Propyl-5a, 17a-cholestane	414.4 > 217.2		4876.22	8226.04	145604.78	27142.42	27571.72
S30nPbb(R+S)	20(S+R)-24-n-Propyl-14b, 17b-cholestane	414.4 > 217.2	3357.64	8880.43	17585.92	342954.75	48805.61	26958.45
S30nPaaR	20S-24-n-Propyl-5a, 17a-cholestane	414.4 > 217.2	2665.47	1820.51	7168.38	217276.73	17649.04	10429.47
C27			176215	1233387	1135300	9153241.2	3705211	2037427
C28			68463.1	573476.5	604862.9	4428396.9	1426363	988435.3
C29			158363	853165.9	1159984	9414548.7	2448101	1423369
C30			9581.46	38532.01	81109.11	984911.73	163151.4	136533.1
C30/(27+28+29+30)			2.32209	1.427872	2.720635	4.1070334	2.10713	2.977325

Table A-4. Selected biomarker peak areas of the penta cyclic and tetra cyclic fractions.

Depth (m)	Count	Depth (m)	Count	Depth (m)	Count	Depth (m)	Count
900.39	1	845.58	44	722.65	87	676.24	130
898.96	2	842.83	45	722.20	88	675.87	131
898.11	3	842.20	46	722.02	89	675.43	132
897.53	4	838.05	47	720.99	90	674.06	133
897.52	5	805.57	48	720.33	91	672.91	134
896.10	6	801.79	49	719.32	92	671.86	135
894.83	7	795.74	50	718.41	93	671.73	136
894.21	8	790.41	51	718.26	94	669.93	137
893.84	9	790.25	52	716.96	95	669.64	138
892.18	10	790.14	53	715.52	96	668.50	139
891.06	11	788.33	54	715.26	97	667.62	140
891.03	12	786.59	55	714.60	98	666.39	141
890.74	13	786.49	56	713.71	99	664.50	142
889.38	14	786.13	57	713.58	100	662.37	143
888.18	15	786.04	58	713.29	101	661.78	144
888.12	16	783.52	59	711.66	102	659.89	145
888.09	17	782.68	60	711.18	103	659.20	146
888.08	18	773.63	61	710.33	104	654.01	147
888.04	19	771.43	62	709.72	105	651.78	148
887.51	20	770.26	63	709.65	106	649.89	149
887.35	21	761.83	64	704.71	107	647.65	150
887.21	22	761.73	65	704.00	108	646.04	151
887.03	23	757.13	66	703.10	109	645.42	152
886.92	24	756.78	67	701.46	110	645.40	153
886.88	25	754.77	68	701.18	111	645.13	154
886.48	26	752.63	69	700.95	112	644.06	155
885.91	27	749.76	70	700.69	113	643.88	156
885.37	28	749.75	71	700.48	114	643.59	157
884.40	29	749.59	72	697.24	115	642.41	158
884.30	30	748.92	73	695.30	116	641.86	159
883.04	31	748.68	74	694.83	117	641.59	160
881.30	32	748.42	75	694.07	118	641.19	161
881.18	33	747.78	76	692.69	119	639.67	162
880.43	34	747.73	77	692.15	120	636.91	163
880.24	35	747.06	78	692.13	121	631.89	164
880.00	36	734.75	79	690.76	122	630.68	165
878.58	37	732.65	80	689.50	123	624.89	166
874.76	38	732.51	81	687.57	124	621.99	167
871.76	39	730.61	82	683.43	125	620.33	168
868.75	40	730.57	83	682.69	126	616.77	169
867.94	41	729.08	84	681.89	127	615.81	170
867.23	42	728.82	85	678.86	128	608.16	171
866.12	43	726.88	86	678.35	129	607.63	172

Table A-5. Cumulative belemnite counts from the Mochras core generated by Clemens Ullmann.

Appendix B — Data from Chapter 3

depth (m)	declination	inclination	depth (m)	declination	inclination
607.26	220.5	35.9	760.73	182.7	-20.5
611.43	237	53.7	762.64	334.7	29.9
613.26	25.2	-30.2	764.77	46.7	-43.7
617.35	183.9	16.1	768.81	11.8	33.8
634.50	200	46.3	770.69	336.9	-28.3
636.35	204.6	-66.7	772.80	277	-44.3
640.77	52.7	-39.9	774.75	136.2	58.7
642.68	330.1	-25.9	776.35	291.7	-34.4
644.82	184.5	-41.5	778.56	42.9	-50.4
650.77	175.5	5.9	780.36	137.6	30.2
664.54	45.2	-48.6	781.91	49.8	-42.9
673.10	275.9	-63	784.40	191.2	23.8
682.52	175.1	-17.4	785.95	60.8	46.6
683.18	48.1	-42.4	793.80	164.1	19.5
686.49	204.1	63.7	797.36	183.7	-26.7
687.32	191.4	76.8	800.48	353.5	35
692.33	196.3	59.9	807.21	209	12.2
702.11	355.1	61.2	820.09	200.7	48.3
703.94	175.5	1.4	823.04	202.9	-43.4
708.23	174.8	22.1	825.04	170.2	-40.8
709.85	177.9	8	834.03	3.3	31.3
711.84	216	35.2	835.61	348.3	9.5
713.59	343.3	55.1	843.03	188.9	22.5
715.67	301.7	-46.4	843.92	192.9	29.8
721.28	63.9	-46.1	847.12	207.9	43.2
725.53	38.4	-32.6	851.10	166.8	61.7
728.04	220	21.5	856.49	191.7	28.2
733.22	180.4	-23.7	858.57	14.5	57.9
735.43	7.9	-41.7	860.93	128.8	71.9
736.78	35.1	-44.3	862.13	162.4	-16.5
745.41	41.3	-42.4	863.07	240.0	26.8
752.50	173.2	-4.4	863.19	329.8	56.2
756.46	34.1	-43.2			

Table B-1. Declination and inclination data from the Class A samples of the Mochras Core.

Appendix C — Geochemical data from Chapter 4

Depth (m)	$\delta^{13}\text{C}$ (‰) PDB	TOC (%)	HI	Tmax (°C)	Depth (m)	$\delta^{13}\text{C}$ (‰) PDB	TOC (%)	HI	Tmax (°C)
2665.005	-27.83	0.22	286	449	2678.29	-28.90	1.72	385	450
2665.3	-27.93	0.22	182	446	2678.39	-29.84	1.95	376	451
2665.75	-28.84	0.16	150	447	2678.49	-29.58			
2666.035	-28.39	0.36	161	449	2678.68	-29.08	2.5	396	452
2666.25	-27.60	0.09	200	448	2679.09	-28.42	1.29	333	447
2666.5	-27.75	0.08	138	449	2679.31	-29.50	1.21	311	449
2666.9	-28.31	0.66	211	450	2679.5	-30.07	1.92	353	449
2667.175	-27.79	0.23	222	451	2679.6	-29.83			
2667.45	-26.77	0.08	150	446	2679.69	-29.05	2.58	357	446
2667.625	-27.19	0.15	253	450	2679.99	-28.59	1.46	329	448
2668	-27.71	0.14	136	447	2680.09	-29.55			
2668.27	-27.78	0.58	214	444	2680.19	-29.56			
2668.49	-27.81	0.25	180	448	2680.31	-29.17	1.85	351	449
2668.7	-27.02	0.83	270	448	2680.59	-25.84			
2668.98	-27.18	0.72	208	448	2680.68	-27.23	0.85	252	448
2669.2	-28.12	0.89	337	450	2680.99	-28.84	1.64	343	449
2669.57	-27.69	0.14	171	449	2681.38	-28.98	1.28	297	448
2669.89	-27.59	0.09	67	449	2682.95	-28.03	2.49	323	450
2670.08	-27.75	0.18	222	446	2683.22	-29.41	1.03	335	448
2670.39	-27.90	0.1	230	449	2683.3	-29.06	1.03	316	449
2670.66	-27.82	0.2	215	451	2683.41	-28.27	0.92	298	449
2670.88	-28.93	0.07	214	449	2683.6	-29.39	0.95	280	450
2671.19	-28.12	0.06	250	448	2683.69	-29.49			
2671.52	-28.06	0.14	186	452	2683.84	-29.04	1.24	364	450
2671.88	-28.65	0.16	238	451	2683.91	-30.01	1.26	335	448
2672.39	-28.69	0.65	295	444	2684.08	-29.34	1.5	369	452
2672.61	-28.58	0.82	284	449	2684.38	-28.91	1.46	345	451
2672.8	-27.60	0.79	290	447	2684.49	-29.90	1.29	337	449
2673.05	-27.92	0.77	292	445	2684.58	-29.30	1.3	362	446
2673.38	-27.89	0.86	306	450	2684.87	-29.43	1.77	368	449
2673.7	-27.94	0.75	349	451	2684.99	-29.88			
2673.99	-29.03	2.4	351	454	2685.32	-29.31	1.37	350	451
2674.18	-28.07	0.69	306	447	2685.4	-29.69			
2674.42	-28.14	1.29	362	449	2685.49	-29.59	1.07	321	449
2674.73	-27.99	1.73	364	451	2685.55	-28.77	1.01	356	449
2674.945	-28.00				2685.76	-29.51			
2675.23	-28.97	2.06	393	451	2685.87	-28.70	0.82	295	449
2675.44	-28.27	1.28	359	446	2686.16	-31.87	2.45	348	451
2675.57	-29.81	1.68	360	451	2686.44	-29.54	2.1	347	451
2675.77	-29.16	1.74	409	449	2686.63	-28.54	1.45	306	451
2675.98	-29.23	2.32	403	452	2686.79	-29.37			
2676.11	-28.90	2.89	399	451	2686.86	-29.44	1.61	339	450
2676.39	-28.46	0.3	310	449	2687.08	-28.54	1.56	340	451
2676.6	-29.28	2.37	383	452	2687.18	-28.80	1.44	311	451
2676.79	-29.62	3.25	418	453	2687.28	-29.03	1.53	314	451
2677.09	-29.53	2.64	379	452	2687.47	-28.98	1.68	378	450
2677.39	-28.99	1.68	402	448	2687.8	-28.51			
2677.6	-29.13	1.76	429	448	2687.96	-25.99	1.21	174	453
2677.79	-29.63	2.43	428	451	2688.31	-29.12	1.22	252	446
2677.99	-29.01	0.77	344	451	2688.49	-28.90	1.94	375	446

Depth (m)	$\delta^{13}\text{C}$ (‰) PDB	TOC (%)	HI	Tmax (°C)
2688.68	-29.46	2.18	340	450
2688.88	-28.40	2.26	337	450
2689.16	-28.56	1.67	347	449
2689.5	-29.16	1.86	356	447
2689.73	-28.42	1.8	358	447
2690.11	-28.75	1.8	361	449
2690.4	-28.48	1.56	342	450
2690.61	-28.45	2.03	357	448
2690.91	-29.42	0.81	319	440
2691.1	-28.36	1.88	348	450
2691.43	-28.16	1.86	361	451
2691.71	-27.57	0.44	302	448
2691.99	-27.96	1.69	312	452
2692.16	-28.03	1.86	333	447
2692.44	-27.85	2.27	281	452
2692.66	-28.99	2.29	308	452
2692.99	-29.01			
2693.15	-28.24	2.57	331	445
2693.45	-28.31	1.65	303	450
2693.6	-27.47			
2693.9	-27.85	0.72	289	449
2694.39	-27.92	0.86	235	451
2694.68	-28.03	1.44	280	445
2695.05	-27.88			
2695.26	-26.24	0.11	191	438
2695.5	-28.15	1.54	245	454
2695.7	-28.03	1.52	266	450
2695.9	-26.77	1.15	234	447
2696.16	-26.34	1.33	205	450
2696.34	-27.13	1.18	229	449
2696.57	-26.80	0.69	233	451
2696.735	-26.52			
2696.99	-26.98	0.41	180	448
2697.38	-25.83			
2697.6	-26.30	0.83	165	446
2697.8	-25.93	1.2	150	454
2698.38	-26.76	1.49	156	452
2698.69	-27.46	0.91	226	451
2698.99	-27.56	1.22	280	450
2699.21	-26.88	1.14	204	454
2699.505	-26.18	0.81	158	454
2700.73	-26.61	0.77	187	448
2701.02	-27.73	1.11	232	450
2701.39	-27.34	1.74	249	453
2701.505	-26.41			
2701.58	-26.91	0.78	164	452
2701.81	-26.76	0.94	196	449
2702.13	-27.85	1.58	242	453
2702.325	-27.48	0.89	208	449
2702.605	-26.32	0.79	162	452

Depth (m)	$\delta^{13}\text{C}$ (‰) PDB	TOC (%)	HI	Tmax (°C)
2702.92	-24.58	1.16	164	452
2702.995	-25.90			
2703.075	-25.85	1.55	165	454
2703.28	-23.52	0.97	70	457
2703.49	-23.75	1	84	457
2703.695	-23.62	1.1	88	457
2703.89	-23.19	1.68	98	455
2704.08	-23.55	1.07	74	459
2704.38	-23.39	1.29	68	456
2704.65	-23.48	0.66	68	456
2705	-24.98	1.41	181	452
2705.37	-23.26	1.41	71	458
2705.6	-25.49			
2705.83	-24.76	1.24	122	455
2706.045	-24.93	1.1	130	453
2706.22	-25.27	1.31	137	456
2706.41	-24.86	1.33	114	455
2706.61	-25.19	1.42	137	457
2706.86	-25.07	1.17	134	454
2707.035	-26.10	1.15	167	455
2707.13	-24.07			
2707.305	-27.37	1.61	244	450
2707.565	-26.84	1.57	230	449
2707.855	-26.17	0.84	188	453
2708.125	-26.15	1.29	208	453
2708.32	-25.70	0.89	117	453
2708.49	-25.61	1.05	175	449
2708.785	-25.35	0.84	142	453
2709.065	-29.13	0.74	131	452
2709.34	-26.74	0.99	206	449
2709.66	-29.13	1.89	257	450
2709.95	-26.38	0.94	204	451
2710.315	-26.36	0.99	170	450
2710.69	-25.32	0.18	133	449
2711.05	-25.50	0.63	165	453
2711.38	-23.74	0.92	97	455
2711.68	-23.92	0.97	95	457
2711.93	-22.79	2.14	92	460
2712.255	-24.81	0.84	113	453
2712.43	-25.50	0.94	171	452
2712.57	-25.36	1.25	189	451
2712.835	-26.18			
2713.255	-27.18	1	279	449
2713.325	-26.35	0.99	232	448
2713.755	-25.80	1.36	242	450
2713.955	-25.49	0.15	127	447
2714.26	-25.54	0.58	219	448
2714.54	-25.04	0.67	140	449
2714.74	-25.80	0.1	160	446

Table C-1. Bulk organic carbon isotope and Rock Eval data from Core A.

Depth (m)	$\delta^{13}\text{C}$ (‰) PDB	TOC (%)	HI	Tmax (°C)	OI
3087.01	-25.95				
3087.45	-24.39				
3087.77	-23.53				
3088.19	-26.56				
3088.8	-24.44	0.07	29	507	129
3089.09	-21.9	0.1	0	-38	70
3090.13	-23.41	0.15	7	481	120
3090.8	-23.62	0.23	30	518	130
3091.39	-23.73				
3091.7	-24.39				
3091.98	-24.02	0.09	11	499	322
3092.15	-23.8	0.04	0	-38	200
3092.61	-25.06				
3093.04	-24.61				
3093.51	-25.44				
3094.09	-23.24	0.07	14	498	229
3094.51	-22.8	0.12	0	496	33
3095.14	-23.96				
3095.75	-24.12				
3096.21	-26.28	0.24	29	447	62
3096.8	-25.85	0.08	0	-38	425
3097.40	-25.55				
3098	-25.24				
3098.6	-24.4	0.11	27	448	100
3099.18	-26.56	0.42	74	457	38
3099.79	-25.23				
3100.53	-19.34	0.19	47	461	89
3101.01	-21.8	0.25	12	476	36
3101.6	-23.42				
3102.35	-22.97	0.24	17	482	150
3102.8	-25.3	0.9	86	460	2
3103.09	-26.75	1.05	110	463	10
3103.85	-24.60	0.2	30	453	100
3104.5	-22.0	0.47	23	484	19
3104.65	-23.15				
3105.25	-23.03	0.18	11	496	206
3106	-22.89	0.3	20	483	57
3106.74	-26.32	2.25	31	460	4
3108	-24.7	0.54	72	455	46
3108.62	-27.85	0.16	38	461	69
3109.04	-23.37				
3109.95	-25.14				
3111	-23.7	0.39	51	467	23
3111.90	-24.69				

Depth (m)	$\delta^{13}\text{C}$ (‰) PDB	TOC (%)	HI	Tmax (°C)	OI
3112.49	-25.58				
3113.25	-26.7	0.06	17	430	183
3114.90	-25.81				
3115.80	-24.72	0.11	18	439	200
3116.85	-26.2	0.19	42	433	26
3117.75	-27.22	0.08	25	437	88
3118.85	-26.47				
3119.75	-25.5				
3120.50	-26.28	1.16	100	463	12
3121.40	-26.75				
3122.45	-27.3	1.23	165	458	2
3123.50	-25.41				
3124.69	-25.79				
3125.9	-24.8	0.76	108	463	4
3126.90	-27.46	1.05	187	460	9
3128.10	-26.16	0.33	76	457	48
3129.15	-25.1	0.78	151	458	15
3130.35	-27.44	0.94	153	460	12
3131.55	-26.18				
3132.9	-24.5	0.96	71	467	4
3133.95	-27.06	1.18	127	459	14
3135.15	-24.1	0.69	62	469	6
3136.05	-25.65	0.81	79	467	15
3137.4	-24.7	0.81	86	468	4
3138.45	-25.61	0.31	77	460	52
3139.50	-24.73	1.2	78	470	6
3140.55	-23.8	0.16	106	509	169
3141.46	-24.94	0.25	104	458	80
3142.70	-26.23	0.7	113	460	21
3143.75	-25.8	1.12	112	465	6
3144.65	-26.40	0.68	118	456	43
3145.25	-24.71	0.32	50	462	56
3145.99	-22.69	0.75	31	470	8
3146.75	-24.2	0.77	60	468	4
3147.82	-24.71	0.74	127	464	15
3148.70	-24.82	0.76	75	467	9
3149.9	-23.5	0.99	78	467	4
3150.95	-22.72	3.06	7	468	3
3151.71	-21.31	0.23	26	464	374
3152.45	-22.3	0.9	39	483	17
3153.05	-23.82	1.28	62	469	12
3153.75	-24.11	0.99	64	469	16
3154.8	-24.2	0.89	103	465	8
3156.30	-24.18	0.41	27	463	34

Table C-2. Bulk organic carbon isotope and Rock Eval data from Core B.

Depth (m)	S	S +/-	Ca	Ca +/-
2665.020	0.152	0.0044	39.52	0.037
2665.135	0.623	0.0071	20.39	0.028
2665.200	1.153	0.009	6.74	0.016
2665.230	1.011	0.0073	2.26	0.010
2665.260	0.311	0.0045	35.67	0.032
2665.300	0.227	0.005	37.51	0.037
2665.350	0.325	0.0047	33.68	0.031
2665.400	0.475	0.0062	32.77	0.035
2665.450	0.506	0.0054	34.92	0.032
2665.490	0.305	0.0054	36.14	0.036
2665.550	0.120	0.0035	39.34	0.033
2665.610	0.272	0.0052	36.36	0.036
2665.650	0.146	0.0036	40.47	0.034
2665.700	0.172	0.0044	40.30	0.037
2665.750	0.113	0.0034	40.33	0.034
2665.800	0.091	0.004	41.54	0.038
2665.850	0.263	0.0043	36.93	0.032
2665.900	0.400	0.0059	31.15	0.033
2665.925	0.270	0.0044	33.80	0.031
2665.970	0.445	0.0052	32.48	0.031
2665.990	0.277	0.0053	37.66	0.037
2666.065	0.299	0.0045	37.74	0.033
2666.120	0.392	0.006	32.90	0.036
2666.175	0.069	0.0033	36.42	0.032
2666.200	0.144	0.0045	39.31	0.038
2666.250	0.122	0.0035	39.14	0.033
2666.300	0.193	0.0046	39.00	0.037
2666.360	0.159	0.0037	39.65	0.033
2666.400	0.107	0.0041	41.19	0.038
2666.450	0.241	0.004	40.70	0.034
2666.490	0.165	0.0043	41.06	0.038
2666.550	0.171	0.0037	40.08	0.033
2666.600	0.129	0.0043	39.88	0.037
2666.650	0.107	0.0034	39.72	0.033
2666.700	0.146	0.0044	38.57	0.037
2666.750	0.171	0.0039	37.92	0.033
2666.800	0.283	0.0053	34.69	0.035
2666.850	0.209	0.0041	36.52	0.032
2666.905	0.606	0.007	23.91	0.029
2666.950	0.395	0.005	30.56	0.030
2666.990	0.480	0.0062	26.19	0.030
2667.030	0.289	0.0045	32.92	0.031
2667.070	0.195	0.0049	36.06	0.036
2667.130	0.158	0.0038	34.55	0.031
2667.200	0.145	0.0046	38.16	0.037
2667.250	0.229	0.0042	35.09	0.032
2667.300	0.118	0.0043	39.02	0.037
2667.350	0.143	0.0037	38.11	0.033
2667.350	0.143	0.0037	38.11	0.033

Depth (m)	S	S +/-	Ca	Ca +/-
2667.400	0.220	0.0049	37.62	0.036
2667.440	0.110	0.0034	40.08	0.033
2667.470	0.233	0.0049	37.96	0.037
2667.550	0.138	0.0037	39.57	0.034
2667.600	0.120	0.0041	41.20	0.038
2667.650	0.086	0.0033	39.90	0.033
2667.700	0.134	0.0043	41.27	0.038
2667.750	0.087	0.0033	41.14	0.034
2667.780	0.122	0.0043	40.11	0.038
2667.850	0.096	0.0033	40.76	0.034
2667.900	0.095	0.0041	39.95	0.037
2667.940	0.107	0.0034	40.02	0.034
2667.990	0.156	0.0045	39.21	0.037
2668.045	0.276	0.0044	36.61	0.032
2668.100	0.442	0.006	25.84	0.028
2668.150	0.261	0.0043	34.64	0.031
2668.200	0.196	0.0045	38.28	0.035
2668.235	0.106	0.0034	39.99	0.034
2668.300	0.394	0.0057	28.04	0.030
2668.350	0.163	0.0039	36.45	0.032
2668.400	0.304	0.0053	33.96	0.034
2668.450	0.167	0.0039	36.58	0.032
2668.490	0.298	0.0053	32.21	0.033
2668.550	0.462	0.0052	24.64	0.026
2668.600	0.190	0.0045	38.11	0.035
2668.650	0.141	0.0037	38.95	0.033
2668.705	0.788	0.0077	2.58	0.011
2668.750	0.983	0.0072	1.67	0.009
2668.800	0.330	0.0055	30.87	0.032
2668.850	0.531	0.0055	22.88	0.025
2668.925	0.755	0.0074	0.88	0.008
2668.950	1.098	0.0074	4.20	0.012
2668.995	1.146	0.0087	6.07	0.015
2669.045	0.997	0.0071	3.39	0.011
2669.100	0.955	0.0079	10.96	0.019
2669.200	0.829	0.0075	13.77	0.021
2669.300	0.180	0.0045	37.84	0.035
2669.400	0.078	0.0037	41.53	0.036
2669.490	0.192	0.0043	40.64	0.036
2669.600	0.182	0.0044	39.35	0.035
2669.700	0.194	0.0043	40.60	0.036
2669.800	0.281	0.0047	40.35	0.036
2669.900	0.154	0.0041	40.48	0.035
2669.975	0.097	0.0038	40.70	0.035
2670.110	0.045	0.0035	41.56	0.036
2670.240	0.040	0.0034	41.59	0.036
2670.310	0.023	0.003	41.03	0.036
2670.400	0.035	0.0031	40.93	0.035
2670.490	0.072	0.0033	40.42	0.035

Depth (m)	S	S +/-	Ca	Ca +/-
2670.600	0.041	0.0031	40.78	0.035
2670.700	0.075	0.0034	40.49	0.035
2670.800	0.149	0.0038	39.99	0.035
2670.900	0.152	0.0037	40.94	0.035
2670.990	0.049	0.0031	40.49	0.035
2671.050	0.057	0.0031	41.54	0.034
2671.100	0.072	0.0034	40.46	0.036
2671.150	0.089	0.0034	41.20	0.034
2671.200	0.078	0.0034	40.90	0.036
2671.250	0.042	0.003	41.28	0.034
2671.300	0.056	0.0033	39.73	0.035
2671.330	0.096	0.0033	40.61	0.034
2671.400	0.084	0.0035	39.86	0.035
2671.530	0.107	0.0037	39.46	0.035
2671.610	0.086	0.0036	39.24	0.035
2671.650	0.072	0.0033	40.53	0.034
2671.700	0.073	0.0035	39.42	0.035
2671.750	0.046	0.0031	40.22	0.034
2671.800	0.087	0.0036	39.81	0.036
2671.850	0.135	0.0038	38.76	0.034
2671.900	0.195	0.0043	36.32	0.034
2671.965	0.144	0.0038	36.89	0.032
2671.990	0.087	0.0035	38.97	0.035
2672.050	0.056	0.0032	39.24	0.034
2672.100	0.086	0.0035	39.20	0.035
2672.150	0.165	0.0039	37.79	0.033
2672.210	0.212	0.0043	36.45	0.033
2672.250	0.369	0.0049	35.23	0.032
2672.290	0.483	0.0058	28.42	0.030
2672.335	0.686	0.0062	21.78	0.025
2672.400	0.511	0.0059	27.45	0.029
2672.450	0.683	0.0062	23.09	0.026
2672.490	0.508	0.0055	27.09	0.029
2672.550	0.174	0.004	36.99	0.033
2672.600	0.249	0.0048	35.74	0.035
2672.650	0.625	0.0058	17.51	0.022
2672.690	0.553	0.0059	22.61	0.027
2672.750	0.809	0.0066	13.52	0.020
2672.800	0.537	0.0059	22.01	0.027
2672.880	0.489	0.0053	22.87	0.025
2672.900	0.990	0.0076	4.10	0.013
2672.945	0.835	0.0069	1.42	0.009
2672.990	0.578	0.0061	12.59	0.020
2673.045	0.742	0.0067	0.49	0.007
2673.160	0.716	0.0063	1.59	0.009
2673.200	0.960	0.0074	3.04	0.011
2673.250	0.842	0.0067	8.40	0.016
2673.300	1.037	0.0074	2.81	0.011
2673.350	0.650	0.006	12.99	0.020

Depth (m)	S	S +/-	Ca	Ca +/-
2673.380	1.002	0.0072	4.36	0.012
2673.420	0.893	0.0068	13.67	0.020
2673.465	0.894	0.0068	4.05	0.012
2673.510	0.747	0.0064	10.05	0.018
2673.550	0.939	0.0071	4.77	0.013
2673.600	0.652	0.006	12.77	0.020
2673.625	0.871	0.0067	6.97	0.015
2673.700	0.506	0.0056	19.69	0.024
2673.750	0.346	0.0048	28.62	0.028
2673.800	0.901	0.0068	35.06	0.032
2673.850	0.133	0.0039	36.83	0.033
2673.900	0.145	0.0038	39.79	0.034
2673.930	0.124	0.0039	36.76	0.033
2673.975	1.531	0.0086	4.26	0.012
2674.045	0.357	0.0049	32.13	0.030
2674.080	0.594	0.0058	22.24	0.025
2674.150	0.662	0.006	19.05	0.023
2674.200	0.097	0.0038	36.88	0.033
2674.250	0.986	0.0072	5.28	0.013
2674.300	1.283	0.0081	2.49	0.010
2674.350	1.025	0.0073	6.83	0.015
2674.400	1.127	0.0076	5.33	0.013
2674.450	0.980	0.007	11.64	0.018
2674.485	0.703	0.0063	17.12	0.022
2674.545	1.068	0.0073	9.95	0.017
2674.620	0.971	0.0071	5.68	0.014
2674.640	1.099	0.0076	6.20	0.014
2674.715	0.810	0.0066	12.74	0.019
2674.760	1.008	0.0072	3.12	0.011
2674.805	0.766	0.0063	8.27	0.016
2674.850	0.350	0.0049	26.77	0.028
2674.900	0.304	0.0046	25.63	0.027
2674.935	0.028	0.0033	38.30	0.033
2674.995	0.055	0.0033	38.24	0.033
2675.050	0.192	0.0041	34.19	0.031
2675.070	0.042	0.0033	39.48	0.034
2675.120	0.542	0.0057	25.85	0.027
2675.200	0.158	0.004	33.76	0.031
2675.240	1.169	0.0077		
2675.320	1.429	0.0085	1.40	0.008
2675.360	1.126	0.0076	1.44	0.008
2675.405	1.164	0.0077	4.67	0.013
2675.450	1.093	0.0075	3.93	0.012
2675.490	1.423	0.0085	0.41	0.006
2675.550	1.159	0.0078		
2675.600	1.211	0.0079	0.06	0.006
2675.645	1.471	0.0087	0.57	0.007
2675.700	1.292	0.0081		
2675.740	1.396	0.0084	0.09	0.006

Depth (m)	S	S +/-	Ca	Ca +/-
2675.800	1.425	0.0085		
2675.820	1.357	0.0082		
2675.880	1.433	0.0084	0.11	0.006
2675.910	1.096	0.0075		
2675.950	1.129	0.0077	0.05	0.006
2676.055	0.983	0.0072	6.65	0.015
2676.075	1.124	0.0076	3.04	0.011
2676.110	0.994	0.007	4.10	0.012
2676.150	0.415	0.0051	28.13	0.028
2676.220	0.288	0.0047	30.90	0.031
2676.265	0.087	0.0035	37.99	0.033
2676.300	0.182	0.004	35.45	0.032
2676.350	0.105	0.0036	38.67	0.033
2676.390	0.065	0.0034	39.84	0.034
2676.450	0.121	0.0035	33.45	0.030
2676.490	0.129	0.0036	30.14	0.028
2676.545	0.168	0.0038	30.40	0.028
2676.585	0.165	0.004	34.64	0.032
2676.630	0.908	0.0069	2.97	0.010
2676.685	1.006	0.0073	3.27	0.011
2676.745	0.996	0.0072	1.82	0.009
2676.800	0.907	0.0069	0.66	0.007
2676.850	0.865	0.0067	4.59	0.012
2676.895	0.743	0.0064	6.69	0.015
2676.965	0.174	0.0039	35.59	0.031
2676.990	0.483	0.0053	27.37	0.028
2677.025	0.589	0.0061	14.53	0.021
2677.075	1.241	0.0079	0.19	0.006
2677.130	0.974	0.007	13.27	0.020
2677.200	1.176	0.0078	3.23	0.011
2677.245	1.061	0.0074	0.07	0.006
2677.285	1.203	0.0078	1.65	0.009
2677.330	1.099	0.0075	1.54	0.009
2677.370	1.091	0.0075		
2677.425	1.154	0.0079		
2677.445	1.265	0.008		
2677.480	1.231	0.008	0.33	0.006
2677.535	0.985	0.0071	0.18	0.006
2677.595	1.270	0.008	0.13	0.006
2677.650	1.496	0.0085		
2677.700	0.987	0.0072	0.12	0.006
2677.755	1.252	0.0079	0.23	0.006
2677.810	1.072	0.0073	0.74	0.007
2677.835	1.002	0.0072	0.46	0.006
2677.900	0.110	0.0037	35.18	0.032
2677.935	0.262	0.0043	30.20	0.029
2677.985	0.233	0.0043	32.04	0.030
2678.035	0.198	0.0041	36.65	0.032
2678.100	0.090	0.0036	38.76	0.034

Depth (m)	S	S +/-	Ca	Ca +/-
2678.155	0.182	0.0039	36.91	0.032
2678.200	0.119	0.0034	35.69	0.031
2678.300	1.943	0.0095		
2678.325	1.293	0.0082	0.14	0.006
2678.355	0.892	0.0069		
2678.400	0.889	0.0069		
2678.450	0.964	0.0073		
2678.520	0.740	0.0064		
2678.600	0.810	0.0066		
2678.655	0.673	0.0061		
2678.700	0.738	0.0065		
2678.750	0.808	0.0065	0.82	0.007
2678.785	0.805	0.0065	7.05	0.015
2678.830	1.925	0.0096	1.97	0.009
2678.900	0.091	0.0035	38.29	0.033
2678.960	0.523	0.0053	39.63	0.034
2678.985	0.110	0.0037	37.91	0.033
2679.045	0.876	0.0067	22.20	0.025
2679.075	1.147	0.0078	0.15	0.006
2679.110	1.194	0.0078		
2679.200	1.007	0.0073	0.07	0.006
2679.250	0.796	0.0067	0.76	0.007
2679.300	0.997	0.0072		
2679.335	1.897	0.0096	2.04	0.009
2679.390	1.239	0.008	1.17	0.008
2679.420	1.146	0.0076	0.13	0.006
2679.455	1.159	0.0076	0.22	0.006
2679.490	1.130	0.0076	0.11	0.006
2679.535	1.568	0.0088		
2679.570	0.847	0.0065	2.99	0.011
2679.600	1.143	0.0076	0.34	0.006
2679.645	0.835	0.0066	0.32	0.006
2679.685	1.023	0.0073	6.15	0.014
2679.735	0.372	0.005	26.16	0.027
2679.800	0.347	0.0046	40.23	0.034
2679.850	0.926	0.0067	36.15	0.032
2679.900	0.391	0.0048	11.34	0.018
2679.980	1.516	0.0089	3.91	0.012
2679.990	1.331	0.0083	0.36	0.007
2680.040	0.479	0.0055	24.97	0.028
2680.115	1.186	0.0079	0.37	0.007
2680.200	1.246	0.0079	0.20	0.006
2680.240	1.262	0.0079	0.34	0.006
2680.295	1.111	0.0075	0.22	0.006
2680.380	0.987	0.0071	0.20	0.006
2680.420	1.337	0.0083	0.28	0.006
2680.495	0.188	0.0041	37.52	0.033
2680.550	0.284	0.0045	36.72	0.032
2680.600	0.316	0.0048	34.93	0.032

Depth (m)	S	S +/-	Ca	Ca +/-
2680.660	0.058	0.0034	36.67	0.032
2680.700	0.494	0.0054	9.60	0.017
2680.750	0.319	0.0048	17.73	0.023
2680.800	0.893	0.0069	1.36	0.008
2680.855	1.203	0.0078	0.43	0.007
2680.900	0.149	0.0039	37.80	0.033
2680.935	0.089	0.0035	39.67	0.034
2680.985	1.551	0.0086	8.44	0.017
2681.025	1.419	0.0084	0.35	0.006
2681.055	0.866	0.0067		
2681.170	1.272	0.0078	5.63	0.014
2681.200	0.175	0.0041	36.38	0.032
2681.225	0.389	0.0049	34.07	0.031
2681.265	0.238	0.0044	32.14	0.030
2681.320	1.137	0.0076	0.90	0.007
2681.350	1.351	0.008	9.89	0.017
2681.400	0.371	0.0052	21.08	0.025
2681.425	0.326	0.0049	26.90	0.028
2682.875	0.432	0.0051	29.57	0.029
2682.900	0.346	0.0048	31.17	0.030
2682.950	0.515	0.0056	20.35	0.024
2682.975	0.504	0.0056	23.12	0.026
2683.000	0.419	0.0054	27.98	0.028
2683.065	0.611	0.006	17.24	0.023
2683.105	0.931	0.0071	2.00	0.009
2683.135	0.973	0.0072	1.11	0.008
2683.245	0.874	0.0068	1.95	0.009
2683.315	0.795	0.0066	1.11	0.008
2683.345	1.139	0.0076	1.19	0.008
2683.400	0.514	0.0055	0.36	0.006
2683.450	0.756	0.0064	0.32	0.006
2683.500	1.137	0.0078	0.45	0.007
2683.555	0.690	0.0062	0.91	0.008
2683.600	0.612	0.006	0.38	0.007
2683.650	0.467	0.0053	1.07	0.008
2683.700	0.388	0.005	1.36	0.008
2683.750	0.352	0.0047	0.24	0.006
2683.805	0.382	0.0049	0.34	0.006
2683.850	0.481	0.0053	0.20	0.006
2683.890	0.386	0.0049	3.26	0.011
2683.965	0.283	0.0044	0.17	0.006
2684.035	0.622	0.0059	0.96	0.008
2684.080	0.539	0.0055	0.68	0.007
2684.160	0.249	0.0044	30.07	0.029
2684.215	0.067	0.0035	37.55	0.033
2684.250	0.077	0.0035	35.60	0.031
2684.300	0.088	0.0034	22.95	0.024
2684.350	0.082	0.0036	33.62	0.031
2684.400	1.010	0.0073	0.54	0.007

Depth (m)	S	S +/-	Ca	Ca +/-
2684.435	0.930	0.007	0.77	0.007
2684.480	0.903	0.0069	0.35	0.006
2684.550	0.723	0.0063	0.58	0.007
2684.600	0.684	0.0062	1.94	0.009
2684.650	0.794	0.0066	0.69	0.007
2684.700	0.778	0.0066	1.29	0.008
2684.750	0.475	0.0054	0.13	0.006
2684.800	0.712	0.0062	0.73	0.007
2684.850	0.794	0.0064	3.34	0.011
2684.890	0.973	0.0072	4.76	0.013
2684.950	0.172	0.0038	30.77	0.029
2684.950	0.186	0.0039	39.64	0.034
2685.040	0.189	0.0039	28.68	0.027
2685.100	0.175	0.004	34.79	0.031
2685.150	0.225	0.0042	26.55	0.026
2685.200	0.432	0.0051	16.13	0.021
2685.250	0.749	0.0064	1.19	0.008
2685.300	1.072	0.0075	1.28	0.008
2685.350	0.756	0.0064	1.29	0.008
2685.400	0.838	0.0067	1.31	0.008
2685.450	1.170	0.0077	1.13	0.008
2685.490	0.640	0.006	3.20	0.011
2685.550	0.391	0.0049	1.07	0.008
2685.600	0.460	0.0053	2.13	0.009
2685.650	0.302	0.0046	6.31	0.014
2685.700	0.391	0.005	1.14	0.008
2685.750	0.345	0.0048	1.62	0.008
2685.800	0.632	0.0061	2.53	0.010
2685.850	0.384	0.0049	0.99	0.008
2685.900	0.546	0.0057	4.29	0.012
2685.950	0.347	0.0047	2.30	0.010
2685.990	0.474	0.0053	1.67	0.009
2686.050	0.345	0.0048	21.52	0.024
2686.120	0.335	0.0048	22.34	0.025
2686.170	0.289	0.0045	26.52	0.027
2686.200	0.287	0.0045	21.50	0.024
2686.250	0.242	0.0043	33.53	0.030
2686.300	0.231	0.0042	35.59	0.032
2686.350	0.207	0.004	35.07	0.031
2686.400	0.283	0.0046	29.78	0.029
2686.445	0.363	0.0049	23.37	0.026
2686.488	0.255	0.0045	32.59	0.031
2686.550	0.771	0.0065	0.06	0.006
2686.600	0.930	0.0071	0.16	0.006
2686.650	0.836	0.0067	0.13	0.006
2686.700	1.124	0.0076	0.94	0.007
2686.750	0.453	0.0052	0.06	0.006
2686.800	0.242	0.0042		
2686.850	0.278	0.0044		

Depth (m)	S	S +/-	Ca	Ca +/-
2686.890	0.337	0.0047	0.07	0.006
2686.950	0.636	0.006	7.19	0.015
2687.010	0.035	0.0034	36.02	0.032
2687.045	0.232	0.0045	28.15	0.028
2687.080	0.619	0.006	11.12	0.019
2687.180	0.686	0.0063	6.32	0.015
2687.200	0.876	0.0069	0.47	0.007
2687.250	0.900	0.0069	0.22	0.006
2687.300	0.968	0.0072	1.44	0.008
2687.350	1.716	0.0095	0.59	0.007
2687.400	0.804	0.0067	0.12	0.006
2687.450	0.930	0.0069	0.30	0.006
2687.510	0.915	0.0071	0.30	0.006
2687.560	0.895	0.0068	0.11	0.006
2687.610	0.237	0.0045	27.58	0.028
2687.650	0.276	0.0045	24.06	0.026
2687.700	0.523	0.0056	11.40	0.019
2687.750	0.198	0.0043	26.60	0.028
2687.790	0.377	0.0051	26.19	0.027
2687.850	1.357	0.0082	0.80	0.007
2687.895	1.014	0.0073	0.37	0.006
2687.950	0.310	0.0046	1.82	0.009
2687.990	0.195	0.004	3.03	0.011
2688.080	0.043	0.003	2.44	0.010
2688.120	0.104	0.0035	0.72	0.007
2688.160	0.106	0.0034	0.77	0.007
2688.205			1.33	0.008
2688.250	0.372	0.0049	8.59	0.016
2688.290	0.444	0.0054	7.34	0.015
2688.350	0.234	0.0042	1.54	0.008
2688.390	0.272	0.0044	0.30	0.006
2688.425	0.661	0.006	0.29	0.006
2688.550	1.125	0.0078	0.27	0.006
2688.615	0.870	0.0069	0.11	0.006
2688.650	0.886	0.007	0.06	0.006
2688.700	0.668	0.0061	0.91	0.007
2688.730	0.622	0.0059	0.69	0.007
2688.780	0.756	0.0064	0.36	0.006
2688.830	0.093	0.0037	35.97	0.032
2688.895	0.971	0.0072	2.61	0.010
2688.955	0.998	0.0072	1.82	0.009
2688.995	0.608	0.0058	3.40	0.011
2689.075	1.022	0.0072	8.97	0.017
2689.095	0.871	0.0068	5.99	0.014
2689.110	1.168	0.0078	0.52	0.007
2689.120	0.631	0.0061	7.48	0.016
2689.163	0.852	0.007	5.92	0.014
2689.200	0.396	0.005	0.22	0.006
2689.265	0.280	0.0046	0.58	0.007

Depth (m)	S	S +/-	Ca	Ca +/-
2689.390	0.327	0.005	0.35	0.006
2689.420	0.176	0.0038		
2689.480	0.389	0.0053	0.19	0.006
2689.550	0.371	0.0049	6.43	0.014
2689.600	0.603	0.0059	1.11	0.008
2689.650	0.206	0.0041	10.60	0.018
2689.700	0.369	0.0049	0.76	0.007
2689.755	0.270	0.0045	24.20	0.026
2689.800	0.065	0.0035	35.20	0.032
2689.850	0.213	0.0043	29.45	0.029
2689.880	1.206	0.0075	37.04	0.033
2689.940	0.635	0.0059	16.45	0.022
2689.965	0.757	0.0065	2.55	0.010
2690.010	0.502	0.0056	0.12	0.005
2690.130	0.364	0.0049	3.17	0.011
2690.170	0.270	0.0043	0.99	0.007
2690.225	0.428	0.0052	6.75	0.015
2690.290	0.349	0.0048	5.64	0.013
2690.330	0.292	0.0046	7.49	0.015
2690.430	0.291	0.0046	6.25	0.014
2690.465	0.518	0.0057	3.11	0.011
2690.510	0.273	0.0046	10.38	0.018
2690.550	0.251	0.0045	29.70	0.029
2690.600	0.117	0.0043	28.20	0.031
2690.665	0.815	0.0066	0.13	0.006
2690.725	0.019	0.0031	40.87	0.034
2690.760	0.040	0.0031	41.76	0.035
2690.815	0.081	0.0034	41.08	0.035
2690.850	0.123	0.0036	39.76	0.034
2690.895	0.343	0.0048	34.09	0.032
2690.960	0.357	0.0049	33.17	0.031
2690.988	0.355	0.005	28.72	0.029
2691.015	2.973	0.0117	1.18	0.007
2691.110	0.901	0.0069	0.71	0.007
2691.150	0.891	0.0068	0.49	0.006
2691.200	0.300	0.0045	0.05	0.005
2691.250	0.196	0.0039	0.18	0.006
2691.300	0.221	0.0042	8.61	0.016
2691.340	0.415	0.0051	3.51	0.011
2691.410	0.355	0.0049	0.58	0.007
2691.470	0.436	0.0052	14.05	0.020
2691.520	0.334	0.0049	17.64	0.023
2691.565	0.522	0.0055	6.17	0.014
2691.600	0.289	0.0047	28.24	0.028
2691.650	0.051	0.0032	41.17	0.034
2691.700	0.088	0.0036	33.96	0.031
2691.785	0.093	0.0035	39.46	0.034
2691.800	0.154	0.0039	36.98	0.033
2691.850	0.084	0.0033	41.57	0.034

Depth (m)	S	S +/-	Ca	Ca +/-
2691.900	0.415	0.0052	29.39	0.029
2691.925	0.167	0.004	39.18	0.034
2691.960	0.900	0.007	3.89	0.012
2692.035	0.669	0.0062	0.62	0.007
2692.060	0.360	0.0048	0.42	0.006
2692.170	0.601	0.0059	2.73	0.010
2692.200	0.288	0.0046	3.59	0.011
2692.235	0.354	0.0047	2.38	0.010
2692.300	0.466	0.0054	3.06	0.011
2692.335	0.346	0.0048	7.96	0.016
2692.400	0.044	0.0032	40.68	0.034
2692.455	0.586	0.0059	5.17	0.013
2692.485	0.307	0.0048	19.69	0.024
2692.560	0.146	0.0041	30.69	0.029
2692.600	0.479	0.0054	9.84	0.017
2692.635	0.292	0.0047	21.09	0.024
2692.690	0.409	0.005	0.64	0.007
2692.745	0.374	0.0048	2.09	0.009
2692.790	0.342	0.0048	1.16	0.008
2692.830	0.403	0.0049	7.50	0.015
2692.875	0.436	0.0051	5.92	0.014
2692.985	0.730	0.0064	1.11	0.008
2693.015	0.394	0.005	0.72	0.007
2693.020	0.433	0.0052	1.27	0.008
2693.060	0.498	0.0055	2.90	0.011
2693.065	0.531	0.0057	4.53	0.013
2693.100	0.366	0.0049	14.68	0.021
2693.165	0.391	0.0051	6.94	0.015
2693.170	0.397	0.0052	9.63	0.017
2693.210	0.269	0.0045	2.92	0.011
2693.230	0.222	0.0043	12.78	0.019
2693.270	0.421	0.0051	1.62	0.009
2693.340	0.406	0.0051	3.39	0.011
2693.390	0.236	0.0045	24.40	0.026
2693.450	0.167	0.0041	31.68	0.030
2693.485	0.085	0.0035	39.30	0.033
2693.525	0.194	0.0041	35.52	0.032
2693.540	0.147	0.0039	36.52	0.033
2693.560	0.161	0.0039	36.74	0.032
2693.600	0.079	0.0034	41.26	0.035
2693.615	0.118	0.0035	41.08	0.034
2693.650	0.210	0.0042	35.71	0.032
2693.660	0.425	0.0051	27.59	0.028
2693.700	0.401	0.0052	25.40	0.027
2693.735	0.266	0.0046	20.38	0.025
2693.765	0.072	0.0037	34.15	0.032
2693.800	0.250	0.0044	11.05	0.018
2693.845	0.244	0.0043	23.43	0.026
2693.895	0.126	0.0039	34.22	0.032

Depth (m)	S	S +/-	Ca	Ca +/-
2693.940	0.165	0.0037	40.71	0.034
2693.985	0.043	0.0032	40.75	0.034
2694.030	0.044	0.0033	39.28	0.034
2694.075	0.066	0.0034	39.42	0.034
2694.110	0.059	0.0033	39.03	0.033
2694.160	0.074	0.0034	39.08	0.033
2694.200	0.098	0.0036	39.18	0.034
2694.250	0.081	0.0034	40.45	0.034
2694.305	0.138	0.0038	40.00	0.034
2694.350	0.537	0.0057	26.62	0.028
2694.405	0.199	0.0042	12.59	0.019
2694.445	0.268	0.0044	10.10	0.017
2694.485	0.338	0.0049	34.84	0.032
2694.550	0.071	0.0034	39.29	0.033
2694.600	0.059	0.0035	37.60	0.033
2694.650	0.443	0.0052	27.51	0.028
2694.700	0.068	0.0036	36.09	0.032
2694.750	0.211	0.0041	6.11	0.014
2694.800	0.231	0.0042	4.31	0.012
2694.835	0.215	0.0041	3.54	0.011
2694.885	0.123	0.0039	17.64	0.022
2694.930	0.245	0.0045	22.22	0.025
2694.985	0.067	0.0036	28.36	0.028
2695.020	0.130	0.004	32.61	0.030
2695.080	0.120	0.0039	23.73	0.026
2695.175	0.164	0.0041	24.01	0.026
2695.200	0.122	0.0038	35.11	0.032
2695.250	0.251	0.0045	31.18	0.030
2695.305	0.015	0.0031	40.52	0.034
2695.350	0.255	0.0044	37.66	0.033
2695.390	0.210	0.0042	37.11	0.032
2695.440	0.207	0.0042	18.11	0.023
2695.485	0.287	0.0046	23.73	0.026
2695.560	0.134	0.0037	16.49	0.021
2695.610	0.154	0.0038	3.74	0.011
2695.690	0.503	0.0056	21.40	0.025
2695.755	0.032	0.0034	36.91	0.032
2695.795	0.186	0.004	6.94	0.015
2695.825	0.156	0.0039	4.86	0.013
2695.885	0.110	0.0038	15.24	0.021
2695.925	0.184	0.0041	12.94	0.020
2695.985	0.171	0.004	3.72	0.011
2696.030	0.099	0.0035	12.84	0.019
2696.065	0.294	0.0047	18.93	0.023
2696.115	0.035	0.0033	33.45	0.031
2696.175	0.045	0.0034	26.34	0.027
2696.200	0.106	0.0036	10.90	0.018
2696.250	0.071	0.0036	33.70	0.031
2696.300	0.139	0.0039	11.80	0.018

Depth (m)	S	S +/-	Ca	Ca +/-
2696.340	0.112	0.0037	20.42	0.024
2696.390	0.393	0.0052	24.51	0.027
2696.430	0.173	0.004	12.33	0.019
2696.485	0.112	0.0037	35.85	0.032
2696.550	0.209	0.0042	26.11	0.027
2696.595	0.045	0.0031	41.26	0.034
2696.650	0.184	0.0042	30.84	0.030
2696.700	0.154	0.004	35.49	0.032
2696.750	0.044	0.0031	41.31	0.034
2696.800	0.210	0.0041	38.42	0.033
2696.850	0.238	0.0043	32.51	0.030
2696.900	0.109	0.0038	36.59	0.032
2696.940	0.046	0.0031	41.09	0.034
2696.980	0.195	0.0042	33.73	0.031
2697.030	0.215	0.0043	25.00	0.026
2697.080	0.035	0.0033	36.25	0.032
2697.140	0.121	0.0039	31.71	0.030
2697.200	0.120	0.0038	25.33	0.026
2697.250	0.150	0.004	18.92	0.023
2697.300	0.104	0.0037	18.15	0.023
2697.350	0.291	0.0047	11.49	0.018
2697.415	0.196	0.0042	9.40	0.017
2697.450	0.131	0.0039	13.49	0.020
2697.495	0.422	0.0052	2.76	0.010
2697.535	0.191	0.0041	14.80	0.020
2697.600	0.116	0.0038	16.90	0.022
2697.650	0.109	0.0037	26.63	0.027
2697.690	0.170	0.0039	4.37	0.012
2697.755	0.129	0.0037	17.72	0.022
2697.795	0.217	0.0042	9.33	0.017
2697.850	0.123	0.0036	11.63	0.018
2697.900	0.070	0.0034	36.62	0.032
2697.945	0.186	0.004	38.58	0.033
2698.025	0.067	0.0033	38.69	0.033
2698.060	0.090	0.0035	40.11	0.034
2698.095	0.121	0.0036	39.80	0.034
2698.150	0.408	0.0049	37.98	0.033
2698.205	0.322	0.0045	38.25	0.033
2698.250	0.105	0.0039	29.72	0.029
2698.300	0.137	0.0038	13.84	0.020
2698.350	0.159	0.004	18.35	0.023
2698.400	0.144	0.0039	15.93	0.022
2698.450	0.120	0.0036	4.86	0.013
2698.490	0.119	0.0035	1.08	0.008
2698.550	0.218	0.0041	4.43	0.012
2698.600	0.166	0.0038	2.27	0.009
2698.650	0.153	0.0038	1.87	0.009
2698.710	0.065	0.0035	33.10	0.031
2698.765	0.433	0.0051	15.60	0.021

Depth (m)	S	S +/-	Ca	Ca +/-
2698.800	0.288	0.0046	20.66	0.024
2698.850	0.247	0.0044	18.68	0.023
2698.890	0.098	0.0037	32.87	0.030
2698.950	0.109	0.0037	37.65	0.033
2699.015	0.270	0.0044	37.76	0.033
2699.050	0.162	0.0038	37.46	0.033
2699.095	0.131	0.0037	39.93	0.034
2699.150	0.169	0.0038	40.73	0.034
2699.195	0.220	0.0044	29.35	0.029
2699.250	0.121	0.0036	5.43	0.013
2699.300	0.265	0.0045	5.32	0.013
2699.350	0.183	0.004	5.40	0.013
2699.410	0.144	0.0038	5.12	0.013
2699.460	0.142	0.0039	5.68	0.014
2699.515	0.201	0.0042	5.25	0.013
2699.540	0.212	0.0043	5.20	0.013
2699.580	0.114	0.0037	3.33	0.011
2700.645	0.122	0.0036	2.47	0.010
2700.700	0.294	0.0047	4.97	0.013
2700.750	0.165	0.0039	2.77	0.010
2700.800	0.210	0.0042	1.93	0.009
2700.850	0.216	0.0042	5.44	0.013
2700.900	0.189	0.004	2.38	0.010
2700.950	0.167	0.0038	3.01	0.010
2701.050	0.218	0.0041	3.25	0.011
2701.060	0.151	0.0038	3.36	0.011
2701.100	0.226	0.0043	5.49	0.013
2701.150	0.140	0.0042	29.44	0.029
2701.200	0.068	0.0037	37.71	0.034
2701.250	0.289	0.0046	30.91	0.029
2701.300	0.308	0.0047	29.56	0.029
2701.350	0.435	0.0053	23.81	0.026
2701.420	0.054	0.0032	41.19	0.034
2701.450	0.289	0.0044	38.30	0.033
2701.485	0.086	0.0034	41.10	0.034
2701.510	0.101	0.0035	39.93	0.034
2701.550	0.170	0.0041	36.20	0.032
2701.605	0.130	0.0037	5.39	0.013
2701.650	0.174	0.0039	3.72	0.011
2701.700	0.175	0.004	6.78	0.015
2701.735	0.223	0.0043	5.13	0.013
2701.800	0.189	0.004	4.46	0.012
2701.860	0.118	0.0036	8.33	0.016
2701.925	0.152	0.0039	16.57	0.022
2701.980	0.155	0.0039	18.10	0.023
2702.050			41.91	0.035
2702.095	0.281	0.0046	28.51	0.029
2702.150	0.171	0.0039	21.45	0.025
2702.215	0.134	0.004	28.49	0.029

Depth (m)	S	S +/-	Ca	Ca +/-
2702.250	0.017	0.0032	38.99	0.033
2702.300	0.174	0.004	14.09	0.020
2702.340	0.102	0.0036	14.18	0.020
2702.400	0.055	0.0033	9.24	0.017
2702.430	0.093	0.0034	3.75	0.011
2702.485	0.140	0.0037	4.87	0.013
2702.550	0.078	0.0035	7.34	0.015
2702.600	0.117	0.0037	9.61	0.017
2702.650	0.076	0.0036	23.59	0.025
2702.700	0.011	0.0031	37.60	0.032
2702.750	0.039	0.0035	28.18	0.028
2702.800	0.139	0.0042	26.50	0.028
2702.850	0.035	0.0034	29.16	0.029
2702.900			28.52	0.028
2702.950			35.74	0.031
2702.990	0.033	0.0032	32.87	0.030
2703.065	0.113	0.0037	8.91	0.017
2703.100	0.100	0.0038	23.82	0.026
2703.175			7.59	0.015
2703.225			11.67	0.018
2703.275			5.77	0.014
2703.310			5.34	0.013
2703.360			6.89	0.015
2703.400			5.87	0.014
2703.450	0.018	0.0029	4.20	0.012
2703.490	0.025	0.003	3.52	0.011
2703.550			3.39	0.011
2703.600			3.40	0.011
2703.635			3.44	0.011
2703.685			3.32	0.011
2703.750	0.019	0.0031	4.69	0.012
2703.805			6.16	0.014
2703.850			6.01	0.014
2703.900	0.035	0.0031	5.20	0.013
2703.950			2.95	0.010
2703.990			2.23	0.010
2704.025	0.021	0.0029	1.70	0.008
2704.075	0.046	0.0031	3.12	0.011
2704.110	0.055	0.0034	3.89	0.012
2704.180			2.59	0.010
2704.200	0.024	0.0033	3.58	0.012
2704.275	0.059	0.0033	3.23	0.010
2704.325	0.052	0.0032	2.50	0.010
2704.380	0.039	0.0033	3.33	0.011
2704.430	0.028	0.0033	2.99	0.010
2704.490	0.152	0.004	6.22	0.013
2704.550			6.81	0.014
2704.600			7.34	0.015
2704.650			5.11	0.013

Depth (m)	S	S +/-	Ca	Ca +/-
2704.715			4.53	0.012
2704.750	0.013	0.003	4.60	0.012
2704.795	0.024	0.0032	7.53	0.015
2704.850			6.14	0.014
2704.900			5.11	0.013
2704.950	0.060	0.0033	5.44	0.013
2705.000	0.037	0.0031	1.44	0.008
2705.060			3.84	0.012
2705.100	0.011	0.0029	4.88	0.013
2705.150			5.74	0.014
2705.200			2.21	0.010
2705.250	0.025	0.003	2.88	0.011
2705.320	0.009	0.0029	3.61	0.011
2705.400			3.63	0.011
2705.585	0.055	0.0033	0.93	0.007
2705.650	0.158	0.0042	10.32	0.017
2705.700	0.068	0.0034	1.93	0.009
2705.750	0.060	0.0034	3.29	0.011
2705.800	0.052	0.0032	1.39	0.008
2705.850	0.045	0.0032	1.69	0.008
2705.890	0.072	0.0035	1.34	0.008
2705.940	0.049	0.0032	1.28	0.008
2705.990	0.065	0.0033	1.49	0.008
2706.045	0.047	0.0032	1.73	0.009
2706.110	0.070	0.0033	1.63	0.008
2706.135	0.067	0.0032	1.69	0.009
2706.170	0.049	0.0032	1.61	0.008
2706.200	0.058	0.0033	2.04	0.009
2706.250	0.045	0.0032	2.11	0.009
2706.300	0.049	0.0032	1.08	0.008
2706.350	0.034	0.003	1.15	0.008
2706.400	0.051	0.0032	1.29	0.008
2706.450	0.047	0.0031	1.15	0.008
2706.510	0.026	0.003	1.06	0.007
2706.550	0.023	0.003	0.91	0.007
2706.595	0.053	0.0032	1.82	0.009
2706.650	0.029	0.003	1.18	0.008
2706.700	0.036	0.003	1.27	0.008
2706.750	0.063	0.0033	5.99	0.014
2706.800	0.048	0.0031	1.60	0.008
2706.850	0.069	0.0032	1.57	0.008
2706.870	0.068	0.0033	1.06	0.007
2706.925	0.062	0.0032	1.03	0.007
2706.970	0.061	0.0032	1.59	0.008
2707.050	0.141	0.0037	1.56	0.008
2707.100	0.104	0.0036	1.85	0.009
2707.135	0.212	0.0044	6.90	0.015
2707.185	0.191	0.004	6.76	0.014
2707.250	0.148	0.0038	7.66	0.015

Depth (m)	S	S +/-	Ca	Ca +/-
2707.300	0.269	0.0045	13.29	0.020
2707.350	0.189	0.004	21.99	0.024
2707.395	0.026	0.003	40.55	0.034
2707.425	0.060	0.0033	38.65	0.033
2707.470	0.559	0.0056	22.88	0.026
2707.490	0.207	0.0042	22.03	0.025
2707.575	0.186	0.0041	19.80	0.024
2707.600	0.215	0.0042	16.00	0.021
2707.650	0.127	0.0036	17.36	0.022
2707.700	0.128	0.0037	12.05	0.018
2707.720	0.126	0.0038	17.26	0.022
2707.770	0.105	0.0037	20.38	0.024
2707.850	0.048	0.0034	19.28	0.024
2707.900	0.025	0.0033	31.39	0.030
2707.950	0.074	0.0035	13.67	0.020
2707.995	0.086	0.0037	19.03	0.023
2708.050	0.100	0.0037	16.08	0.021
2708.100	0.155	0.004	9.22	0.017
2708.150	0.055	0.0033	7.51	0.016
2708.190	0.120	0.0038	10.44	0.018
2708.250	0.129	0.004	9.11	0.017
2708.300	0.153	0.0039	6.25	0.014
2708.350	0.142	0.0038	6.72	0.014
2708.405	0.203	0.0043	6.81	0.015
2708.450	0.240	0.0045	4.93	0.013
2708.490	0.177	0.0041	9.44	0.017
2708.550	0.134	0.0038	5.26	0.013
2708.600	0.103	0.0038	8.19	0.016
2708.650	0.174	0.0041	6.71	0.014
2708.700	0.210	0.0043	6.93	0.014
2708.750	0.131	0.0041	8.82	0.016
2708.810	0.192	0.0043	7.44	0.015
2708.840	0.241	0.0045	6.64	0.014
2708.890	0.183	0.0042	5.29	0.013
2708.950	0.174	0.0042	8.76	0.016
2708.990	0.182	0.0042	8.12	0.016
2709.030	0.176	0.0042	11.76	0.018
2709.070	0.159	0.0041	9.93	0.017
2709.125	0.042	0.0035	21.13	0.024
2709.180	0.017	0.0035	23.43	0.026
2709.200	0.044	0.0036	20.55	0.024
2709.250	0.051	0.0035	10.53	0.017
2709.300	0.011	0.0033	33.39	0.031
2709.350	0.043	0.0035	21.20	0.025
2709.400	0.122	0.0037	36.26	0.032
2709.430	0.071	0.0032	40.57	0.034
2709.475	0.126	0.0037	38.28	0.033
2709.515	0.281	0.0045	25.35	0.026
2709.570	0.191	0.004	5.37	0.013

Depth (m)	S	S +/-	Ca	Ca +/-
2709.615	0.111	0.0036	5.80	0.013
2709.680	0.148	0.0038	3.26	0.011
2709.815			40.46	0.034
2709.855			40.10	0.033
2709.920			33.09	0.030
2709.975	0.030	0.0032	24.21	0.026
2710.050	0.027	0.0032	26.92	0.028
2710.100	0.015	0.0032	34.58	0.032
2710.150			33.26	0.031
2710.200	0.126	0.004	29.78	0.029
2710.250	0.165	0.0041	20.44	0.024
2710.300			35.91	0.031
2710.350	0.015	0.0029	11.40	0.018
2710.400	0.087	0.0033	39.90	0.033
2710.440	0.051	0.003	40.51	0.033
2710.490	0.055	0.0031	40.38	0.033
2710.550	0.031	0.0029	40.82	0.033
2710.600	0.060	0.0032	40.06	0.033
2710.650	0.085	0.0033	39.21	0.033
2710.690	0.145	0.0037	36.58	0.032
2710.750	0.239	0.0043	5.58	0.013
2710.800	0.241	0.0044	9.82	0.017
2710.870	0.090	0.0038	30.80	0.029
2710.900	0.069	0.0037	18.80	0.023
2710.950	0.075	0.0037	29.12	0.028
2710.990	0.023	0.0036	29.70	0.030
2711.050	0.019	0.0032	8.65	0.016
2711.100			4.51	0.012
2711.150	0.037	0.0032	2.75	0.010
2711.200	0.016	0.0033	10.54	0.018
2711.250	0.029	0.0032	3.30	0.011
2711.300	0.100	0.0036	0.93	0.007
2711.350	0.009	0.0029	2.55	0.010
2711.400	0.010	0.0029	3.14	0.011
2711.440	0.035	0.0031	3.79	0.011
2711.480			5.40	0.013
2711.570	0.014	0.003	2.04	0.009
2711.610			1.88	0.009
2711.660			3.56	0.011
2711.700	0.031	0.0031	2.52	0.010
2711.750	0.038	0.0031	1.69	0.009
2711.800	0.024	0.003	1.04	0.007
2711.850	0.020	0.003	1.60	0.009
2711.860	0.010	0.0028	1.20	0.008
2711.915			1.10	0.008
2711.955	0.012	0.0029	0.83	0.007
2711.995	0.065	0.0034	1.22	0.008
2712.025	0.060	0.0033	2.10	0.009
2712.075	0.029	0.003	3.22	0.011

Depth (m)	S	S +/-	Ca	Ca +/-
2712.110	0.083	0.0035	2.73	0.010
2712.185	0.106	0.0036	6.96	0.014
2712.200	0.144	0.0039	3.98	0.012
2712.300			33.04	0.029
2712.350	0.058	0.0034	18.91	0.023
2712.400	0.047	0.0034	31.97	0.030
2712.435	0.092	0.0034	8.77	0.016
2712.490	0.068	0.0034	38.25	0.033
2712.550	0.067	0.0037	31.01	0.030
2712.600	0.012	0.0032	21.55	0.024
2712.635	0.052	0.0033	36.64	0.032
2712.700	0.076	0.0033	39.34	0.033
2712.740	0.138	0.0037	39.05	0.033
2712.780	0.055	0.0033	37.31	0.032
2712.855			33.86	0.030
2712.900	0.063	0.0036	28.78	0.028
2712.950	0.049	0.0035	26.91	0.027
2712.990	0.052	0.0035	27.28	0.027
2713.070	0.049	0.0033	37.10	0.032
2713.100	0.020	0.0031	36.47	0.032
2713.165	0.125	0.0039	29.97	0.029
2713.210	0.064	0.0032	39.19	0.033
2713.240	0.072	0.0034	33.64	0.030
2713.300	0.096	0.0033	41.29	0.034
2713.350	0.069	0.0037	27.40	0.028
2713.400	0.055	0.0034	34.01	0.031
2713.440	0.083	0.0034	35.28	0.031
2713.470	0.031	0.0029	40.08	0.033
2713.545	0.036	0.0029	39.83	0.033
2713.600	0.117	0.0038	32.60	0.030
2713.655	0.738	0.0065	21.51	0.024
2713.700	0.184	0.0041	33.96	0.031
2713.750	0.172	0.0037	39.16	0.033
2713.800	0.407	0.005	36.52	0.032
2713.830	0.206	0.0042	14.16	0.019
2713.875	0.131	0.0037	31.94	0.029
2713.925	0.136	0.0038	36.03	0.031
2713.990	0.132	0.0039	31.80	0.030
2714.050	0.134	0.0038	32.67	0.030
2714.100	0.143	0.0039	33.62	0.031
2714.150	0.074	0.0034	36.35	0.032
2714.200	0.079	0.0034	38.53	0.033
2714.250	0.662	0.0062	28.26	0.028
2714.320	1.759	0.009	33.94	0.031
2714.360	0.240	0.0044	32.52	0.030
2714.400	0.142	0.0039	32.67	0.030
2714.450	0.097	0.0036	36.25	0.032
2714.490	0.337	0.0044	39.51	0.033
2714.550	0.407	0.0047	37.65	0.032

Depth (m)	S	S +/-	Ca	Ca +/-
2714.600	0.475	0.0049	40.19	0.034
2714.650	0.123	0.0035	39.61	0.033
2714.700	0.078	0.0035	36.98	0.032
2714.750	0.114	0.0036	38.11	0.033
2714.800	0.121	0.0038	35.17	0.031
2714.835	0.307	0.0046	36.97	0.032
2714.885	0.045	0.0034	4.01	0.012
2714.900	0.314	0.005	14.11	0.021
2714.980	0.226	0.0043	2.35	0.009
2715.065	0.245	0.0044	3.27	0.011
2715.095	0.349	0.0051	3.88	0.012
2715.150	0.311	0.0048	1.16	0.008
2715.220	6.366	0.0168	1.21	0.007
2715.270	0.154	0.0039	2.08	0.009
2715.320	3.237	0.013	0.19	0.006
2715.370	0.149	0.0039	3.24	0.011
2715.425	1.175	0.0081	0.62	0.007
2715.495	0.102	0.0036	1.51	0.008
2715.550			1.86	0.009
2715.580	0.206	0.0042	3.82	0.012
2715.640	0.112	0.0037	2.11	0.009
2715.690	0.221	0.0044	3.29	0.011
2715.740	0.016	0.003	4.75	0.012
2715.790	0.060	0.0034	1.76	0.009
2715.850	0.098	0.0035	8.85	0.016
2715.900			7.09	0.015
2715.950			8.07	0.016
2715.990	0.066	0.0033	3.37	0.011
2716.050	0.079	0.0035	5.40	0.013
2716.100	0.028	0.0032	7.34	0.015
2716.160	0.031	0.0032	9.48	0.017
2716.215	0.038	0.0033	8.86	0.016
2716.250	0.368	0.0051	8.65	0.016
2716.300	0.050	0.0035	19.53	0.023
2716.350			9.73	0.018
2716.400	0.057	0.0034	16.51	0.021
2716.450	0.048	0.0034	17.33	0.022
2716.490	0.039	0.0032	11.61	0.018
2716.550			11.72	0.019
2716.590			9.92	0.018
2716.650	0.081	0.0036	8.89	0.016
2716.700			5.42	0.013
2716.750			23.50	0.026
2716.800	0.031	0.0032	8.67	0.016
2716.835	0.015	0.0031	5.82	0.014
2716.920	0.019	0.0031	12.10	0.018
2716.945	0.057	0.0033	3.42	0.011
2716.990	0.053	0.0034	3.63	0.011
2717.130	0.024	0.003	3.55	0.011

Depth (m)	S	S +/-	Ca	Ca +/-
2717.150	0.016	0.0032	5.93	0.014
2717.200	0.016	0.0031	9.99	0.017
2717.250	0.039	0.0031	1.26	0.008
2717.300	0.053	0.0033	0.75	0.007
2717.355	0.018	0.0031	1.02	0.007
2717.400	0.037	0.0031	13.17	0.019
2717.450	0.018	0.0032	1.39	0.008
2717.520			32.93	0.030
2717.545	0.023	0.003	3.23	0.011
2717.600	0.038	0.0032	6.58	0.015
2717.650	0.015	0.0032	8.24	0.016
2717.700	0.043	0.0031	3.10	0.011

Depth (m)	S	S +/-	Ca	Ca +/-
2717.800	0.110	0.0036	9.24	0.016
2717.900	0.021	0.003	8.09	0.016
2717.990			0.74	0.007
2718.130	0.045	0.0033		
2718.200	0.043	0.0033		
2718.300				
2718.420			0.86	0.007
2718.490			0.91	0.007
2718.600			16.08	0.022
2718.700	0.039	0.0031	0.94	0.007
2718.800				
2718.850	0.012	0.0029	5.13	0.013

Table C-3. Sulphur and Calcium element concentrations from Core A measured by HH-XRF.

Depth (m)	Mo	Mo +/-
2676.685	0.0011	0.0002
2678.300	0.0011	0.0002
2679.990	0.0009	0.0002
2680.855	0.0019	0.0002
2688.650	0.001	0.0002
2714.835	0.0021	0.0002

Table C-4. Molybdenum element concentrations from Core A measured by HH-XRF.

Carbon-isotope data																							
Depth (m)	C13	C14	C15	C16	C17	C18	C19	C20	C21	C22	C23	C24	C25	C26	C27	C28	C29	C30	C31	C32	C33	C34	
2672.53			-32.3	-32.1	-32.5	-33.4	-33.0	-32.2	-31.7	-31.7	-31.8	-31.9	-31.9	-31.8	-31.7	-31.6	-31.8	-32.8	-31.6				
2675.23		-31.7	-31.5	-31.6	-31.7	-32.9	-32.6	-32.0	-31.6	-31.5	-31.7	-31.5	-31.7	-31.5	-31.6	-31.5	-31.4	-31.8	-31.8	-31.2			
2676.68	-31.5	-32.2	-32.6	-33.3	-33.8	-35.3	-34.4	-33.1	-32.0	-31.6	-31.7	-31.6	-31.6	-31.4	-31.7	-31.8	-31.7	-31.8	-31.7	-31.2			
2681.17	-30.6	-30.7	-30.9	-31.0	-31.6	-31.8	-31.4	-31.3	-31.7	-32.1	-32.0	-31.9	-31.8	-31.8	-31.7	-31.6	-31.7	-31.9	-31.5	-31.6			
2684		-32.0	-32.0	-32.5	-32.5	-32.9	-32.5	-32.3	-32.2	-32.3	-32.5	-32.7	-32.7	-32.7	-33.0	-32.8	-32.8	-32.6	-32.7				
2685.94			-30.5	-30.7	-31.1	-31.5	-31.4	-31.3	-31.4	-31.8	-32.0	-32.0	-32.2	-32.3	-32.4	-32.7	-33.0	-33.5	-33.0	-32.9	-32.7		
2691.25	-28.6	-29.0	-29.4	-29.7	-31.6	-31.6	-30.7	-30.7	-31.0	-31.0	-31.4	-30.9	-31.3	-31.2	-31.1	-31.7	-31.5	-31.5	-31.1	-31.2	-31.7	-32.7	
2695.57			-28.5	-29.2	-29.5	-30.1	-30.2	-30.2	-29.9	-30.0	-30.1	-30.0	-29.9	-29.9	-30.0	-29.7	-30.0	-30.4	-30.1	-30.2	-31.0	-31.1	
2697.8			-31.3	-30.5	-31.1	-32.0	-31.4	-30.9	-30.5	-30.4	-30.3	-30.5	-30.4	-31.0	-30.4	-30.0	-29.7	-31.9	-29.3				
2699.39					-31.4	-32.2	-31.2	-30.4	-30.3	-30.2	-30.0	-30.2	-30.2	-30.2	-30.1	-30.2	-30.6	-31.5	-30.2	-30.7			
2702.13			-33.4	-33.1	-33.6	-34.9	-34.1	-32.5	-30.9	-30.6	-30.6	-30.6	-30.5	-30.2	-30.4	-30.2	-30.4	-31.6					
2703.89				-32.1	-33.2	-34.8	-34.9	-33.3	-31.2	-30.8	-30.9	-31.1	-31.2	-30.5	-30.9	-31.6	-31.9	-34.1					
2705.135				-31.1	-31.2	-32.1	-31.4	-30.9	-30.6	-30.6	-30.7	-30.4	-30.4	-30.3	-30.3	-30.2	-30.4	-31.0	-30.7				
2706.22					-33.5	-34.8	-34.7	-33.2	-31.2	-30.2	-30.2	-30.2	-30.1	-29.8	-30.1	-30.2	-30.7						
2708.125			-31.5	-31.5	-31.9	-32.8	-32.2	-31.4	-30.8	-30.8	-31.0	-30.9	-31.0	-30.7	-30.8	-30.6	-31.9	-32.2	-30.9				

Standard deviation																							
Depth (m)	C13	C14	C15	C16	C17	C18	C19	C20	C21	C22	C23	C24	C25	C26	C27	C28	C29	C30	C31	C32	C33	C34	
2672.53			0.2	0.1	0.1	0.3	0.3	0.1	0.1	0.1	0.1	0.1	0.2	0.2	0.1	0.0	0.3	0.6	0.6				
2675.23		0.2	0.2	0.1	0.3	0.0	0.1	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.3	0.3	0.6			
2676.68	0.3	0.1	0.0	0.0	0.1	0.0	0.1	0.3	0.2	0.4	0.1	0.3	0.5	0.2	0.6	0.9	0.4	0.3	0.2	0.2			
2681.17	0.1	0.1	0.1	0.0	0.2	0.1	0.0	0.0	0.1	0.2	0.3	0.2	0.1	0.0	0.0	0.0	0.2	0.1	0.3	0.3			
2684		0.4	0.0	0.1	0.1	0.0	0.3	0.0	0.0	0.2	0.1	0.1	0.3	0.4	0.3	0.2	0.2	0.1	0.1				
2685.94			0.0	0.0	0.2	0.0	0.1	0.1	0.1	0.1	0.3	0.2	0.4	0.4	0.3	0.3	0.4	0.1	0.2	0.6	0.6		
2691.25	0.1	0.2	0.0	0.0	0.4	0.4	0.1	0.1	0.1	0.4	0.9	0.1	0.1	0.2	0.3	0.5	0.2	0.0	0.4	0.5	0.6	0.2	
2695.57			1.3	0.0	0.2	0.2	0.1	0.1	0.4	0.3	0.1	0.4	0.3	0.4	0.3	0.3	0.2	0.0	0.2	0.5	0.2	1.3	
2697.8			0.5	0.3	0.3	0.0	0.1	0.4	0.2	0.6	0.1	0.6	0.2	0.3	0.7	0.8	1.2	0.4	1.9				
2699.39					0.2	0.1	0.2	0.2	0.1	0.2	0.1	0.3	0.3	0.4	0.3	0.1	0.1	0.4	0.5	0.4			
2702.13			0.1	0.2	0.1	0.1	0.1	0.2	0.2	0.2	0.1	0.1	0.1	0.1	0.1	0.3	0.0	0.5					
2703.89				0.3	0.5	0.5	0.2	0.1	0.2	0.1	0.0	0.1	0.3	0.5	0.3	0.6	0.2	1.4					
2705.135				0.2	0.0	0.2	0.1	0.1	0.0	0.0	0.1	0.1	0.2	0.1	0.2	0.1	0.4	0.1	0.7				
2706.22					0.4	0.9	0.0	0.2	0.1	0.2	0.0	0.2	0.2	0.2	0.2	0.3	1.1						
2708.125			1.2	0.1	0.1	0.0	0.4	0.3	0.1	0.0	0.2	0.1	0.1	0.0	0.3	0.4	0.1	1.1	0.1				

Table C-5. Compound-specific carbon isotope data of *n*-alkanes (chain length 13–34) from Core A.

Depth (m)		2669.03	2672.53	2674.5	2675.23	2676.68	2677.5
Peak name	Ion	Peak area	Peak area	Peak area	Peak area	Peak area	Peak area
17a,21b-hopane	412.4 > 191.2	854032	4423	13135	26025	65561.1	9621.41
Gammacerane	412.4 > 191.2	170904	497	1735	3344	5387.7	1144.51
Gamm/17a,21b-hopane		0.20011	0.11248	0.13212	0.12851	0.08218	0.11895

Depth (m)		2679.6	2681.17	2684	2685.94	2687.28	2689.99
Peak name	Ion	Peak area	Peak area	Peak area	Peak area	Peak area	Peak area
17a,21b-hopane	412.4 > 191.2	33000	30562.1	817299	1269070	2964842	4462
Gammacerane	412.4 > 191.2	5899	7112.52	124998	142845	243886	368
Gamm/17a,21b-hopane		0.17876	0.23272	0.15294	0.11256	0.08226	0.08241

Depth (m)		2691.25	2695.57	2697.8	2699.39	2702.13	2703.89
Peak name	Ion	Peak area	Peak area	Peak area	Peak area	Peak area	Peak area
17a,21b-hopane	412.4 > 191.2	91989.7	1546143	370947	336685	671375	162904
Gammacerane	412.4 > 191.2	8161.55	73839.4	20454.4	24962.1	49968.3	14336
Gamm/17a,21b-hopane		0.08872	0.04776	0.05514	0.07414	0.07443	0.088

Depth (m)		2705.14	2706.22	2708.13	2710.73
Peak name	Ion	Peak area	Peak area	Peak area	Peak area
17a,21b-hopane	412.4 > 191.2	412242	151948	680763	1351722
Gammacerane	412.4 > 191.2	31602.2	15381.1	72893.2	94583.2
Gamm/17a,21b-hopane		0.07666	0.10123	0.10708	0.06997

Table C-6. Biomarker results from Core A.

Appendix D

Palynology

-- Data generated and interpreted by James Riding (BGS)

[D1] Methodology

Palynological study was undertaken on 18 samples from Core A and 3 samples from Core B to constrain the age of the sediments and the prevailing palaeoclimatic and palaeoecological conditions. The samples were prepared using the standard acid digestion method including mild oxidation with cold nitric acid (Wood et al., 1996); the rock samples, prepared organic residues, and microscope slides are all housed in the collections of the British Geological Survey, Keyworth, Nottingham NG12 5GG, United Kingdom.

[D2] Results and discussions

[D2.1] Core-A

The 18 samples studied for their palynological content produced moderately abundant organic residues that are relatively rich in palynomorphs. The palynofloras are of low diversity; preservation throughout was poor to fair, but this did not prevent identification of the majority of the genera present. The palynomorphs were mid-brown in colour, thereby indicating that the succession examined is moderately thermally mature. The selected palynomorphs are illustrated in Figure D.1 and the distribution of palynomorphs and kerogen macerals recognized in Core A are listed in Table D-1.

Gymnosperm pollen, dominantly *Classopollis* spp., comprise between 73.7% and 99.7% of the overall associations; specifically, the 18 samples were overwhelmingly dominated by this Mesozoic pollen genus. An identification to species level was not possible, but the forms are probably largely referable to *Classopollis*

classoides or *Classopollis meyeriana*. Most specimens were dispersed grains, but some tetrads (groups of four grains) are also present. Other gymnosperm pollen types, present in far lower proportions, comprise undifferentiated bisaccate pollen, *Cerebropollenites macroverrucosus*, *Chasmatosporites* spp., indeterminate forms, *Perinopollenites elatoides* and *Vitreisporites pallidus*. The specimens of *Chasmatosporites* are commonly somewhat problematical to speciate, but the majority appear to be *Chasmatosporites apertus* or *Chasmatosporites hians*.

Pteridophyte spores are also present in relatively low numbers, and include relatively prominent *Cyathidites* spp. and *Ischyosporites variegatus*. Other spores recorded include *Cibotiumspora juriensis*, *Contignisporites* sp., *Neoraistrickia* sp., *Osmundacidites wellmanii*, indeterminate forms and ?*Kraeuselisporites* sp. Spores are most prominent in the sample at 2714.98 m., comprising 15.00% of the overall assemblage.

Aquatic palynomorphs are relatively sporadic and sparse where present. Acritarchs are only present in Core A and are most prominent (21.9% of the overall palynomorph assemblage) in the sample at 2684.49 m. They, however, mainly occur in the intervals of 2702.49 m to 2710.73 m and 2684.49 m to 2695.8 m and are largely spinose acritarchs, mostly *Micrhystridium* spp., *Veryhachium collectum* and *Veryhachium* spp. Foraminiferal test linings. Dinoflagellate cysts ?*Nannoceratopsis* sp., *Pareodinia halosa* and ?*Skuadinium* sp., and the prasinophyte *Halosphaeropsis liassica* were also encountered.

Amorphous organic material was especially common in the uppermost part of the succession of Core A between 2665.19 m and 2685.94 m. In the lowermost succession, between 2697.7 m and 2718.8 m, woody tissue was the most common kerogen maceral type.

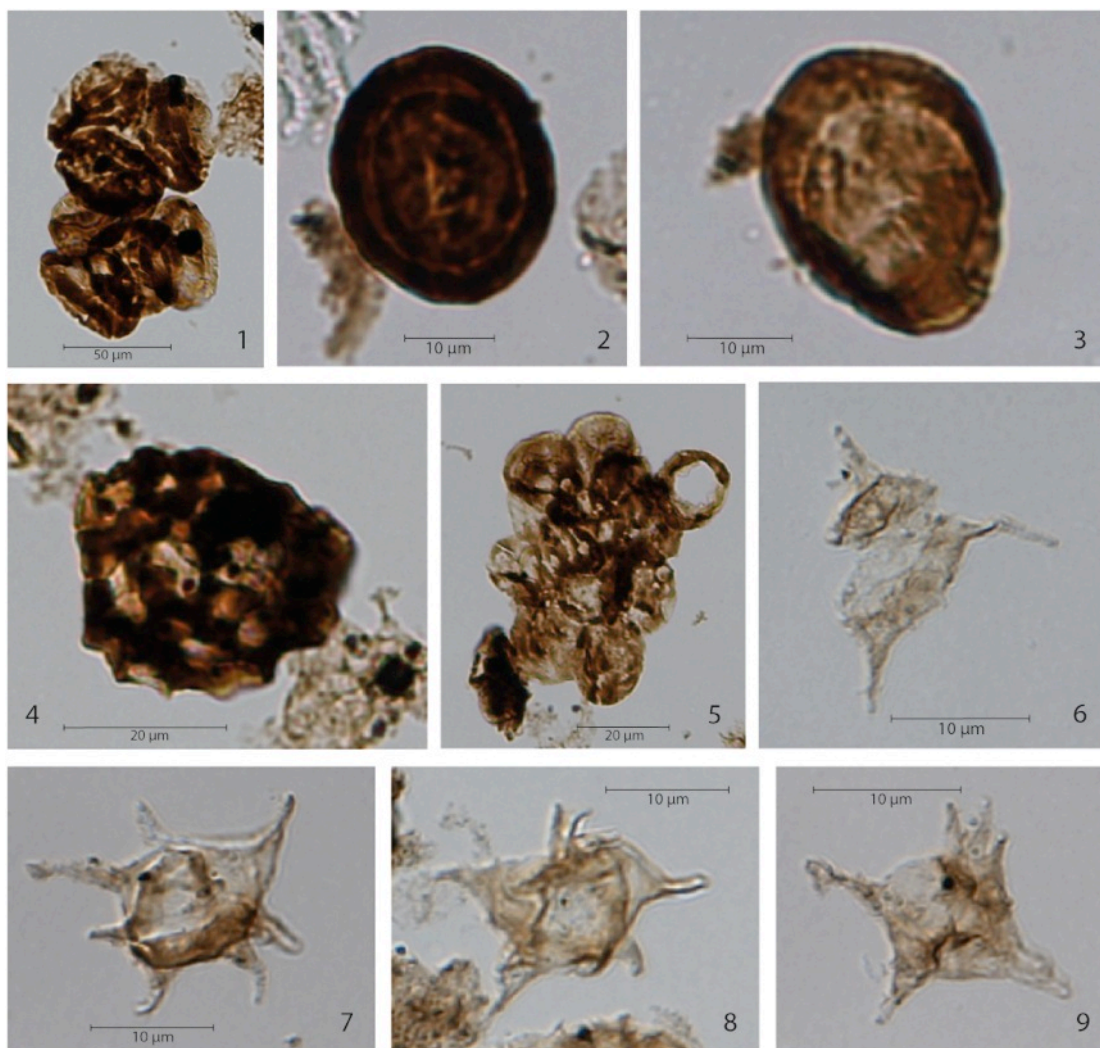


Figure D.1 Photomicrographs of selected palynomorphs.

Pollen:

1. Two tetrads of *Classopollis*. 2693.35m Core A. BGS sample MPA 66166/slide 3 at S57/2.
2. *Classopollis* spp. 3094.58m Core B. BGS sample MPA 66168/slide 1 at K39.
3. *Classopollis* spp. 3094.58m Core B. BGS sample MPA 66168/slide 1 at K39.

Spore:

4. *Ischyosporites variegatus* (Couper 1958) Schulz 1967. 2693.35m Core A. BGS sample MPA 66166/slide 3 at S63/4.

Aquatic palynomorphs:

5. A clump of the spherical prasinophyte *Halosphaeropsis liassica* Mädlér 1963. 2693.35m Core A. BGS sample MPA 66166/slide 3 at C60/3.
6. *Veryhachium* sp. 2693.35m Core A. BGS sample MPA 66166/slide 3 at E55/4.
7. *Micrhystridium* sp. 2702.49m Core A. BGS sample MPA 66167/slide 1 at O62/3.
8. *Micrhystridium* sp. 2693.35m Core A. BGS sample MPA 66166/slide 4 at M66/4.
9. *Veryhachium collectum* Wall 1965. 2702.49m Core A. BGS sample MPA 66167/slide 1 at R65/1.

[D2.2] Core–B

The palynomorphs and the kerogen macerals are identified in 3 samples from Core B (Table D-2) and the selected palynomorphs are illustrated in Figure D.1. The palynomorphs are consistently dark brown in colour, indicating that the interval studied is moderately to highly thermally mature. Gymnospermous pollen was again overwhelmingly dominant, comprising between 89.1% to 99.2% of the overall palynofloras. This group is principally represented by *Classopollis* spp., but tetrads of this pollen grain are extremely rare throughout. Bisaccate pollen proved relatively common at 3094.58 m, and *Cerebropollenites macroverrucosus*, *Chasmatosporites* spp. and *Perinopollenites elatoides* were also found. *Cyathidites* spp. dominates the spore floras, and is most common in the sample at 3094.58m where they make up 10.5% of the terrestrially derived palynomorphs. Other spores comprise *Contignisporites* sp., *Ischyosporites variegatus*, *Neoraistrickia* sp. and *Osmundacidites wellmanii*.

Aquatic palynomorphs proved singularly sparse. Such forms are entirely absent in the sample at 3149.9m and single specimens were encountered in the samples at 3094.58m and 3115.65m. A questionable, indeterminate acritarch and one specimen of the freshwater/brackish alga *Botryococcus* are present in the samples at 3115.65m and 3094.58m, respectively. Palynomorphs and woody tissue are generally the most common kerogen macerals. However, amorphous organic material was especially prominent (36% of the overall kerogen) in the sample at 3115.65m.

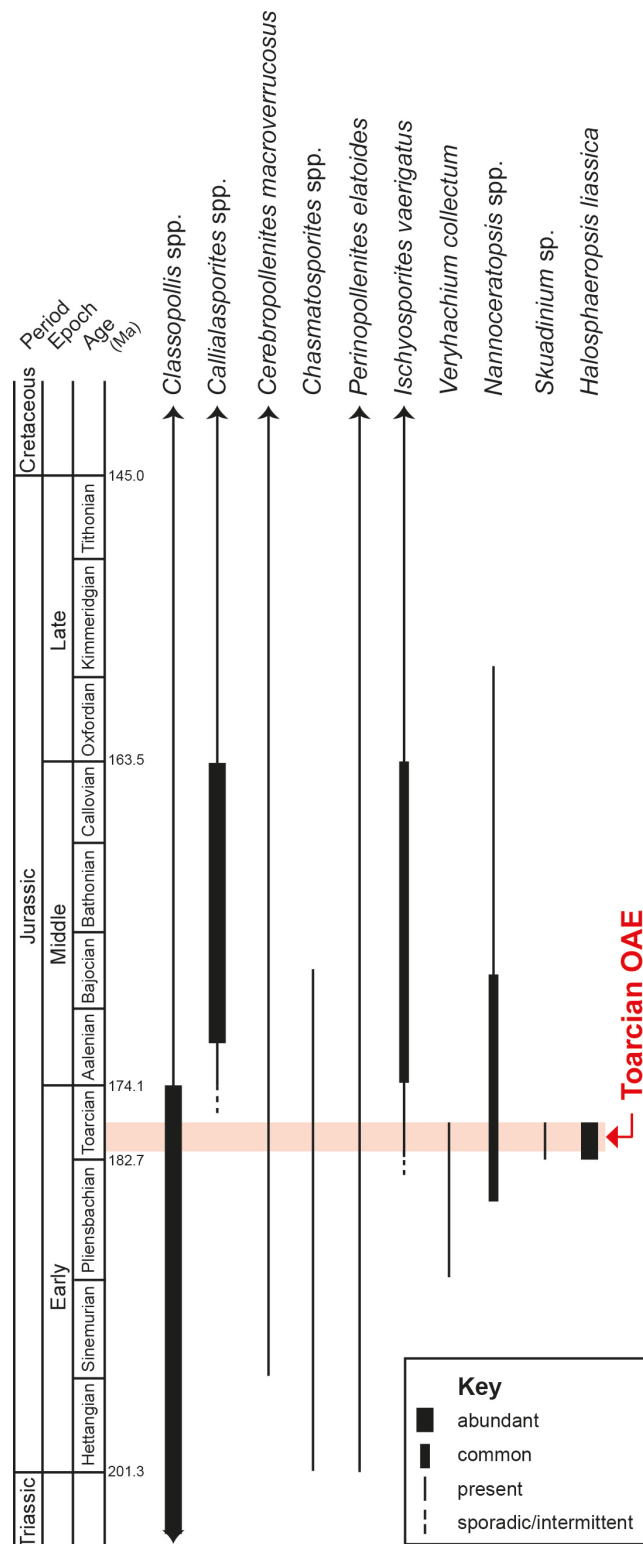


Figure D.2 A range chart of selected palynomorphs. This chart illustrates the known semi-quantitative stratigraphical extents of ten selected palynomorph genera and species that were recorded in this study in order to demonstrate the age-diagnostic nature of these forms. These data form part of the basis for the age model in this study and complement Re-Os radiometric age dating and carbon-isotope stratigraphy. The information herein was compiled from works cited in the bibliography.

[D2.3] Palynostratigraphy

Due to the relatively uniform nature of the palynomorph and kerogen associations within and between the two wells studied, both successions are interpreted as being coeval, and from the same, single genetic sedimentary succession. Despite the relatively low diversity nature of the palynofloras, and the total dominance of the relatively long-ranging pollen *Classopollis* spp., the assemblages are unequivocally indicative of the Early Jurassic (Early Toarcian). The stratigraphical ranges of selected taxa are illustrated in Figure D.2.

The material studied is referable to the Australasian *Classopollis torosa* Oppel Zone, which has been interpreted as being of Hettangian to Early Toarcian age (fig. 46 in Helby et al., 1987). The Chinese craton was, during the Jurassic, located across the Tethys Ocean, at a similar palaeolongitude to Australia. *Classopollis classoides* was also typically abundant in the Toarcian of Europe (e.g. Couper, 1958; Srivastava, 1976; Vakhrameyev, 1981; Bucefalo Palliani and Riding, 1998). The entire lack of the characteristic Araucarian pollen genus *Callialasporites*, and the absence of significant proportions of typically Middle Jurassic spore genera such as *Leptolepidites* and *Neoraistrickia*, precludes a Middle Jurassic age (Srivastava, 1987, fig. 3; Srivastava, 1987; Riding et al., 1991). The range base of the distinctive monosaccate genus *Callialasporites* is close to the Early–Middle Jurassic transition, interpreted as a response to significantly cooler palaeotemperatures in the Middle Jurassic as opposed to the Early Jurassic in Europe. Korte *et al.* (2015) gave a thorough account of the isotopic evidence for this major palaeoclimatic shift. Furthermore, this bio-event appears to be broadly coeval globally (Helby et al., 1987, fig. 13; Quattrocchio et al., 2011). The presence of *Cerebropollenites macroverrucosus* indicates that the succession is no older than Sinemurian age (Morbey and Dunay, 1978; Dybkjær,

1991). The genus *Chasmatosporites* is also biostratigraphically significant, being a characteristically Early Jurassic form, and is only infrequently observed stratigraphically higher than the Toarcian (Srivastava, 1987; Guy-Ohlson, 1986a). Moreover, *Perinopollenites elatoides* is typical of the Early Jurassic in Europe (Srivastava, 1987, 2011; Weiss, 1989; Riding et al., 2013).

The pteridopyle spores are also significant in that the association of *Cibotiumspora juriensis*, *Contignisporites* sp. and *Ischyosporites variegatus* is consistent with a late Early Jurassic age (Guy-Ohlson, 1986b). The most stratigraphically significant fern spore is *Ischyosporites variegatus*. Consistent records of this distinctive, thick-walled, reticulate species, which has affinities to the family Schizaeaceae, range from the Early Jurassic (Pliensbachian–Toarcian transition) to the Early Cretaceous (Albian) of Europe and surrounding regions (Schulz and Mai, 1966; Schulz, 1967; Srivastava, 1975; Vigran and Thusu, 1975; van Erve, 1978). This species is most prominent in the Middle Jurassic (Aalenian–Bathonian) (Couper, 1958; Srivastava, 1987, 2011; Weiss, 1989; Schweitzer et al., 1987; Mehlqvist et al., 2009). However, the range base of *Ischyosporites variegatus* is at the Pliensbachian–Toarcian transition, and the oldest occurrences of consistent records of this species are of earliest Toarcian age. These datum levels were established both in compilations (e.g. Dybkjær, 1991, fig. 4; Shurygin et al., 1995, fig. 5), and by primary studies of well-dated material (Schulz and Mai, 1966, p. 30; Herngreen and de Boer, 1974, table 7; Michelsen, 1979, p. 148; Hoelstad, 1985, figs. 5, 6; Lund and Pedersen, 1985; Guy-Ohlson, 1988, p. 815; Koppelhus and Batten, 1996, fig. 6A; Koppelhus and Dam, 2003; Barrón et al., 2013, fig. 2; Mogutcheva, 2014). Andsberg and Dybkjaer (2003, p. 273) stated that the range base of the genus *Ischyosporites* is Toarcian in age, although subsequently Barrón et al. (2013, fig. 2) reported an occurrence from the

uppermost Pliensbachian of Portugal. Despite the latter record, the best example of this datum in a study using independently dated material was given by Koppelhus and Dam (2003), who undertook a detailed study of the palynology, sedimentology and sequence stratigraphy of the Lower and Middle Jurassic strata of Jameson Land, East Greenland. These authors recorded *Ischyosporites variegatus* from the Toarcian successions that they studied (Koppelhus and Dam, 2003, figs. 4A, 10, 12). However, a single-specimen occurrence of *Ischyosporites variegatus* was reported from one Sinemurian sample (number 341168). Due to the apparently anomalous nature of this occurrence, this record is deemed to be probably either a misidentification, or the result of contamination. *Ischyosporites variegatus* was not recorded throughout the Pliensbachian of East Greenland by Koppelhus and Dam (2003). However, Guy-Ohlson (1990, table 1) reported very sparse and sporadic occurrences of this species from the mid–late Pliensbachian of Sweden. There are some sporadic reports of spores assigned to *Ischyosporites* sp. from the Late Pliensbachian of Europe (e.g. Rogalska, 1971; Barrón et al., 1999, fig. 2), which may have resulted in the Pliensbachian record of *Ischyosporites variegatus* in the compilation of Guy-Ohlson (1989, fig. 3).

To summarise, we contend that there are no reports of consistent occurrences of *Ischyosporites variegatus* from strata older than Early Toarcian in the Northern Hemisphere (Mehlqvist et al., 2009). *Ischyosporites variegatus* was also present in Gondwana, and had a similar temporal distribution. Filatoff (1975, figs. 5, 8) reported the range of *Ischyosporites variegatus* as being Early Toarcian to Callovian in the Perth Basin, Western Australia (Filatoff, 1975). Previously, Balme (1957) had demonstrated that this species occurs throughout the Lower Cretaceous in Western Australia.

Wall (1965) demonstrated the abundance and diversity of spinose acritarchs in the Lower Jurassic of the UK. These associations are especially rich in species of *Micrhystridium* and *Veryhachium*. The acritarch species *Veryhachium collectum* was found between 2685.94 m and 2710.73 m in Core A. This taxon was reported from the Pliensbachian by Wall (1965, table 2) and Koppelhus and Dam (2003, fig. 4B); however, these acritarchs generally range stratigraphically higher than the lowest reported occurrences, so that the presence of *Veryhachium collectum* is deemed to be entirely compatible with an Early Toarcian age of the studied succession.

Dinoflagellate cysts proved relatively rare, another trait of the Lower Toarcian worldwide (Woollam and Riding, 1983; Riding et al., 1999, 2010). These palynomorphs are confined to Core A. The occurrences of ?*Nannoceratopsis* and *Pareodinia halosa* are entirely consistent with an Early Toarcian age (Prauss, 1989). For example, the range base of *Nannoceratopsis* is Upper Pliensbachian (Riding and Thomas, 1992). The occurrence of a single specimen of ?*Skudinium* sp. at 2710.73 m is significant. This genus is distinctively biconical in outline, and was initially described from the Lower Toarcian of the North West Shelf of Australia (Riding and Helby, 2001). The assessment of the Early Toarcian of the *Skudinium* Suite has been based on the ranges of other dinoflagellate cysts and spores, plus evidence from pollen, foraminifera, calcareous nannofossils and eustacy/sequence stratigraphy (Riding and Helby, 2001). Subsequently, *Skudinium* was confirmed as a reliable marker for the Lower Toarcian of Australia in a comprehensive review (Riding et al., 2010, fig. 8).

Multi-specimen clumps of the prasinophyte species *Halosphaeropsis liassica* were encountered, albeit rarely, in samples at 2710.73 m, 2702.49 m and 2693.35 m and questionably at 2685.94 m in Core A. These occurrences are extremely significant in that this taxon is typical of marine sediments deposited during the Toarcian Oceanic

Anoxic Event (T-OAE) in Europe (Lund and Pedersen, 1985; Prauss et al., 1991; Bucefalo Palliani and Riding, 2000; Bucefalo Palliani et al., 2002). *Halosphaeropsis liassica* was an opportunistic species, which thrived in the environmentally stressed conditions that were developed during the T-OAE (Bucefalo Palliani et al., 2002). This species has not been reported in significant numbers in sediments other than those deposited during the T-OAE, and is interpreted as being linked to this event in the same way that the dinoflagellate cyst *Apectodinium augustum* is linked to the Paleocene–Eocene Thermal Maximum (PETM) (Sluijs et al., 2007; Kender et al., 2012).

The high levels of amorphous organic material observed between 2665.19 m and 2685.94 m in Core A are consistent with the imprint of the T-OAE in the Sichuan Basin strata, with partially-degraded biogenic material being abundantly preserved under anoxic conditions (Bucefalo Palliani and Riding, 2000). The 18 samples studied here from Core A and 3 samples from Core B, are stratigraphically coincident with a marked negative compound-specific and bulk organic $\delta^{13}\text{C}$ excursion, so that the new palynostratigraphy supports the observed negative CIE in the lacustrine Da'anzhai Member to be that of the T-OAE, as recognized in the marine realm.

[D2.4] Palaeoecology

The occurrences of marine palynomorphs in the samples between 2702.49 m to 2710.73 m and 2684.49 m to 2695.8 m in Core A are unequivocal evidence of marine influence. The marine palynomorphs in these intervals are sufficiently abundant and diverse enough to draw this conclusion. However, where marine forms are sparse, e.g. in the sample at 2702.49 m, the specimens observed may have been introduced by unknown vectors or record reworking or other means of contamination. All the samples that lack marine palynomorphs (i.e. samples at 2718.8 m and 2714.98 m,

2700.9 m and 2697.7 m, and between 2681.17 m and 2665.19 m) are interpreted as representing a definitively lacustrine depositional environment. The occurrence of *Botryococcus*, in the absence of marine palynomorphs, at 3094.58 m in Core B is entirely consistent with a freshwater depositional environment, especially given the palaeontological and organic geochemical evidence.

The dominance of the pollen genus *Classopollis* is clearly significant. Its palaeoecology has been much discussed and it is conventionally interpreted as being thermophilic and a reliable proxy for warm/hot climatic conditions (Srivastava, 1976; Vakhrameyev, 1981; Pocock and Jansonius, 1961; Volkheimer et al., 2008). The parent plants were representatives of the thermophilic and xerophytic family Cheirolepidiaceae (Francis, 1983). Vakhrameyev (1970) interpreted the Cheirolepidiaceae as drought-resistant, thermophilous, xerophytic shrubs and trees. The Cheirolepidiaceae have been interpreted to have thrived in coastal and upland slope habitats (Filatoff, 1975; Batten, 1975). It appears that *Classopollis* lived in a wide variety of habitats that included salt-marsh or mangrove settings under semi-arid to arid conditions.

Chasmatosporites is possibly related to the Order Cycadales (Pocock and Jansonius, 1969), representatives of which thrive in modern subtropical and tropical areas. The spore *Ischyosporites variegatus* belongs to the largely tropical Family Schizaeaceae (Couper, 1958). Hence, much of the non-*Classopollis* pollen and spores are consistent with the evidence for a warm climate provided by the consistent superabundance of *Classopollis* spp.

[D2.5] Conclusions

The palynology of the 21 samples from Core A and Core B unambiguously defines a stratigraphical interval that corresponds to the Toarcian Oceanic Anoxic Event (T-OAE). The acritarch, dinoflagellate cyst, pollen, prasinophyte and spore floras are all indicative of an Early Toarcian age. Specifically, the occurrences of the acritarch *Veryhachium collectum*, the dinoflagellate cyst ?*Skuadinium* sp., the superabundance of the pollen *Classopollis* spp. (in the absence of *Callialasporites* spp.) and the prasinophyte *Halosphaeropsis liassica*, and the consistent presence of the spore *Ischyosporites variegatus* are especially biostratigraphically significant. Stratigraphic correlation with a negative compound-specific and bulk organic-matter carbon-isotope excursion reinforces this interpretation. The consistent superabundance of the gymnosperm pollen *Classopollis* spp. is indicative of sustained hot/warm climatic conditions. Most samples accumulated in freshwater lacustrine settings, although the presence of acritarchs between 2702.49 m to 2710.73 m and 2684.49 m to 2695.8 m in Core A possibly suggest a transient connection or connections between the lake and the sea.

Collection Number	Depth	POLLEN								SPORES								ACRITARCHS				D. CYSTS				MISC.		POLLEN / SPORES		TERR. vs MARINE		KEROGEN (%)			
		<i>Cerebropollenites macroverrucosus</i>	<i>Chasmatosporites apertus/hians</i>	<i>Classopollis</i> sp. (single grains)	<i>Classopollis</i> sp. (tetrads)	<i>Perinopollenites elatoides</i>	pollen - indeterminate	<i>Vitresporites pallidus</i>	<i>Cibotiumspora jurensis</i>	<i>Contignisporites</i> sp.	<i>Cyathidites australis</i>	<i>Cyathidites minor</i>	<i>Cyathidites</i> spp.	<i>Ischyosporites variegatus</i>	<i>Retitritrites</i> sp.	spinose spore, <i>Krauseisporites</i>	trilete spores, indeterminate	acritarchs - indeterminate	<i>Michrystidium</i> spp.	<i>Verhachium collectum</i>	<i>Verhachium</i> spp.	dinoflagellate cys - indeterminate	? <i>Nannoceratopsis</i> spp.	<i>Paradinia halosa</i>	<i>Skudinium</i> sp.	foraminiferal test linings	<i>Halosphaeropsis llassica</i>	gymnosperm pollen (nos. and overall %)	pteridophyte spores (nos. and overall %)	terrestrially-derived palys (nos. and overall %)	indigenous marine palys (nos. and overall %)	wood	plant tissue	palynomorphs	amorphous organic material
1	2665.19	5	2	255	6	...	...	...	...	...	2	3	...	3	...	X	4	...	...	...	...	...	...	...	...	...	...	268/95.7	12/4.3	280/100	0/0	12	5	8	75
2	2669.03	19	4	263	11	...	...	...	...	...	3	1	4	6	...	X	4	...	...	...	...	...	...	...	...	...	...	297/94.3	18/5.7	315/100	0/0	18	2	13	67
3	2673.57	27	2	245	38	...	...	...	...	...	1	3	14	1	...	...	2	X	X	...	X	...	...	...	...	...	...	312/93.7	21/6.3	333/100	0/0	15	5	47	33
4	2676.11	5	2	X	173	46	...	...	...	...	X	...	1	X	...	...	X	...	...	...	...	...	...	...	...	X	...	226/99.6	1/0.4	227/100	0/0	7	5	23	65
5	2677.50	26	...	1	239	11	?X	...	...	...	1	1	6	1	...	X	2	...	...	...	...	...	...	...	...	...	...	277/96.2	11/3.8	288/100	0/0	10	5	15	70
6	2681.17	14	...	X	33	3	...	1	...	...	...	...	3	2	...	...	2	...	...	...	...	...	...	...	...	...	...	51/87.9	7/12.1	58/100	0/0	14	2	2	82
7	2684.49	11	1	3	221	17	...	X	...	...	X	2	5	...	2	...	6	...	36	12	27	?X	...	...	...	...	...	253/73.7	15/4.4	268/78.1	75/21.9	30	14	26	30
8	2685.94	18	...	7	257	29	...	...	...	X	...	...	6	X	...	X	3	...	3	1	1	...	...	...	...	...	?X	311/95.7	9/2.8	320/98.5	5/1.5	15	5	43	37
9	2691.25	12	...	7	259	6	1	...	X	...	...	...	...	X	...	...	...	X	26	3	4	...	...	...	...	...	...	285/89.6	0/0	285/89.6	33/10.4	25	5	67	3
10	2693.35	44	X	5	237	1	8	10	...	...	X	X	5	1	...	...	7	12	2	X	3	...	X	X	X	X	...	305/91.0	13/3.9	318/94.9	17/5.1	25	8	39	28
11	2695.80	30	2	2	287	6	...	X	...	...	...	...	1	X	...	...	...	...	9	3	2	...	...	...	...	...	...	327/95.6	1/0.3	328/95.9	14/4.1	30	5	42	23
12	2697.70	19	X	2	283	3	X	...	...	...	...	...	1	X	...	...	...	...	X	X	...	...	...	...	...	...	...	307/99.7	1/0.3	308/100	0/0	37	13	34	16
13	2700.90	27	1 + ?1	...	273	20	X	...	...	...	...	...	2	2	...	...	3	...	...	...	...	...	...	...	...	...	...	321/97.9	7/2.1	328/100	0/0	75	12	12	1
14	2702.49	17	...	2	259	2	7	...	...	...	3	X	X	X	...	X	X	X	X	X	1	...	X	...	...	...	...	287/98.6	3/1.0	290/99.7	1/0.3	19	10	61	10
15	2705.14	41	8	...	268	4	...	...	...	...	...	...	5	2	...	...	3	...	7	X	2	...	...	...	...	...	...	321/94.5	10/2.9	331/97.4	9/2.6	22	5	61	12
16	2710.73	11	X	X	227	2	...	...	...	...	...	...	3	X	...	2	...	...	1	2	1	...	...	...	?X	...	X	240/96.4	5/2.0	245/98.4	4/1.6	28	7	42	23
17	2714.98	...	...	267	...	...	...	...	...	...	2	...	31	...	...	...	14	...	...	...	...	...	...	...	...	...	...	267/85.0	47/15.0	314/100	0/0	64	5	28	3
18	2718.80	...	...	246	X	...	...	...	...	...	...	...	1	...	...	...	X	...	...	...	...	...	...	...	...	...	...	246/99.6	1/0.4	247/100	0/0	70	5	18	7

Table D-1. The distribution of palynomorphs and kerogen macerals recognized in eighteen samples from Core A. The numbers refer to grains counted and percentages of the overall assemblage as appropriate. An “X” indicates that the respective taxon was present but only outside the count and an ellipsis (...) indicates that the respective taxon is absent. The pollen:spore and terrestrial:marine ratios are also presented.

Depth(m)	POLLEN							SPORES							AQS.		POLLEN/SPORES		KEROGEN (%)				
	bisaccate pollen - undifferentiated <i>Cerebropollenites macroverrucosus</i> <i>Chasmatosporites apertus/hians</i> <i>Chasmatosporites major</i> <i>Classopollis classopollis</i> (single grains) <i>Classopollis classopollis</i> (tetrads) <i>Perinopollenites elatoides</i>							<i>Contignisporites</i> sp. <i>Cyathidites australis</i> <i>Cyathidites minor</i> <i>Cyathidites</i> spp. <i>Ischyosporites variegatus</i> <i>Neoraistrickia</i> sp. <i>Osmundacidites wellmannii</i> trilete spores, indeterminate							acritarchs - indeterminate <i>Botryococcus</i>		gymnosperm pollen (nos. and per cent.) pteridophyte spores (nos. and per cent.)		wood plant tissue palynomorphs amorphous organic material				
3094.58	21	...	4	X	237	1	...	...	12	3	11	2	X	X	4	...	X	263/89.1	32/10.9	26	14	51	9
3115.65	4	?X	X	:	204	:	X	X	X	:	6	3	:	:	1	?X	...	208/95.4	10/4.6	31	14	19	36
3149.9	6	:	:	:	239	:	:	:	:	:	2	:	:	:	:	:	:	245/99.2	2/0.8	45	14	23	18

Table D-2. The distribution of palynomorphs and kerogen macerals recognized in three samples from Core B. The numbers refer to grains counted and percentages of the overall assemblage as appropriate. An “X” indicates that the respective taxon was present but only outside the count and an ellipsis (...) indicates that the respective taxon is absent. The pollen:spore and terrestrial:marine ratios are also presented.

Appendix E

Re-Os geochronology

-- Data generated and analysed by David Selby (Durham University)

[E1] Methodology

Rhenium-osmium (Re-Os) analysis was conducted for two stratigraphic intervals close to the top and base of the black-shale interval (at 2676.87 to 2677.79 m and 2692.31 to 2693.26 m) in Core A. For each interval, 8 individual horizons separated by 10 cm were sampled. Samples were crushed at the Department of Earth Sciences, University of Oxford, following the procedures described Cumming et al. (2012). The selected core samples were first polished to remove all cutting and drilling marks to eliminate any potential contamination with rhenium or osmium. Samples were subsequently air-dried at 60°C for ~12 hours and broken into rock-chips, without direct metal contact. Samples (1-6 g) were then crushed and homogenized into a fine powder (~30 µm) in a silica mill (Kendall et al., 2009).

Re-Os geochronology was performed at the Laboratory for Sulphide and Source Rock Geochronology and Geochemistry at the Durham Geochemistry Centre, Durham University (UK). The Re and Os from the sample powder was isolated using estimated analytical protocols of Cumming et al. (2012) and Selby and Creaser (2003). In brief, the ~0.5g of sample powder, plus a known amount of a tracer (spike) solution of ^{190}Os and ^{185}Re was loaded into a carius tube and digested with 8mL of the $\text{Cr}^{\text{VI}}\text{-H}_2\text{SO}_4$ solution for 48 hours at 220°C. The $\text{Cr}^{\text{VI}}\text{-H}_2\text{SO}_4$ solution was used because it is known to liberate hydrogenous Re and Os preferentially, thereby limiting the incorporation of detrital Re and Os (Selby and Creaser, 2003; Kendall et al., 2004, 2013; Rooney et al., 2010). Osmium was extracted from $\text{Cr}^{\text{VI}}\text{-H}_2\text{SO}_4$ solution using

the solvent extraction (CHCl_3) and further purified using micro-distillation. Rhenium was extracted from the Os-extracted $\text{Cr}^{\text{VI}}\text{-H}_2\text{SO}_4$ solution using NaOH-Acetone extraction, and further purified using anion chromatography.

The purified Re and Os fractions were analysed for their isotope compositions using negative thermal ionisation mass spectrometry using a ThermoElectron TRITON mass spectrometer via static Faraday collection for Re and ion-counting using a secondary electron multiplier in peak-hopping mode for Os. The Re and Os fractions were loaded onto Ni and Pt filaments, respectively (Selby, 2007). Total procedural blanks during this study were 12 ± 2 pg and 0.1 ± 0.5 pg (1σ S.D., $n = 2$) for Re and Os, respectively, with an average $^{187}\text{Os}/^{188}\text{Os}$ value of 0.25 ± 0.06 ($n = 2$).

Uncertainties for $^{187}\text{Re}/^{188}\text{Os}$ and $^{187}\text{Os}/^{188}\text{Os}$ were determined by full error propagation of uncertainties in Re and Os mass-spectrometer measurements, blank abundances and isotopic compositions, spike calibrations and reproducibility of standard Re and Os isotopic values. The Re-Os isotopic data, including the 2σ calculated uncertainties for $^{187}\text{Re}/^{188}\text{Os}$ and $^{187}\text{Os}/^{188}\text{Os}$ and the associated error correlation function (ρ), were regressed to yield a Re-Os date using Isoplot V. 4.0 and the λ ^{187}Re constant of $1.666 \times 10^{-11} \text{a}^{-1}$ (Ludwig, 1980, 2008; Smoliar et al., 1996). The age uncertainty, including the uncertainty of 0.35 % in the ^{187}Re decay constant, only affects the third decimal place (Selby, 2007; Smoliar et al., 1996). Two in-house Re and Os (DROsS) solution standards are analysed to monitor the long-term reproducibility of mass-spectrometer measurements. For this study, the Re solution standard yields an average $^{185}\text{Re}/^{187}\text{Re}$ ratio of 0.59841 ± 0.0015 (1 S.D., $n = 2$), with the Os-isotope reference solution (DROsS) yielding an $^{187}\text{Os}/^{188}\text{Os}$ ratio of 0.16093 ± 0.00007 (1 S.D., $n = 2$), which is in agreement with previous studies (Du Vivier et al., 2015).

[E2] Re-Os Geochronology

Rhenium-osmium (Re-Os) analysis was conducted for two stratigraphic intervals close to the top and base of the black-shale interval (at 2676.87 to 2677.79 m and 2692.31 to 2693.26 m) in Core A. For each interval, 8 individual horizons separated by 10 cm were sampled. The two sampled intervals possess different Re abundances, but similar common Os values (^{192}Os). For example, the interval of 2692.31–2693.26 m possesses 3.5 to 6.8 ppb Re, whereas the interval between 2676.87 m and 2677.79 m contains 9.5 to 22.8 ppb Re, with the ^{192}Os abundances being between 37.3 and 87.9 ppt (Table E-1). Given the difference and similarity in the Re and Os abundances, the Re-Os isotope compositions for the two intervals are distinct.

Batch /Sample	Depth (m)	Re (ppb)	±	Os (ppt)	±	^{192}Os (ppt)	±	$^{187}\text{Re}/^{188}\text{Os}$	±	$^{187}\text{Os}/^{188}\text{Os}$	±	rho	Os at 183Ma
RO-A-1	2692.31	6.0	0.0	206.1	1.8	69.8	0.7	170.2	1.9	1.801	0.026	0.684	1.28
RO-A-2	2692.56	4.1	0.0	123.7	1.1	41.6	0.5	196.3	2.5	1.869	0.029	0.705	1.27
RO-A-3	2692.66	4.5	0.0	175.4	1.5	59.8	0.7	148.9	1.7	1.740	0.026	0.682	1.29
RO-A-4	2692.73	3.5	0.0	190.8	1.6	65.8	0.7	105.7	1.2	1.634	0.024	0.666	1.31
RO-A-5	2692.84	6.8	0.0	179.9	1.6	59.8	0.7	225.6	2.6	1.986	0.029	0.693	1.30
RO-A-6	2692.99	6.8	0.0	188.8	1.6	63.1	0.7	213.4	2.4	1.930	0.028	0.690	1.28
RO-A-7	2693.06	5.5	0.0	173.8	1.5	58.5	0.6	188.6	2.2	1.871	0.028	0.690	1.30
RO-A-8	2693.26	5.1	0.0	154.2	1.4	52.1	0.6	196.3	2.3	1.832	0.028	0.692	1.23
RO-B-1	2676.87	22.8	0.1	288.2	2.2	87.9	0.7	516.4	4.2	2.839	0.027	0.713	1.26
RO-B-2	2676.99	9.5	0.0	122.4	1.2	37.3	0.5	508.3	7.1	2.835	0.045	0.821	1.28
RO-B-3	2677.09	18.1	0.1	231.7	1.8	70.6	0.6	508.9	4.5	2.850	0.029	0.748	1.30
RO-B-4	2677.18	20.9	0.1	221.5	1.8	65.1	0.6	640.4	5.8	3.232	0.033	0.764	1.28
RO-B-5	2677.3	13.8	0.0	174.1	1.6	53.1	0.6	518.8	6.0	2.839	0.039	0.768	1.25
RO-B-6	2677.39	17.7	0.1	181.8	1.6	53.2	0.5	661.9	6.7	3.273	0.037	0.802	1.25
RO-B-7	2677.69	17.3	0.1	191.8	1.6	57.1	0.5	604.0	5.9	3.095	0.033	0.788	1.25
RO-B-8	2677.79	14.0	0.0	160.4	1.6	48.1	0.6	577.3	7.0	3.021	0.043	0.785	1.26

Table E-1. Re-Os radio-isotopic dating data.

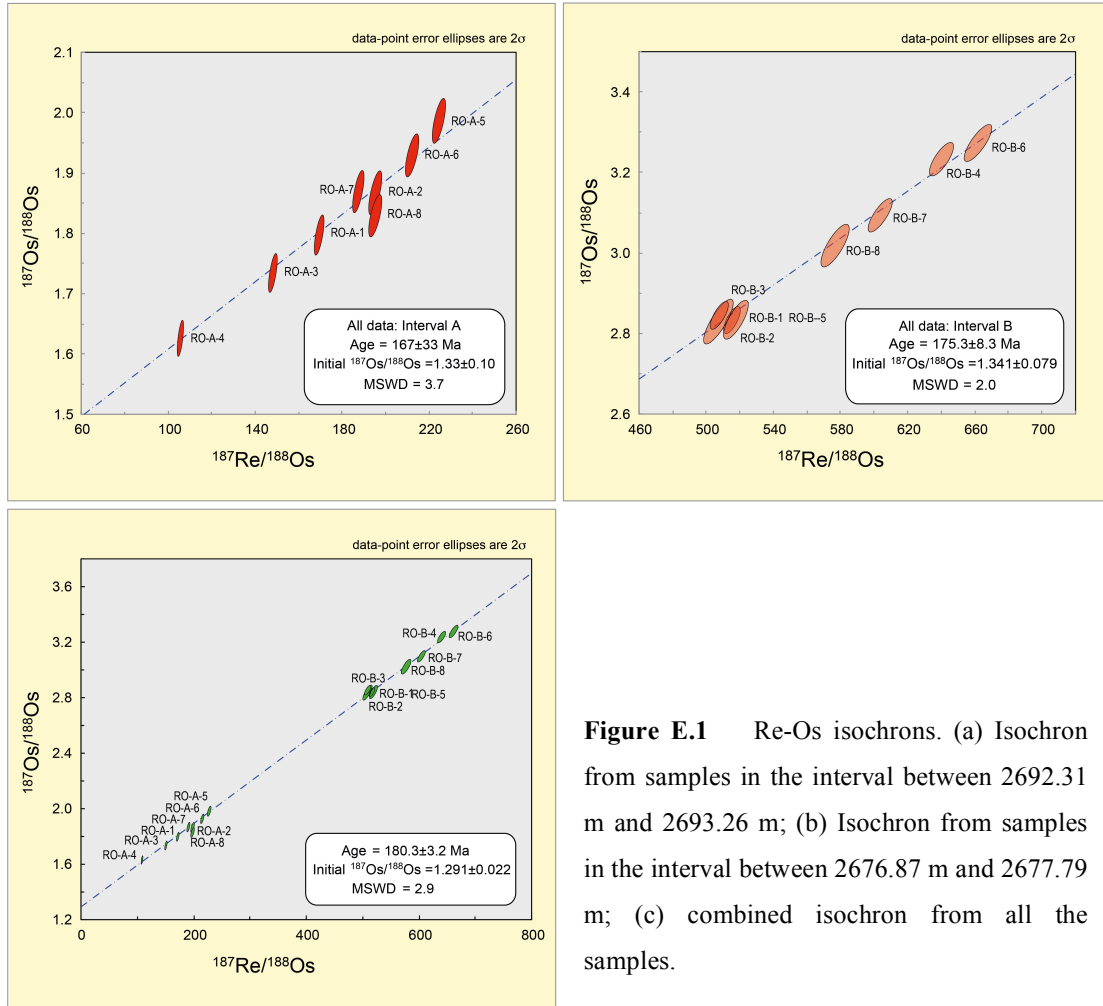


Figure E.1 Re-Os isochrons. (a) Isochron from samples in the interval between 2692.31 m and 2693.26 m; (b) Isochron from samples in the interval between 2676.87 m and 2677.79 m; (c) combined isochron from all the samples.

For samples in the interval between 2692.31 m and 2693.26m, the $^{187}\text{Re}/^{188}\text{Os}$ values have relatively little range (~ 149 and 226), and are positively correlated with $^{187}\text{Os}/^{188}\text{Os}$ values (~ 1.63 to 1.98). For this sampled interval, 3 samples have very similar Re-Os isotope compositions. All the Re-Os data yield a statistically imprecise Model 3 age of 167 ± 33 Ma (MSWD = 3.7), with an initial $^{187}\text{Os}/^{188}\text{Os}$ of 1.33 ± 0.10 (Figure E.1 a). Two samples deviate by -0.44 and -2.4 % from the overall regression line (RO-A-2 and RO-A-8). If these two samples are removed from the regression analysis, the Re-Os data yield a Model 1 Re-Os age of 174 ± 14 Ma (MSWD = 1.0), with an initial $^{187}\text{Os}/^{188}\text{Os}$ of 1.32 ± 0.04 . The other sampled interval (2676.87–2677.79 m) also possesses a limited range in the $^{187}\text{Re}/^{188}\text{Os}$ values (~ 508 to 662). The $^{187}\text{Re}/^{188}\text{Os}$ data positively correlate with the $^{187}\text{Os}/^{188}\text{Os}$ data, and yield a Model 3 Re-

Os age of 175.3 ± 8.3 Ma (MSWD = 2.0), with an initial $^{187}\text{Os}/^{188}\text{Os}$ of 1.34 ± 0.08 (Figure E.1 b). Four of the 8 samples yield very similar Re-Os data.

In addition to plotting the data separately, we consider the Re-Os data as a whole to determine a more statistically meaningful Re-Os date, given: 1) the small amount of geological time between the sampled intervals (both intervals are within the stratigraphic interval of the negative CIE and the duration of the negative CIE has been estimated to be 300–900 kyrs (Kemp et al., 2005; Suan et al., 2008; Boulila et al., 2014), which is well below the uncertainty of the Re-Os date; 2) the similar initial $^{187}\text{Os}/^{188}\text{Os}$ compositions of each sampled interval (Figure E.1 a, b); and 3) the better spread of the range of the Re-Os isotope compositions. Collectively the entire Re-Os data set yields a Model 3 Re-Os age of 180.3 ± 3.2 Ma (MSWD = 2.9), with an initial $^{187}\text{Os}/^{188}\text{Os}$ of 1.29 ± 0.02 (Figure E.1 c).

Appendix F — Data from Chapter 5

depth (m)	PI		Tmax(°C)		TOC(%)		HI	
	AE	WR	AE	WR	AE	WR	AE	WR
2669.03	0.04	0.2	443	449	0.34	0.69	156	243
2672.53	0.04		444		0.62		173	
2674.5	0.04		445		1.05		242	
2675.23	0.02	0.2	444	451	1.59	2.06	306	393
2676.68	0.01	0.21	448	455	2.54	2.99	331	389
2677.5	0.02	0.15	444	449	1.66	1.93	283	386
2679.6	0.02		444		1.64		261	
2681.17	0.01	0.21	447	450	1.89	2.25	274	301
2684	0.03	0.2	446	453	0.88	1.21	276	380
2685.94	0.03	0.2	444	452	0.67	0.92	216	311
2687.28	0.01	0.23	445	451	1.05	1.53	222	314
2689.99	0.04		448		1.59		269	
2691.25	0.02	0.16	446	453	1.66	1.88	232	340
2695.57	0.03	0.18	449	453	0.8	1.04	150	207
2697.8	0.02	0.19	448	454	1	1.2	111	150
2699.39	0.03	0.22	449	451	0.64	0.78	130	201
2702.13	0.02	0.3	446	453	1.15	1.58	200	242
2703.89	0.08	0.31	455	455	1.43	1.68	64	98
2705.135	0.02	0.21	444	453	0.84	0.96	131	209
2706.22	0.04	0.34	453	456	1.07	1.31	87	137
2708.125	0.02	0.29	452	453	1	1.29	141	208
2710.73	0.05	0.17	449	453	1.5	1.73	161	194

AE: after extraction

WR: whole rock

Table F-1. Rock Eval results from the whole rock samples and the residue samples after extraction.

Core A		Core B	
Depth (m)	$\delta^{13}\text{C}$ (‰)	Depth (m)	$\delta^{13}\text{C}$ (‰)
	PDB		PDB
2669.03	-25.94125	3102.8	-25.62806
2672.53	-27.09842	3120.50	-25.48797
2674.5	-27.64153	3130.35	-26.40096
2675.23	-28.62506	3143.75	-25.85371
2676.68	-28.8102	3153.05	-23.48775
2677.5	-29.0243		
2679.6	-28.59826		
2681.17	-28.24619		
2684	-28.78491		
2685.94	-28.30009		
2687.28	-27.75591		
2689.99	-27.82098		
2691.25	-27.59652		
2695.57	-25.73		
2697.8	-25.37744		
2699.39	-25.84074		
2702.13	-26.55374		
2703.89	-22.69607		
2705.135	-26.47045		
2706.22	-24.38665		
2708.125	-25.54732		
2710.73	-25.41445		

Table F-2. Organic carbon isotope data of the residue samples after extraction from cores A and B.

Peak name	2669.03	2676.68	2677.5	2681.17	2684	2685.94	2687.28	2691.25	2695.57	2697.8	2699.39	2702.13	2703.89	2705.135	2706.22	2708.125	2710.73
Area	Area	Area	Area	Area	Area	Area	Area	Area	Area	Area	Area	Area	Area	Area	Area	Area	Area
nC17	49.080	102.149	189.917	109.482	92.279	74.814	92.345	134.577	39.277	4.108	8.711	21.934	6.356	63.205	25.175	22.297	100.726
pr	9.376	13.590	32.193	17.259	9.018	10.002	9.217	18.437	6.540	0.866	1.132	2.297	0.323	10.229	1.120	1.649	26.501
nC18	53.242	94.098	183.495	108.443	76.838	79.134	63.318	120.562	39.049	3.887	9.028	16.039	0.919	62.057	6.159	9.157	109.163
ph	6.753	14.930	25.254	14.525	5.985	7.425	6.754	13.715	4.475	0.613	0.994	2.815	0.228	6.914	1.239	1.271	16.911
nC19	48.940	76.589	178.576	110.397	78.860	77.895	63.235	110.331	36.908	3.812	8.202	14.160	0.804	54.848	6.114	8.328	88.830
nC20	43.740	58.710	186.587	110.897	77.514	73.813	60.239	111.164	37.539	3.480	7.364	10.348	0.627	50.386	4.366	7.246	68.220
nC21	39.683	48.292	183.139	109.552	77.279	69.767	58.512	105.163	35.993	3.270	6.861	8.284	0.432	45.902	3.027	6.749	57.168
nC22	37.006	43.433	183.726	107.988	75.542	66.509	56.288	102.337	34.369	3.036	6.321	7.521	0.526	42.896	2.724	6.621	48.724
nC23	36.745	44.821	194.948	109.156	74.673	66.275	56.085	105.636	34.500	2.879	6.389	7.074	0.747	41.943	2.406	5.993	47.750
nC24	32.112	39.059	178.923	97.821	61.604	57.952	48.152	93.200	29.833	2.331	5.462	5.959	0.321	35.393	1.888	4.953	38.495
nC25	32.866	40.923	180.402	93.315	60.463	58.088	46.111	94.643	30.686	2.311	5.474	5.880	0.471	34.543	2.104	5.013	39.121
nC26	26.969	32.526	155.569	78.457	46.216	48.580	39.725	88.133	25.988	1.790	4.626	5.082	0.276	30.312	1.536	3.901	31.163
nC27	25.063	29.802	148.252	69.338	43.693	45.952	37.713	84.286	24.556	1.567	4.267	4.415	0.239	27.643	1.194	3.432	27.006
nC28	19.174	23.885	121.668	55.900	31.234	34.884	29.016	66.622	19.667	1.170	3.224	3.363	0.203	21.056	0.933	2.594	20.648
nC29	17.752	22.301	113.812	48.760	25.487	31.412	25.368	62.361	18.581	1.032	3.091	3.122	0.230	19.686	1.050	2.487	19.243
nC30	13.682	17.770	92.710	38.679	18.547	23.916	20.057	50.054	15.006	0.800	2.375	2.370	0.129	15.730	0.563	1.783	13.899
nC31	10.361	14.446	79.239	33.487	12.417	18.655	13.502	39.151	12.560	0.635	2.227	1.874	0.133	13.308	0.489	1.442	11.504
nC32	7.505	10.623	60.069	25.620	7.951	13.363	8.899	29.150	9.317	0.332	1.974	1.183	0.130	10.676	0.135	0.845	8.627
nC33	5.269	7.464	38.249	17.341	4.460	9.004	5.241	18.893	6.926	0.329	2.319	0.867	0.036	8.565	0.259	0.713	6.193
nC34	3.844	5.684	25.010	12.612	3.340	6.639	3.716	13.454	4.947	0.154	2.989	0.676	0.031	7.349	1.079	0.475	4.558
nC35	3.198	5.316	17.894	10.904	2.551	5.938	2.779	12.023	4.150	0.147	4.033	0.752	0.114	8.163	0.389	0.332	3.960
nC36	2.581	5.116	12.171	8.626	2.170	4.791	2.355	9.366	3.615		4.638	0.468		7.916	0.144	0.339	3.870
nC37	2.721	6.648	10.858	7.428	3.068	4.709	3.132	8.746	4.241		6.105	1.081		9.015	0.603	0.773	5.673
nC38	1.961	6.121	7.011	6.529	1.704	4.117	1.775	5.606	2.427		5.943	0.268		7.048	0.190	0.294	6.623
Pr/Ph	1.388	0.910	1.275	1.188	1.507	1.347	1.365	1.344	1.461	1.412	1.139	0.816	1.416	1.480	0.904	1.298	1.567
Pr/n17	0.191	0.133	0.170	0.158	0.098	0.134	0.100	0.137	0.166	0.211	0.130	0.105	0.051	0.162	0.045	0.074	0.263
Ph/n18	0.127	0.159	0.138	0.134	0.078	0.094	0.107	0.114	0.115	0.158	0.110	0.176	0.248	0.111	0.201	0.139	0.155
Pr/(Pr+Ph)	0.581	0.477	0.560	0.543	0.601	0.574	0.577	0.573	0.594	0.585	0.533	0.449	0.586	0.597	0.475	0.565	0.610

Table F-3. Peak areas of the *n*-alkanes and acyclic isoprenoids of the total lipid extraction from Core A.

Peak name	Ion	2669.03	2676.68	2677.5	2681.17	2684	2685.94	2687.28	2691.25	2695.57	2697.8	2699.39	2702.13	2703.89	2705.14	2706.22	2708.13	2710.73
		Area	Area	Area	Area	Area	Area	Area	Area	Area	Area	Area	Area	Area	Area	Area	Area	Area
33H S	17a,21b,22(S)-trishomohopane	454.5 > 191.2	104275	7070.28	1462.31	5323.2	95752	103074	381458	9951.64	165380	46325.4	44179.4	65661.9	15902	53070	12418.8	67549
33H R	17a,21b,22(R)-trishomohopane	454.5 > 191.2	66458	4731.17	829.757	3031.49	53216	65878.3	228760	6913.95	107006	26352.7	28384.9	42266.7	9291.62	30131.5	6804.38	38901.9
32H S	17a,21b,22(S)-bishomohopane	440.4 > 191.2	348915	15759	3237.4	12840.2	238119	316224	878982	24257.7	382578	93387.9	81343	144496	28557	111358	24486.4	128168
32H R	17a,21b,22(R)-bishomohopane	440.4 > 191.2	145944	11044.9	2019.62	8745.96	163951	209074	586715	17355.8	270052	65510.8	55085.5	96698.5	18411.8	75254.5	14008	82122.7
31H S	17a,21b,22(S)-homohopane	426.4 > 191.2	277699	20179.6	3513.62	13874	261388	367437	101295.4	27879.6	419606	112863	95378.9	171222	45530.5	115203	39619.3	169208
31H R	17a,21b,22(R)-homohopane	426.4 > 191.2	234534	14322.6	2678.03	10160.8	192825	268882	723161	21235.4	334993	86836	83469.1	129551	35860.7	91261.1	31480.9	126052
Standard	374.4 > 219.2	6239191	135191	21356	76960.8	9135718	5443173	1.06E+07	177431	7734019	2.67E+07	2.30E+07	1.01E+07	2.67E+07	9491468	1.09E+07	3.53E+07	4688839
	9,15-dimethyl-25,27-hopane	412.4 > 191.2	1358510	47881.3	14343.5	79231.9	2836313	2055890	4444516	247109	2520019	744864	661630	696086	60395.3	1307478	54897.4	817097
30EE	dinorhopane (early eluting hopane)																	1899118
30D	15a-methyl-17a-27-norhopane (diahopane)	412.4 > 191.2	1194145	60612.2	16247.3	75244.9	3018546	2295426	5519874	254693	2800435	649410	600973	812524	55638.9	1088952	57253.9	717268
30H	17a,21b-hopane	412.4 > 191.2	854032	65561.1	9666.31	30562.1	817299	1269070	2964842	91989.7	1546143	370947	336685	671375	162904	412242	151948	680763
29D	15a-methyl-17a-27,30-dinorhopane (diahopane)	398.4 > 191.2	312508	21813.9	5310.14	23091.7	845434	717750	1885317	104584	872929	205348	166484	278177	13775.3	319938	18068.7	189357
29H	398.4 > 191.2	473048	35531.6	4824.12	13195.9	400383	515160	1237171	35260.5	536624	203081	169395	361685	135900	178657	138393	386610	609622
29Ts	18a-30-norneohopane	398.4 > 191.2	589697	49423.3	11384	41766.2	1108907	1156423	3863060	128540	1198875	314808	224764	399213	34058.8	355115	40865.3	315058
29Nsp	17b,18a-21-methyl-28-nor-spergulane	398.4 > 191.2	57734.8	3749.15	786.172	3052.28	156562	136516	365803	35113.5	294246	56556.7	4925.2	96457.2	5588.64	96092.8	3917.89	50757.9
29M	17b,21a-30-norhopane	398.4 > 191.2	141514	6792.93	1738.03	8086.88	288365	229792	32091.2	344558	87021	59662.7	100175	6723.63	113937	5669.1	74155.2	196976
27D	370.4 > 191.2	89674.3	6166.1	1545.4	7493.8	212385	169561	398637	28530.9	200898	50455.1	47472.6	64211	5456.39	89343.9	6649.35	44302.3	150123
27Ts	18a-22,29,30-trisnorhopane	370.4 > 191.2	719747	54615.6	11254.9	50332.8	1645951	1311416	3743924	256956	2056294	555091	438211	682183	60174.8	820996	61951.7	527442
27Tm	17a-22,29,30-trisnorhopane	370.4 > 191.2	197470	22305	3230.34	7235.78	314222	298353	748436	33808.1	291115	89057.8	88570.2	167816	56196.7	105308	54192.7	177639
29Nsp/29H		0.12205	0.10552	0.16297	0.23131	0.39103	0.265	0.29568	0.99583	0.54833	0.27849	0.29473	0.26669	0.04112	0.53786	0.02831	0.13129	0.4003
30EE/30H		1.5907	0.73033	1.48386	2.59249	3.47035	1.62	1.49907	2.68627	1.62987	2.00801	1.96513	1.03681	0.37074	3.17163	0.36129	1.20027	1.40496
29Ts/29H		1.24659	1.39097	2.35981	3.16509	2.76961	2.24478	3.12249	3.64543	2.23411	1.55016	1.32686	1.10376	0.25062	1.9877	0.29529	0.81492	1.40611
Ts/Tm		3.64485	2.44858	3.48412	6.9561	5.23819	4.39552	5.00233	7.60043	7.06351	6.23293	4.94761	4.06506	1.07079	7.79614	1.14317	2.96917	5.53108
29D/29H		0.66063	0.61393	1.10075	1.74991	2.11156	1.39326	1.52389	2.96604	1.62671	1.01116	0.98281	0.76911	0.10136	1.7908	0.13056	0.48979	1.06799
30D/30H		1.39824	0.92451	1.68082	2.46204	3.69332	1.80875	1.86178	2.76872	1.81124	1.75068	1.78497	1.21024	0.34154	2.64153	0.3768	1.05362	1.48687
29M/29H		0.29915	0.19118	0.36028	0.61283	0.72022	0.44606	0.64599	0.91012	0.64208	0.4285	0.35221	0.27697	0.04947	0.63774	0.04096	0.19181	0.32311
S/(S+R)31H		0.54213	0.58488	0.56748	0.57725	0.57547	0.57744	0.58346	0.56764	0.56764	0.56516	0.5333	0.56927	0.5594	0.55798	0.55723	0.57308	0.55163
S/(S+R)32H		0.70508	0.58794	0.61582	0.59483	0.59223	0.60199	0.5997	0.58293	0.58621	0.58772	0.59623	0.59908	0.608	0.59673	0.6361	0.60948	0.57331
S/(S+R)33H		0.61075	0.5991	0.63799	0.63715	0.64277	0.61008	0.62512	0.59006	0.60715	0.63741	0.60883	0.60838	0.63119	0.63785	0.64603	0.63456	0.59086
Steranes/hopanes		0.73544	0.74571	0.59479	0.54317	0.65562		0.45322	0.49134	0.45723	0.93228	1.13478	0.70739	1.4059	0.60161	1.49933	1.08672	0.48176

Table F-4. Peak areas of selected biomarkers of pentacyclic triterpenoids and the related ratios.

Peak name	Ion	2669.03	2676.68	2677.5	2681.17	2684	2685.94	2687.28	2691.25	2695.57	2697.8	2699.39	2702.13	2703.89	2705.14	2706.22	2708.13	2710.73
Area	Area	Area	Area	Area	Area	Area	Area	Area	Area	Area	Area	Area	Area	Area	Area	Area	Area	Area
17a,21b,22(S)-trishomohopane	454.5 > 191.2	104275	7070.28	1462.31	5323.2	95752	103074	381458	9951.64	165380	46325.4	44179.4	65661.9	15902	53070	12418.8	67549	128732
17a,21b,22(R)-trishomohopane	454.5 > 191.2	66458	4731.17	829.757	3031.49	53216	65878.3	228760	6913.95	107006	26352.7	28384.9	42266.7	9291.62	30131.5	6804.38	38901.9	89139.9
17a,21b,22(S)-bishomohopane	440.4 > 191.2	348915	15759	3237.4	12840.2	238119	316224	878982	24257.7	382578	93387.9	81343	144496	28557	111358	24486.4	128168	283300
17a,21b,22(R)-bishomohopane	440.4 > 191.2	145944	11044.9	2019.62	8745.96	163951	209074	586715	17355.8	270052	65510.8	55085.5	96698.5	18411.8	75254.5	14008	82122.7	210844
17a,21b,22(S)-homohopane	426.4 > 191.2	277699	20179.6	3513.62	13874	261388	367437	1012954	27879.6	419606	112863	95378.9	171222	45530.5	115203	39619.3	169208	326708
17a,21b,22(R)-homohopane	426.4 > 191.2	234534	14322.6	2678.03	10160.8	192825	268882	723161	21235.4	334993	86836	83469.1	129551	35860.7	91261.1	31480.9	126052	265549
Standard	374.4 > 219.2	6239191	135191	21356	76960.8	9135718	5443173	1.06E+07	177431	7734019	2.67E+07	2.30E+07	1.01E+07	2.67E+07	9491468	1.09E+07	3.53E+07	4688839
9,15-dimethyl-25,27-dinorhopane (early eluting hopane)	412.4 > 191.2	1358510	47881.3	14343.5	79231.9	2836313	2055890	4444516	247109	2520019	744864	661630	696086	60395.3	1307478	54897.4	817097	1899118
15a-methyl-17a-27-norhopane (diahopane)	412.4 > 191.2	1194145	60612.2	16247.3	75244.9	3018546	2295426	5519874	254693	2800435	649410	600973	812524	55638.9	1088952	57253.9	717268	2009830
17a,21b-hopane	412.4 > 191.2	854032	65561.1	9666.31	30562.1	817299	1269070	2964842	91989.7	1546143	370947	336685	671375	162904	412242	151948	680763	1351722
15a-methyl-17a-27,30-dinorhopane (diahopane)	398.4 > 191.2	312508	21813.9	5310.14	23091.7	845434	717750	1885317	104584	872929	205348	166484	278177	13775.3	319938	18068.7	189357	651071
17a,21b-30-norhopane	398.4 > 191.2	473048	35531.6	4824.12	13195.9	400383	515160	1237171	35260.5	536624	203081	169395	361685	135900	178657	138393	386610	609622
18a-30-norneohopane	398.4 > 191.2	589697	49423.3	11384	41766.2	1108907	1156423	3863060	128540	1198875	314808	224764	399213	34058.8	355115	40865.3	315058	857197
17b,18a-21-methyl-28-nor-spergulane	398.4 > 191.2	57734.8	3749.15	786.172	3052.28	156562	136516	365803	35113.5	294246	56556.7	49925.2	96457.2	5588.64	96092.8	3917.89	50757.9	244031
17b,21a-30-norhopane	398.4 > 191.2	141514	6792.93	1738.03	8086.88	288365	229792	799202	32091.2	344558	87021	59662.7	100175	6723.63	113937	5669.1	74155.2	196976
27D	370.4 > 191.2	89674.3	6166.1	1545.4	7493.8	212385	169561	398637	28530.9	200898	50455.1	47472.6	64211	5456.39	89343.9	6649.35	44302.3	150123
27Ts	370.4 > 191.2	719747	54615.6	11254.9	50332.8	1645951	1311416	3743924	256956	2056294	555091	438211	682183	60174.8	820996	61951.7	527442	1699003
27Tm	17a-22,29,30-trisnorhopane	370.4 > 191.2	197470	22305	3230.34	7235.78	314222	298353	748436	33808.1	291115	89057.8	88570.2	167816	56196.7	105308	54192.7	177639
29Nsp/29H	0.12705	0.10552	0.16297	0.23131	0.39103	0.265	0.29568	0.99583	0.54833	0.27849	0.29473	0.26669	0.04112	0.53786	0.02831	0.13129	0.4003	
30EE/30H	1.5907	0.73033	1.48386	2.59249	3.47035	1.62	1.49907	2.68627	1.62987	2.00801	1.96513	1.03681	0.37074	3.17163	0.36129	1.20027	1.40496	
29Ts/29H	1.24659	1.39097	2.35981	3.16509	2.76961	2.24478	3.12249	3.64543	2.23411	1.55016	1.32686	1.10376	0.25062	1.9877	0.29529	0.81492	1.40611	
Ts/Tm	3.64485	2.44858	3.48412	6.9561	5.23819	4.39552	5.00233	7.60043	7.06351	6.23293	4.94761	4.06506	1.07079	7.79614	1.14317	2.96917	5.53108	
29D/29H	0.66063	0.61393	1.10075	1.74991	2.11156	1.39326	1.52389	2.96604	1.62671	1.01116	0.98281	0.76911	0.10136	1.7908	0.13056	0.48979	1.06799	
30D/30H	1.39824	0.92451	1.68082	2.46204	3.69332	1.80875	1.86178	2.76872	1.81124	1.75068	1.78497	1.21024	0.34154	2.64153	0.3768	1.05362	1.48687	
29M/29H	0.29915	0.19118	0.36028	0.61283	0.72022	0.44606	0.64599	0.91012	0.64208	0.4285	0.35221	0.27697	0.04947	0.63774	0.04096	0.19181	0.32311	
S/(S+R)/31H	0.54213	0.58488	0.56748	0.57725	0.57547	0.57744	0.58346	0.56764	0.55607	0.56516	0.5333	0.56927	0.5594	0.55798	0.55723	0.57308	0.55163	
S/(S+R)/32H	0.70508	0.58794	0.61582	0.59483	0.59223	0.60199	0.5997	0.58293	0.58621	0.58772	0.59623	0.59908	0.608	0.59673	0.6361	0.60948	0.57331	
S/(S+R)/33H	0.61075	0.5991	0.63799	0.63715	0.64277	0.61008	0.62512	0.59006	0.60715	0.63741	0.60883	0.60838	0.63119	0.63785	0.64603	0.63456	0.59086	
Stenanes/hopanes	0.73544	0.74571	0.59479	0.54317	0.65562		0.45322	0.49134	0.45723	0.93228	1.13478	0.70739	1.4059	0.60161	1.49933	1.08672	0.48176	

Table F-5. Peak areas of selected biomarkers of tetracyclic triterpenoids and the related ratios.

Depth (m)	Peak name		Ratio C19/C23
	C23/3	C19/3	
2669.03	437078.8	316719.3	0.72
2676.68	57998.53	30004.91	0.52
2677.5	23876.9	16302.82	0.68
2681.17	21968.57	27804.97	1.27
2684	387489.8	767281.2	1.98
2685.94	1190115	1583039	1.33
2687.28	831941.3	910386.5	1.09
2691.25	40639.13	74813.73	1.84
2695.57	287203.1	476425.8	1.66
2697.8	130907.8	123698.3	0.94
2699.39	134890.1	148701.1	1.10
2702.13	186818.8	128626.6	0.69
2703.89	99973.21	29526.05	0.30
2705.135	130250	278483	2.14
2706.22	92523.45	30890.63	0.33
2708.125	262086.8	160834.7	0.61
2710.73	404736.1	322653.5	0.80

Table F-6. Selective biomarker peak area of the tricyclic terpanes from Core A.

Ion	DBT	3-MP	2-MP	9-MP	1-MP	Phenan- threne	Standard	DBT/ Phenan- threne	MPI-1
	184	192	192	192	192	178	188		
Depth (m)									
2669.03		6383	6188.8	20178	7993.42	10447.1	41100.4		0.49
2672.53	517.48	19907	24739	51538	35493.1	25628.3		0.0202	0.59
2674.5	527.62	18904	22689	47178	31395.2	21433.6		0.0246	0.62
2675.23	2582.4	35674	41034	78993	52460.8	102205	158.988	0.0253	0.49
2676.68	16199	233730	255892	524273	326183	753156	184877	0.0215	0.46
2677.5	25818	377031	433727	834669	556791	978175	55140.1	0.0264	0.51
2679.6	379.06	13024	14928	33716	21925.8	13531.8		0.0280	0.61
2681.17	55851	681400	806193	2E+06	1048864	1812663	115046	0.0308	0.50
2684	7406.6	64547	75226	142869	95802.1	195301	66095.4	0.0379	0.48
2685.94		50116	48713	137123	60178.8	95716.2	180885		0.51
2687.28	17446	175911	202742	371840	249752	458535	112360	0.0380	0.53
2689.99	367.15	16711	20914	42777	28689	11084.7		0.0331	0.68
2691.25	1948.2	182548	191531	432863	233079	444716	126857	0.0044	0.51
2695.57		52078	53746	122635	63454	115717	47448		0.53
2697.8	4788.2	31512	37362	58315	39902	79863.6	111108	0.0600	0.58
2699.39	9046.3	86981	105236	185363	125761	167383	285878	0.0540	0.60
2702.13	3996.9	25373	29660	51931	35636.3	65495	53538.3	0.0610	0.54
2703.89	3186.1	14764	18013	17453	12789.7	53124	62671.2	0.0600	0.59
2705.135	8670.4	63958	77228	133310	90337.7	146436	65691.8	0.0592	0.57
2706.22	4235	23089	27397	37322	26419.2	72345.3	87434.2	0.0585	0.56
2708.125	3557.4	22372	26125	44089	31922.6	63321	72667.8	0.0562	0.52
2710.73	7871.6	241479	259932	489663	285950	602337	91818.9	0.0131	0.55

MP: Methylphenanthrene

DBT: Dibenzothiophene

MPI-1: $1.5 \times [2\text{-MP} + 3\text{-MP}] / [\text{Phenanthrene} + 1\text{-MP} + 9\text{-MP}]$

Table F-7. Selective biomarker peak area of the aromatic fractions from Core A.

Appendix G — Data from Chapter 6

Sample	Number	Height	TOC	TIC	$\delta^{13}\text{C}_{\text{org}}$	$\delta^{13}\text{C}_{\text{carb}}$	$\delta^{18}\text{O}_{\text{carb}}$	Tmax	TOC	HI	OI	MINC
		(m)	(%)	(%)	(‰)	(‰)	(‰)	(°C)	(%)			(%)
K-M	200	15.4	0.73	8.87	-27.89	0.67	-6.11	434	0.6	190	108	7.27
K-M	201	15.3	1.05	4.78	-27.85	0.40	-5.36					
K-M	202	15.2	1.25	6.37	-28.10	0.29	-4.63					
K-M	203	15.1	1.43	2.99	-28.27	0.16	-4.91					
K-M	205	14.9	1.20	4.29	-27.77	-0.06	-5.03	434	1.23	183	50	5.78
K-M	206	14.8	1.45	5.28	-27.90	0.03	-5.07					
K-M	207	14.7	1.31	4.75	-27.98	-0.04	-5.40					
K-M	208	14.6	1.65	4.85	-28.43	0.09	-5.18					
K-M	209	14.5	1.77	5.95	-28.44	0.03	-4.97	428	1.67	296	25	4.75
K-M	210	14.4	1.78	4.91	-28.39	0.30	-5.05					
K-M	211	14.3	1.85	5.93	-28.35	0.18	-5.26					
K-M	212	14.2				-0.12	-5.18					
K-M	213	14.1	1.84	6.09	-28.51							
K-M	214	14	2.23	4.54	-28.58	0.12	-5.50	430	2.49	235	30	4.91
K-M	215	13.9	2.03	4.20	-28.27							
K-M	216	13.8	1.80	4.71	-28.00	0.14	-5.46	425	1.76	264	23	4.75
K-M	217	13.7	2.05	4.24	-27.81							
K-M	218	13.6	2.07	4.67	-28.18	0.12	-5.27					
K-M	219	13.5	1.21	4.36	-27.73			432	0.9	219	56	7.8
K-M	220	13.4	2.03	4.17	-27.83	0.04	-5.52					
K-M	221	13.3	2.87	4.04	-28.00							
K-M	222	13.2	2.28	4.03	-27.92	-0.04	-5.35	426	2.35	334	25	6.47
K-M	223	13.1	3.18	4.29	-27.80							
K-M	224	13	3.14	3.59	-28.04	-0.31	-5.41					
K-M	225	12.92	7.41	4.54	-28.55			428	7.18	577	19	2.89
K-M	226	12.8	1.43	3.93	-27.88	0.18	-4.88					
K-M	227	12.7	1.38	4.53	-27.76							
K-M	228	12.6	0.92	7.86	-27.71	0.32	-7.59					
K-M	229	12.5	1.39	4.75	-27.78							
K-M	230	12.4	1.51	4.33	-27.78	0.22	-5.35					
K-M	231	12.3	1.57	4.27	-27.94							
K-M	232	12.2	1.82	4.15	-27.98	0.35	-5.22					
K-M	233	12.1	2.21	3.39	-28.04							
K-M	234	12	2.30	4.31	-27.44	0.24	-5.33	432	2.24	329	36	4.44
K-M	235	11.9	1.64	5.45	-27.28							
K-M	236	11.8	1.95	3.93	-27.18	0.36	-5.09	431	1.65	258	100	4
K-M	237	11.7	1.16	6.11	-27.55							
K-M	238	11.6	1.40	4.77	-27.66	0.23	-5.84	430	1.42	192	82	9.98
K-M	239	11.5	1.48	5.63	-27.63							
K-M	240	11.4	1.20	4.01	-27.47	0.11	-5.35					
K-M	241	11.3	1.34	5.47	-26.95			436	1.16	127	91	3.5
K-M	242	11.2	1.42	3.79	-27.26	0.09	-5.33					
K-M	243	11.1	1.75	5.49	-28.40							
K-M	244	11	1.71	3.71	-28.73	0.07	-5.24	434	1.74	244	35	3.82
K-M	245	10.89	2.00	3.93	-28.43							
K-M	246	10.78	7.60	1.94	-28.32	-0.40	-6.05					
K-M	247	10.7	1.63	4.32	-28.12							
K-M	248	10.61	0.80	8.72	-28.47	0.84	-6.97	436	0.71	224	76	6.88

K-M	249	10.48	1.52	3.53	-28.31							
K-M	250	10.36	1.59	4.27	-28.58	0.18	-5.13	430	1.65	301	50	8.68
K-M	95	10.25	1.67	6.04	-28.35	0.31	-5.10					
K-M	94	10.14	0.50	8.21	-27.01	0.91	-6.66					
K-M	93	10.03	2.06	5.44	-28.83	0.29	-4.79	436	1.86	342	53	4
K-M	92	9.92	1.75	3.72	-28.35	0.20	-5.11					
K-M	91	9.81	1.91	5.90	-28.55	0.16	-4.97	429	1.84	272	46	3.82
K-M	90	9.7	1.63	4.20	-28.31							
K-M	89	9.59	1.60	5.47	-28.18	0.21	-5.03	428	1.49	238	42	4.25
K-M	88	9.48	1.70	3.67	-28.20	-0.07	-5.20					
K-M	87	9.37	2.30	4.32	-28.52	-0.19	-5.22	426	2.35	346	27	4.63
K-M	86	9.28	2.01	5.12	-27.82	-0.25	-5.48					
K-M	85	9.17	2.59	3.94	-27.95	-0.10	-4.63	434	2.51	367	28	4.84
K-M	84	9.06	2.14	6.21	-28.54	0.28	-5.90					
K-M	83b	8.96	1.20	3.94	-28.76	0.63	-6.91	429	1.07	385	47	13.2
K-M	83	8.87	1.97	4.54	-28.15							
K-M	82	8.78	2.25	4.03	-28.23	-0.09	-5.35					
K-M	81b	8.73	0.82	5.48	-27.71	0.68	-7.00	430	0.53	108	132	8.69
K-M	81	8.63	2.05	5.82	-28.37	-0.39	-4.98					
K-M	79	8.51	2.95	4.07	-28.71							
K-M	78	8.41	2.00	5.33	-28.31	0.22	-5.61	434	1.4	274	70	5.97
K-M	77	8.27	2.42	4.54	-28.71							
K-M	76	8.13	1.77	5.50	-28.78	0.45	-5.96	429	2.89	214	25	11.69
K-M	75b	8.06	1.13	3.97	-28.65							
K-M	75	8	1.96	4.12	-28.72	0.22	-5.32					
K-M	74b	7.93	0.89	8.98	-28.54	0.84	-6.75	433	0.76	236	84	6.38
K-M	74	7.88	1.88	4.94	-28.80	0.21	-5.50					
K-M	73	7.8	1.81	4.60	-28.47	0.07	-5.31	428	1.82	337	41	4.56
K-M	72	7.73	2.16	4.51	-28.44	0.18	-5.13					
K-M	71	7.6	1.00	7.76	-27.53	0.16	-6.05	435	0.86	124	114	5.97
K-M	70	7.46	3.18	4.52	-28.59	-0.06	-5.34					
K-M	69	7.4	1.30	5.39	-27.95	-0.10	-5.66					
K-M	68	7.29	1.55	5.25	-28.14	-0.12	-5.86					
K-M	67	7.18	2.01	6.38	-29.07	-0.24	-5.16					
K-M	66	7.07	2.56	4.37	-29.50	-0.21	-5.06	433	2.46	407	27	4.31
K-M	65	6.96	1.78	3.71	-28.63	-0.51	-5.11					
K-M	64	6.86	2.36	4.54	-29.03	-1.09	-5.06					
K-M	63	6.8	4.20	4.71	-28.77	-0.89	-5.64	425	4.31	558	12	9.79
K-M	62	6.73	4.66	4.79	-28.73	-0.88	-5.56					
K-M	61	6.66	4.62	4.52	-28.87	-0.95	-5.63	426	4.81	541	19	5.36
K-M	60	6.59	5.67	4.46	-28.74	-0.68	-5.70					
K-M	59	6.52	6.95	4.71	-29.20	-0.67	-6.39	433	6.87	614	11	3.92
K-M	58	6.45	5.25	3.42	-29.62	-1.13	-5.77					
K-M	57	6.39	1.49	4.31	-28.26	-0.13	-5.72	429	1.39	317	58	13.19
K-M	56	6.31	1.66	6.20	-28.34	-0.08	-5.75					
K-M	55	6.23	2.06	4.49	-28.90	-0.35	-5.81					
K-M	54	6.15	1.12	7.58	-28.28	-0.81	-6.57	434	1.02	346	53	7.51
K-M	53	6.06	2.56	4.60	-29.24	-0.45	-5.67					
K-M	52	5.97	2.54	5.91	-28.89	-0.81	-5.56					
K-M	51	5.88	2.66	6.99	-29.07	-0.72	-5.64	422	2.99	432	12	9.76

K-M	50	5.79	2.46	5.24	-28.68	-0.80	-5.45					
K-M	49	5.7	2.21	4.54	-28.78	-0.77	-5.64	429	2.14	441	24	5.28
K-M	48	5.61	2.43	5.55	-28.69	-0.26	-6.22					
K-M	47	5.54	1.57	5.01	-28.96	-0.59	-8.50	430	1.09	314	61	8.19
K-M	46	5.51	7.54	4.50	-30.60	-0.49	-5.56					
K-M	45	5.4	6.72	5.62	-30.83	-0.63	-6.07	426	9.32	482	8	7.76
K-M	44	5.33	7.94	4.62	-30.73	0.15	-5.46	436	7.73	720	15	4.34
K-M	43	5.26	6.76	5.61	-30.62	0.02	-6.05					
K-M	42	5.18	5.43	4.56	-30.33	-0.26	-5.48	426	5.48	649	13	6.2
K-M	41	5.1	8.20	7.05	-30.26	-0.65	-5.22	430	8.07	657	13	4.1
K-M	40	5.02	6.56	4.79	-29.95	-0.95	-5.48					
K-M	39	4.94	6.25	5.32	-30.16	-0.54	-5.57					
K-M	38	4.86	5.49	4.52	-29.93	-0.53	-5.57					
K-M	37	4.78	5.78	7.93	-30.02	-0.33	-5.74	422	5.79	596	19	6.48
K-M	36	4.7				0.16	-5.60					
K-M	35	4.62	5.70	4.80	-29.86	-0.05	-5.86	431	5.58	632	19	4.66
K-M	34	4.54	6.59	4.71	-29.73	-0.22	-6.39					
K-M	33	4.46	5.19	3.53	-29.28			430	5.24	545	29	4.36
K-M	32	4.38	5.60	4.47	-29.42	-0.02	-5.51					
K-M	31	4.3	6.98	3.48	-29.77							
K-M	30	4.22	9.99	4.29	-29.93	-0.16	-6.51	420	10.9	601	14	8.3
K-M	29	4.14	6.64	8.79	-29.71			432	6.66	592	25	4.1
K-M	28	4.06	10.30	4.08	-29.88							
K-M	27	3.98	9.53	6.20	-30.19			431	9.3	696	13	4.2
K-M	26	3.9	8.58	4.39	-29.78	-0.01	-6.54					
K-M	25	3.82	8.97	4.67	-29.29			431	8.83	604	16	4.12
K-M	24	3.74	6.95	4.60	-28.94	-0.32	-5.87					
K-M	23	3.67	1.49	8.50	-28.00			437	1.23	279	81	6.17
K-M	22	3.61	3.07	6.33	-28.84	0.61	-5.14					
K-M	21	3.5	2.98	8.44	-28.80							
K-M	20	3.39	3.15	6.33	-28.65	0.33	-5.54	432	2.93	461	31	6.73
K-M	19	3.28	4.41	4.64	-28.14							
K-M	18	3.17	4.36	5.65	-28.56	0.29	-5.52	425	4.34	566	18	8.22
K-M	17	3.06	4.73	4.38	-28.12							
K-M	16	2.95	5.16	5.55	-28.38	0.19	-5.47	423	6.82	442	12	14.73
K-M	15	2.84	5.46	4.16	-28.82			430	5.29	555	22	5.49
K-M	14	2.73	5.66	5.72	-28.73	0.29	-5.48					
K-M	13	2.62	1.08	3.63	-27.45			440	0.99	211	83	6.96
K-M	12	2.4	1.70	6.51	-28.04	0.76	-4.94					
K-M	11	2.3	2.35	4.05	-28.88			426	4.03	267	10	12.71
K-M	10	2.2	2.74	5.50	-28.99	0.61	-4.72					
K-M	9	2.1	2.16	4.05	-28.85			431	2.06	428	43	5.81
K-M	8	1.9	2.00	6.20	-28.76	0.77	-4.96	425	1.98	435	21	7.5
K-M	7	1.7	1.97	4.26	-28.72							
K-M	6	1.4	2.14	6.13	-28.25	0.55	-4.91					
K-M	5	1.08	2.94	4.19	-28.04			431	2.78	432	32	5.64
K-M	4	0.96	3.01	5.22	-27.90	0.23	-4.91					
K-M	3	0.84	3.96	4.69	-28.15			427	4.08	524	13	12.37
K-M	2	0.72	7.22	4.53	-27.60	-0.37	-5.38					
K-M	1	0.6	8.15	4.18	-27.33			431	8.06	532	15	4.46

Table G-1. TOC and TIC data in columns 4 and 5 are from Coloumat measurement. Data in columns 9–13 are from Rock Eval pyrolysis.

Sample Height(m)	Sample Number (KM)	POLLEN						SPORES				MICROPLANKTON						POLLEN /SPORES		TERR. vs MARINE		KEROGEN (%)				
		bisaccate pollen (undifferentiated)	<i>Cerebropollenites macroverrucosus</i>	<i>Chasmatosporites</i> spp.	<i>Classopollis meyeriana</i> (single grains)	<i>Classopollis meyeriana</i> (tetrads)	<i>Perinopollenites elatoides</i>	<i>Cyathidites</i> spp.	<i>Densosporites</i> sp. (reworked)	<i>Krausselisporites reissingeri</i>	trilete spores (indeterminate)	acritarchs (indeterminate)	<i>Micrhystridium</i> spp.	<i>Botryococcus braunii</i>	foraminiferal test linings	scolecodont (undifferentiated)	<i>Tasmanites</i> spp.	gymnosperm pollen (nos. and per cent.)	pteridophyte spores (nos. and per cent.)	terrestrially-derived palynomorphs (nos. and per cent.)	indigenous marine palynomorphs (nos. and per cent.)	wood	plant tissue	palynomorphs	amorphous organic material	
1.90	8	16	...	...	287	14	...	...	...	2	...	...	...	...	...	43	317/87.6	2/0.5	319/88.1	43/11.9	20	5	18	57		
2.95	16	6	...	...	293	7	...	...	...	...	1	...	...	...	...	12	306/95.9	0/0	306/95.9	13/4.1	25	5	10	60		
3.39	20	6	3	...	309	12	...	...	...	1	...	1	...	...	...	26	330/92.2	1/0.3	331/92.5	27/7.5	17	5	13	65		
3.67	23	3	...	...	237	6	...	...	...	...	...	...	...	...	...	38	246/86.6	0/0	246/86.6	38/13.4	65	5	8	22		
3.82	25	2	...	...	167	9	...	...	...	...	...	2	...	1	...	4	178/96.2	0/0	178/96.2	7/3.8	13	5	8	74		
3.98	27	...	...	...	103	...	...	...	...	...	...	1	...	...	...	7	103/92.8	0/0	103/92.8	8/7.2	10	3	8	79		
4.22	30	2	...	...	213	1	...	...	...	1	...	...	...	1	...	5	216/96.9	1/0.4	217/97.3	6/2.7	10	3	13	74		
4.78	37	4	...	...	303	4	...	...	...	?1	2	...	...	1	...	14	311/94.5	3/0.9	315/95.7	14/4.3	17	3	15	65		
5.18	42	11	...	...	258	6	?1	...	...	...	...	...	...	1	...	8	276/96.8	0/0	276/96.8	9/3.2	15	3	8	74		
5.40	45	1	...	...	183	15	...	...	...	1	...	...	...	...	...	4	199/97.5	1/0.5	200/98	4/2	8	...	12	80		
6.15	54	8	...	...	424	23	...	1	...	1	...	5	...	...	...	18	455/94.8	2/0.4	457/95.2	23/4.8	23	3	20	54		
7.29	68	4	3	4	215	5	...	1	1	1	...	5	...	...	...	13	231/91.3	4/1.6	235/92.9	18/7.1	45	5	12	38		
8.41	78	5	?1	...	328	6	...	2	...	...	...	19	...	...	...	1	32	340/86.3	2/0.5	342/86.8	52/13.2	40	5	13	42	
11.00	244	25	...	2	429	27	1	1	...	1	...	26	...	...	...	5	484/93.6	2/0.4	486/94	31/6	12	3	17	68		

Table G-2. Palynology data from the Kilve section counted by James Riding.