

Using Uranium- and Thorium-Series Isotopes as Tracers for Trace-metal Inputs to the Oceans

by

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“What we know is a drop.

What we don’t know is an ocean.”

-- Sir Isaac Newton

Abstract

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This thesis explores the use of U-Th series isotopes as tracers to study ocean mixing and chemical inputs to the open ocean from atmospheric dust, rivers, continental shelves and ocean sediments.

The use of Th isotopes as an improved tracer of dust input has been tested by measuring ^{232}Th and ^{230}Th concentrations of upper-ocean seawater at six stations along a meridional Atlantic section that spans the Saharan dust plume. The results of ^{232}Th -derived dust fluxes show good agreements with dust model depositions, and suggest that thorium may be a more accurate tracer of dust input than Aluminium, which is frequently used for this purpose.

A new technique has been developed for the precise measurement of $^{228}\text{Ra}/^{226}\text{Ra}$ ratios and ^{228}Ra and ^{226}Ra concentrations in seawater by multi-collector ICP mass spectrometry (MC-ICP-MS). This methods offers improved analytical precision and detection limits relative to previous decay-counting approaches, though is more labour intensive. The accuracy of this method has been proved in the GEOTRACES Ra intercalibration, and shows consistent results with decay counting measurements from other labs. This technique has been applied to water samples in Loch Etive, a Scottish fjord, and in the Cape Basin during the UK-GEOTRACES cruise (GA10E) to investigate ocean mixing and trace-metal fluxes in the oceans.

In Loch Etive, Ra data provide an estimation of sedimentary ^{228}Ra flux of $5.5 \pm 0.3 (\times 10^9 \text{ atoms m}^{-2} \text{ yr}^{-1})$ in the inner loch deep basin. Short-lived Ra isotope ($^{223}\text{Ra}_{\text{ex}}$) has also been used to estimate surface water transport rate, which is $\sim 2.4 \pm 0.2 \text{ cm s}^{-1}$ from the mouth to the head of the loch. In the Cape Basin, seawater ^{228}Ra and ^{226}Ra activities have been used to estimate vertical and horizontal mixing in the surface ocean. The horizontal mixing (K_y) from the continental shelf to the open ocean is $3.8 \pm 0.8 (\times 10^7 \text{ cm}^2 \text{ s}^{-1})$ and the vertical mixing (K_z) in the upper 400 m layer is $0.9 - 2.1 \text{ cm}^2 \text{ s}^{-1}$. These mixing rates enable the calculation of nutrient flux in the surface ocean. The calculated vertical nitrate fluxes in the Cape Basin are $0.4 - 0.5 \text{ mmol N m}^{-2} \text{ d}^{-1}$. This finding shed light on the nutrient inputs to the South Atlantic Subtropical Gyre.

Extended Abstract**Using Uranium- and Thorium-Series Isotopes as Tracers for Trace-metal Inputs to the Oceans**

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This thesis investigates the use of U- and Th-series isotopes as tracers to study ocean mixing and the inputs of chemical species to the open ocean from atmospheric dust, rivers, continental shelves and ocean sediments. Assessing ocean mixing rates and the fluxes of trace metals into, out of, and within the ocean provide information about the relationship between biological activity and micronutrient supply. Radium isotopes (^{226}Ra , half-life $T_{1/2} = 1602$ years; ^{228}Ra , $T_{1/2} = 5.75$ years; ^{223}Ra , $T_{1/2} = 11.4$ days; ^{224}Ra , $T_{1/2} = 3.66$ days) are used to assess chemical fluxes, ocean mixing, eddy diffusion and carbon export in the oceans. Thorium isotopes (^{232}Th , $T_{1/2} = 1.4 \times 10^{10}$ years; ^{230}Th , $T_{1/2} = 7.5 \times 10^4$ years; ^{228}Th , $T_{1/2} = 1.9$ years; ^{234}Th , $T_{1/2} = 24.1$ days) are used to estimate Th residence time, particle dynamics and dust fluxes in the oceans.

The use of Th isotopes as a tracer of dust input to the surface ocean has been tested by measuring ^{232}Th and ^{230}Th concentrations of upper-ocean seawater at six stations along a meridional Atlantic section that spans the Saharan dust plume. The highest ^{232}Th concentrations and $^{232}\text{Th}/^{230}\text{Th}$ ratios are observed at stations expected to have high dust inputs. The lateral input of ^{232}Th from Mediterranean Outflow Water is detected at 1000 m in the North Atlantic. Surface-water Th residence times calculated from ^{230}Th and ^{234}Th are generally consistent with one another and range from 1.23 to 2.55 years. The results of ^{232}Th -derived dust fluxes show good agreements with models of dust deposition if Th solubility is 1 to 5% in the north Atlantic (yielding fluxes of $0.4\text{--}19.2 \text{ g m}^{-2} \text{ yr}^{-1}$) and 5 to 10% in the south Atlantic (fluxes of $0.2\text{--}0.7 \text{ g m}^{-2} \text{ yr}^{-1}$).

A new technique has been developed for the precise measurement of $^{228}\text{Ra}/^{226}\text{Ra}$ ratios and ^{228}Ra and ^{226}Ra concentrations in seawater by multi-collector ICP mass spectrometry (MC-ICP-MS). This technique provides a lower detection limit ($0.1 \text{ fg } ^{228}\text{Ra}$), higher precision (2%) and a shorter counting time (20 minutes) for measurement of ^{228}Ra and ^{226}Ra concentrations, although it is more labour intensive. Measurements of ^{228}Ra and ^{226}Ra concentrations made with this technique show good

agreement with consensus numbers from other labs by decay-counting techniques within the GEOTRACES Ra intercalibration. In this thesis, the technique is used to measure seawater ^{228}Ra and ^{226}Ra in Loch Etive (a Scottish fjord), and on samples from the UK-GEOTRACES cruise (GA10E) along 40°S in the South Atlantic.

Loch Etive provides an ideal environment to estimate the sedimentary ^{228}Ra flux since it has no groundwater input and limited water ventilation in the deep basin. ^{228}Ra concentrations in Etive deep-waters indicate a sedimentary ^{228}Ra flux of $5.5 \pm 0.3 (\times 10^9 \text{ atoms m}^{-2} \text{ yr}^{-1})$, which is comparable with the global range of sedimentary ^{228}Ra inputs from shelf sediments in the literature. Shelf sediments around the head of the loch also provide additional inputs of ^{224}Ra and ^{228}Ra to the surface water, which alter the activity ratio of $^{228}\text{Ra}/^{226}\text{Ra}$ in the surface water by about 11 ~ 19%. Short-lived Ra isotopes (^{223}Ra and ^{224}Ra) have also been used to study water transport and vertical diffusivity in Loch Etive. Surface water transport rate is $\sim 2.4 \pm 0.2 \text{ cm s}^{-1}$ from the mouth to the head of the loch, based on the distribution of $^{223}\text{Ra}_{\text{ex}}$ activities in surface water. Thus, seawater traveling from the mouth to the head of the loch takes 17 ± 2 days.

In the Cape Basin, SE Atlantic Ocean (UK-GEOTRACES-GA10E), the activities of ^{228}Ra and ^{226}Ra were measured at the surface and in the water column. The gradients of ^{228}Ra were used to estimate isopycnal and diapycnal mixing in the ocean. In surface water, The horizontal mixing (K_x) from the continental shelf to the open ocean is $3.8 \pm 0.8 (\times 10^7 \text{ cm}^2 \text{ s}^{-1})$ and the vertical mixing (K_z) in the upper 400 m layer is $0.9 - 2.1 \text{ cm}^2 \text{ s}^{-1}$. Based on ^{228}Ra -derived vertical mixing in the surface ocean, the calculated upward nitrate fluxes in the Cape Basin are $0.4 - 0.5 \text{ mmol N m}^{-2} \text{ d}^{-1}$, and the organic carbon fluxes are $3.1 - 3.3 \text{ mmol C m}^{-2} \text{ d}^{-1}$. The vertical mixing has also been applied to calculate phosphate fluxes of $0.03 \text{ mmol P m}^{-2} \text{ d}^{-1}$ and silicate fluxes of $0.14 - 0.33 \text{ mmol Si m}^{-2} \text{ d}^{-1}$ in this region. These Ra-derived mixing rates will also prove useful in assessing inputs of other chemical species (including the micronutrient, Fe) to the Cape Basin.

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List of Abbreviations

A	activity of radioactive nuclide
ag	attogram 10^{-18} g
AABW	Antarctic Bottom Water
AAIW	Antarctic Intermediate Water
ACL	Agulhas Current Leakage
AMT	Atlantic Meridional Transect
ARC	Agulhas Return Current
BEC	Benguela Current
cps	counts per second
CTD	conductivity, temperature, depth
dpm	disintegrations per minute
$\Delta\text{NO}_3^-/\Delta z$	gradient of nitrate over the depth z
$\delta^{234}\text{U}$	$[(^{234}\text{U}/^{238}\text{U})-1] \times 1000$
e.g.	exempli gratia (for example)
et al.	et alii (and others)
F_{dust}	dust flux
$F_{\text{sed}}(^{228}\text{Ra})$	sedimentary ^{228}Ra flux
F_{nitrate}	nitrate flux
$F_{232\text{Th}}$	^{232}Th flux
fg	femtogram 10^{-15} g
GEOSECS	Geochemical Ocean Sections Study
ICP-MS	inductively coupled plasma mass spectrometry
i.e.	id est (that is)
K_d	distribution coefficient
K_x	horizontal eddy diffusion coefficient
K_z	vertical eddy diffusion coefficient
LDPE	low-density polyethylene
λ	decay constant
MC-ICP-MS	multi-collector inductively coupled plasma mass spectrometry
mg	milligram 10^{-3} g
μg	microgram 10^{-6} g
MOW	Mediterranean Outflow Water

NADW	North Atlantic Deep Water
ng	nanogram 10^{-9} g
POC	particulate organic carbon
pg	picogram 10^{-12} g
RaDeCC	radium delayed coincidence counter
Ra _{ex}	excess Ra, derived only from within the water column
σ	standard error of the mean
SAPs	in situ stand alone pump system
SASW	Subantarctic Surface Water
S.D.	standard deviation
S.E.	standard error
SGD	submarine groundwater discharge
S _{Th}	Th solubility
T _{1/2}	half-life
τ_{Th}	Th removal residence time
$\tau_{\text{daughter-mean-life}}$	mean life of daughter, $T_{1/2}/\ln(2)$
TIMS	thermal ionization mass spectrometry
TTO	Transient Tracers in the Oceans
w	mean water transport rate
WMDW	Western Mediterranean Deep Water
X	horizontal distance
yr	year
Z	vertical depth
(²²⁸ Ra/ ²²⁶ Ra)	activity ratio of ²²⁸ Ra/ ²²⁶ Ra
[²³² Th/ ²³⁰ Th]	atomic ratio of ²³² Th/ ²³⁰ Th
[²³² Th] _{dust}	²³² Th dust concentration
²²³ Ra _{ex} and ²²⁴ Ra _{ex}	excess of ²²³ Ra and ²²⁴ Ra

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Declaration

I declare that the contents of this thesis are all my own work, except where otherwise stated.

Yu-Te (Alan) Hsieh

Chapter 1

Introduction

1.1 Ocean productivity

The ocean plays a very important role in the Earth's climate system. Ocean productivity controls the global carbon cycle between the oceans and the atmospheres. Phytoplankton, microscopic organisms in the ocean, and plants take carbon dioxide from the atmosphere through different photosynthetic processes in the surface ocean converting carbon into organic compounds to be restored in the ocean. In addition, phytoplankton forms the base of the ocean food chain, which has a very significant impact on marine biosphere and even human fishing. Such primary production through photosynthetic processes requires nutrients and light. Sunlight is available in the top few hundred metres of the ocean (the photic zone) for much of the day. Thus, nutrient availability in the ocean becomes the most important limiting factor in ocean productivity.

Comparisons of global ocean productivity (e.g. chlorophyll concentration) and nutrient distribution (e.g. nitrate concentration) generally show a good correlation in the surface ocean (Fig. 1.1). The global distribution of ocean productivity shows clear patterns of low productivity in the ocean gyres and high productivity around upwelling zones (e.g. equatorial current) and coastal areas. It also shows some local patterns of high productivity in the low productivity zones (e.g. Gulf Stream rings in the north-west Atlantic and island effects in the Southern Ocean). Thus, early studies of ocean productivity have traditionally focused on investigating the source, fluxes and uptake of carbon, nitrogen, phosphorus and silicon, the so-called macronutrients, in the oceans (Dugdale and Goering, 1967). They have found that the major sources of these macronutrients are enriched around coastal regions, where coastal upwelling forces nutrient-rich cold deep water to the surface.

Over the past two decades, however, macronutrients have come no longer to be considered as the only limiting factor in ocean productivity in the surface ocean. Many studies have shown that some regions have high levels of nutrients but low chlorophyll (HNLC), for example, in the Southern Ocean, sub-Arctic and the equatorial Pacific (Fig. 1.1) (Barber and Chavez, 1991; Minas et al., 1986). Thus, micronutrients, nutrients required by living things throughout their life in small quantities (e.g. Mn, Fe, Co, Ni, Cu, Zn and Cd), also need to be considered in ocean productivity. These elements are

important as cofactors in enzymes and as structural elements in proteins, although most of their biochemical functions are still not completely understood (Morel and Price, 2003).

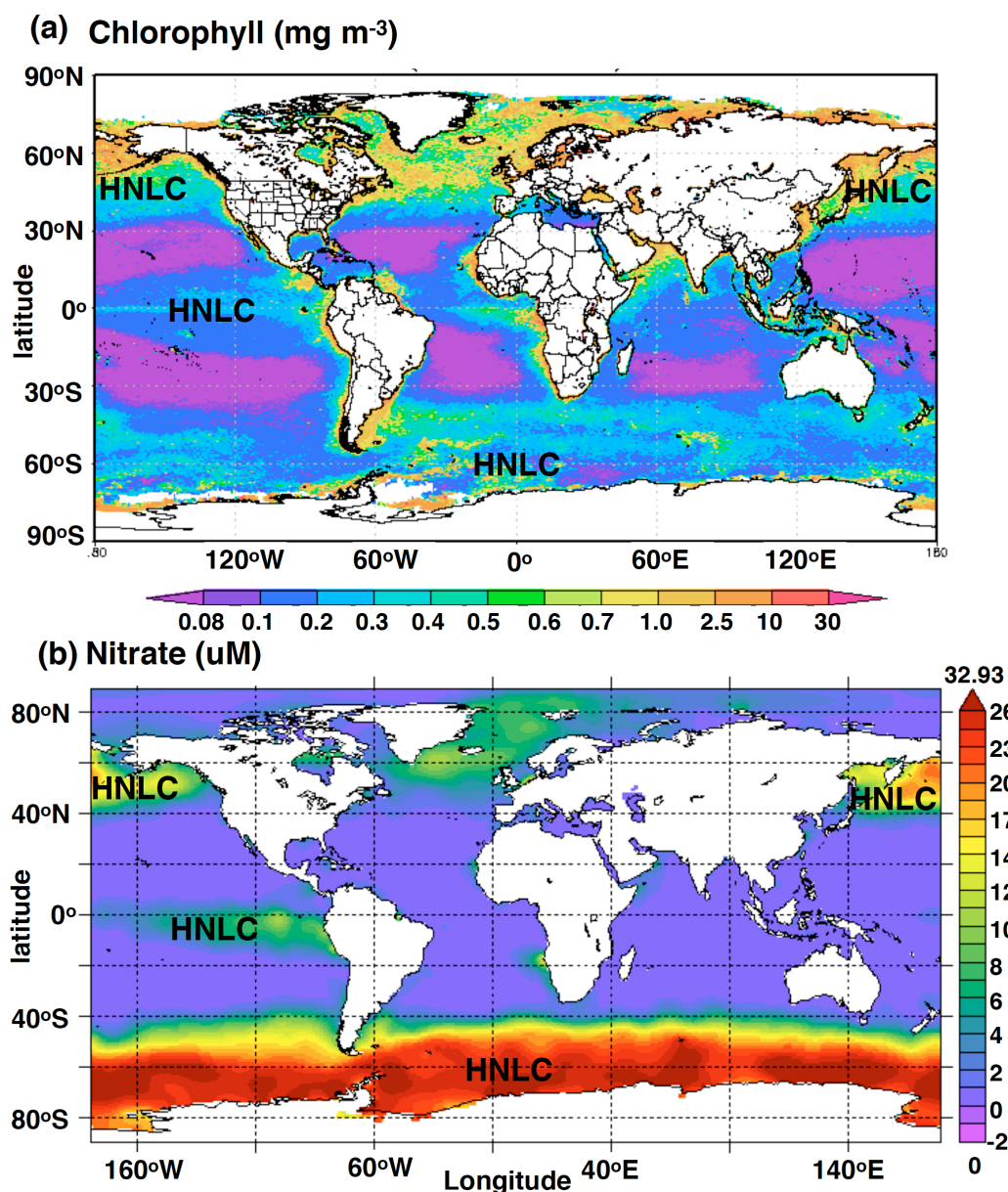


Figure 1.1 Schematic diagrams of (a) ocean productivity (chlorophyll) and (b) nutrient (nitrate) in the oceans. In most areas, ocean productivity is generally limited by light, temperature and macronutrient inputs to the oceans. In some regions, however, there have high nutrient concentrations but low chlorophyll values, which are the so-called HNLC regions (e.g. equatorial Pacific Ocean, subarctic Pacific Ocean and the Southern Ocean). In these regions, ocean productivity should also be limited by other factors (e.g. micronutrients), most of which have not been well studied. The average nitrate data are from the World Ocean Atlas 2001 (January-December 2001) and the average chlorophyll data are from the SeaWiFS satellite (January-December 2001).

Iron is one of the most important micronutrients in marine productivity. The iron hypothesis was first proposed by Martin in the late 1980s (Martin et al., 1994; Martin and Fitzwater, 1988). Dissolved

iron concentrations are very low in those HNLC regions (approximately 0.3 – 0.4 nM in the Southern Ocean). In Martin's incubation experiment, phytoplankton growth is found to increase in HNLC waters on adding iron. To test the hypothesis on a large scale, Fe addition experiments have been carried out by adding iron directly to the HNLC regions (Boyd et al., 2007). However, the amount of carbon export by ocean iron fertilization shows huge uncertainty (Buesseler et al., 2008). Additionally, this method only results in very little removal of carbon dioxide from the atmosphere, compared to the rapid global increases. Thus, research directions have changed to focus on understanding natural oceanic iron inputs and carbon biogeochemistry in the oceans (e.g. GEOTRACES programme).

1.2 Micronutrient inputs to the oceans

Atmospheric inputs, continental runoff, sediments and hydrothermal activity are considered to be the four major sources providing trace elements and micronutrients to the oceans. Ocean mixing, biological activity, particle scavenging and remineralisation play important roles in the internal chemical cycles within the ocean. To understand the controls on life in the ocean, chemical inputs to the ocean need to be quantified first.

Table 1.1 Global iron fluxes to the ocean

Source	Flux (Tg year ⁻¹)
Fluvial particulate total iron	625 - 962
Fluvial dissolved iron	1.5
Glacial sediments	34 - 211
Atmospheric	16
Coastal erosion	8
Hydrothermal	14
Authigenic	5

From Jickells et al. (2005).

Iron inputs to the oceans have been more extensively studied than other micronutrients. Jickells et al. (Jickells et al., 2005) reviewed the global iron inputs to the oceans (Table 1.1); this review highlighted the importance of atmospheric dust to the oceanic iron input and marine biogeochemistry and hence to the feedback between climate change and dust production. In Fig 1.2, Jickells et al. illustrate the complex cycles relating how dust iron input drives marine productivity and then changes the global climate state. This also leads to a feedback between changing global temperature and

precipitation, which changes soil moisture, vegetation cover and the production of dust. All of these cycles are based on the assumption that atmospheric dust input is the major source of iron to the surface ocean.

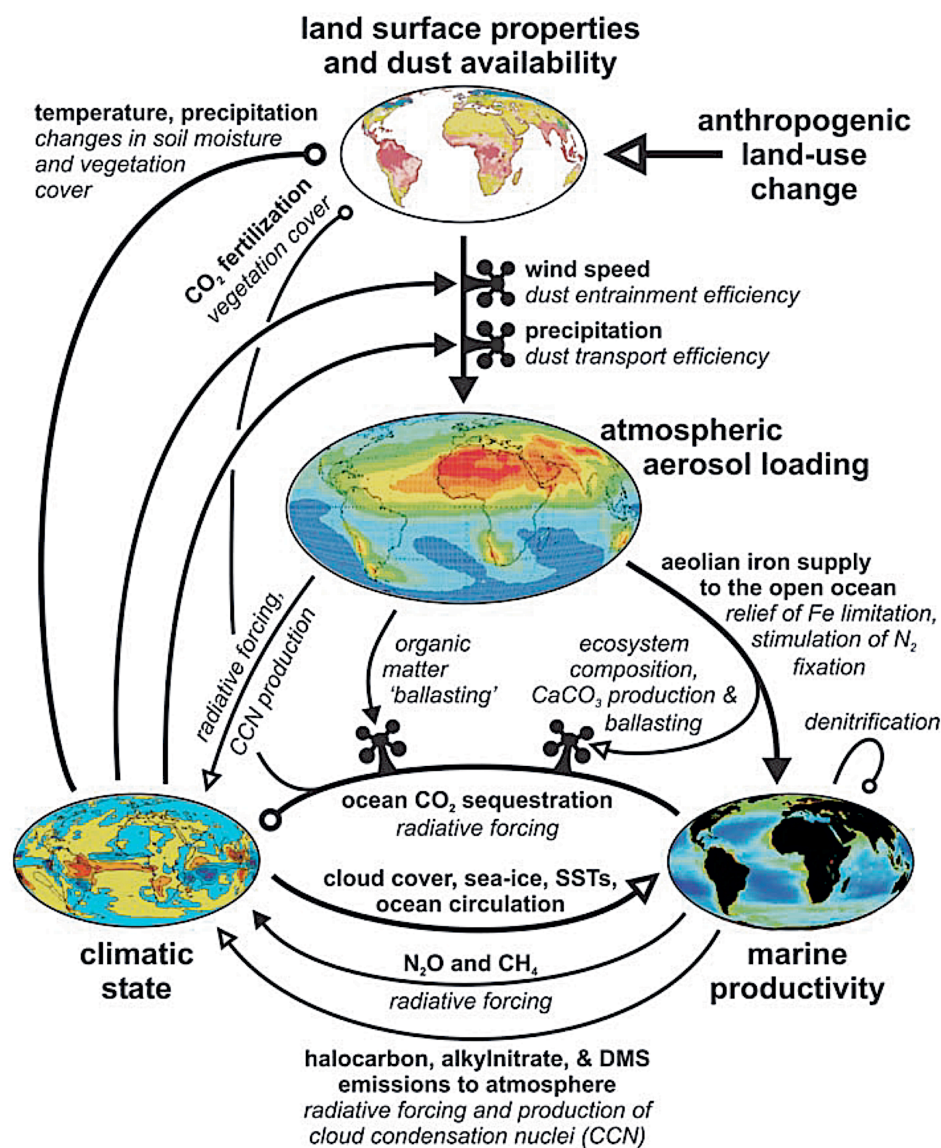


Figure 1.2 Global iron and dust connections. Atmospheric dust provides iron input to the oceans and then changes marine productivity and climate state. The change of climate state could also lead to a feedback on the dust production. From Jickells et al. (2005).

Dust models have been used to estimate atmospheric dust deposition and iron input to the oceans (Fig. 1.3). In low dust input regions, dust models can overestimate iron input by more than 50% (Mahowald et al., 2009) compared to the observed values, indicating that dust deposition models have huge uncertainties (Fig. 1.4). Improved geochemical tracers are thus required to quantify atmospheric dust deposition to the oceans. Dissolved aluminium has been commonly used for this purpose to study

dust input to the oceans (Measures et al., 2005; Measures et al., 2008; Measures and Vink, 2000; Vink and Measures, 2001). In Fig. 1.5 (Measures and Vink, 2000), the distribution of dissolved aluminium concentrations is generally consistent with a modelled global dust deposition in the oceans (Duce et al., 1991). This method assumes that the solubility of Al from dust ranges from 3 to 5% and that there is a constant residence time of 5 years in the mixed layer. However, one of the potential problems is assuming a constant Al residence time (5 years) in the surface ocean. In model results (Han et al., 2008), Al residence time can vary from months to 73 years in the surface ocean (Fig. 1.6). Thus, a better constraint for residence times of geochemical tracers is required. Instead of using Al as a dust proxy, Th isotopes have been investigated in this thesis as an improved geochemical tracer for dust input to the oceans. The combination of ^{232}Th and ^{230}Th (or ^{234}Th) provides an assessment of Th removal rates and residence time in the surface ocean.

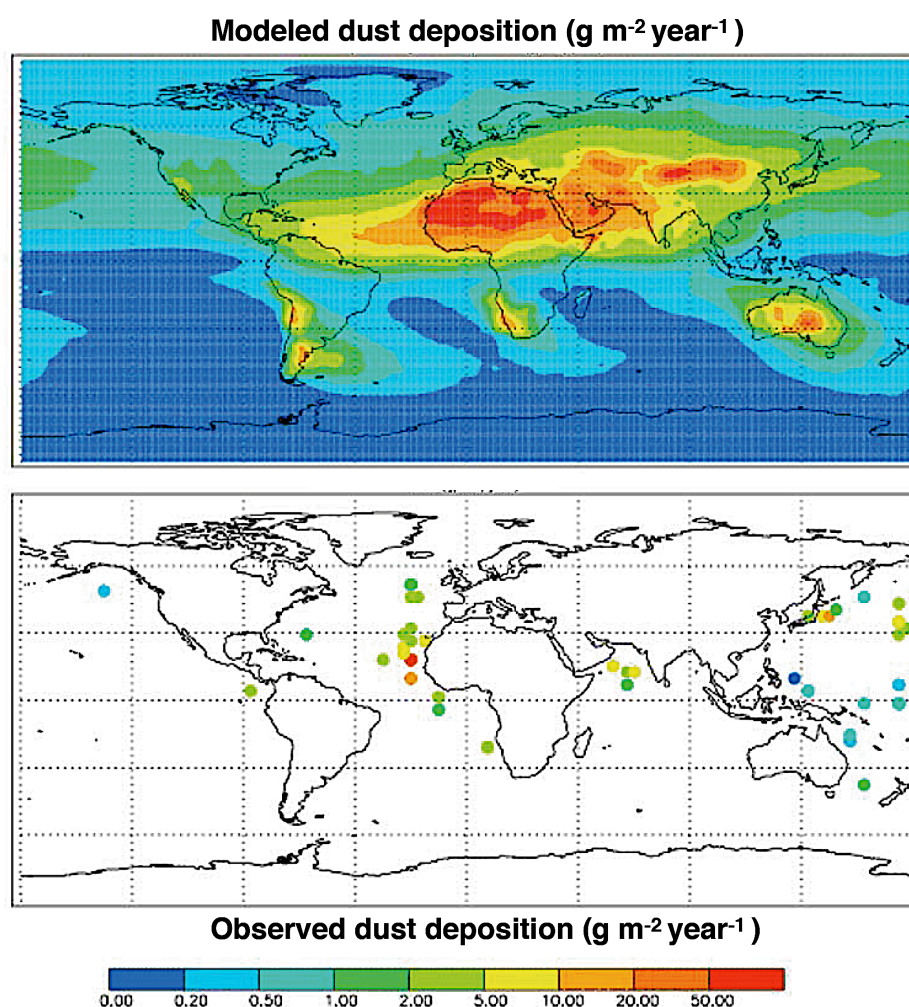


Figure 1.3 Comparison of (a) dust deposition models (Luo et al., 2003; Ginoux et al., 2004; Tegen et al., 2004) and (b) sediment trap in situ observation data (Kohfeld and Harrison, 2001). From Mahowald et al. (2005).

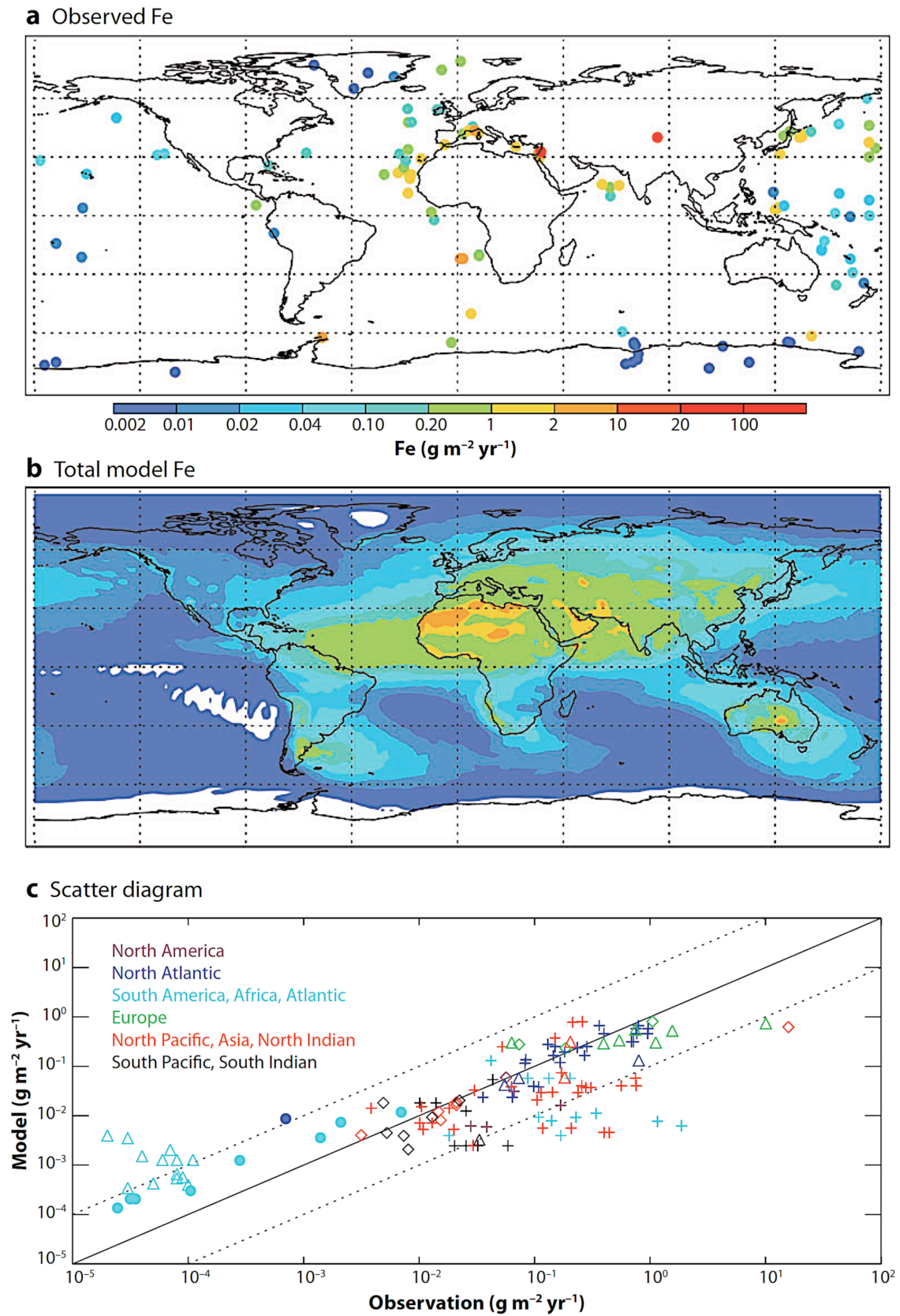


Figure 1.4 Global distribution of dust iron input. Dust deposition of iron input in (a) the observations and (b) a dust model. (c) Scatter diagram of iron deposition between modeled and observed data. From Mahowald et al. (2009).

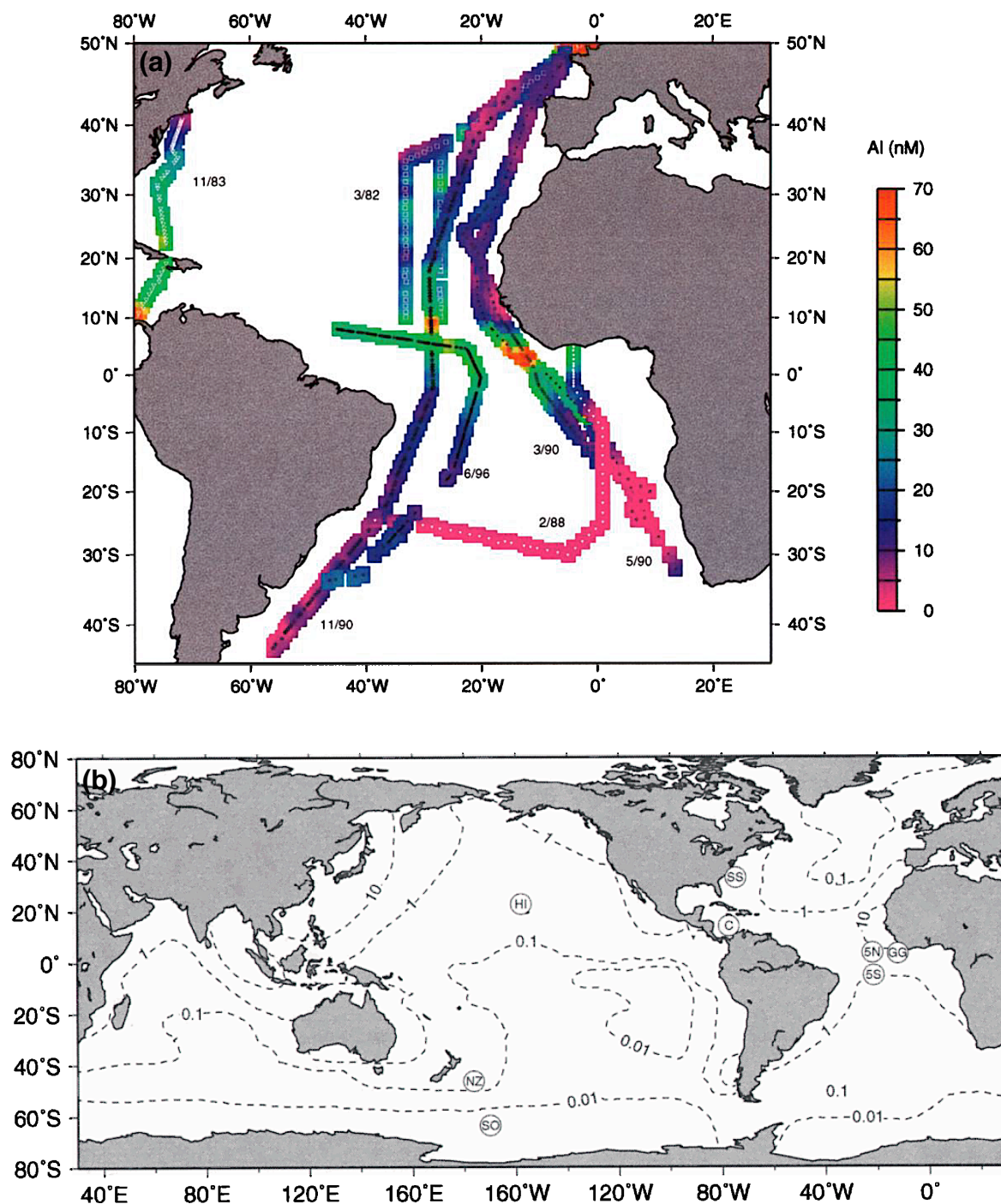


Figure 1.5 Comparison of (a) surface seawater dissolved aluminium (Measures and Vink, 2000) and (b) dust deposition model (Duce et al., 1991). The unit of dust deposition is $\text{g m}^{-2} \text{yr}^{-1}$. From Measures and Vink (2000).

Dust is not the only source of iron to the oceans. The global dust iron flux is, however, only 1-2% of the total global iron fluxes (Table 1.1). Knowledge of multiple iron sources and iron cycles is required to fully understand the correlation between iron inputs and marine productivity in the oceans. Boyd and Ellwood (Boyd and Ellwood, 2010) reviewed the biogeochemical iron cycle in the oceans.

They emphasised the significance of recycled iron and multiple iron sources to the oceans. For example, in the Southern Ocean, iron can come from dust, shelf sediments, icebergs and upwelling from below. However, the balance between these iron fluxes is not clear and thus requires further investigation.

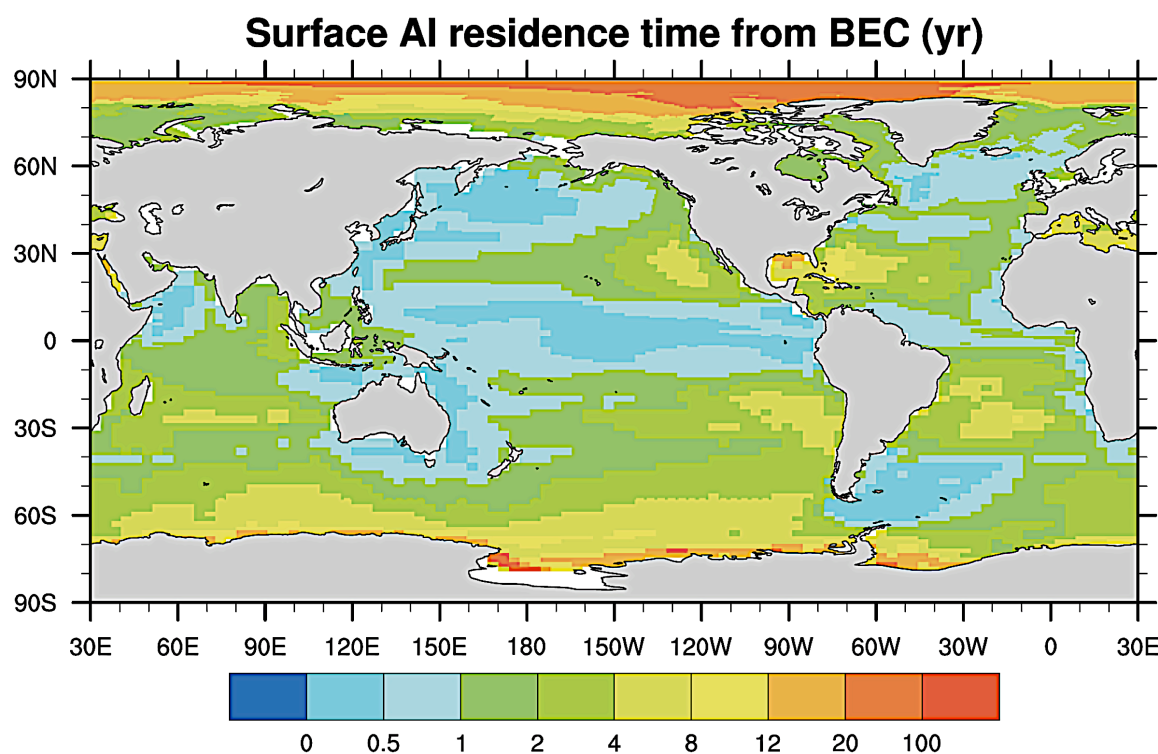


Figure 1.6 Modeled aluminum residence time in surface ocean. From Han et al. (2008).

Continental shelf and slope marine sediments also both play important roles in supplying micronutrients to the ocean (Hutchins et al., 1998; Johnson et al., 1999). The benthic iron fluxes from the continental shelf sediments can be determined from dissolved pore-water concentration gradients (Shaw et al., 1990) or direct measurements using in situ benthic chambers (Elrod et al., 2004; Severmann et al., 2010). Iron fluxes from continental shelf sediments to the open ocean have been estimated by radium-derived ocean mixing rates (Charette et al., 2007; Dulaiova et al., 2009). As Ra has a similar source from shelf sediments as iron, but not from atmospheric dust, Ra can be used as a tracer for tracing iron from the continental shelf. However, Ra comes not only from sediments, but also from riverine and submarine groundwater discharge (SGD) to the oceans (Moore et al., 2008). Therefore, precise estimates of Ra sources and fluxes to the oceans are highly required.

This thesis aims to develop and apply new tools, using U-Th series nuclides, to contribute to our understanding of processes in the ocean, particularly dust inputs and ocean mixing rates. Development of these tools is motivated primarily by the need to improve understanding of micronutrient cycles in the ocean, although the relevance of the results extend more widely to other chemical cycles and ocean processes. In this thesis, the applications have been involved in several marine study programmes (e.g. GEOTRACES and AMT (Atlantic Meridional Transect)). The results are compared with data from early programmes (e.g. GEOSECS (Geochemical Ocean Sections Study) and TTO (Transient Tracers in the Oceans) from the 1960s to the 1980s).

1.3 U-Th series isotopes in the oceans

U-Th series chemistry has been extensively applied to study ocean processes in a wide range of areas from paleoceanography to modern oceanography. The U-Th decay series have three naturally occurring radioactive decay chains starting from ^{238}U , ^{235}U and ^{232}Th and ending up with stable lead isotopes (Fig. 1.7). The equations for radioactive decay can be written as follows:

$$\frac{dN_1}{dt} = -\lambda_1 N_1 \quad (1.1)$$

$$\frac{dN_2}{dt} = -\lambda_1 N_1 + \lambda_2 N_2 \quad (1.2)$$

where N_1 is the number of atoms of the parent nuclide and N_2 is the number of atoms of the daughter nuclide; t is time and λ is the decay constant of the parent nuclide ($\lambda = \ln 2 / T_{1/2}$, $T_{1/2}$ is the half-life). In general, these are used for the activity of a nuclide instead of a number of atoms when dealing with radioactive nuclides. The activity (A) of a number of atoms of a nuclide is the total rate of decay ($A = \lambda N$) and the units are disintegrations per minute (d.p.m.). Solving the two equations above for the first two nuclides in a decay chain gives (Bateman, 1910):

$$N_1 = N_1^0 e^{-\lambda_1 t} \quad (1.3)$$

$$N_2 = \frac{\lambda_1}{\lambda_2 - \lambda_1} N_1^0 (e^{-\lambda_1 t} - e^{-\lambda_2 t}) + N_2^0 e^{-\lambda_2 t} \quad (1.4)$$

If it is assumed that there is no initial N_2 , then Eqn. 1.4 can be simplified to:

$$N_2 = \frac{\lambda_1}{\lambda_2 - \lambda_1} N_1^0 (e^{-\lambda_1 t} - e^{-\lambda_2 t}) \quad (1.5)$$

Normally, each decay series starts with a long-lived parent; thus, $\lambda_1 \ll \lambda_2$ and $\exp(-\lambda_2 t) \approx 0$ as t increases. In addition, if $t \ll T_{1/2}$, the decay rate of N_1 becomes insignificant. In this case, Eqn. 1.5 can be further simplified to:

$$N_2 \approx \frac{\lambda_1}{\lambda_2 - \lambda_1} N_1^0 e^{-\lambda_1 t} \approx \frac{\lambda_1}{\lambda_2 - \lambda_1} N_1 \quad (1.6)$$

Since $\lambda_1 \ll \lambda_2$, $\lambda_2 - \lambda_1 \approx \lambda_2$, further simplification of Eqn. 1.6 can be made:

$$N_2 \approx \frac{\lambda_1}{\lambda_2} N_1 \quad (1.7)$$

$$N_2 \lambda_2 \approx \lambda_1 N_1 \quad (1.8)$$

When the activities of all of the nuclides in the decay chain are the same, this becomes the so-called secular equilibrium. Thus, the activity ratio of a parent and a daughter is equal to 1 in secular equilibrium; U-Th series isotopes tend towards secular equilibrium with time. The disequilibrium of U-Th series isotopes can be used to assess ocean processes at different timescales. To make the level and direction of disequilibrium clear, units would be used in activities and activity ratios in this thesis, except where otherwise stated.

In the U-Th series decay chains, varied geochemical properties of the elements (e.g. U, Th, Pa, Ra Ac and Rn) enable investigations of geological process in different oceanic environments to be made (e.g. in seawater, suspended particles and sediments). U-Th series nuclides have a wide range of half-lives, which permits applications in different processes at time scales from days to 10^5 years. The distribution of these nuclides in the oceans is controlled by their input and output mechanisms. Studies of these isotopes in dissolved and particulate phases could provide important information about particle dynamic process, ocean mixing, chemical fluxes and biological reactivity in the oceans (Cochran, 1992; Rutgers van der Loeff and Geibert, 2008).

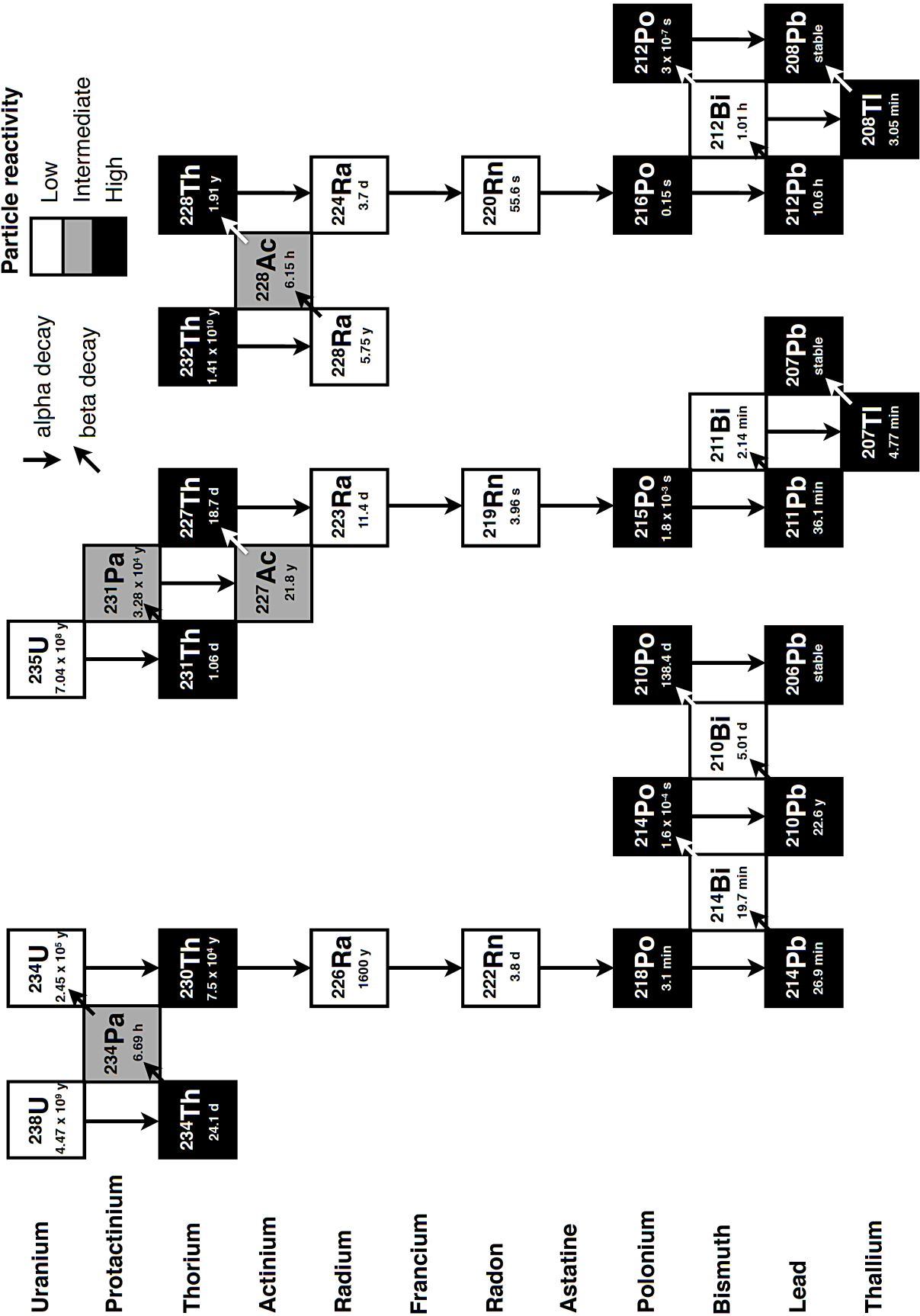


Figure 1.7 Schematic of the U and Th decay chains.

1.3.1 Distribution of U-Th series isotopes in the oceans

This thesis is focused on the applications of Th and Ra isotopes to study mixing and chemical fluxes in the oceans. In the following section, some relevant details about the distribution, input and removal processes of Th and Ra isotopes and their parents, U isotopes, in the oceans are summarised.

Uranium isotopes

Uranium has three isotopes in natural marine environments: ^{238}U , ^{235}U and ^{234}U . U is soluble and stabilized as $\text{UO}_2(\text{CO}_3)_3^{4-}$ in seawater. The residence time of U is $2 \times 10^5 - 4 \times 10^5$ years in the oceans (Palmer and Edmond, 1993). U is also very sensitive to anoxic and oxic conditions. Under anoxic conditions, the soluble U (VI) is converted to insoluble U (IV) and removed from seawater. The distribution of ^{238}U follows a relationship with salinity in seawater (Chen et al., 1986). The average seawater U concentration ranges from 3.162 to 3.231 ng g^{-1} , normalised to salinity of 35 ‰, and it is uniformly distributed in the oceans (Chen et al., 1986) (Fig. 1.8). U-234 is produced by ^{238}U radioactive decay. The activity ratio of seawater $^{234}\text{U}/^{238}\text{U}$ in the open ocean shows a mean value of 1.146 (Robinson et al, 2004) which is higher than secular equilibrium because of sediment α -recoil that preferentially releases more ^{234}U from minerals than ^{238}U during chemical weathering. The variation of $^{234}\text{U}/^{238}\text{U}$ in seawater is a response to different riverine inputs due to changes in continental weathering (Henderson, 2002).

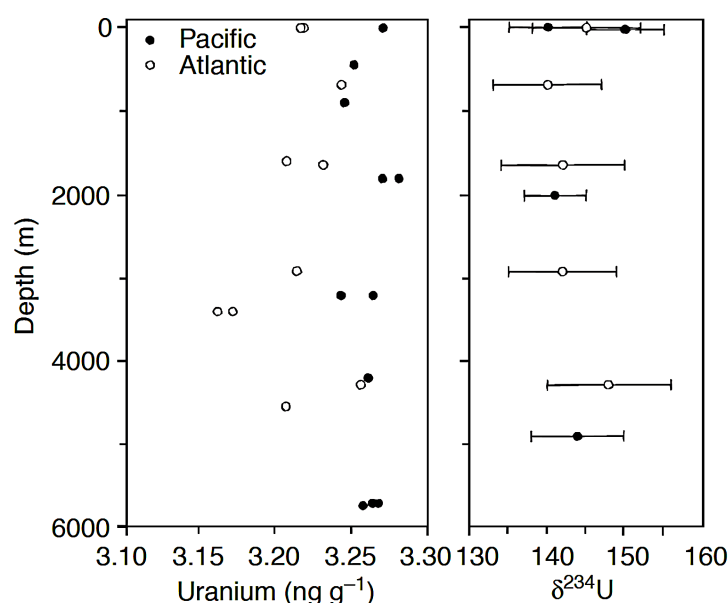


Figure 1.8 Seawater ^{238}U concentration and $\delta^{234}\text{U}$ profiles in the Pacific and the Atlantic Ocean. Data from Chen et al. (1986). Figures from Krishnaswami (2001).

Thorium isotopes

Thorium is more insoluble than uranium and it is particle reactive in seawater. It generally exists as a neutral hydroxide species in seawater. Th-232 enters the oceans mainly from detrital inputs (both atmospheric and fluvial inputs). Most ^{232}Th remains on particles and sinks down to the deep sea. Seawater ^{232}Th concentrations are only around a few tens of picograms per litre in the open ocean seawater (Chen et al., 1986). In Fig. 1.9, a figure of seawater ^{232}Th concentrations against distance from continents shows a trend of higher activities in coastal water in the pre-1980 data (Huh et al., 1989). However, this trend is not shown in the post-1980 data. Huh et al. (Huh et al., 1989) suggest that the difference is due to sampling and analytical artefacts in the old data. The post-1980 data indicate that atmospheric and fluvial inputs are both important in supplying ^{232}Th to the oceans. Seawater ^{232}Th concentration depth profiles in the open Atlantic and Pacific Oceans both show a higher concentration of ^{232}Th in the surface water (Chen et al., 1986; Roy-Barman et al., 1996) (Fig. 1.10), which suggests that ^{232}Th in the surface open ocean is highly associated with atmospheric dust inputs.

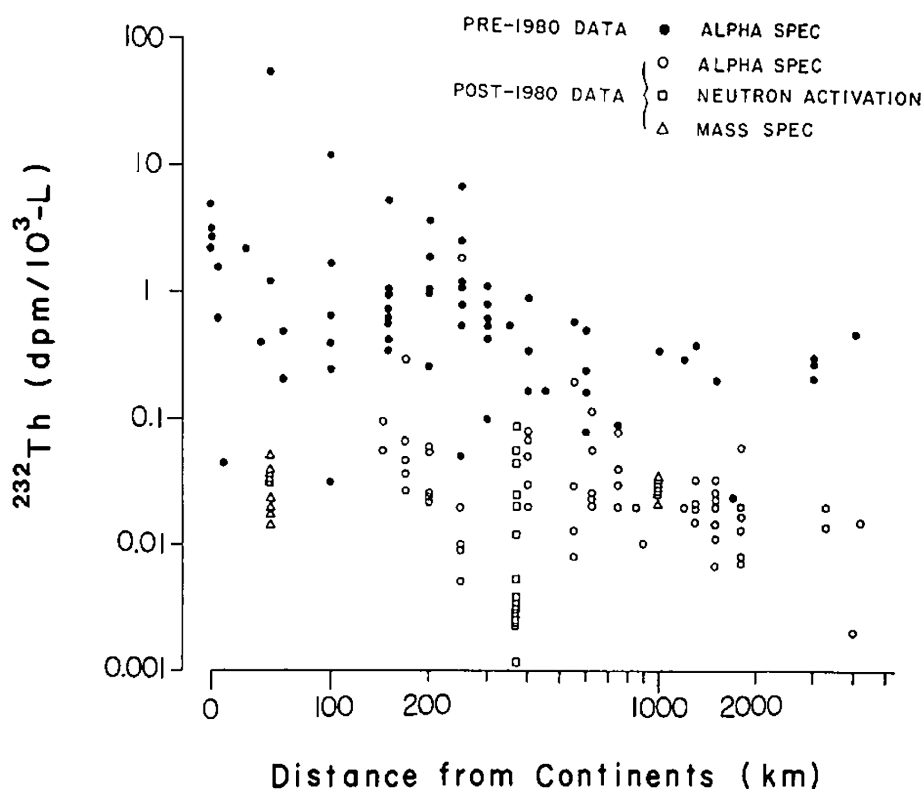


Figure 1.9 Seawater ^{232}Th concentration against distance from continents. From Huh (1989).

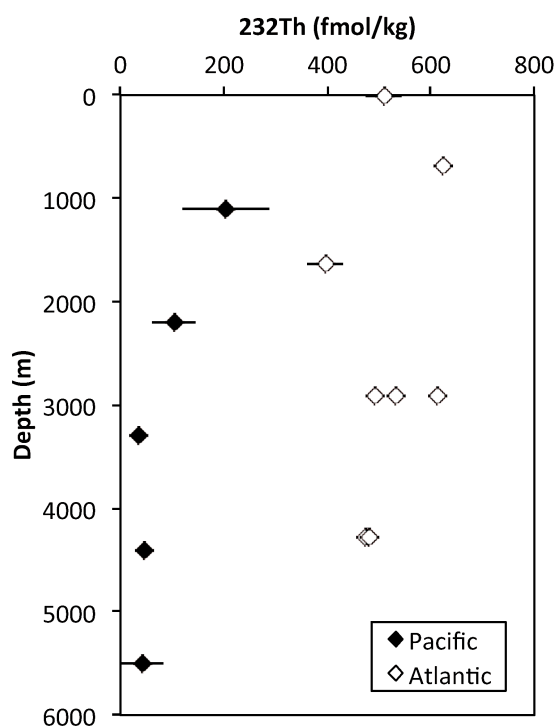


Figure 1.10 Seawater ^{232}Th concentration (particulate + dissolved) profiles in the Pacific and the Atlantic Ocean. Data for North West Pacific from Nozaki et al. (1987) and for North Atlantic from Chen et al. (1986).

Seawater ^{234}Th , ^{230}Th and ^{228}Th primarily occur from in situ decay of uranium and radium isotopes in the oceans (Fig. 1.7). Seawater ^{234}Th , ^{230}Th and ^{228}Th concentrations are determined by their production rates, radioactive decay and particulate scavenging in the oceans (Nozaki et al., 1981; Sarin et al., 1996) (Fig. 1.11). The depth profile of dissolved seawater ^{230}Th in the Pacific Ocean shows a linear increase with depth. Particle scavenging and reversible exchange of Th between suspended particles and soluble phases have been used to explain the distribution of ^{230}Th in the water column (Nozaki et al., 1981). In the surface water, activities of ^{234}Th , ^{230}Th and ^{228}Th show significant depletion relative to their parents, ^{238}U , ^{234}U and ^{228}Ra respectively, due to particle scavenging. However, ^{234}Th and ^{228}Th return to secular equilibrium with their parents a few hundred metres below the surface ocean due to their short half-lives and the lower removal rate at greater depth (Fig. 1.11b and c). The distribution of ^{228}Th is then similar to its parent, ^{228}Ra , which shows a high concentration in both the surface and deep seawater, and a low concentration in the intermediate seawater (Cochran et al., 2000). Overall, studies of deficiency of Th isotopes (^{234}Th , ^{230}Th and ^{228}Th) relative to their parents (^{238}U , ^{234}U

and ^{228}Ra) allow the quantification of particulate removal, remineralisation and Th residence time in the oceans (Buesseler et al., 1992; Buesseler et al., 2006; Cochran et al., 2000; Savoye et al., 2006).

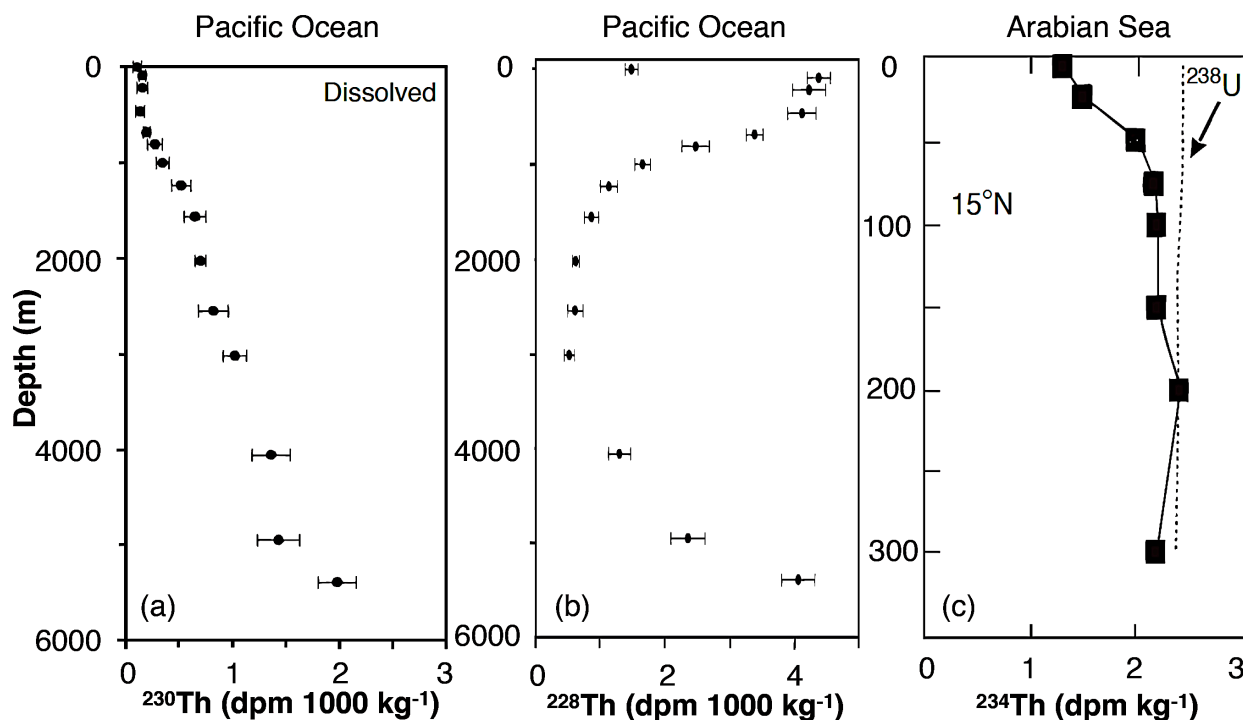


Figure 1.11 Seawater ^{230}Th , ^{228}Th and ^{234}Th concentration (dissolved) profiles in the Pacific Ocean (^{230}Th and ^{228}Th) and the Arabian Sea (^{234}Th). Data for ^{230}Th and ^{228}Th from Nozaki et al. (1981) and for ^{234}Th from Sarin et al. (1996). Figures adapted from Krishnaswami (2001).

Radium isotopes

Radium isotopes, ^{228}Ra , ^{226}Ra , ^{224}Ra , and ^{223}Ra , enter the oceans mainly through sediment diffusion, river and groundwater discharges. Ra is relatively soluble and found as a divalent cation (Ra^{2+}) in seawater. The depth profiles of ^{226}Ra concentration ($T_{1/2} = 1600$ years) in the oceans show an increase with depth (Fig. 1.12). The distribution of ^{226}Ra concentration in the oceans is derived from sediment diffusion, particle scavenging, biological cycling, ocean mixing and radioactive decay. The average ^{226}Ra concentration is ~ 0.13 picograms per litre (28.8 dpm 100L^{-1}) in seawater (Broecker et al., 1976; Chung and Craig, 1980). In deep seawater, the Pacific Ocean shows higher ^{226}Ra concentration than the Atlantic Ocean because waters in the deep Pacific Ocean are “older” and have had longer to accumulate ^{226}Ra from underlying sediment, and also because the ^{226}Ra fluxes from deep-sea sediments are thought to be higher in the low sedimentation-rate sediments of the Pacific (Cochran and Krishnaswami, 1980).

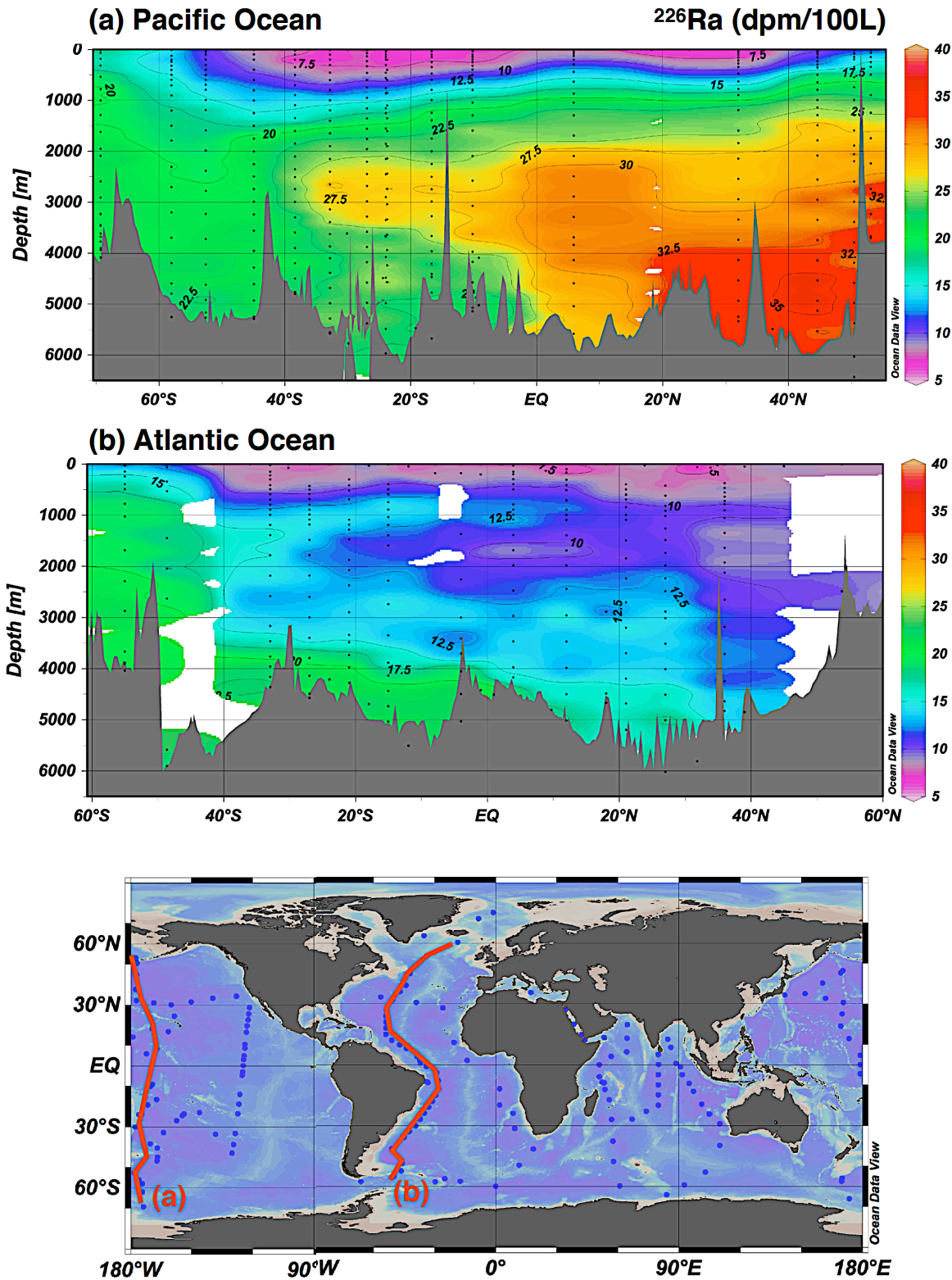


Figure 1.12 Vertical profiles of ^{226}Ra in the (a) Pacific and (b) Atlantic Oceans. Data from the GEOSECS ^{226}Ra dataset (Ostlund et al., (1987)) available at http://climotope.earth.ox.ac.uk/data_compilations. This figure was produced for this thesis.

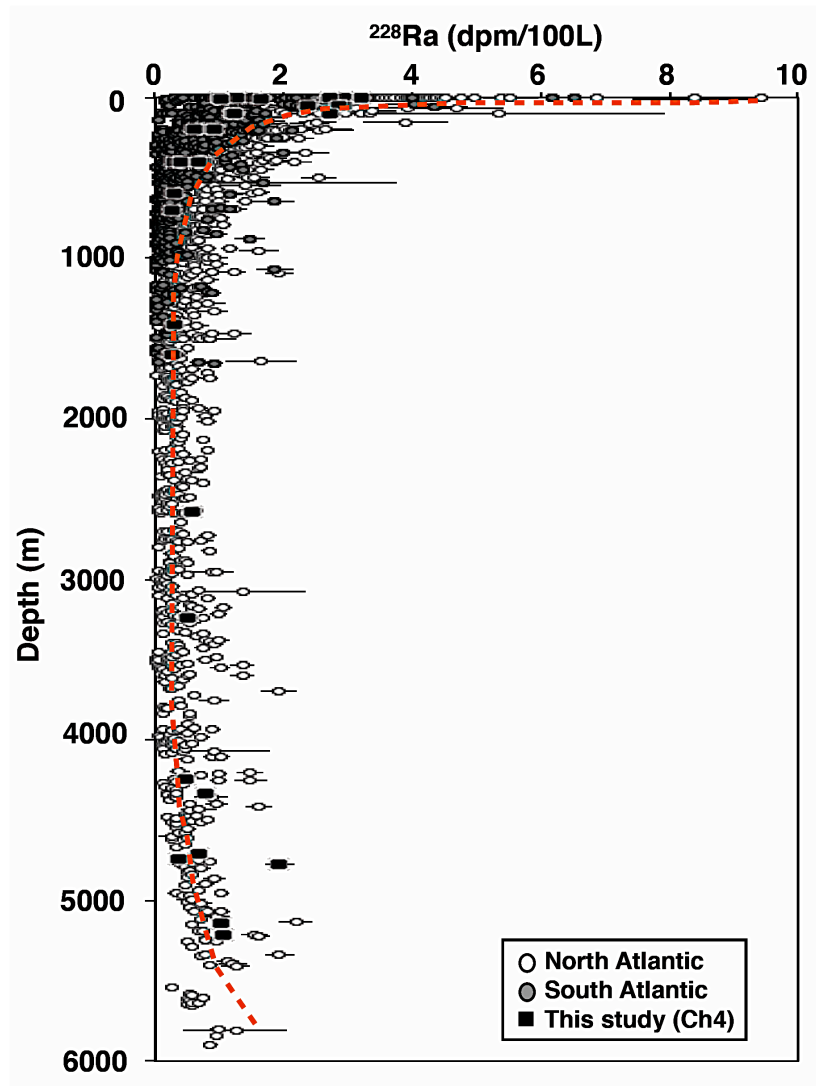


Figure 1.13 Vertical profiles of ^{228}Ra in the Atlantic Ocean. The red line is the average distribution of ^{228}Ra in the water column. Data are from the TTO ^{228}Ra dataset (provides by Bob Key) and the results of chapter 4 in this thesis. This figure was produced for this thesis.

Ra-228 has a shorter half-life ($T_{1/2} = 5.75$ years) than ^{226}Ra . Ra-228 is always found significantly in excess in seawater over its parent, ^{232}Th . Ra-228 is produced by ^{232}Th decay in sediments and released from sediments into porewater and then into seawater. The vertical depth profiles of ^{228}Ra show higher concentrations in the upper and deep layers of the water column (Fig. 1.13), reflecting the fact that ^{228}Ra enters the oceans mainly from sediments on the continental shelves and deep-sea basins. The concentrations of seawater ^{228}Ra range from 0.00165 to 1.65 femtograms per litre (0.1 – 100 dpm 100L⁻¹). In the surface ocean, ^{228}Ra concentration is a function of distance from the coast, due to decay as horizontal mixing transports it offshore. In Fig. 1.14, ^{228}Ra concentration in the surface ocean shows a decreasing trend with the distance from the coast of California. The two different off-shore ^{228}Ra

mixing gradients represent two mixing coefficients, 4×10^5 and 4×10^7 $\text{cm}^2 \text{s}^{-1}$, showing the interrupted lateral mixing by the boundary current along the continental margins. Similar observations have been seen in the Kuroshio Current and Peru Current systems in previous studies (Knauss et al., 1978; Yamada and Nozaki, 1986).

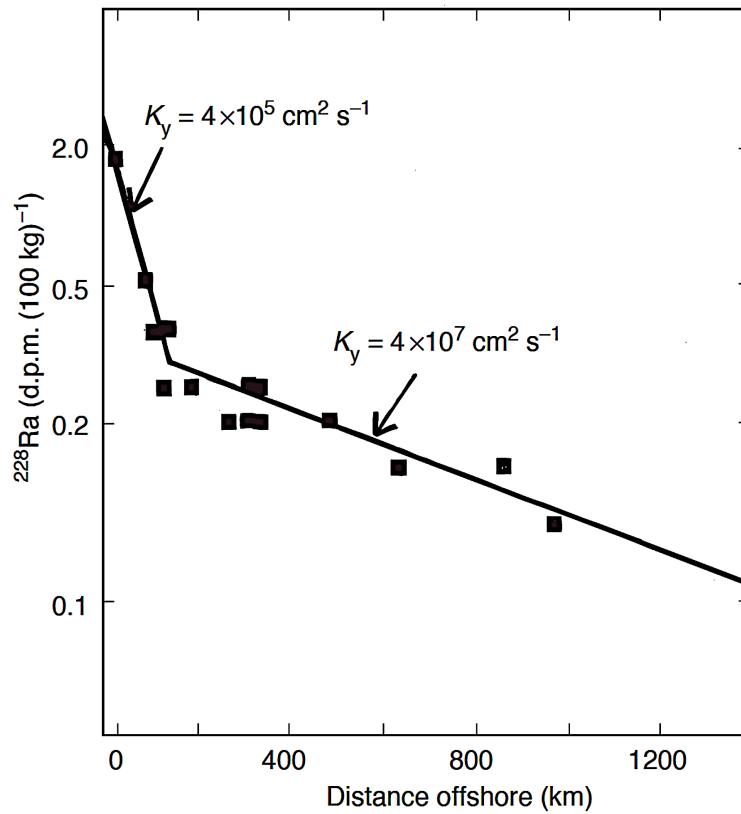


Figure 1.14 Surface seawater ^{228}Ra concentration as a function of distance from the California coast. K_y is the horizontal diffusion coefficient. Data from Knauss et al. (1978). Figure from Krishnaswami (2001).

The shorter-lived Ra isotopes, ^{224}Ra ($T_{1/2} = 3.66$ days) and ^{223}Ra ($T_{1/2} = 11.4$ days), also show an exponential decrease in surface water with distance from the coasts (Charette et al., 2007) (Fig. 1.15). Ra-224 and ^{223}Ra are released from sediments and river and groundwater discharges in the coastal areas and transported off-shore by horizontal ocean mixing (Moore, 2000). The short half-lives allow the estimates of short-term ocean mixing from few days to weeks. In the open ocean, ^{224}Ra and ^{223}Ra generally show secular equilibrium with their parents, ^{228}Th and ^{227}Ac respectively, due to their short half lives.

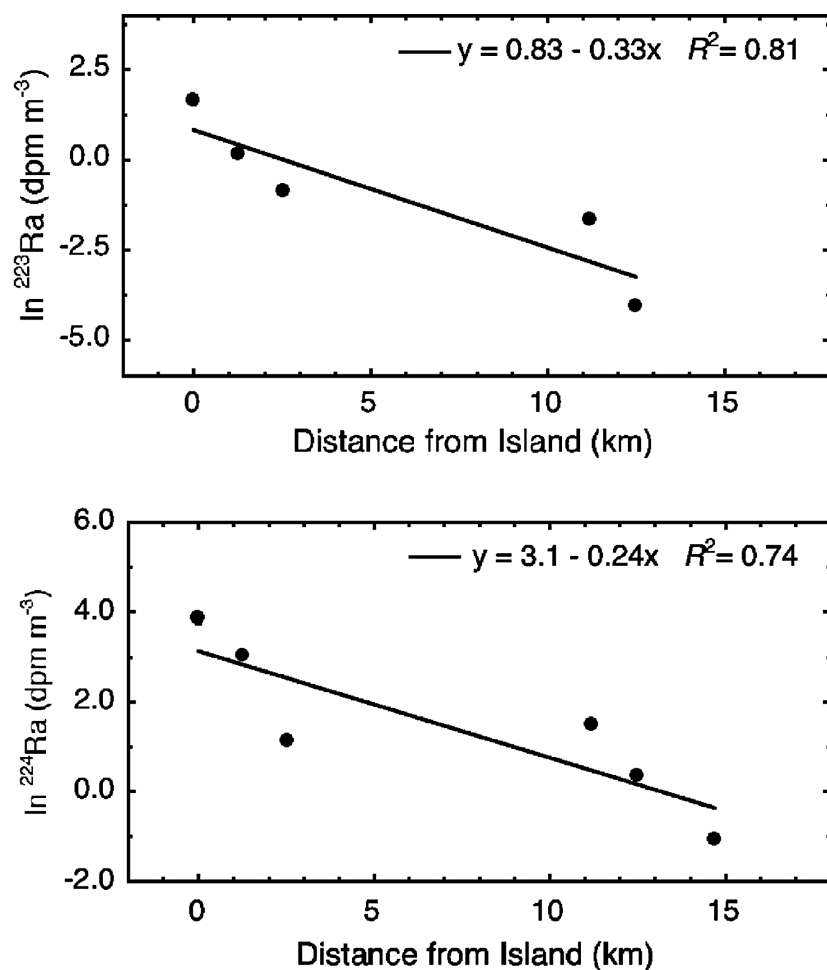


Figure 1.15 Off-island transects of ln (²²⁴Ra) and ln (²²³Ra) in the Southern Ocean. From Charette et al. (2007).

1.3.2 Input and removal of U-Th series isotopes in the oceans

There are several major inputs of uranium- and thorium-series isotopes to the oceans: rivers, groundwater discharges, marine sediments, atmospheric dust, hydrothermal input and in situ production of daughter isotopes in the oceans. In order to balance the inputs of uranium- and thorium-series isotopes in the oceans, there are also several removal mechanisms: radioactive decay, particle scavenging, oxide absorption, biological uptake and oceanic mixing. The ocean cycles of the U-Th series elements have been summarised previously in Cochran (1992), Cochran and Masqué (2003), Henderson and Anderson (2003), and Rutgers van der Loeff and Geibert (2008). The pathways and nuclide cycles of U, Th, and Ra isotopes in the oceans are illustrated in a schematic overview (Fig. 1.16).

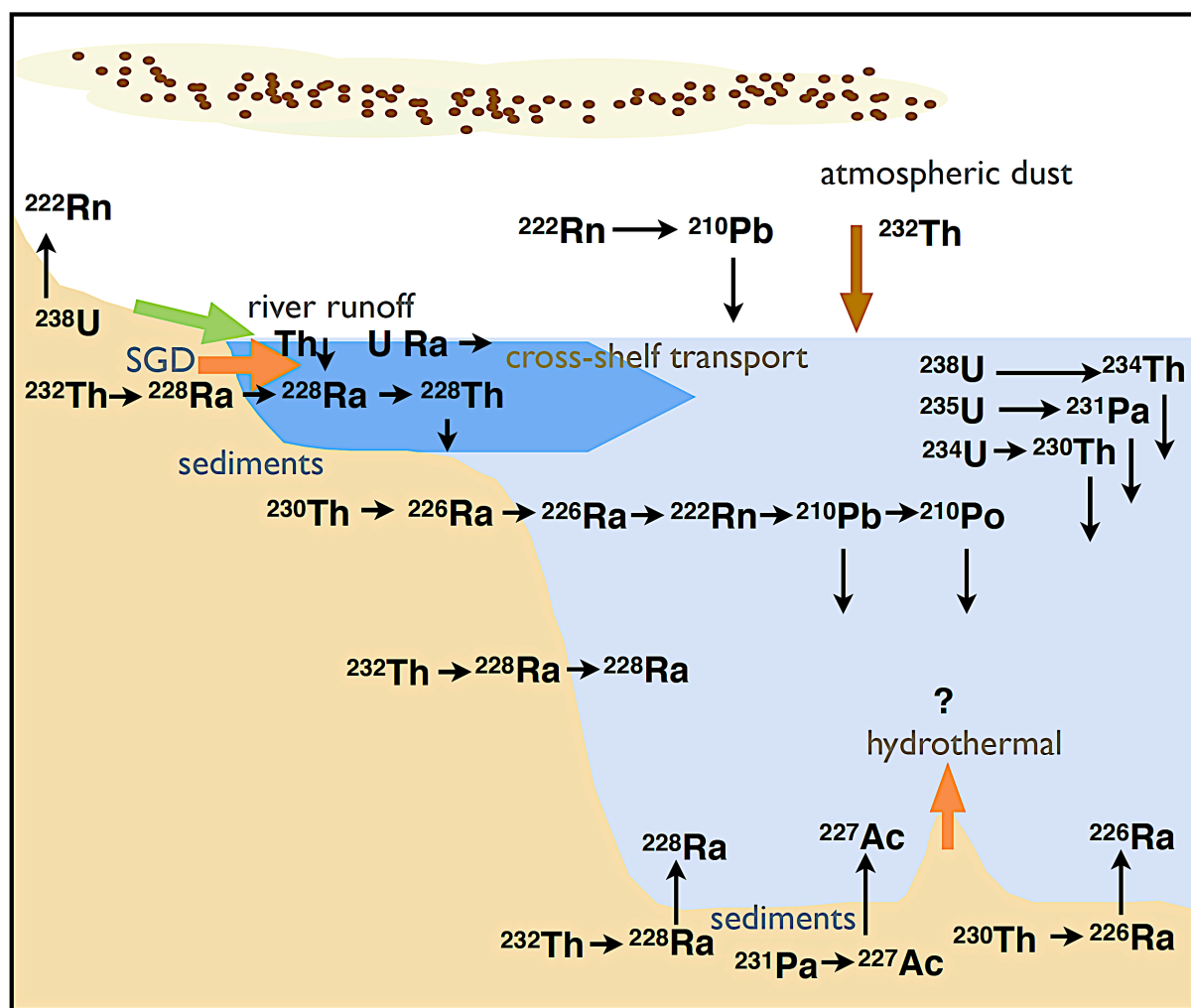


Figure 1.16 Schematic diagram of the U and Th decay series cycles in the oceans. The major sources of U and Th decay series nuclides to the oceans are atmospheric dust, continental inputs (SGD and river runoff), sediments, hydrothermal and authogenic inputs. Solid horizontal arrows represent radioactive decay and diffusion out of sediments. Solid vertical arrows represent scavenging or particle settling (downward) and elements released from sediments (upward). Adapted from Cochran (1992).

Uranium isotopes

A new assessment of oceanic uranium budget for the Holocene has been summarised in Dunk et al. (2002). Riverine input is the major U input to the oceans. The total riverine U flux is $1.0 (\pm 0.3) \times 10^{10}$ g yr⁻¹ (Palmer and Edmond, 1993). Groundwater also provides a significant input to the oceans of $0.2 (\pm 0.2) \times 10^{10}$ g yr⁻¹. Since groundwater U concentrations and isotopic compositions are highly variable (Porcelli and Swarzenski, 2003), the uncertainty in groundwater U flux is significantly high. In contrast, the U flux from atmospheric dust input is minor, $0.04 (\pm 0.02) \times 10^{10}$ g yr⁻¹. These U fluxes, discussed above, are enough to balance the total removal of U of $1.1 (\pm 0.3) \times 10^{10}$ g yr⁻¹ in the oceanic budget. Thus, new assessments of oceanic U budget challenge some previous assessments of the additional input

of ^{234}U ($6.2 \times 10^4 \text{ g } ^{234}\text{U yr}^{-1}$) from pelagic deep-sea sediments (Cochran and Krishnaswami, 1980; Ku et al., 1977). Furthermore, an additional source of U input ($0.14 \times 10^{10} \text{ g yr}^{-1}$, up to 15% of the global riverine flux) from the Amazon continental shelf sediments is still debatable (Mckee et al., 1987), because the behaviour of U in estuarine environments represents a large uncertainty (Porcelli et al., 1997).

U is removed from seawater by marine sediments and oceanic basalt alteration. Total U removal flux by sediments is $\sim 0.68 \times 10^{10} \text{ g yr}^{-1}$, which is about 60% of the total U input to the oceans (Barnes and Cochran, 1990). Biogenic carbonate (e.g. corals and molluscs) also plays an important role in U removal in the oceans of about $0.3 (\pm 0.1) \times 10^{10} \text{ g yr}^{-1}$ (Dunk et al., 2002). Basalt alteration U uptake is $0.14 (\pm 0.08) \times 10^{10} \text{ g yr}^{-1}$ (Dunk et al., 2002; Henderson and Anderson, 2003). Based on the U budget and the seawater U concentration, U residence time is about $4 \times 10^5 \text{ yr}$ in the ocean (Henderson and Anderson, 2003).

Thorium isotopes

The only input of ^{232}Th is from detrital materials. The total detrital flux of ^{232}Th from both atmospheric and fluvial inputs is $\sim 1150 \text{ } \mu\text{g m}^{-2} \text{ yr}^{-1}$ to the global ocean (Robinson et al., 2008), based on the globally averaged detrital material input to the oceans, $\sim 32 \times 10^{15} \text{ g yr}^{-1}$ (Syvitski et al., 2003), and the average detrital ^{232}Th concentration of $\sim 13 \text{ } \mu\text{g g}^{-1}$ (Taylor and McLennan, 1985). As the atmospheric input is about 32 times lower than the total detrital inputs (Syvitski et al., 2003), the atmospheric ^{232}Th input is $\sim 36 \text{ } \mu\text{g m}^{-2} \text{ yr}^{-1}$ to the global ocean. Deep-sea sediments also provide ^{232}Th to the deep ocean, as indicated by observations of increased ^{232}Th concentrations near the sea floor (Nozaki and Horibe, 1983). However, the flux of ^{232}Th from deep-sea sediments is not well constrained.

Th-230 is produced in situ from ^{234}U decay in seawater, this being by far the major input of ^{230}Th to the oceans. The production rate of ^{230}Th is $0.57 \text{ fg L}^{-1} \text{ yr}^{-1}$ (given $\lambda_{234} = 2.8263 \times 10^{-6} \text{ yr}^{-1}$; seawater $\delta^{234}\text{U}$ of 146.6; and ^{238}U concentration of 3.33 ng g^{-1} (Robinson et al., 2004)). Assuming that total volume of the earth's ocean to be $1.347 \times 10^9 \text{ km}^3$ (Garrison, 2005), the total ^{230}Th input from seawater ^{234}U decay is $\sim 7.68 \times 10^5 \text{ g yr}^{-1}$. In contrast, expected detrital ^{230}Th input is $\sim 0.16 \times 10^4 \text{ g yr}^{-1}$, based on the total detrital ^{232}Th input of $\sim 0.42 \times 10^9 \text{ g}$ and a lithogenic material $^{230}\text{Th}/^{232}\text{Th}$ ratio of $\sim 4.0 \times$

10^{-6} mol/mol (Roy-Barman et al., 2009), which is only 0.2% of the ^{230}Th input from seawater ^{234}U production. ^{234}Th and ^{228}Th are also produced *in situ* from ^{238}U and ^{228}Ra decay respectively in seawater.

Th isotopes are particle-reactive and removed from seawater by particle scavenging and radioactive decay. The distribution of ^{230}Th in the water column shows a linear increase with depth (Fig. 1.11), which is explained by reversible particle scavenging and sorption equilibrium in the oceans (Bacon and Anderson, 1982; Nozaki et al., 1987). The seawater $^{230}\text{Th}/^{234}\text{U}$ activity ratio is always in a state of disequilibrium, because the ocean Th residence time (0.5 – 20 years), controlled by Th removal, is much shorter than the half-life of ^{230}Th (7.5×10^4 years). For example, observed seawater $^{230}\text{Th}/^{234}\text{U}$ activity ratios range from 0.2 – 2 ($\times 10^{-4}$) in the equatorial Pacific (Luo et al., 1995), which is about 10^4 – 10^5 times lower than the secular equilibrium ratio of 1. For $^{234}\text{Th}/^{238}\text{U}$ and $^{228}\text{Th}/^{228}\text{Ra}$, particle scavenging quickly removes seawater ^{234}Th and ^{228}Th in the upper 100 – 200 m surface ocean (Fig. 1.11), which causes $^{234}\text{Th}/^{238}\text{U}$ and $^{228}\text{Th}/^{228}\text{Ra}$ activity ratios to be in disequilibrium in the surface layer. Thus, the U-Th series disequilibrium activity ratios can be used to assess particle removal flux in the surface ocean. However, due to the short half-lives of ^{234}Th (24.1 days) and ^{228}Th (1.91 years), the activity ratios of $^{234}\text{Th}/^{238}\text{U}$ and $^{228}\text{Th}/^{228}\text{Ra}$ return to secular equilibrium at a depth of a few hundred metres below the surface ocean.

Radium isotopes

Sediment is the major input for Ra isotopes into the oceans. Ra-226 and ^{228}Ra are produced from ^{230}Th and ^{232}Th respectively in sediments and then released into pore water and diffused into seawater. The estimated sedimentary flux of ^{226}Ra is $0.3 \sim 0.9 \text{ ng m}^{-2} \text{ yr}^{-1}$ (Cochran and Krishnaswami, 1980). For ^{228}Ra , the average sedimentary fluxes are $19 \text{ pg m}^{-2} \text{ yr}^{-1}$ from the continental shelf fine sediments, $0.4 \text{ pg m}^{-2} \text{ yr}^{-1}$ from the continental shelf coarse sediments, and $3 \text{ pg m}^{-2} \text{ yr}^{-1}$ from the continental slope sediments (Moore et al., 2008). Moore et al. (2008) summarised the major inputs of ^{228}Ra to the Atlantic Ocean from previous literature (Table 1.2). The overall sedimentary ^{228}Ra flux is about 37% of the total ^{228}Ra inputs to the surface ocean, although with large uncertainties.

Table 1.2 ^{228}Ra inputs to the surface Atlantic Ocean

Source	Flux (10^{23} atoms year $^{-1}$)
Sedimentary	
Shelf mud	1
Shelf sand	0.05
Slope	0.25
River	
Dissolved	0.03
Desorbed	0.22
Dust	0.03
SGD	1.9

From Moore et al. (2008).

Other Ra sources also contribute significant inputs of Ra to the oceans. Upwelling supplies $0.3 \text{ ng } ^{226}\text{Ra m}^{-2} \text{ yr}^{-1}$ to the surface ocean (Ku and Luo, 1994). Riverine input contributes less than 2% of the total ^{226}Ra inputs to the oceans and 7% of the total ^{228}Ra inputs to the surface ocean (Moore, 1967; Moore et al., 2008). The input of submarine groundwater discharge (SGD) has been evaluated in the surface Atlantic Ocean, contributing 90% of the total ^{226}Ra in the East coast of North America (Moore, 1996). In addition, $\approx 54\%$ ($\sim 72 \text{ g } ^{228}\text{Ra yr}^{-1}$) of the total ^{228}Ra in the surface Atlantic ocean is also thought to come from SGD (Moore et al., 2008). Compared to other sources, atmospheric Ra input is insignificant. Hydrothermal Ra input is poorly constrained. The short-lived Ra isotopes, ^{224}Ra and ^{223}Ra , are produced by decay from ^{228}Ra and ^{227}Ac respectively. Sedimentary, riverine and groundwater inputs are the three major sources of short-lived Ra isotopes in the coastal areas. However, their fluxes to the oceans have still not been quantified.

Radium is removed from seawater by particulate scavenging and burial mechanisms. The average particulate removal of ^{226}Ra is about 50% of the total removal of ^{226}Ra ($\sim 0.25 \text{ ng m}^{-2} \text{ yr}^{-1}$) (Ku and Luo, 1994; Moore and Dymond, 1991) and burial of ^{226}Ra is about 8% of the total ^{226}Ra removal ($\sim 0.04 \text{ ng m}^{-2} \text{ yr}^{-1}$) (Li et al., 1973). The remaining 42% is removed from seawater by radioactive decay ($\sim 0.2 \text{ ng m}^{-2} \text{ yr}^{-1}$). The residence time of ^{226}Ra is ~ 500 years in the oceans (Moore and Dymond, 1991). Compared to the residence time of ^{226}Ra in seawater, the mean lives of ^{228}Ra , ^{224}Ra and ^{223}Ra are much shorter. Thus, ^{228}Ra , ^{224}Ra and ^{223}Ra are mainly removed by radioactive decay in the oceans

rather than particulate removal. For example, 98.4 % of the total removal of ^{228}Ra is by radioactive decay ($1.35 \text{ pg m}^{-2} \text{ yr}^{-1}$) and 1.6% is by particulate removal ($0.22 \text{ pg m}^{-2} \text{ yr}^{-1}$) (Moore et al, 2008).

1.4 Applications of thorium and radium isotopes in the oceans

1.4.1 Applications of Th isotopes in the oceans

Before the 1980s, thorium isotopes, ^{232}Th and ^{230}Th , were commonly measured by alpha counting. Due to their low concentrations in seawater, the low precision and accuracy of ^{232}Th and ^{230}Th measurements restricted the application of Th isotopes in the oceans. Since the 1980s, however, mass spectrometry has improved the detection limit and analytical precision for Th isotopes (Chen et al., 1986). The sample size required for measuring seawater ^{232}Th and ^{230}Th has reduced from 100 L to 10 L or smaller. However, radio decay counting methods remain the most suitable techniques for the analysis of ^{234}Th and ^{228}Th (Rutgers van der Loeff et al., 2006).

Th-232 enters the oceans mainly by terrestrial inputs, such as atmospheric dust and riverine input. Seawater $^{232}\text{Th}/^{230}\text{Th}$ ratios and ^{232}Th concentration profiles in the Pacific and Atlantic Oceans show high ratios and high concentrations in the surface ocean, which is due to atmospheric dust input to the surface ocean (Cochran et al., 1987; Huh et al., 1989; Nozaki et al., 1987). In Fig 1.17, the comparison of loess and dust ^{232}Th data shows that the average ^{232}Th concentration is 10.7 ppm in lithogenic materials and sediments (McGee et al., 2007). The atomic ratio of $^{232}\text{Th}/^{230}\text{Th}$ also shows a constant value of $\sim 200,000$ in the upper continental crust (Taylor and McLennan, 1985). Thus, the fluxes of ^{232}Th to the oceans can be converted to detrital fluxes to the oceans. For example, the approach of using ^{230}Th -normalised ^{232}Th fluxes in marine sediments has been used to calculate detrital fluxes to the oceans in several previous studies (Anderson et al., 2006; McGee et al., 2007; Winckler et al., 2008). Detrital fluxes provide an important estimate of the aeolian iron supply to the oceans, which enables us to understand the correlation between the aeolian iron supply and biogeochemical cycles, as well as paleoclimate change.

In the open ocean, ^{234}Th , ^{230}Th and ^{228}Th are mainly produced by radioactive decay of ^{238}U , ^{234}U and ^{228}Ra respectively in water columns. Since Th is a highly particulate-reactive element, the disequilibrium activity ratios of $^{234}\text{Th}/^{238}\text{U}$, $^{230}\text{Th}/^{234}\text{U}$ and $^{228}\text{Th}/^{228}\text{Ra}$ in seawater have been used to

investigate particulate scavenging, Th residence time and particle fluxes in the oceans (Broecker et al., 1973; Luo et al., 1995; Savoye et al., 2006).

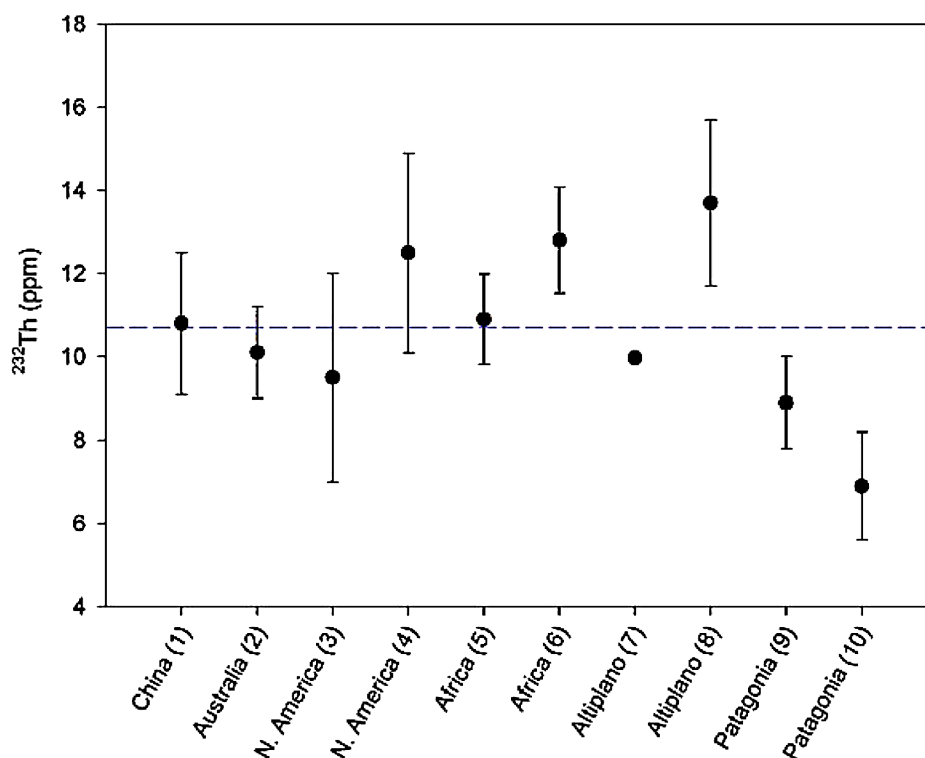


Figure 1.17 Comparison of ^{232}Th concentration in loess and dust from various dust sources. From McGee et al. (2007).

The distribution of ^{230}Th and its input and removal in the oceans have been summarised above. It is constantly produced from ^{234}U in seawater and removed by particle scavenging through the whole water column to the seafloor. Early studies of ^{230}Th in the ocean showed a linear increase of dissolved ^{230}Th with depth (Fig. 1.11), which is explained by the balance between its production and reversible particle scavenging (Bacon and Anderson, 1982; Moore, 1981; Nozaki et al., 1981). Thus, high particle fluxes around the continental margins generally enhance the removal of seawater ^{230}Th to sediments, the so-called “boundary scavenging” (Anderson et al., 1983; Bacon, 1988; Roy-Barman, 2009). Furthermore, due to the different removal rates and different particle chemical affinities between ^{230}Th and ^{231}Pa , these two nuclides have been extensively used to constrain ocean circulation and productivity in the past (Henderson and Anderson, 2003; McManus et al., 2004; Negre et al., 2010; Yu et al., 1996).

The constant and uniform production of ^{230}Th and particle removal in seawater can be used to normalise downward material and chemical fluxes to the seafloor, this having been extensively used to reconstruct past dust fluxes and mass accumulation rates in marine sediments (Adkins et al., 2006; Anderson et al., 2006; Bacon, 1984; Francois et al., 2004; McGee et al., 2007; Singh et al., 2011; Winckler et al., 2008). The use of ^{230}Th normalization is based on the assumptions that ^{230}Th flux to the seafloor is constant with no advection input. However, studies have observed advection ^{230}Th input in some regions (Scholten et al., 2008; Venchiarutti et al., 2008), which also needs to be considered in a model of ^{230}Th distribution in the oceans (Roy-Barman, 2009). Thus, in order to estimate these downward fluxes precisely, a model has been used to constrain the global ^{230}Th fluxes to deep-sea sediments (Henderson et al., 1999).

Short-lived Th isotopes, ^{234}Th and ^{228}Th , have also been used to normalise downward particle fluxes in the modern ocean (e.g. Th removal flux and particulate organic carbon (POC) flux). The first observation of ^{234}Th deficiency to ^{238}U in the upper 100 m surface water was found in the Indian Ocean (Bhat et al., 1968). They found that biogenic material plays an important role in scavenging ^{234}Th from seawater in the surface ocean before sinking down to the deep ocean. During the sinking process, remineralisation of this material occasionally happens and ^{234}Th is released to seawater at depth.

An one-dimensional steady state scavenging model has been used to calculate Th residence time (Th removal rate) in seawater based on the disequilibrium of Th isotopes to their parents in the surface ocean (Broecker et al., 1973). Th residence time can be calculated by the following equation with respect to particle scavenging:

$$\tau_{\text{Th}} = \frac{A_{\text{daughter}} / A_{\text{parent}}}{1 - A_{\text{daughter}} / A_{\text{parent}}} \cdot \tau_{\text{daughter-mean-life}} \quad (1.9)$$

where τ_{Th} is the residence time of ^{234}Th , ^{230}Th or ^{228}Th ; A is the radioactive decay rate (activity) of the respective daughters and parents ($^{234}\text{Th}/^{238}\text{U}$, $^{230}\text{Th}/^{234}\text{U}$ or $^{228}\text{Th}/^{228}\text{Ra}$); and $\tau_{\text{daughter-mean-life}}$ is the mean life of the daughter ($1/\lambda$).

Broecker et al. (Broecker et al., 1973) determined a Th residence time of 0.7 year in the surface ocean by measuring seawater $^{228}\text{Th}/^{228}\text{Ra}$. Li et al. (Li et al., 1980) also measured the seawater $^{228}\text{Th}/$

^{228}Ra ratio to calculate Th residence time in the upper 350 m surface Atlantic Ocean, with values ranging from 0.5 to 20 years. Many studies have used more than one pair of Th nuclides to study Th removal rates in the oceans. Kaufman et al. (Kaufman et al., 1981) used both $^{228}\text{Th}/^{228}\text{Ra}$ and $^{234}\text{Th}/^{238}\text{U}$ ratios to calculate the Th residence time in New York Bight and they generally found consistent results from both nuclides. However, they also found some discrepancies between ^{228}Th and ^{234}Th residence times, which may be due to their different half-lives responding to particle scavenging at different timescales. Another problem for the relative long-lived Th isotopes, ^{230}Th and ^{228}Th , is that upwelling may bring additional inputs of ^{230}Th and ^{228}Th to the surface layer, which would cause longer Th residence times for ^{230}Th and ^{228}Th than for ^{234}Th . Luo et al. (Luo et al., 1995) found the upward mixing contributes additional inputs of ^{230}Th and ^{228}Th from the deep water to the surface ocean in the equatorial Pacific upwelling regions.

Particulate organic carbon (POC) export can be assessed by using the disequilibrium of ^{234}Th to ^{238}U and ^{228}Th to ^{228}Ra in surface water, which provides important information about primary productivity, new production and carbon cycles in the oceans (Buesseler et al., 1992; Buesseler et al., 2006; Charette and Moran, 1999; Cochran et al., 2000). Buesseler et al. (Buesseler et al., 1992) used the deficiency of ^{234}Th to ^{238}U to calculate the ^{234}Th -derived particle sinking flux in the bottom of the euphotic zone. The ^{234}Th -derived particle sinking flux can also be converted to POC by multiplying by the ratio of $\text{POC}/^{234}\text{Th}$ in these sinking particles:

$$POC_{flux} = \left[\lambda \int (A_{^{238}\text{U}} - A_{^{234}\text{Th}}) dz \right] \times \frac{POC}{^{234}\text{Th}} \quad (1.10)$$

Due to the short half-life of ^{234}Th , this method reflects POC fluxes for the preceding weeks before measurement rather than the long-term or annual average removal. For example, it might overestimate the long-term annual POC flux during a seasonal bloom when the ^{234}Th profile is not in steady state (Thomalla et al., 2006). This equation has also been applied to long-lived ^{230}Th and ^{228}Th . However, lateral inputs and upwelling may contribute extra ^{230}Th and ^{228}Th to the surface open ocean, which may underestimate POC seasonal fluxes (Cai et al., 2002; Coppola et al., 2006; Luo et al., 1995; Santschi, 1984).

1.4.2 Applications of Ra isotopes in the oceans

Radium isotopes can be measured by alpha spectrometry, gamma spectrometry and mass spectrometry. Decay counting techniques are commonly used to measure Ra isotopes in seawater samples. Alpha spectrometry has been used to directly measure the alpha-emitting ^{226}Ra (Moore, 1969). The beta-emitting ^{228}Ra isotope can also be indirectly measured by alpha spectrometry via its daughters, ^{228}Th or ^{224}Ra (Moore, 1969; Moore et al., 1985). However, the alpha-counting technique for ^{228}Ra measurements requires a longer waiting time (3 to 18 months) for the in-growth of ^{228}Th . In addition, it needs chemical separations. In contrast, gamma spectrometry provides a simple preparation for both ^{226}Ra and ^{228}Ra measurements. However, gamma spectrometry has the disadvantages of weak emission probability and high background interference from the cosmic ray. Therefore, it generally relies on the use of large samples to increase sensitivity or underground labs to reduce the cosmic-ray background noise for seawater samples (Dulaiova and Burnett, 2004; van Beek et al., 2010). Measurements of ^{224}Ra and ^{223}Ra can be achieved using a radium delayed coincidence counting system (RaDeCC) (Moore and Arnold, 1996) and gamma spectrometry (van Beek et al., 2010).

Mass spectrometry has improved the analytical precision and reduced the sample size needed for measuring seawater ^{226}Ra concentrations. Thermal ionization mass spectrometry (TIMS) has been used for the determination of ^{226}Ra concentration (Cohen and Onions, 1991; Ollivier et al., 2008). The disadvantage is that a complicated chemical separation procedure is required to concentrate Ra in a small volume, to separate the matrix components, to remove the possible interferences and to prepare the source on the filament. Inductively coupled plasma mass spectrometry (ICP-MS) and multi collector-ICP-MS have improved the measurements of ^{226}Ra concentration in seawater (Foster et al., 2004; Ghaleb et al., 2004). Furthermore, ICP-MS techniques enable a simple introduction of the liquid sample into the ion source, which allows for a shorter analysis time. The use of multiple ion counting also provides fast and precise ^{226}Ra and ^{228}Ra measurements in seawater samples (Foster et al. 2004).

Radium isotopes have been extensively used as tracers for ocean circulation, ocean mixing, nutrient and micronutrient fluxes, SGD, and sediment inputs to the oceans. The distribution of ^{226}Ra and ^{228}Ra in the oceans is mainly controlled by radioactive decay, sediment and groundwater inputs, biological cycling and ocean mixing (Fig. 1.12 and Fig. 1.13). The use of Ra isotopes as tracers for

ocean mixing has been summarised in Ku and Luo (2008). Ra-226 has been applied to study basin-scale ocean mixing (Broecker et al., 1976; Chan et al., 1976; Chung, 1980; Chung and Craig, 1980; Ku and Lin, 1976; Ku and Luo, 1994; Rhein and Schlitzer, 1988); Ra-228 has also been used as a tracer for ocean diapycnal mixing (Cai et al., 2002; Charette et al., 2007; Huh and Ku, 1998; Ku et al., 1995; Moore et al., 1985; Nozaki and Yamamoto, 2001; Sarmiento et al., 1990; Trier et al., 1972; van Beek et al., 2008) and isopycnal mixing (Kaufman et al., 1973; Knauss et al., 1978; Li et al., 1980; Moore et al., 1980; Reid and Sackett, 1982; Yamada and Nozaki, 1986). This approach relies on the assumption that the change of ^{228}Ra with time is a function of ocean mixing and radioactive decay:

$$\frac{\partial A}{\partial t} = K \frac{\partial^2 A}{\partial x^2} - \lambda A \quad (1.11)$$

where K is the eddy diffusion coefficient; x is the offshore distance or water depth; A is the activity of ^{228}Ra and λ_{Ra228} is $3.82 \times 10^{-9} \text{ s}^{-1}$. At steady state with the boundary conditions $A = A_0$ at $x = 0$ and $A = 0$ at $x \rightarrow \infty$, Eqn. 1.11 can be solved:

$$A = A_0 \exp\left[-x \sqrt{\frac{\lambda}{K}}\right] \quad (1.12)$$

The use of ^{228}Ra as a tracer for ocean mixing shows global horizontal eddy diffusivity (K_x) values ranging from 10^5 to $10^7 \text{ cm}^2 \text{ s}^{-1}$ (Table 1.3). For example, Kanuss et al. (Kanuss et al., 1978) used the change of ^{228}Ra gradient in the surface ocean to demonstrate offshore mixing values of 4×10^5 and $4 \times 10^7 \text{ cm}^2 \text{ s}^{-1}$ across the Peru current system in the Pacific Ocean (Fig. 1.14). Horizontal eddy diffusivity shows increased values with increasing length scale. Below the surface ocean, ^{228}Ra has been used to estimate horizontal eddy diffusivities along thermoclines. In the Atlantic Ocean, the distribution of ^{228}Ra below 3000 m provides an estimate for K_x of $8 \times 10^7 \text{ cm}^2 \text{ s}^{-1}$ in the abyssal circulation (Sarmiento et al., 1982). Vertical profiles of seawater ^{228}Ra have also been used to calculate vertical eddy diffusivities (K_z) in the oceans, ranging from 10^{-1} to $10^2 \text{ cm}^2 \text{ s}^{-1}$ (Table 1.3). Furthermore, these ^{228}Ra -derived ocean mixing diffusivities also provide the opportunities to quantify macronutrient and micronutrient fluxes with horizontal and vertical ocean mixing to the surface open ocean (Cai et al., 2002; Charette et al., 2007; Ku et al., 1995; Nozaki and Yamamoto, 2001; Sarmiento et al., 1990). Overall, ^{228}Ra -derived

ocean mixing is consistent with the typical range of horizontal (isopycnal) mixing, 10^4 to 10^8 $\text{cm}^2 \text{s}^{-1}$, and vertical (diapycnal) mixing, 10^{-1} to 10^2 $\text{cm}^2 \text{s}^{-1}$ in the oceans (Polzin et al., 1997; Toole et al., 1994).

Table 1.3 Summary of ^{228}Ra -derived eddy diffusion coefficient

Eddy diffusion coefficient ($\text{cm}^2 \text{s}^{-1}$)	Location	Reference
K_x (horizontal distance)		
4×10^5 (0-200 km)	Kuroshio current, the coast of Japan	Yamada and Nozaki, 1986
4×10^7 (> 200 km)	Kuroshio current, the coast of Japan	Yamada and Nozaki, 1986
4×10^5 (0-200 km)	Peru current, the coast of California	Knauss et al., 1978
4×10^7 (> 200 km)	Peru current, the coast of California	Knauss et al., 1978
1×10^6	North East America, North Atlantic	Kaufman et al, 1973
1×10^6 (0-200 km)	Baja California, North East Pacific	Huh and Ku, 1998
5×10^7 (1000 km)	Baja California, North East Pacific	Huh and Ku, 1998
8×10^7 (deep ocean, ~3000 km)	Atlantic abyssal circulation	Sarmiento et al. 1982
K_z (vertical depth)		
0.1 (0-150 m)	Equatorial Atlantic	Moore, 1972
0.5 (150-225 m)	Equatorial Atlantic	Moore, 1972
16 ± 3 (102-200 m)	North Atlantic	Trier et al., 1972
11 ± 3 (650-891 m)	North Atlantic	Trier et al., 1972
21 ± 5 (4070-4893 m)	North Atlantic	Trier et al., 1972
0.23 (0-300 m)	South China Sea	Cai et al., 2002
11-100 (0-300 m)	Crozet Plateau region, Southern Ocean	Charette et al., 2007
1.5 (300-1000 m)	Crozet Plateau region, Southern Ocean	Charette et al., 2007
1.5 ± 1.3 (0-500 m)	Kerguelen Plateau, Southern Ocean	van Beek et al., 2008
5-17 (1700 m)	San Nicolas Basin	Hammond et al., 1990
1-3 (850 m)	San Pedro Basin	Hammond et al., 1990
15-30 (3000-5000 m)	Baja California, North East Pacific	Huh and Ku, 1998
120 (3000-4000 m)	Baja California, North East Pacific (24° 16.9' N, 115° 8.9' W)	Huh and Ku, 1998

There are a few potential problems needed further investigation for using ^{228}Ra as a tracer of ocean mixing, which have been summarised in Cochran (1992) and Ku and Luo (2008). First of all, the use of ^{228}Ra as a tracer to estimate vertical mixing is based on the assumption that there is no lateral input to change the vertical gradient of ^{228}Ra . However, horizontal mixing is generally 10^5 to 10^8 times faster than vertical mixing (Table 1.3). Advection water masses in contact with slope sediments may provide lateral ^{228}Ra inputs to alter the vertical gradients of ^{228}Ra ; this has been observed on the continental slopes or around the continental margins (Hammond et al., 1990; Moore and Santschi, 1986). The second problem with the use of ^{228}Ra as a tracer for ocean mixing is assuming that the ^{228}Ra distribution in the ocean is in steady state. Previous studies have found a non-steady ^{228}Ra distribution

in the Gulf of Mexico (Reid et al., 1979) and temporal variations in ^{228}Ra in the sub-Arctic Ocean (Moore et al., 1980). These suggest that using ^{228}Ra as a tracer for ocean mixing requires further investigation into its sources, fluxes and spatial and temporal variations in the oceans.

Ra-^{228} has also been used to estimate riverine (Chen et al., 2010; Key et al., 1985; Moore and Shaw, 2008), SGD (Charette and Buesseler, 2004; Krest et al., 2000; Moore, 2003; Moore et al., 2008; Rama and Moore, 1996) and sedimentary (Crotwell and Moore, 2003; Hammond et al., 1990; Hancock et al., 2000; Hancock et al., 2006; Moore et al., 1995; Rama and Moore, 1996; Santschi et al., 1979) inputs to the ocean. Moore et al. (2008) have demonstrated the use of a ^{228}Ra inventory to assess SGD input to the surface Atlantic, which assumes that the output of ^{228}Ra by radioactive decay must be balanced by riverine, SGD and sedimentary ^{228}Ra inputs to the oceans. The mass balance and inventory of ^{228}Ra in the upper Atlantic Ocean suggest that SGD input is about 80 to 160% of freshwater input to the Atlantic Ocean (Fig. 1.18) (Moore et al., 2008).

To better constrain SGD flux to the ocean requires precise assessments to be made of the ^{228}Ra inventory, riverine and sedimentary ^{228}Ra fluxes and the average ^{228}Ra concentration in SGD. As discussed above, apart from SGD, sediment provides the most important input of ^{228}Ra to the Atlantic Ocean, about 37% of total ^{228}Ra loss in the surface Atlantic (Table 1.2). In contrast, riverine and dust inputs are only 7% and < 1 % respectively. Thus, a better understanding of sedimentary ^{228}Ra fluxes would allow a more precise constraint of SGD flux to the oceans.

Sedimentary ^{228}Ra fluxes have been estimated in different regions of the oceans (e.g. continental shelves and slopes, lagoons, marshes, coral reefs, estuarine environments and deep-sea basins). In general, continental shelf sediments show higher ^{228}Ra fluxes in the range $0.1 - 110 (\times 10^9) \text{ atoms m}^{-2} \text{ yr}^{-1}$, than other regions (Moore et al., 2008). The highest sedimentary ^{228}Ra flux has been found on the Amazon shelf, $110 \times 10^9 \text{ atoms m}^{-2} \text{ yr}^{-1}$ (Moore et al., 1995). Additionally, coarse sediments have lower ^{228}Ra fluxes than fine sediments (Hancock et al., 2006). There are very few studies about sedimentary ^{228}Ra fluxes on the continental slopes. Hammond et al. (Hammond et al., 1990) estimated sedimentary ^{228}Ra fluxes to be in the range $5 - 11 (\times 10^9) \text{ atoms m}^{-2} \text{ yr}^{-1}$ on the San Pedro and the San Nicolas Basin slopes. Deep-sea sediments also show a lower sedimentary ^{228}Ra flux, $1.4 - 4.3 (\times 10^9) \text{ atoms m}^{-2} \text{ yr}^{-1}$, than the continental shelf sediments (Cochran and Krishnaswami, 1980). Most of these fluxes are

derived from the diffusion models based on the vertical gradients of ^{228}Ra in sediment porewater. The sedimentary ^{228}Ra fluxes normally show a very large uncertainty of up to 50% (Moore et al., 2008), which might be due to complex ^{228}Ra end-members in coastal areas and variable factors (e.g. bioturbation and partition coefficients) controlling ^{228}Ra diffusion from sediments (Cochran and Krishnaswami, 1980; Hancock et al., 2000).

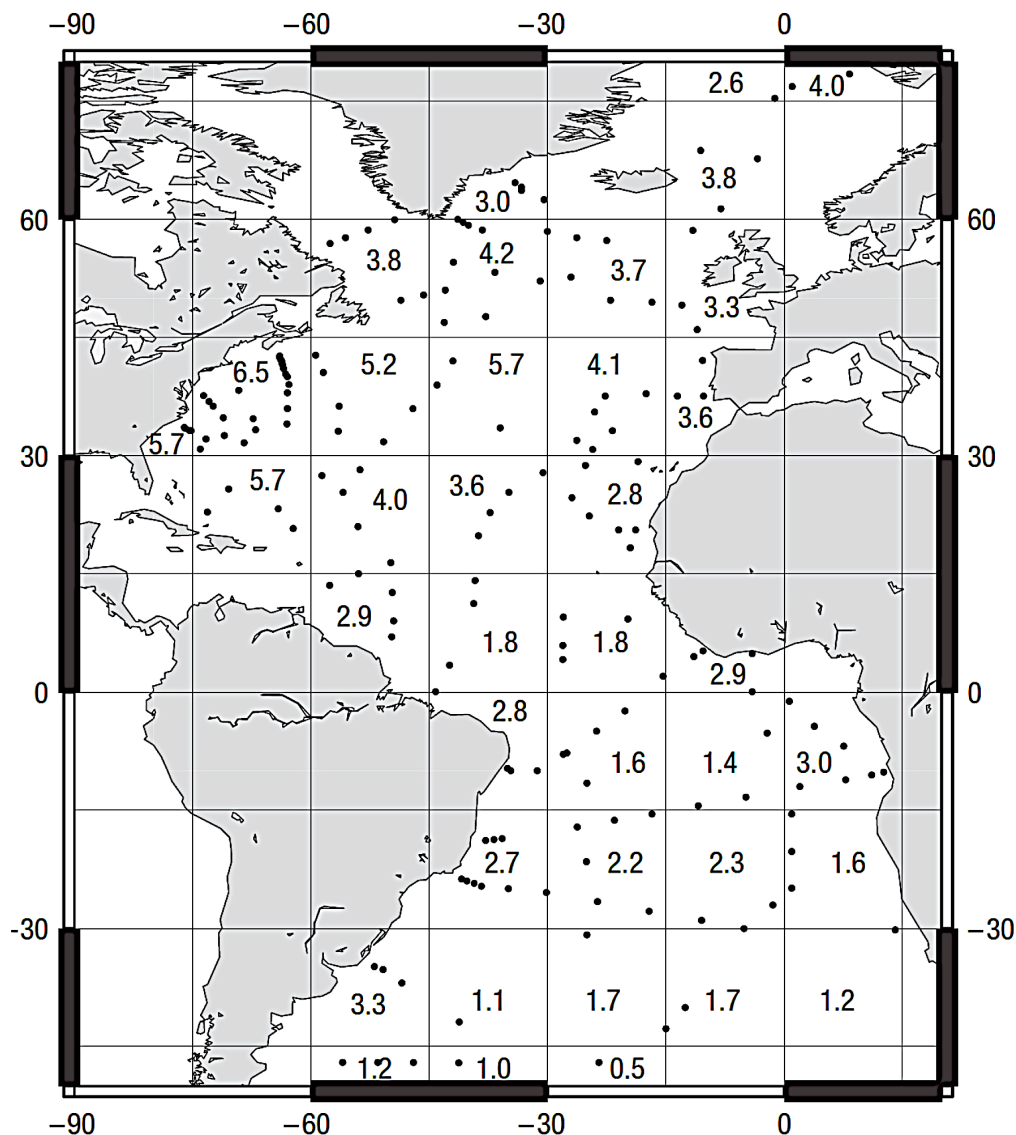


Figure 1.18 ^{228}Ra inventory in the surface Atlantic Ocean (< 1000 m). The unit is $10^{10} \text{ atoms m}^{-2}$. Each number represents the average ^{228}Ra inventory within each $15^\circ \times 15^\circ$ box. Based on the figure, total upper Atlantic ^{228}Ra inventory is 2.9×10^{24} atoms per year, resulting 3.48×10^{23} atoms decay per year. The loss of ^{228}Ra needs to balance by the ^{228}Ra inputs from sediment, river and dust, and the rest is inferred to SGD (Table 1.2). From Moore et al. (2008).

The short-lived Ra isotopes, ^{224}Ra and ^{223}Ra , have been used to study ocean mixing and SGD in coastal areas. Groundwater is not only an important source for ^{228}Ra but it also provides a significant amount of ^{223}Ra and ^{224}Ra to salt marshes (Rama and Moore, 1996). Combining four Ra isotopes (^{228}Ra , ^{226}Ra , ^{224}Ra and ^{223}Ra , the so-called Ra quartet) in coastal regions, ^{224}Ra and ^{223}Ra estimate coastal mixing rates K_x range from 3.6×10^6 to $4.2 \times 10^6 \text{ cm}^2 \text{ s}^{-1}$; these mixing rates multiply with horizontal gradients of ^{226}Ra and ^{228}Ra can also provide estimates of ^{226}Ra and ^{228}Ra offshore fluxes (Moore, 2000). The total removal of ^{226}Ra and ^{228}Ra requires balancing by the inputs of ^{226}Ra and ^{228}Ra from SGD, sediments and rivers. Another application of ^{223}Ra and ^{224}Ra is to estimate water ages, which has been explored in the Mississippi river plume (Moore and Krest, 2004). Ra-223 and ^{224}Ra have also been used to estimate horizontal mixing and to determine horizontal iron fluxes to the Southern Ocean (Charette et al., 2007; Dulaiova et al., 2009).

To sum up, U-Th series nuclides show great potential to assess ocean mixing rates and chemical inputs to the ocean. This thesis is focused on developing these nuclides as new tools to have better constraints on ocean processes and chemical cycles in marine environments, which would improve our understanding of biogeochemistry, the global carbon cycle and, hence, climate change.

1.5 Outline of the thesis

The chapters of this thesis are written in the format of paper manuscripts. Each chapter includes an abstract, introduction, methodology, results and discussion. Chapters cover a range of research projects, each related to the development and use of U-Th series measurements to assess ocean processes.

The second chapter begins with a study developing new chemical tracers for dust input to the surface ocean, ^{232}Th and ^{230}Th . Seawater samples collected from an Atlantic meridional transect (AMT12) have been analysed for ^{232}Th and ^{230}Th concentrations to calculate ^{232}Th -derived dust fluxes and ^{230}Th removal rate in the surface ocean. The results are compared with dissolved Al data and dust models in the Atlantic Ocean. This study also provides an estimation of Th solubility in different regions of the Atlantic Ocean, highlighting the importance of understanding Th solubility in future

studies. This chapter also discusses the advantages and disadvantages of using Th isotopes and dissolved Al to determine dust fluxes to the oceans.

Chapter 3 gives an overview of analytical techniques for Ra isotopes over the last two decades, including different decay counting techniques and mass spectrometry. This chapter then discusses the details of the newly developed technique for precisely measuring seawater $^{228}\text{Ra}/^{226}\text{Ra}$ ratios and ^{228}Ra and ^{226}Ra concentrations using MC-ICP-MS. The results of GEOTRACES Ra intercalibration are reported in this chapter for comparison of the newly developed method with other techniques.

This new analytical method has been applied to two marine settings for studying ocean mixing, and nutrient and micronutrient fluxes to the oceans. Chapter 4 describes the use of the Ra quartet (^{228}Ra , ^{226}Ra , ^{224}Ra and ^{223}Ra) in Loch Etive, a Scottish sea loch, to study overturn circulations in the fjord system and to evaluate Ra fluxes from different sources to the oceans. This chapter also provides the details of applications of ^{223}Ra and ^{224}Ra to the study of water transport rates.

Chapter 5 focuses on the study of ^{226}Ra and ^{228}Ra during the UK-GEOTRACES cruise (GA10E) in the South East Atlantic. This chapter demonstrates the use of ^{228}Ra as a tracer to study offshore 1-D diffusional and horizontal model mixing. Such an application can also be used to calculate vertical mixing in the water column, which is important in the estimation of chemical fluxes transported from the deep oceans. For example, the distribution of nitrate and ^{228}Ra -derived vertical mixing can be used to calculate vertical nitrate flux and total carbon export in the South East Atlantic and Agulhas Current Leakage.

Chapter 2

Combining seawater ^{232}Th and ^{230}Th concentrations to determine dust fluxes to the surface ocean

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2.1 Abstract

Aeolian dust is a significant source of iron and other nutrients to the surface ocean, but constraining the size of this flux is difficult. Chemical tracers, such as Al, are useful, but are limited by lack of information about their rate of removal from surface seawater. In this study, we test the use of Th isotopes as an improved tracer of dust input by measuring ^{232}Th and ^{230}Th concentrations of upper-ocean seawater at six stations along a meridional Atlantic section that spans the Saharan dust plume. Open ocean ^{232}Th , like Al, is dominantly derived from dust dissolution, while ^{230}Th is produced in seawater by U decay and provides an assessment of Th removal rates. The highest ^{232}Th concentrations and $^{232}\text{Th}/^{230}\text{Th}$ ratios, particularly in the surface waters, are observed at stations expected to be influenced by input of Saharan dust. The pattern of ^{232}Th concentration is in agreement with dissolved Al distributions and SeaWiFS aerosol imagery, supporting the use of ^{232}Th as a proxy for short-term dust addition. Deeper in the water column, ^{232}Th concentration may also reflect longer-term dust inputs. In addition, lateral input of ^{232}Th from Mediterranean Outflow Water is detected at 1000 m in the north Atlantic.

Surface-water residence times are calculated separately from ^{230}Th and ^{234}Th using a simple scavenging model and values from the two isotopes are generally consistent with one another. Th-230 residence times appear to reflect the longer-term value, however, rather than exhibiting the strong seasonal influence seen for ^{234}Th . These Th residence times allow dust flux to the surface ocean to be calculated using the known concentration of Th in dust, and assumed values for the solubility of dust Th in seawater. Resulting dust fluxes show good agreements with models of dust deposition if Th

solubility is 1 to 5% in the north Atlantic (yielding fluxes of $0.4 - 19.2 \text{ g m}^{-2} \text{ yr}^{-1}$) and 5 to 10% in the south Atlantic (fluxes of $0.2 - 0.7 \text{ g m}^{-2} \text{ yr}^{-1}$). Despite the need for better constraints on the fractional solubility of dust Th, this study demonstrates the power of combining Th isotope measurements to constrain dust fluxes to the surface ocean.

2.2 Introduction

Atmospheric dust plays important roles in many aspects of the earth system, including influencing the planet's radiative balance and climate (Mahowald et al., 2006; Wang et al., 2009). Biogeochemically, aeolian dust is considered to be a major source of micronutrients such as Fe to the surface ocean (Jickells et al., 2005). Dust inputs therefore influence primary productivity, the nature of nutrient cycling, and the oceanic carbon cycle (Fung et al., 2000; Mahowald et al., 2009; Martin et al., 1990; Sarthou et al., 2007). Tracing the sources and reconstructing fluxes of dust to the ocean are therefore important for our understanding of the carbon cycle and climate change in the present and the past (e.g. Jickells et al., 2005; Moore and Braucher, 2008; Watson et al., 2000).

Previous studies estimating dust fluxes to the ocean have focused on directly measuring aeolian aerosols (Arnold et al., 1998) and modelling (Duce et al., 1991). However, dust models are not considered entirely accurate, and only the portion of the dust that dissolves in seawater plays a role in biogeochemical cycles (Boyd and Ellwood, 2010) rather than the entire mass of dust. Dissolved Al provides a more direct measure of the dissolved portion of dust input to the surface ocean and has been successfully used to assess dust input in some settings (Measures and Vink, 2000; Measures et al., 2005). The removal rate of Al from surface waters is, however, poorly constrained which places some limitation on the use of surface-ocean Al concentrations as a proxy for dust input.

Thorium isotopes (^{232}Th , $T_{1/2} = 1.4 \times 10^{10}$ years; ^{230}Th , $T_{1/2} = 75,690$ years; ^{228}Th , $T_{1/2} = 1.9$ years; ^{234}Th , $T_{1/2} = 24.1$ days) have been applied to a wide variety of questions in oceanography (e.g. Henderson and Anderson, 2003; Cochran and Masqué, 2003). Recently, such use has extended to reconstruction of past dust fluxes to the ocean, through analysis of marine sedimentary records (Anderson et al., 2006; McGee et al., 2007; Winckler et al., 2008). Thorium isotopes may also be useful as a tracer of dust input in the modern ocean. In seawater, the insoluble nature of Th means that the

primordial long-lived isotope – ^{232}Th – is a clear fingerprint of recent lithogenic addition and, in the open ocean, is likely to be dominantly supplied by the dissolution of dust, in a manner similar to Al. Thorium has the advantage over Al, however, that the radiogenic isotopes, ^{230}Th and ^{234}Th , may provide a direct way to assess the removal rates of Th isotopes, and therefore allow quantification of the input of ^{232}Th from dust sources. Th-230 and ^{234}Th are produced by decay of homogeneously distributed U isotopes in seawater and transported downward by reversible scavenging with sinking particles (Henderson et al., 1999; Nozaki et al., 1981). Both ^{230}Th (Andersson et al., 1995; Bhat et al., 1968; Broecker et al., 1973; Guo et al., 1995; Huh et al., 1989; Luo et al., 1995) and ^{234}Th (Bacon et al., 1996; Buesseler et al., 1992; Cochran et al., 2000; Kaufman et al., 1981) have been widely used to assess the removal of material from seawater, but have not previously been coupled to measurements of ^{232}Th to assess dust fluxes in the modern ocean.

In this study, we test the use of Th isotopes as a measure of dust input to the modern ocean. We measure Atlantic profiles of ^{232}Th and ^{230}Th to demonstrate spatial variation of ^{232}Th associated with Saharan dust inputs, and use ^{230}Th data (and existing ^{234}Th data; Thomalla et al., 2006) to calculate Th removal rates from surface water and hence rates of dust addition.

2.3 Samples and previous data

Samples were collected from six stations (CTD-17, 27, 34, 42, 52, 61) along a meridional transect (AMT 12, May–June, 2003; Jickells, 2003) between 50°S and 50°N (Fig. 2.1). These stations range from the low dust setting of the South Atlantic Gyre, through the major Saharan dust plume in the northern tropics of the Atlantic, into the reasonably low dust North Atlantic Gyre (Fig. 2.1a). Two previous cruises with similar tracks provide data that are useful for direct comparison with results from this study. The dissolved Al data from the A16N CLIVAR line (Measures et al., 2008) enables comparison of ^{232}Th with the Al dust proxy. And ^{234}Th data from the AMT 14 cruise (Thomalla et al., 2006) are used in conjunction with our ^{230}Th and ^{232}Th results. Two existing ^{232}Th – ^{230}Th profiles (Moran et al., 2002; Vogler et al., 1998) provide an indication of the temporal variability of Th isotopes in the Atlantic.

Unfiltered seawater samples of 20 L at 25 m, and 10 L at 50, 100, 200, 500 and 1000 m were collected at each of the six stations using Niskin bottles mounted on a CTD rosette. To compare total and dissolved Th in the surface layer, additional 20 L samples were collected at 25 m from CTD 17, 27, 42 and 61, and filtered through 142 mm diameter 0.2 μm pore-size cellulose nitrate filter on board ship. Time pressure during the cruise prevented a larger filtering campaign.

2.4 Analytical techniques

2.4.1 Chemical pre-treatment and column chemistry

All samples were acidified with 7 mL of 10 N HCl per litre and stored in cubitainers prior to analysis. A mixed ^{236}U – ^{229}Th spike (Oxford Water Spike, ^{236}U ~ 60 ng/g and ^{229}Th ~ 500 fg/g; Robinson et al., 2004) and 10 mg of pre-cleaned Fe were added to samples which were then shaken and left overnight. Distilled NH^+ solution was added to increase the pH to ~ 8 for iron hydroxide co-precipitation. Samples were left to stand for two days for the precipitate to settle. Re-suspension was performed after one day to provide more opportunity for scavenging of U and Th to the Fe-precipitate. The precipitate was centrifuged and rinsed with 18 M Ω (Milli-Q) water. Finally, the precipitate was dissolved in concentrated 7.5 N HNO_3 , evaporated to dryness and redissolved in 4 mL of 7.5 N HNO_3 for column purification.

Column separation and purification of U and Th were carried out using anion exchange resin (Dowex Bio-Rad AG1X8 100–200 mesh) (Edwards et al., 1987). Samples were loaded on prewashed and conditioned 2 mL columns in 4 mL of 7.5 N HNO_3 . The column was then washed with 7.5 N HNO_3 , converted to Cl^- and Th eluted with 6 N HCl, and the remaining U eluted with H_2O . Because of the relatively high U concentrations in seawater, the Th fraction was passed through the same column a second time to remove any residual U. The chemical blank has been monitored and corrected for every batch of chemistry. The full procedural blank is 10 ± 3 (n = 4) pg of ^{232}Th , 0.5 ± 0.1 (n = 4) fg of ^{230}Th and 0.3 ± 0.1 (n = 4) ng of ^{238}U , which is less than 1 – 5% of total Th in each sample and is insignificant for U.

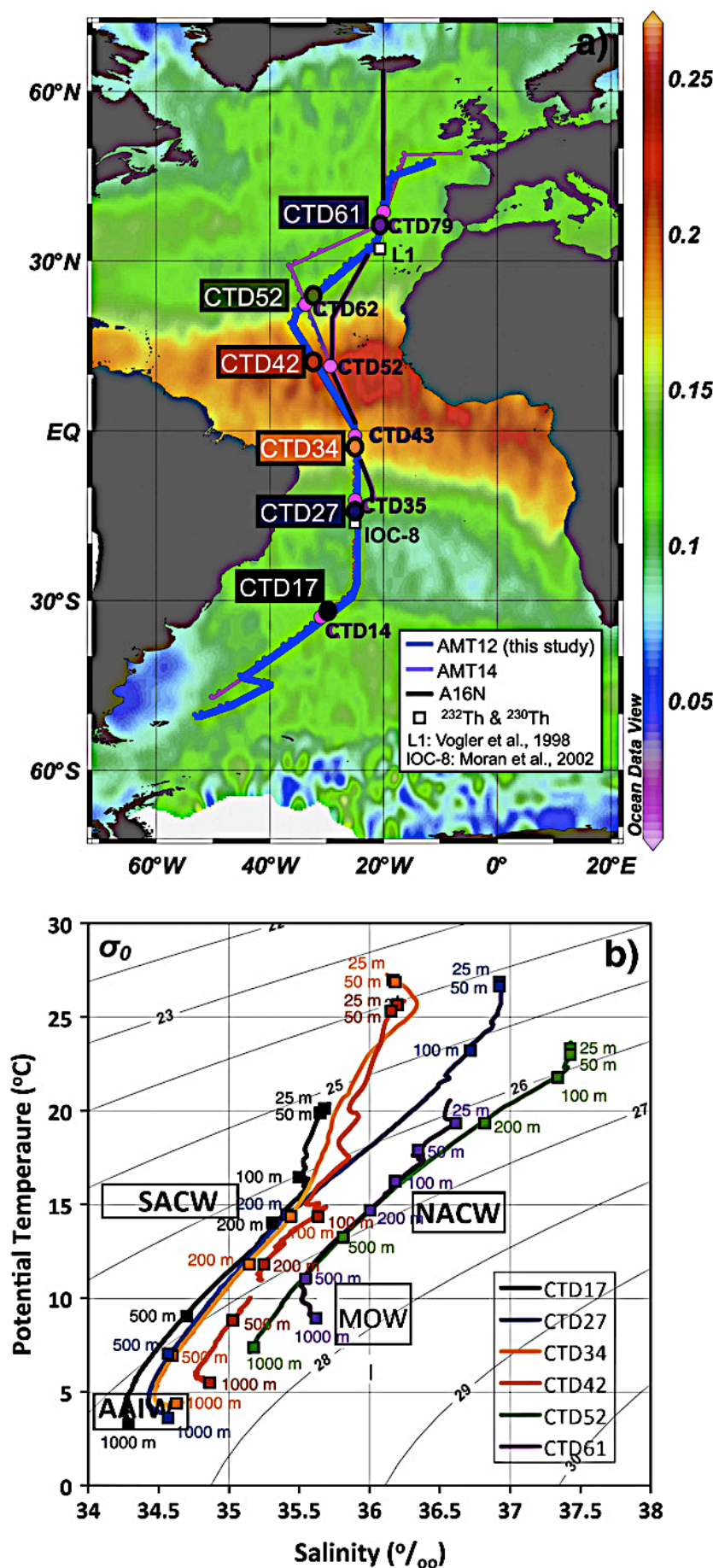


Figure 2.1 (a) Map of sample locations, overlaid with a SeaWiFS image of aqua aerosol optical thickness at 869 nm (unitless). The Saharan dust plume is indicated by warmer colours. Six stations (CTD17–CTD61) are labelled with coloured boxes on the map, and the colour also repeated in all results figures. The blue line is the AMT 12 cruise track (12 May to 17 June 2003) studied here; the dark purple line is the AMT 14 cruise track (28 April to 1 June 2004) from which comes the ^{234}Th data (Thomalla et al., 2006); the black line is the A16N cruise track (4 June to 11 August 2003), used for dissolved Al (Measures et al., 2008). White squares are reference stations for ^{232}Th and ^{230}Th data comparison with L1 (Vogler et al., 1998) and IOC-8 (Moran et al., 2002).

(b) Temperature–Salinity (T–S) diagram and hydrography. The six stations are shown in different colours. The sampling depths are shown in squares with colours matched to their stations. Four water masses, SACW (South Atlantic Central Water), NACW (North Atlantic Central Water), AAIW (Antarctic Intermediate Water) and MOW (Mediterranean Outflow Water), are identified in the black boxes in the diagram. The increased salinity at station CTD 61 shows two water masses mixing between MOW and the Atlantic seawater in the deep water-column. MOW, flowing from the Strait of Gibraltar and spreading across the north Atlantic, has a signature of high salinity (Armi et al., 1988).

2.4.2 Mass spectrometry

Measurements of ^{232}Th and ^{230}Th were performed using a Nu Instrument MC-ICP-MS with protocols adapted from previous methods (Mason and Henderson, 2010; Robinson et al., 2004; Thomas et al., 2006). The measurement routine involved 3 parts: (1) Standard bracketing with the CRM-145 U standard was applied to assess mass discrimination and ion-counter gain before and after each sample. (2) Instrumental memories of ^{229}Th , ^{230}Th , and ^{232}Th were detected on an ion counter before each sample. (3) ^{229}Th and ^{230}Th were measured dynamically on an ion counter equipped with an energy filter to improve abundance sensitivity from U, while ^{232}Th was measured on a Faraday cup during the ^{229}Th analysis step. The abundance sensitivity from all U isotopes contributes $< 1\%$ to the ^{230}Th and ^{232}Th beams and is corrected. U-235 was measured on a Faraday cup in each step to normalise signal instability. The method has been tested during the GEOTRACES intercalibration of Th and Pa measurements in seawater (Anderson et al., submitted for publication). The total uncertainties of ^{232}Th and ^{230}Th measurements are typically 2 – 4% (2σ).

2.4.3 In-growth and lithogenic ^{230}Th corrections

In-growth of ^{230}Th must be corrected if samples have been collected and stored for long periods, particularly for low-Th surface waters (Robinson et al., 2004). The in-growth rate of ^{230}Th is $0.57\text{fg kg}^{-1}\text{yr}^{-1}$ (given $\lambda^{234} = 2.8263 \times 10^{-6}\text{yr}^{-1}$; seawater $\delta^{234}\text{U}$ of 146.6; and ^{238}U concentration of 3.33 ng/g). Six years elapsed between collection in 2003 and analysis so in-growth of ^{230}Th is $\approx 3.43\text{ fg/kg}$. In-grown ^{230}Th for each sample was calculated from its measured U concentration and subtracted from the measured value to assess initial ^{230}Th concentration. The in-growth correction can be up to 70% for surface seawater with low initial ^{230}Th concentrations but can be made with high precision because the uncertainty associated with this correction depends only on uncertainty of the half-life of ^{234}U ($\pm 2\%$) (Cheng et al., 2000), and the concentration of ^{234}U ($\pm 4\%$). These uncertainties are insignificant compared to the analytical uncertainty.

In the ocean, ^{230}Th is not only derived from in situ radioactive decay of dissolved ^{234}U in seawater, but also from lithogenic input (Roy-Barman et al., 2002). Lithogenic input elevates the ^{230}Th concentration therefore causing an overestimate of Th residence time in surface seawater. For example,

in high dust deposition surface water, ^{230}Th residence time without lithogenic correction is about 30% higher than the value with lithogenic correction. We correct lithogenic ^{230}Th from the measured ^{230}Th before the calculation of Th residence time using:

$$^{230}\text{Th}_{\text{sw}} = ^{230}\text{Th}_{\text{measured}} - ^{232}\text{Th}_{\text{measured}} \times \left[^{230}\text{Th}/^{232}\text{Th} \right]_{\text{litho}} \quad (2.1)$$

where $^{230}\text{Th}_{\text{sw}}$ is the molar ^{230}Th concentration produced by in situ decay of ^{234}U in seawater; $^{230}\text{Th}_{\text{measured}}$ and $^{232}\text{Th}_{\text{measured}}$ are the measured molar concentrations of the sample; and $[^{230}\text{Th}/^{232}\text{Th}]_{\text{litho}}$ is the atom ratio in lithogenic materials, expected to fall between 3.2×10^{-6} and 5.4×10^{-6} mol/mol (Anderson et al., 1990; Henderson and Anderson, 2003). Typical $[^{230}\text{Th}/^{232}\text{Th}]$ ratios are 4.4×10^{-6} mol/mol in the continental crust (Andersson et al., 1995), 4.9×10^{-6} mol/mol in the Saharan dust (Rydell and Prospero, 1972) and 4.0×10^{-6} mol/mol in a sediment trap in the west Mediterranean sea (Roy-Barman et al., 2009). Here we follow Roy-Barman et al. (2009) in assuming a $[^{230}\text{Th}/^{232}\text{Th}]$ of 4.0×10^{-6} mol/mol and we associate a 30% uncertainty with this value which encompasses other estimates of the ratio.

2.5 Results

Seawater ^{232}Th and ^{230}Th concentrations and isotopes ratios are given in Table 2.1. In cases where both filtered and unfiltered samples were measured there is generally close agreement. As seen in previous studies (e.g. Moran et al., 1997; Vogler et al., 1998), Th in the unfiltered samples is mostly in the dissolved phase. However, some filtered samples have slightly higher values than unfiltered samples, which is possibly due to contamination during filtration. Based on this observation, we focus our discussion only on the larger unfiltered dataset for the remainder of the paper. Two samples (CTD52 – 50 m and CTD61 – 200 m) show significantly lower concentrations of both ^{232}Th and ^{230}Th , which strongly suggests a spiking problem (labelled with superscript a in Table 2.1). These samples are not plotted on figures nor considered in the discussion. Three other samples (CTD17 – 200 m, CTD27 – 50 m and CTD34 – 200 m) also have unusually high ^{232}Th concentrations and may have encountered contamination during the sampling or analysis. Because such contamination cannot be clearly demonstrated, however, we leave these analyses in figures and discussion.

Table 2.1 ^{232}Th and ^{230}Th concentrations and isotope ratios

Station	Latitude	Longitude	Seawater sample	Depth (m)	^{232}Th (pg/kg)	2 S.E.	^{230}Th (fg/kg)	2 S.E.	$^{232}\text{Th}/^{230}\text{Th}$	2 S.E.
CTD17	31,78,53 S	29,70,94 W	filtered	25	35.2	0.4	1.13	0.03	30862	814
			unfiltered	25	27.3	0.3	0.98	0.02	27771	596
			unfiltered	50	17.0	3.0	0.56	0.19	29797	11146
			unfiltered	100	14.1	0.4	0.62	0.14	22656	5322
			unfiltered	200	82.8	1.7	2.63	0.18	31190	2262
			unfiltered	500	44.3	1.2	4.37	0.22	10062	583
			unfiltered	1000	34.4	1.1	6.92	0.38	4930	310
CTD27	13,92,63 S	24,99,75 W	filtered	25	26.1	0.2	0.80	0.02	32345	700
			unfiltered	25	20.8	0.2	0.89	0.02	22995	553
			unfiltered	50	143.5	5.1	0.96	0.21	148496	32457
			unfiltered	100	10.4	0.3	0.39	0.16	26130	10902
			unfiltered	200	21.4	1.1	2.02	0.51	10503	2698
			unfiltered	500	29.4	0.9	5.98	0.32	4874	300
			unfiltered	1000	21.8	0.8	4.82	0.30	4489	325
CTD34	02,23,61 S	24,99,91 W	unfiltered	25	64.1	0.8	0.93	0.02	68154	1591
			unfiltered	50	39.8	0.9	0.53	0.08	74281	11819
			unfiltered	100	48.4	1.1	1.85	0.16	25900	2349
			unfiltered	200	117.5	3.2	2.14	0.20	54397	5372
			unfiltered	500	69.3	1.7	4.16	0.24	16498	1021
			unfiltered	1000	77.5	2.1	7.54	0.35	10194	550
CTD42	09,56,32 N	32,28,63 W	filtered	25	150.7	1.5	1.59	0.02	93793	1740
			unfiltered	25	150.0	1.9	1.42	0.02	104434	2164
			unfiltered	50	81.6	3.7	0.66	0.21	122025	38312
			unfiltered	100	97.0	2.5	2.03	0.18	47350	4270
			unfiltered	200	73.9	1.3	2.38	0.17	30709	2313
			unfiltered	500	105.7	3.3	3.53	0.27	29659	2480
			unfiltered	1000	100.2	2.6	3.54	0.25	28034	2103
CTD52	24,22,87 N	32,57,38 W	unfiltered	25	86.4	0.9	1.70	0.03	50303	915
			unfiltered	50	18.6 ^a	0.5	0.18 ^a	0.14	102076 ^a	81834
			unfiltered	100	85.1	2.0	1.76	0.15	47916	4274
			unfiltered	200	72.9	1.5	3.94	0.27	18360	1302
			unfiltered	500	71.6	2.0	4.85	0.27	14610	922
			unfiltered	1000	68.6	1.5	8.00	0.33	8496	404
CTD61	36,73,59 N	20,81,40 W	filtered	25	17.9	0.2	0.77	0.02	23209	511
			unfiltered	25	26.9	0.3	1.43	0.02	18602	349
			unfiltered	50	39.2	2.8	2.18	0.17	17810	1917
			unfiltered	100	39.2	0.8	1.59	0.15	24403	2383
			unfiltered	200	18.2 ^a	1.4	0.24 ^a	0.28	75624 ^a	88719
			unfiltered	500	65.7	2.6	4.25	0.37	15311	1458
			unfiltered	1000	64.5	1.2	5.84	0.23	10932	473

Thorium concentration is expressed in units of pg/kg for ^{232}Th and fg/kg for ^{230}Th . [$^{232}\text{Th}/^{230}\text{Th}$] is expressed in activity ratio. The half-life used in this study is 75.690 ka for ^{230}Th (Cheng et al., 2000) and 14.0100 Ga for ^{232}Th (Holden, 1990). All errors are 2 standard errors.

^aData are considered to have spiking problem.

Th-232 concentrations range from 10.4 pg/kg to 150.0 pg/kg (Fig. 2.2a), with depth variability at each station typically smaller than the changes observed between stations. The highest ^{232}Th concentrations are observed at the station directly under the Saharan Dust plume (CTD 42) with stations immediately to the north and south also showing higher ^{232}Th concentrations than samples

further from the dust plume. The average ^{232}Th concentration at CTD 27 (41.2 ± 20.6 pg/kg) is in close agreement with the value measured close by in 1996 at station IOC-8 (33.9 ± 16.9 pg/kg; Moran et al., 2002). Average values at CTD 61 (40.2 ± 37.0 pg/kg) are lower than a nearby measurement at station L1 in 1996 (73.4 ± 56.8 pg/kg, Vogler et al., 1998), with both profiles showing a notable increase in ^{232}Th ($\approx$ factor 2) at 1000 m relative to 25 m – a feature not seen in other station data.

Th-230 concentration profiles increase with depth at all stations from $0.53 - 1.70$ fg/kg at 25 m to $4.82 - 8.00$ fg/kg at 1000 m (Fig. 2.2b). Previous measurements from the north Atlantic show very similar concentrations (Vogler et al., 1998), while those from the South Atlantic (Moran et al., 2002) are systematically higher than our new measurements.

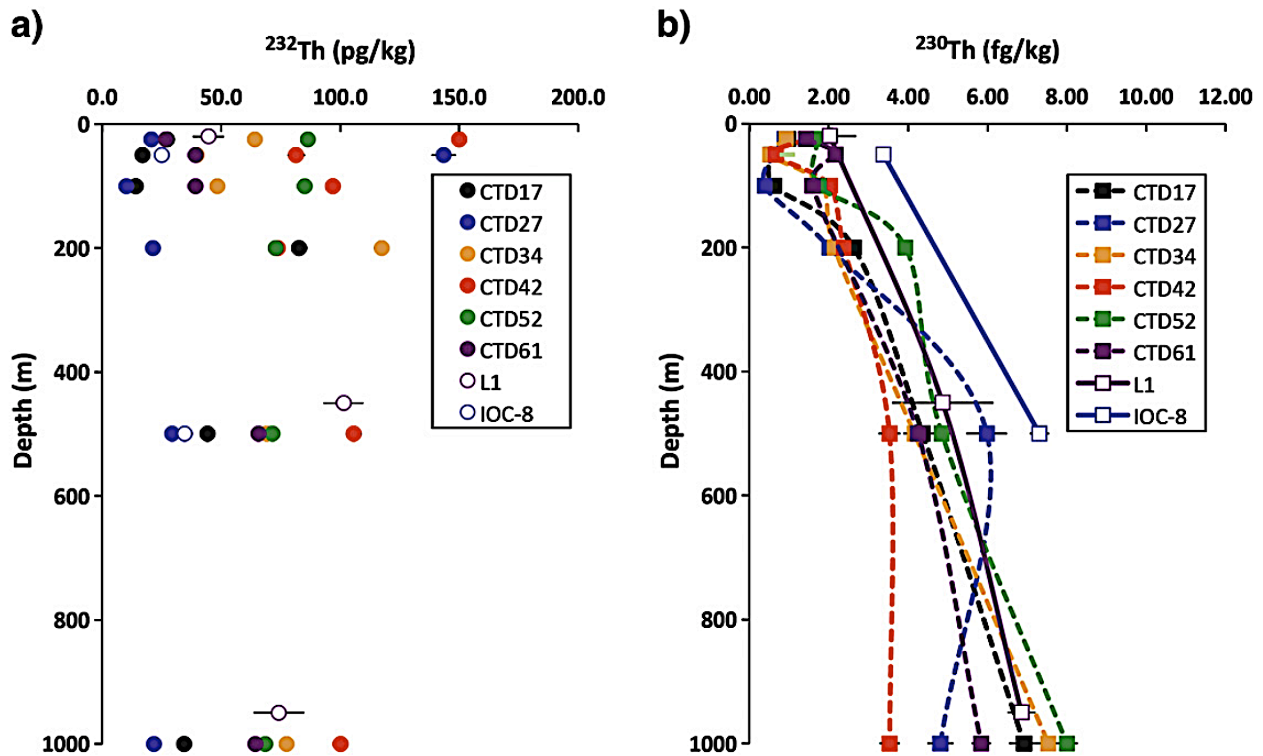


Figure 2.2 Water-column profiles of (a) ^{232}Th and (b) ^{230}Th concentrations. The open symbols are data from reference stations: L1 (Vogler et al., 1998) and IOC-8 (Moran et al., 2002) and are plotted in the same colour as the closest station from this study.

Depth profiles of $^{232}\text{Th}/^{230}\text{Th}$ (atom ratio) range from 4,489 (CTD 27, 1000 m) to 122,025 (CTD 42, 50 m) (Fig. 2.3). Near the surface, at 25 m, the maximum ratio of 104,434 is found at CTD 42, and the minimum ratio of 22,995 is at CTD 27. In general, $^{232}\text{Th}/^{230}\text{Th}$ profiles at each station can

be explained by constant ^{232}Th with depth and an increasing ^{230}Th concentration. We demonstrate this in Fig. 2.3, which is constructed by assuming a constant ^{232}Th concentration identical to that at 25 m and the observed ^{230}Th depth profile. These calculated profiles demonstrate the general constancy of ^{232}Th with depth, and allow easy recognition of where deviations from this behaviour occur. Such deviations are seen in several samples in the mid-water column, and the largest such deviation is at CTD 61, which shows enrichment of ^{232}Th as deep as 1000 m.

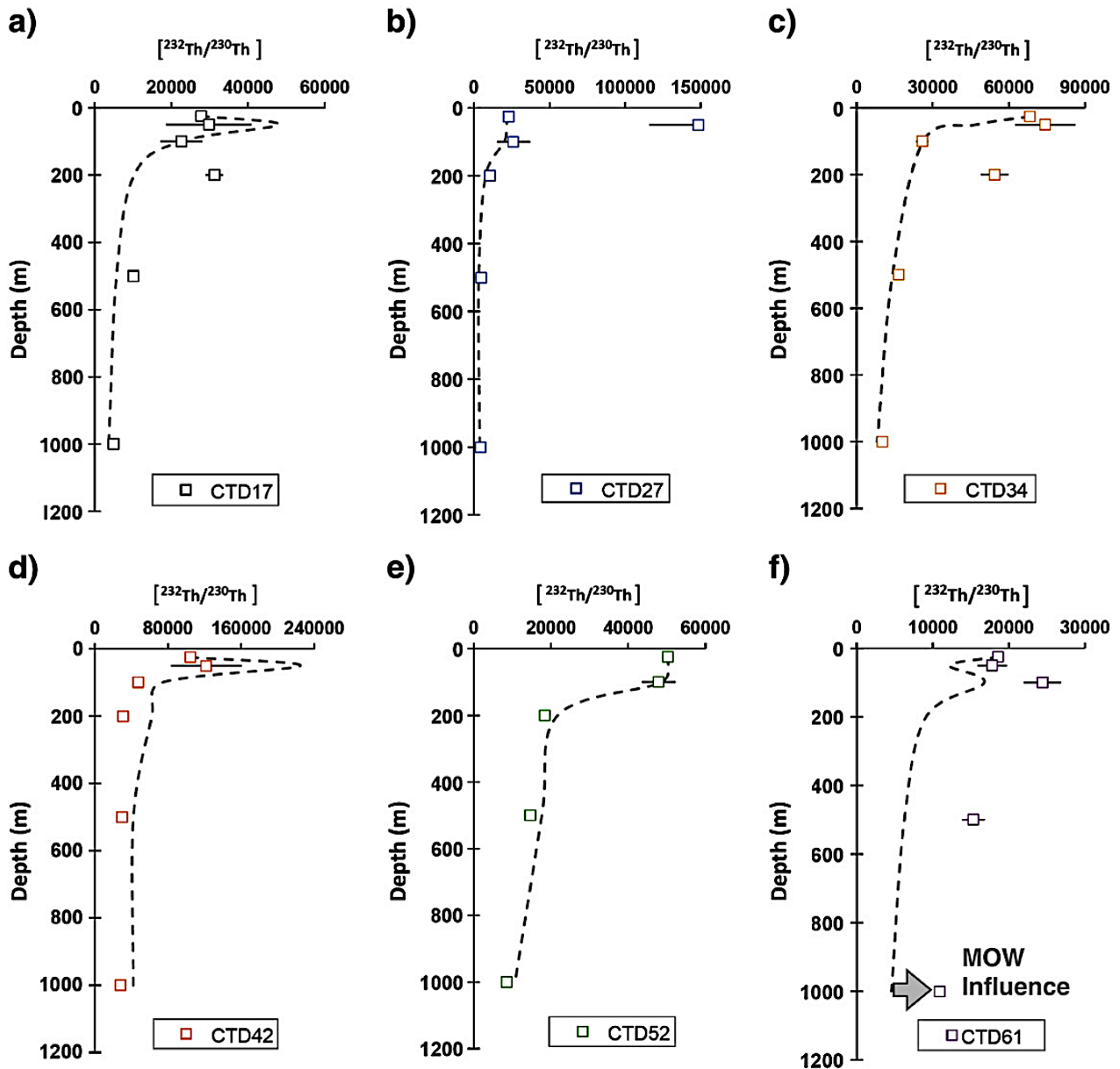


Figure 2.3 Water-column $[^{232}\text{Th}/^{230}\text{Th}]$ profiles. The depth profile of $[^{232}\text{Th}/^{230}\text{Th}]$ from each station is similar to the typical profile (dashed line) given by the extrapolation of $^{232}\text{Th}/^{230}\text{Th}$ to depth from the surface ^{232}Th concentration and the profiles of ^{230}Th (see text). However, the $[^{232}\text{Th}/^{230}\text{Th}]$ profile at some stations, particularly CTD 61 (f) is offset from the dashed line, demonstrating the potential advection of excess ^{232}Th .

U-238 concentrations show a similar relationship of ^{238}U to salinity as seen in previous studies (e.g. Owens et al., 2011). The average $\delta^{234}\text{U}$ in our samples is 146 ± 4 (‰) (2S.D., $n = 40$) which is also consistent with published values (e.g. Chen et al., 1986; Robinson et al., 2004). These data were used for the in-growth ^{230}Th correction but are not considered further in this discussion.

2.6 Discussion

2.6.1 Dust flux control of open-ocean ^{232}Th

The highest ^{232}Th concentrations, particularly in surface waters (e.g. 25 m), are observed at stations expected to be strongly influenced by input of dust from the Sahara (Fig. 2.4a). Aeolian and fluvial inputs are the major sources of ^{232}Th to the ocean (Guo et al., 1995; Huh et al., 1989; Robinson et al., 2004; Roy-Barman et al., 1996) so it is not a surprise that dust inputs would dominate in the open ocean far from any riverine inputs. Normalising to ^{230}Th (Fig. 2.4b) further strengthens the relationship with expected dust inputs (based on satellite optical depth measurements – Fig. 2.4c) and a well-defined peak in $[\text{Th}/^{230}\text{Th}]$ coincides with the band of maximum optical depth measurements (Fig. 2.4b). These data clearly indicate strong control of open-ocean $[\text{Th}/^{230}\text{Th}]$ by dust input, and suggest the use of Th isotopes as a proxy with which to constrain the size of this ocean input.

In the centre of the dust plume (CTD 42), a $[\text{Th}/^{230}\text{Th}]$ ratio greater than 100,000 is observed in surface waters. Previous studies reporting $[\text{Th}/^{230}\text{Th}]$ ratios this high (e.g. 116,000 – 205,000; Cochran et al., 1987) have been in coastal regions and influenced by riverine inputs. Stations in this study are far from any such riverine input, however, and there is no hint of freshwater inputs from hydrographic observations (e.g. Fukumori and Wunsch, 1991). In surface waters influenced by the high dust fluxes of the Saharan plume, rates of addition of ^{232}Th to seawater appear comparable with that from riverine sources at the ocean margin.

Th-232 (and $^{232}\text{Th}/^{230}\text{Th}$ ratios) also show similar patterns to that of the other commonly used chemical dust proxy, Al, along this Atlantic transect (Fig. 2.4a). Although at lower measurement resolution, variation of ^{232}Th concentration in surface waters is consistent with the surface dissolved Al distribution (Measures et al., 2008) with both peaking at $\approx 10^\circ\text{N}$. This observation further supports the use of ^{232}Th in a similar manner as that of Al to assess fluxes of dust to the surface ocean.

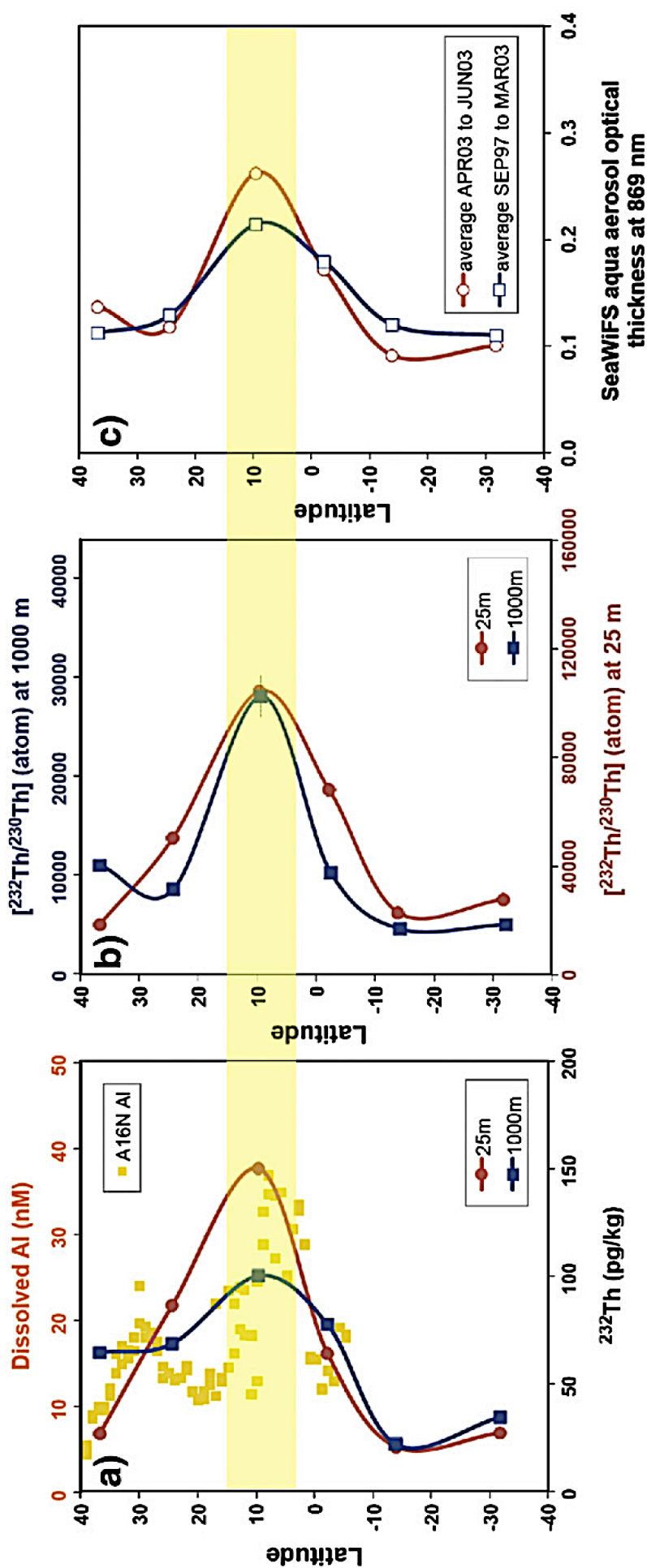


Figure 2.4 Latitudinal dependence of (a) ^{232}Th (pg/kg) and dissolved Al (nM), (b) $^{232}\text{Th}/^{230}\text{Th}$, and (c) SeaWiFS data of aqua aerosol optical thickness at 869 nm along the AMT 12 transect (average SeaWiFS aerosol data from the $1^\circ \times 1^\circ$ grid square corresponding to sample locations). The yellow band indicates the high dust zone of the Saharan dust plume. In (a) and (b), the red line is the data at 25 m seawater and the blue line is at 1000 m. Yellow squares in (a) are the dissolved Al data from A16N transect (Measures et al., 2008). In (c), the short-term data while the AMT 12 carried out (April–June in 2003) are presented in red and the long-term average data (September 1997 – March 2003) are presented in blue. The SeaWiFS aerosol data are downloaded from <http://reason.gsfc.nasa.gov/OPS/Giovanni/>, NASA ocean colour time-series online visualisation and analysis.

Th-232 data from different depths may also provide information about dust inputs over different timeframes. The short residence time of Th in surface waters mean that ^{232}Th concentrations will be biased by input in the preceding months. Smoothing during downward transport, on the other hand, means that deeper ^{232}Th concentrations may reflect a longer-term average of dust inputs. To investigate the influence of temporal variation in dust inputs on ^{232}Th , we compare ^{232}Th concentrations at 25 m and 1000 m with the average aerosol data from April to June in 2003 (i.e. the same period as the sample collection) and the long-term data averaged from September 1997 to March 2003. Th-232 concentrations show a significant difference between 25 m and 1000 m under the centre of the dust plume (Fig. 4a) with the concentration of ^{232}Th at 25 m about 50% higher than at 1000 m. A similar offset between the short-term and long-term averaged aerosol data is found at the same location (Fig. 4c) with the short-term aerosol depth about 25% higher than the long-term average. These observations hint that surface water ^{232}Th distributions reflect short-term dust inputs to the ocean while, in deep waters, mixing during scavenging and downward transport causes ^{232}Th concentrations to reflect the long-term average dust input. An ability to assess seasonal changes in dust input in this way, if supported by additional data, would be important because aerosol inputs of micronutrients to the ocean are thought to exhibit strong seasonality (e.g. Gao et al., 2001).

2.6.2 Lateral input of ^{232}Th

To use ^{232}Th as a tracer of atmospheric dust input, the assumption must be made that there are no other inputs of ^{232}Th to open-ocean surface waters. Th-232, however, has an average ocean residence time of ~20 years in seawater (Henderson and Anderson, 2003) allowing the possibility of lateral input of ^{232}Th , and/or supply to the surface from upwelling. In some regions, high ^{232}Th flux from lateral input is more likely due to the influence of seawater with re-suspended sediments or higher detrital materials (e.g. continental margins with strong advection or upwelling; Roy-Barman, 2009).

To investigate the influence of lateral ^{232}Th input in samples of this study, we draw a surface extrapolated [$^{232}\text{Th}/^{230}\text{Th}$] profile at each station to compare to our data (Fig. 2.3). The extrapolated profiles of [$^{232}\text{Th}/^{230}\text{Th}$] are produced by taking the surface (25 m) ^{232}Th concentration and the profiles of ^{230}Th to produce a hypothetical [$^{232}\text{Th}/^{230}\text{Th}$] profile that assumes the ^{232}Th at depth is equal to the present surface concentration.

Several measurements fall off the $^{232}\text{Th}/^{230}\text{Th}$ profiles expected if dust input from above is the only source of ^{232}Th (Fig. 2.3). These high values require an additional source of ^{232}Th , either from sample contamination during collection or measurement, or by lateral transport in the water column. Inspection of the T–S values of all but one of the five samples with such anomalously high $^{232}\text{Th}/^{230}\text{Th}$ (Fig. 2.1b) do not indicate any additional water mass is present and therefore argues against lateral transport as the explanation. Recent intercalibration efforts in the GEOTRACES programme have demonstrated the susceptibility of seawater ^{232}Th measurements to intermittent contamination (Anderson et al., submitted for publication) and this may be the case for some of the samples in this study. In one case, however, the high $^{232}\text{Th}/^{230}\text{Th}$ is much more likely to be caused by lateral advection. At CTD61, high values are observed at 1000 m, coincident with a clear trend in temperature and salinity towards Mediterranean Overflow Waters (MOW) (Fig. 2.1b).

The influence of MOW at CTD61 is likely to explain the high ^{232}Th concentrations. Waters at these depths also have dissolved Al concentrations (~ 20 nM) about 2 times higher than surface water dissolved Al (~ 10 nM) at the same latitude (36°N) probably through the influence of MOW (Measures et al., 2008). Western Mediterranean Deep Water (WMDW) has a very high dissolved Al of ~ 120 nM when it exits from the Strait of Gibraltar then spreads into the North Atlantic (Measures and Edmond, 1988). The concentration of ^{232}Th in the western Mediterranean Sea (≈ 500 pg/kg; Roy-Barman et al., 2002) is also about 5 to 10 times higher than the average ^{232}Th concentration in the surface layer of Atlantic. Labelling of MOW with high ^{232}Th from the Mediterranean therefore provides a good explanation for the high $^{232}\text{Th}/^{230}\text{Th}$ at this station. In the future, a time-series data collection of ^{232}Th and ^{230}Th around this area would help to understand the distribution and flow rate of MOW and to evaluate the chemical impact of particulate and dissolved Th from MOW to the north Atlantic.

2.6.3 Th removal residence times in surface seawater

To convert ^{232}Th concentrations in seawater into ^{232}Th input fluxes requires information about the removal rate of ^{232}Th . This might be derived from the other, shorter-lived radioactive isotopes – ^{228}Th , ^{234}Th and ^{230}Th . Indeed, ^{234}Th is routinely used to assess downward fluxes of carbon in the ocean (Buesseler et al., 1992; Cochran et al., 2000; Kaufman et al., 1981). The use of ^{228}Th is less frequent, due to difficulty in analysing this nuclide and the variability of its parent (^{228}Ra), while ^{230}Th is not

normally used to calculate residence times in this way. In this section we assess the use of ^{230}Th for derivation of surface-ocean Th residence times, and compare residence times calculated with ^{230}Th , with those from ^{234}Th .

The removal residence times of Th in surface seawater were calculated using a simple scavenging model (Broecker et al., 1973):

$$\tau_{\text{Th}} = \frac{A_{\text{daughter}} / A_{\text{parent}}}{1 - A_{\text{daughter}} / A_{\text{parent}}} \cdot \tau_{\text{daughter-mean-life}} \quad (2.2)$$

where τ_{Th} is the removal residence time of ^{230}Th or ^{234}Th ; A is the radioactive decay rate (activity) of the respective daughters and parents (^{230}Th – ^{234}U and ^{234}Th – ^{238}U); and $\tau_{\text{daughter-mean-life}}$ is the mean life of daughter ($1/\lambda$). We use ^{230}Th data (corrected for lithogenic ^{230}Th) from this study and ^{234}Th data from Thomalla et al. (2006). Literature ^{234}Th data are not from the same year, or from exactly the same locations, as the ^{230}Th data reported here, but they are reasonably close, and interannual variations at each station are not expected to be large relative to the changes observed seasonally in a single year. We therefore consider this comparison to provide worthwhile information even though not conducted on identical samples.

Comparisons of ^{234}Th and ^{230}Th (and ^{228}Th) in surface water have been made in some previous studies. Santschi (1984) found a good correlation between particle fluxes and ^{230}Th , ^{228}Th and ^{234}Th residence times through the water column although the half-life of these Th isotopes range over six orders of magnitude. However, Luo et al. (1995) found longer Th residence times of ^{230}Th and ^{228}Th than ^{234}Th in the equatorial upwelling regions because of the vertical upward mixing of the long-lived ^{230}Th and ^{228}Th . Coppola et al. (2006) also found that ^{230}Th and ^{234}Th partition differently between large and small particles, with a larger fraction of ^{234}Th than ^{230}Th on the large particles. Their results still showed similarity, however, between the distributions of particulate organic carbon (POC) and ^{230}Th . This suggests that the use of ^{230}Th to estimate POC flux may be possible.

In our results, removal residence times calculated from ^{230}Th are generally in agreement with the values calculated from ^{234}Th for the upper mixed layer (< 25 m) in the Atlantic. Residence times of

^{230}Th range from 1.23 (± 0.37) to 2.55 (± 0.77) years, and of ^{234}Th from 0.27 (± 0.09) to 1.79 (± 0.45) years (Fig. 2.5). These results are reassuring for the use of ^{230}Th to calculate Th residence times in surface seawater, although it has a half-life more than a million times longer than ^{234}Th (the more routinely used radionuclide for estimating particulate organic carbon (POC) flux in surface ocean).

Residence times for Th show a general trend of slower removal rates in the sub-tropical gyres and faster removal in the tropics (Fig. 2.5). Similar observations have also been found in previous studies using ^{228}Th (and its parent ^{228}Ra) in the Atlantic (Li et al., 1980) and Pacific (Luo et al., 1995). Due to the strong upwelling in tropical areas, high particulate fluxes increase the Th scavenging rate. A short ^{234}Th residence time of 0.25 years is found in the Atlantic equatorial upwelling region, which is related to a high POC flux (Charette and Moran, 1999). In sub-tropical regions, lower Th removal rates imply lower particulate fluxes and slower downward transport of Th through the water column.

Despite the broad agreement in patterns of thorium removal assessed with ^{230}Th and ^{234}Th , there are differences in the absolute values calculated with the two nuclides at some locations. For instance, our results show a longer residence time for ^{230}Th than ^{234}Th , presumably due to upward mixing which will impact ^{230}Th more than ^{234}Th (with its much shorter half life). The other mismatch between ^{230}Th and ^{234}Th is at 36–38°N where the ^{230}Th calculated residence time is 2.55 years compared to significantly shorter residence time of 0.27 years for ^{234}Th . Such short ^{234}Th residence times are, in general, associated with particulate scavenging during seasonal bloom (Buesseler et al., 1992). At the time of the ^{234}Th measurements (April–May 2004), SeaWiFS chlorophyll data show a strong seasonal bloom in the northern temperate Atlantic, which induces a high ^{234}Th flux of 3332 dpm $\text{m}^{-2} \text{day}^{-1}$ and a huge disequilibrium of ^{234}Th – ^{238}U (at CTD 79 in Thomalla et al., 2006). The annual average chlorophyll concentration is, however, some 5 to 7 times lower than that seen during the bloom in this region (Fig. 5 in Thomalla et al., 2006). This suggests that the annual average Th residence time should also be 5 to 7 times higher, within error of the ^{230}Th residence time observed.

Comparison of ^{234}Th and ^{230}Th data suggest that these isotopes provide somewhat different, but complementary, information about Th removal. Th-234 is more appropriate (due to its short half-life and correspondingly short residence time) for estimation of the surface water POC export, which varies on a short time scale. In contrast, the residence time of ^{230}Th is not set by its half-life, is longer than

that for ^{234}Th , and is likely to be similar to that for ^{232}Th . Future studies might usefully compare ^{234}Th and ^{230}Th residence times through a year, and assess the scavenging effect of particle size and composition on the various Th isotopes. Given present understanding, however, the use of ^{230}Th to assess removal rates of ^{232}Th appears appropriate and allows quantification of ^{232}Th input.

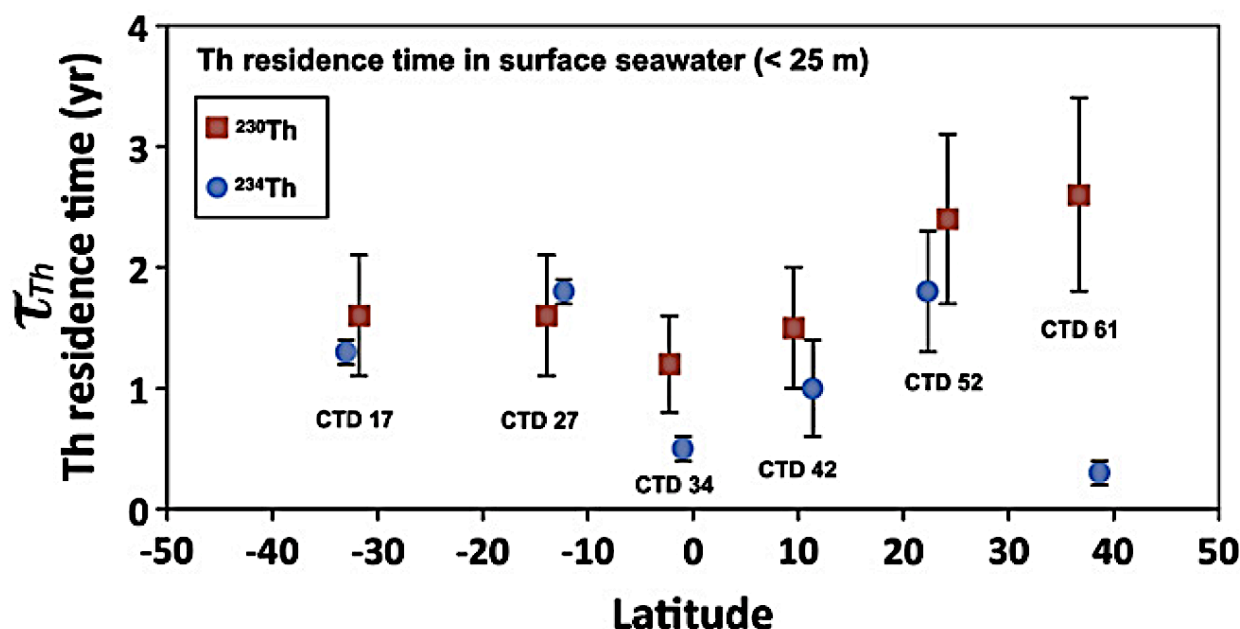


Figure 2.5 The residence time of ^{230}Th and ^{234}Th in surface seawater (< 25 m). The ^{234}Th residence time is calculated with data from AMT 14 (Thomalla et al., 2006). The activity ratio of ($^{230}\text{Th}/^{234}\text{U}$) is calculated using ^{230}Th half-life of 75.690 ka and ^{234}U half-life of 245.250 ka (Cheng et al., 2000). A ratio of [$^{230}\text{Th}/^{232}\text{Th}$] of 4.0×10^{-6} is used for lithogenic correction. Error bars are two standard errors.

2.6.4 Quantifying dust input with Th isotopes

Combining observed ^{232}Th concentrations in surface waters with ^{230}Th -derived residence times for Th allows calculation of the output flux of ^{232}Th from the surface ocean and, by assuming steady-state, the input flux of ^{232}Th from dust dissolution. To calculate this dust input requires consideration of the two forms of Th (dissolved and particulate) and of the transfer between them as dust dissolves in surface seawater.

Although ^{232}Th enters the ocean in a different form than ^{230}Th and ^{234}Th , the seawater inventory of all three isotopes is dominated by the dissolved fraction in which their behaviour is expected to be chemically identical. Use of ^{230}Th residence times to assess ^{232}Th removal is therefore valid despite the different input mechanisms. Ideally, the dissolved-fraction data for ^{232}Th would help to ensure of that ^{230}Th and ^{232}Th were comparable but, in practise, some 80 – 90% ^{232}Th is present in the dissolved form

(i.e. operationally defined as passing through a 0.2 micron filter) so the presence of some particulate ^{232}Th in the unfiltered seawater samples measured in this study makes only a small difference to the calculations. This dominance of dissolved ^{232}Th in seawater reflects faster removal of particulate Th by settling, than removal of dissolved Th by scavenging. To a first approximation, ^{232}Th that does not dissolve is removed downwards sufficiently fast as to be insignificant to the ^{232}Th budget of seawater. It is the fraction that does dissolve that dominates the budget and allows an assessment of dust fluxes.

The ^{232}Th removal flux ($\mu\text{g m}^{-2} \text{ yr}^{-1}$) is calculated by multiplying the ^{232}Th concentration ($\mu\text{g m}^{-3}$) by a constant mixed layer depth of 25 m (based on the average mixed layer depth in our study sites), and then dividing by the ^{230}Th -derived removal residence time (yr) at 25 m (Table 2.2). The assumption of a constant mixed layer is not completely accurate, but this assumption has also been made in the commonly used Al-based approach (Measures and Brown, 1996; Measures and Vink, 2000) and represents a good starting point, allowing direct comparison with such Al studies. Calculated removal fluxes of ^{232}Th ranges from 0.26 to 2.50 $\mu\text{g m}^{-2} \text{ yr}^{-1}$ for the surface Atlantic. To turn this removal flux into a dust flux to the surface ocean requires an assessment of the solubility of ^{232}Th from dust on addition to seawater. This solubility can then be inserted into the following equation:

$$F_{\text{dust}} = \frac{F_{^{232}\text{Th}}}{[^{232}\text{Th}]_{\text{dust}} \times S_{\text{Th}}} \quad (2.3)$$

where F_{dust} is the dust flux; $F_{^{232}\text{Th}}$ is the removal flux of ^{232}Th ; $[^{232}\text{Th}]_{\text{dust}}$ is the ^{232}Th dust concentration (assumed to be 13 ppm; Taylor and McLennan, 1985); and S_{Th} is Th solubility.

Assessing metal solubility from dust in seawater is a complex issue and, for those metals where extensive data exists (e.g. Fe) it has been shown that solubility is highly variable (e.g. Baker and Croot, 2010). There are very few estimates of the solubility of Th, although Roy-Barman (2009) assumed that the Th solubility from lithogenic materials was only 1%. If we assume 1% dissolution (Fig. 2.6a blue line), dust fluxes range from 2.0 to 19.2 $\text{g m}^{-2} \text{ yr}^{-1}$ across the Saharan dust gradient, compared to 0.1 to 9.8 $\text{g m}^{-2} \text{ yr}^{-1}$ in global dust deposition models (Fig. 2.6b Mahowald et al., 2005). In the south Atlantic, dust fluxes assessed with a 1% Th solubility are therefore up to an order of magnitude higher than model estimates. This might be explained by inaccuracy of the model results (which rely on

assumptions of atmospheric dust removal mechanisms) or by a higher solubility of Th from dust in this region. Direct assessment of Th solubility from dust in different regions is required, and the present uncertainty in such solubility represents the largest uncertainty in the use of Th isotopes as dust input tracers. Never-the-less, the overall similarity in $^{232}\text{Th}/^{230}\text{Th}$ ratios and expected dust fluxes across the Saharan plume points to the significant potential of Th isotopes as a quantitative tool to assess dust inputs.

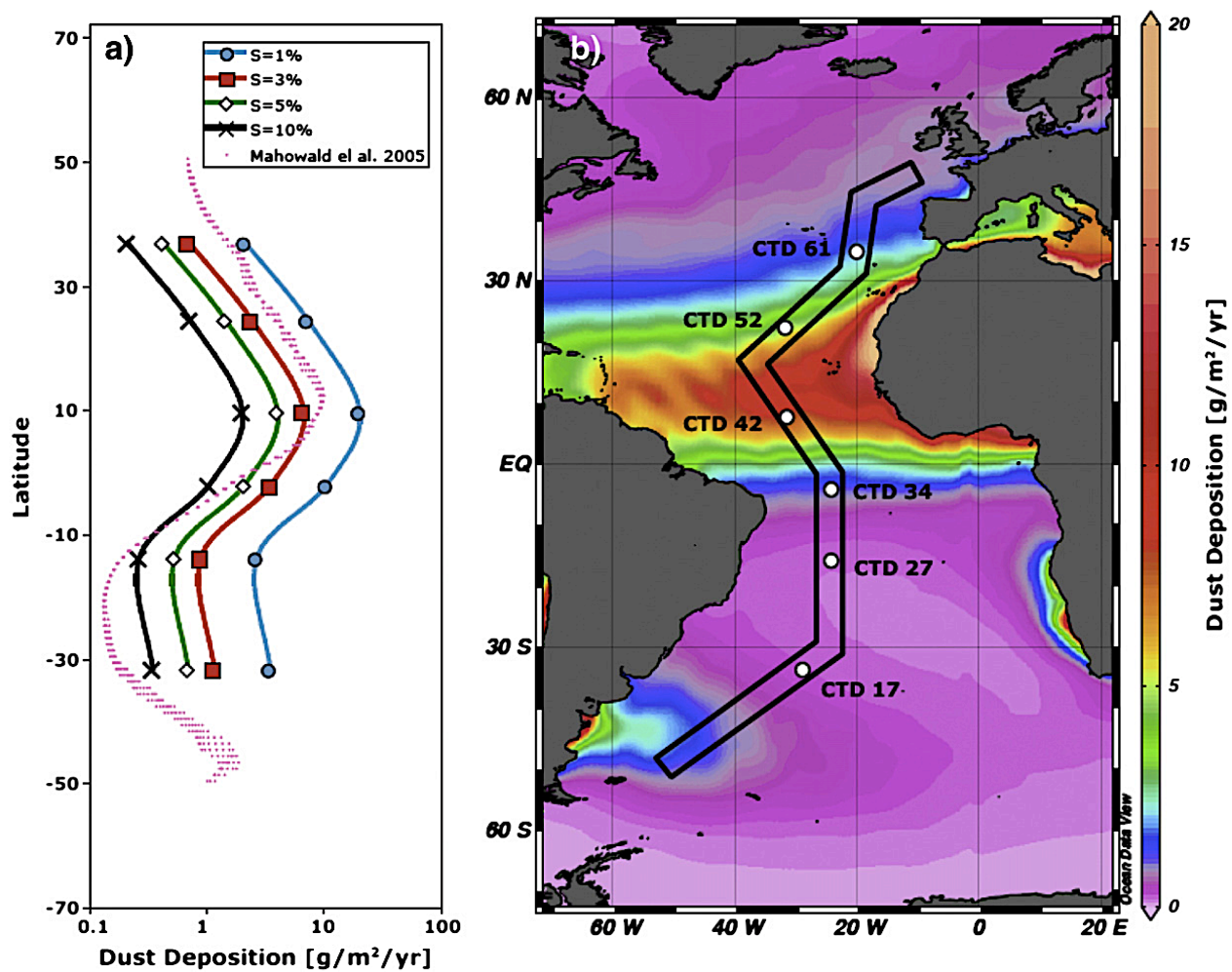


Figure 2.6 The comparison of (a) ^{232}Th estimated dust deposition (in log scale) and (b) the global dust deposition model (Mahowald et al., 2005). Dust deposition is expressed in units of $\text{g m}^{-2} \text{yr}^{-1}$. The dust depositions estimated from ^{232}Th are calculated from Th solubility ranges from 1% to 10%. The light red dots in (a) are the dust model output from the black section in the dust model map in (b).

Table 2.2 Th flux, dust deposition model and Th solubility in the ocean

AMT12 Station	^{232}Th flux ($\mu\text{g m}^{-2} \text{yr}^{-1}$) at 25m	Model dust deposition ($\text{g m}^{-2} \text{yr}^{-1}$)	Th solubility (%)
CTD17	0.43 ± 0.13	0.20 ± 0.04	16.9 ± 6.1
CTD27	0.33 ± 0.10	0.18 ± 0.04	13.9 ± 5.0
CTD34	1.30 ± 0.39	1.55 ± 0.31	6.5 ± 2.3
CTD42	2.50 ± 0.75	8.98 ± 1.80	2.1 ± 0.8
CTD52	0.90 ± 0.27	4.13 ± 0.83	1.7 ± 0.6
CTD61	0.26 ± 0.08	1.54 ± 0.31	1.3 ± 0.5

Global dust deposition models are cited from Mahowald et al. (2005) with 20% uncertainty. The solubility is calculated assuming an average ^{232}Th concentration of 13 ppm from pelagic sediments (Taylor and McLennan, 1985).

2.6.5 Comparisons of Al and Th as dust tracers

To use a metal, such as Al or Th, as a tracer of dust inputs to the oceans requires making a number of assumptions: i. conditions can be considered to be at steady state; ii. the mixed layer depth has a constant thickness or can be otherwise constrained; iii. the metal has a known residence time at the measurement site; iv. the metal content of dust is known (and ideally can be considered invariant); v. the metal solubility in dust is known; vi. dust is the only source of that metal to the surface seawater.

Aluminium and ^{232}Th show similar geochemical characteristics and in many ways meet these assumptions to the same degree. Both are dominantly sourced from the continents and are also fairly uniformly distributed in continental rocks so that reasonable assumptions can be made about dust composition. Both have sufficiently short residence times in surface waters that, in the surface open ocean, there is not likely to be significant input from non-dust sources. If there is an issue with lateral transport for ^{232}Th , it must be even worse for Al because the average residence time of Th is shorter than that of Al in the surface ocean.

The major potential advantage of ^{232}Th relative to Al is that the use of ^{230}Th (or ^{234}Th) provides an assessment of the local residence time of Th. This differs from Al, where previous studies (e.g. Measures and Brown, 1996; Measures and Vink, 2000) have assumed a constant residence time, typically of 5 years. Modelling studies provide some indication of the variability of Al residence time, suggesting that

it may change from months to several decades (Han et al., 2008), and demonstrating the limitations of the assumption of constant residence time. The ability to constrain residence time may, therefore, make ^{232}Th a more robust proxy for dust input than Al.

The major limitation in using ^{232}Th to assess dust fluxes is variability in the solubility of Th solubility from dust. In this it is similar to Al, but the situation is worsened for Th because, unlike Al, there has been little previous study of Th solubility. Robinson et al. (2008) measured $^{232}\text{Th}/^{230}\text{Th}$ from leached fractions of bottom sediments to reconstruct the flux of dissolved ^{232}Th to the ocean. They found that adsorbed fractions of ^{232}Th , interpreted as scavenged dissolved ^{232}Th , ranged from 35 – 50% of total ^{232}Th . However, this estimation may include ^{232}Th from other sources since bottom sediments have settled through the whole water column. Limited previous work has suggested that Th solubility might vary significantly, however. Arraes-Mescoff et al. (2001) found Th solubility from 1 to 13% in marine suspended particles collected in the Ligurian Sea, and Roy-Barman et al. (2002) estimated Th solubility from aeolian dust from 3 to 5% in the western Mediterranean Sea.

Some assessment of Th solubility can be made by comparing our new data with previous models of dust deposition. We have calculated Th solubility in Table 2.2 by assuming that modelled dust depositions are broadly correct (with 20% uncertainty) (Mahowald et al., 2005) and that dust contains a constant Th concentration of 13 ppm (Taylor and McLennan, 1985). Th solubility calculated in this way ranges from 1 to 16%. Models of dust deposition have considerable uncertainty, however, so this cannot be considered a robust calibration of solubility. It is nevertheless reassuring that this range is broadly similar to that seen in previous studies (Arraes-Mescoff et al., 2001; Roy-Barman et al., 2002).

The solubility of Al may also help in constraining Th solubility because the geochemical characteristics of Th and Al are somewhat similar. Published Al solubility ranges widely from 0.1 to 86% (Baker et al., 2006; Buck et al., 2010; Measures et al., 2010; Prospero et al., 1987). In the Atlantic, Baker et al. (2006) assessed the Al solubility in the Saharan plume as $\approx 3\%$, with higher solubility of $\approx 9\%$ elsewhere. Buck et al. (2010) also found a wide range of Al solubility of 5 – 27% in samples collected from the A16N CLIVAR cruise in the North Atlantic. This range of solubility is rather similar to that observed for Th in this study, suggesting a similar set of processes are at work for the two tracers.

In general, ^{232}Th -dust fluxes show agreement with existing dust models if Th solubility is 1 to 5% in the north Atlantic (where dust input is high) and 5 to 10% in the south Atlantic (where dust input is low). This range of solubility is similar to those found for dissolved Al, with higher Al solubility in low, than in high dust regions (Baker et al., 2006; Luo et al., 2005; Prospero et al., 1987). Relative to the range of Al solubility in the Atlantic (5 – 27%; Buck et al., 2010), the solubility of Th seems slightly lower (1 – 16%), but the spatial pattern of solubility is nevertheless similar.

Better constraints on the solubility of Al and Th and their concentrations in dust will be required to fully quantify dust flux to the ocean using these elements, and variations of mixed layer thickness and the advection input should also be considered in future studies. This study, however, has demonstrated that, although Th shares some limitations with Al as a proxy for dust input, the ability to assess Th removal time with shorter-lived nuclides offers it a significant potential advantage.

2.7 Conclusions

Seawater thorium isotopes, ^{230}Th and ^{232}Th , can be used as proxies to calculate Th removal rates and dust input in the surface ocean. Seawater ^{232}Th concentrations and $^{232}\text{Th}/^{230}\text{Th}$ show a good correlation with dissolved Al and with SeaWiFS aerosol optical data across the Saharan dust plume. Deeper in the water-column, variation of ^{232}Th concentration may reflect the temporal variation of dust input and, in some locations, the lateral advection of Th (e.g. from the Mediterranean).

Thorium residence times calculated by ^{230}Th – ^{234}U are broadly in agreement with results calculated by ^{234}Th – ^{238}U . In contrast to the short-lived ^{234}Th , however, ^{230}Th residence time is likely to approximate the annual Th removal rate, which is more appropriate for calculating the long-term average ^{232}Th flux in the ocean.

Dust fluxes are calculated from measured ^{232}Th concentrations, ^{230}Th -derived removal rates, typical continental Th concentrations, and dust Th solubility of 1 to 10%. The ^{232}Th estimated dust deposition of $2.0 - 19.2 \text{ g m}^{-2} \text{ yr}^{-1}$ and $0.2 - 1.9 \text{ g m}^{-2} \text{ yr}^{-1}$ show good agreements with a dust model (Mahowald et al., 2005) if Th solubility is 1 to 5% in the north Atlantic (high dust input) and 5 to 10% in the south Atlantic (low dust input). Further studies of Th solubility will help to better constrain the ^{232}Th estimated dust flux and allow Th isotopes to be used as a quantitative tool to assess the input of dust (and related nutrients) to the surface ocean.

Chapter 3

Precise measurement of $^{228}\text{Ra}/^{226}\text{Ra}$ ratios and Ra concentrations in seawater

samples by multi-collector ICP mass spectrometry

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3.1 Abstract

We have developed a method for the precise measurement of $^{228}\text{Ra}/^{226}\text{Ra}$ ratios and ^{228}Ra and ^{226}Ra concentrations in seawater by multi-collector ICP mass spectrometry (MC-ICP-MS). The measurement of Ra isotopes has typically relied on decay-counting techniques with large-volume seawater samples. Adapting pre-concentration approaches from such previous studies, our new protocol pumps 50 to 150 L of seawater through Mn-fibre cartridges to pre-concentrate Ra. The Mn-fibres are ashed and then leached with 6N HCl to remove Ra which is then precipitated with SrSO_4 . The SrSO_4 is converted to SrCO_3 for dissolution, before purification of Ra using two ion-exchange columns – one with AG50-X8 resin and the other with Sr Spec resin. The resulting purified Ra aliquot from the Mn-fibre is used to assess the $^{228}\text{Ra}/^{226}\text{Ra}$ ratio of seawater. A separate, 120 to 500 mL sample of the same seawater is also collected and used to assess ^{226}Ra concentrations by MC-ICP-MS, by applying isotope dilution with a ^{228}Ra spike. Seawater ^{228}Ra concentrations are calculated by multiplying $^{228}\text{Ra}/^{226}\text{Ra}$ ratios from the Mn-fibre by ^{226}Ra concentrations from the isotope dilution measurement.

Measurements of $^{228}\text{Ra}/^{226}\text{Ra}$ ratios on an in-house Ra standard demonstrate an internal precision of 1.7% (2 S.E.) and an external repeatability of 2% (2 S.D.) Similar external repeatability is demonstrated for four 100 litre seawater samples from Southampton Docks. The accuracy of the technique, relative to commonly used decay-counting approaches, has been demonstrated for seawater ^{228}Ra and ^{226}Ra concentrations using samples collected as part of the GEOTRACES intercalibration effort. Using comparable volumes of seawater to those for existing analytical techniques, MC-ICP-MS

provides a lower detection limit (≈ 0.1 fg ^{228}Ra), higher precision (2%) and a shorter counting time (20 minutes) for measurement of ^{228}Ra and ^{226}Ra concentrations (although it requires a longer pretreatment time for Ra purification). This technique will allow study of ^{228}Ra in the ocean interior where concentrations are low and will extend the powerful use of this isotope to understand mixing and trace-element fluxes in the oceans.

3.2 Introduction

Measurements of the two relatively long-lived radium isotopes (^{226}Ra , $T_{1/2} = 1600 \pm 7$ yrs; ^{228}Ra , $T_{1/2} = 5.75 \pm 0.03$ yrs) (Knoing et al., 2006) have been widely applied in oceanography. In coastal and open-ocean settings, ^{226}Ra and ^{228}Ra are used to provide important information on processes such as diffusion (Kadko et al., 1987), horizontal and vertical mixing (Broecker et al., 1967; Broecker et al., 1976; Chung and Craig, 1980; Ku and Luo, 1994; Kaufman et al., 1973; Moore, 1969; Moore, 1972; Moore and Santschi, 1986), water-mass and particulate residence time (Li et al., 1980; Rutgers van der Loeff et al., 1995), pore-water and sediment benthic fluxes (Bollinger and Moore, 1993; Bollinger and Moore, 1984; Cochran and Krishnaswami, 1980; Webster et al., 1995; Webster et al., 1994; Hancock et al., 2000; Hammond et al., 1990; Moore et al., 1996), and submarine groundwater discharge (SGD) (Rama and Moore, 1996; Moore, 1996; Moore et al., 2008). Ra-228, the shorter lived of the two isotopes, is particularly suited for the study of oceanic processes with time-scales of months to years because of its 5.75 year half-life. For instance, ^{228}Ra is continually supplied to the ocean by the decay of insoluble ^{232}Th in shelf sediments (Moore, 1969) and can therefore be used to evaluate the mixing rates between shelf waters and the open ocean (Rutgers van der Loeff et al., 1995; Rutgers van der Loeff et al., 2003; Turekian et al., 1996), and to investigate the fluxes of nutrients and trace elements from the shelf to the open ocean (Charette et al., 2007).

Ra-228 concentrations in seawater are particularly low, typically ranging from 0.00165 to 1.65 femtograms/L (i.e. equivalent to 10^{-1} to 10^2 disintegrations per minute / 100 L – a unit commonly used in the literature). The measurement of ^{228}Ra in seawater requires large-volume seawater samples and is limited in precision and detection limits. Improvements in either or both of these by the development of new analytical approaches to the measurement of Ra would allow significant new applications of these isotopes to oceanic problems.

3.3 Previous approaches to ^{228}Ra analysis in seawater

Radium isotopes have been measured using a variety of decay-counting or mass-spectrometry techniques in previous studies. For ^{228}Ra , the majority of previous seawater measurements have relied on decay counting techniques, because they provide a relatively easy and low-cost analytical method.

Alpha spectrometry was first used to measure seawater ^{228}Ra concentrations in the late 1960s. Moore et al. (1969) developed a method relying on ^{228}Th in-growth in which Ra was concentrated from 600 – 700 L seawater samples using BaSO_4 precipitation, before waiting at least 5 months to allow ^{228}Th to partially equilibrate with ^{228}Ra . Th-228 was then separated from Ra and measured in an alpha spectrometer using ^{230}Th as a yield tracer. Ra-226 was also measured on the Ra portion, using a ^{222}Rn scintillation technique (Broecker, 1965), to calculate the $^{228}\text{Ra}/^{226}\text{Ra}$ activity ratio of the same sample. The unknown chemical yield of this approach was addressed by also measuring ^{226}Ra activity on a separate 20 L sample of the same seawater. The precision of this technique is about 30% (2-sigma) on the ^{228}Ra concentration. Improvements to these protocols since they were first developed have since lowered the precision to $\approx 10\%$ (2-sigma) (Moore et al., 1985). In contrast to other decay counting techniques, alpha spectrometry is limited by its complicated chemical procedures, multiple counting steps and long waiting time for ^{228}Th in-growth. However, its advantage is a low background providing a low analytical detection limit of ~ 1.15 fg (0.7 dpm) ^{228}Ra .

Gamma spectrometry has been used successfully to measure high activities of ^{228}Ra and ^{226}Ra in coastal seawater (Moore, 1984). A germanium detector measures gamma ray emissions from ^{214}Bi and ^{214}Pb (^{226}Ra daughters) and ^{228}Ac (^{228}Ra daughter), having waited about 3 to 4 weeks for equilibrium of ^{228}Ac with ^{228}Ra . However, due to high background and the low detection efficiency of most germanium detectors, this method was initially only applicable for volumes of at least 100 L seawater with high Ra activities. Improved, well-type detectors, subsequently extended the method to smaller sample volumes of 20 L for ^{226}Ra measurements (Reyss et al., 1995). In addition, recent application of underground gamma spectrometry has improved the analytical detection limit and the precision, enabling measurement of ^{228}Ra under lower background surroundings (van Beek et al., 2007; van Beek et al., 2010). This improved gamma spectrometry gives an analytical detection limit of 0.76 fg (0.46 dpm) ^{228}Ra and a precision for ^{228}Ra of $\approx 6\%$ (2-sigma), obtained with a counting time of 1 to 2 days

(van Beek et al., 2010). In the absence of underground counting facilities, the detection limit for ^{228}Ra increases to ≈ 10 fg (6 dpm) (Parekh et al., 2003). Sample pretreatment for gamma counting consists only of ashing Mn-fibres (used to preconcentrate Ra from large volumes of seawater) to reduce the fibre volume before insertion in the gamma counter (Dulaiova and Burnett, 2004). Gamma spectrometry therefore provides the advantage of simpler sample pretreatment and shorter waiting time than alpha-counting. However, for measurement of the low activity of ^{228}Ra seen in the open ocean, gamma spectrometers in most labs remain restricted by high detector background.

More recently, ^{228}Ra has also been measured using delayed coincidence counting (Moore, 2008). Radium Delayed Coincidence Counting (RaDeCC), relies on the closely spaced decays caused when ^{223}Ra and ^{224}Ra decay, and is commonly used to measure these shorter lived Ra isotopes (Charette et al., 2007; Moore and Arnold, 1996; Smith et al., 2007; Moore and Krest, 2004). This technique neatly circumvents the need for lower backgrounds and heavy instrument shielding. Ra-228 can be measured using delayed coincidence by storing samples (e.g. scavenged on a Mn-fibre) for at least 6 months until the in-growth of ^{228}Th from ^{228}Ra is easily distinguishable from the initial ^{228}Th absorbed to the fibre. The in-growth of ^{224}Ra is measured by RaDeCC and used to calculate the theoretical in-growth of ^{228}Th to estimate initial ^{228}Ra in the sample. This technique provides the advantage of measuring four different half-lived Ra isotopes, ^{228}Ra , ^{226}Ra , ^{224}Ra and ^{223}Ra , from the same sample. However, this method requires long-term storage of samples at appropriate moisture levels to ensure efficiency. It provides an estimated detection limit of 0.8 fg (0.5 dpm) ^{228}Ra and a precision of 11% (2-sigma).

Mass spectrometry techniques have been used successfully to measure ^{226}Ra concentrations in seawater. Cohen and O’Nions (1991) developed a method for measuring seawater ^{226}Ra concentration using thermal ionization mass spectrometry (TIMS) by isotope dilution with a ^{228}Ra spike. This method demonstrated the advantage of high ionization efficiency for Ra by TIMS, providing a low detection limit of 0.1 fg and enabling measurements of only 1 fg ^{226}Ra (equivalent to ≈ 20 ml of seawater – much reduced relative to decay counting approaches). The high precision of 1% (2-sigma) is obtained with ~ 1 hour counting time, which is faster and more precise than decay counting techniques. Ghaleb et al. (2004) presented an alternative preconcentration technique using MnO_2 precipitation to

extract Ra from seawater before TIMS measurements. Inductively coupled plasma mass spectrometry (ICP-MS) (Varga, 2008) and multi-collector ICP-MS (MC-ICP-MS) (Foster et al., 2004) have also been developed to measure seawater ^{226}Ra concentrations. These ICP-MS techniques generally provide shorter measuring time (< 30 minutes) than TIMS, but rely on somewhat larger sample sizes (e.g. 120 ml) (Foster et al., 2004). Overall, mass spectrometry for ^{226}Ra analysis has the disadvantage of longer pre-processing times, but the significant advantages of smaller sample size, higher precision and shorter measuring time than decay counting techniques.

In atom terms, ^{228}Ra concentrations are typically at least 100 times lower in seawater than ^{226}Ra concentrations, making analysis of ^{228}Ra by mass spectrometry considerably more demanding than ^{226}Ra . Two recent studies have presented approaches to the measurement of $^{228}\text{Ra}/^{226}\text{Ra}$ ratios and ^{228}Ra concentrations in waters by mass spectrometry. One used TIMS to measure near-shore seawater samples (Ollivier et al., 2008). This study used 0.25 – 2 L of coastal seawater, a pre-concentration technique relying on the precipitation of MnO_2 and quoted precisions of 1.72% (2-sigma). The other study applied a MC-ICP-MS to measure lake water (Sharabi et al., 2010), using 60 L of water, preconcentration with MnO_2 precipitation and an external precision of 10% (2-sigma). In this study, we build on these mass spectrometry approaches and present a new analytical protocol for measuring seawater $^{228}\text{Ra}/^{226}\text{Ra}$ ratios and ^{228}Ra and ^{226}Ra concentrations by MC-ICP-MS. This technique is suitable for analysis of low ^{228}Ra concentration seawater, and we demonstrate its use on seawaters, including those from the GEOTRACES intercalibration effort, which allow direct comparison with decay-counting approaches.

3.4 Overview of analytical approach

The measurement protocol described in this paper provides concentrations for ^{226}Ra and ^{228}Ra , as well as a direct $^{228}\text{Ra}/^{226}\text{Ra}$ ratio. These values are delivered by measurement of two discrete subsamples for each seawater sample. A relatively small-volume seawater sample (~120 – 500 mL) is spiked with an enriched ^{228}Ra isotope tracer. Following chemical purification of Ra, mass spectrometry on this sample yields a ^{226}Ra concentration for the seawater with a precision of ~3%. This portion of the analysis follows the approach of Foster et al. (2004), and is not described in detail here. Low concentrations of

^{228}Ra in seawater require significantly larger sample sizes (~ 100 L) which cannot readily be collected without shipboard preconcentration. A second large-volume subsample is therefore preconcentrated on a Mn-fibre cartridge and, following chemical purification, the $^{228}\text{Ra}/^{226}\text{Ra}$ ratio is analyzed by MC-ICP-MS. The combined ^{226}Ra concentration and $^{228}\text{Ra}/^{226}\text{Ra}$ ratio provide a ^{228}Ra concentration for seawater. The preconcentration, purification and mass spectrometry of this larger-volume sample is the focus of this paper.

3.5 Chemical purification of radium

In broad terms, Ra purification from large seawater volumes is performed by preconcentration on Mn cartridges, ashing and leaching of these cartridges, precipitation of Ra with SrSO_4 , conversion to SrCO_3 and ion exchange separation. The sequence is shown in Figure 2.1 and described below.

3.5.1 Reagents

Nitric and hydrochloric acids were purified in a sub-boiling distillation system. Milli-Q 18.2 M Ω water was used throughout this work. Mn-fibres and PVC cartridges were purchased from SCI (Scientific Computer Instruments), SC, USA. Analytical grade sulphuric acid from Fisher Scientific UK Ltd., with a non-detectable Ra blank, was used to precipitate SrSO_4 . Strontium solution (0.3 M) was cleaned of Ra before addition to samples by adding sufficient concentrated H_2SO_4 to precipitate approximately 10% of the Sr as $\text{Sr}(\text{Ra})\text{SO}_4$. Sodium carbonate solution (1 M) was prepared and cleaned for Ra following the procedure described in Foster et al. (2004). Bio-Rad AG50-X8 (200-400 mesh) resin was used to separate Ra and Ba from other elements. An Eichrom Sr-spec. resin (50-100 mesh) was used for the selective separation of Ra from Ba. A ^{228}Ra spike was used to determine seawater ^{226}Ra concentrations and chemical blanks. The ^{228}Ra spike was prepared by milking a high ^{232}Th standard in 2003 (by Michael Staubwasser at Oxford) and has a calibrated $^{228}\text{Ra}/^{226}\text{Ra}$ ratio of 3.915 ± 0.063 (2 S.E., $n = 5$) at the 1st January 2003. The calibration was performed relative to the NIST ^{226}Ra solution (SRM 4966). The spike concentration of ^{228}Ra and ^{226}Ra (also relative to the 1st January 2003) were 5.995 ± 0.057 (10^{-16} mol/g) and 1.531 ± 0.015 (10^{-16} mol/g) (2 S.E., $n = 6$), respectively. At the time of analysis for the work reported here, the spike had a $^{228}\text{Ra}/^{226}\text{Ra}$ ratio of 1.511 (30th August 2010), which is significantly lower than the initial ratio of 3.915 on the 1st January 2003. To achieve high

precision measurements, spike is added to the sample to getting a mixed $^{228}\text{Ra}/^{226}\text{Ra}$ ratio of ~ 0.7 , which sets the percentage of ^{226}Ra from the spike to less than 50% and also provides enough ^{228}Ra atoms for counting. As spike $^{228}\text{Ra}/^{226}\text{Ra}$ falls further with time, error magnification will become an issue and manufacture of a new spike is recommended. An in-house $^{228}\text{Ra}/^{226}\text{Ra}$ standard was mixed using the spike solution and NIST ^{226}Ra to give a ratio of ~ 0.0029 , similar to that observed in oceanic settings.

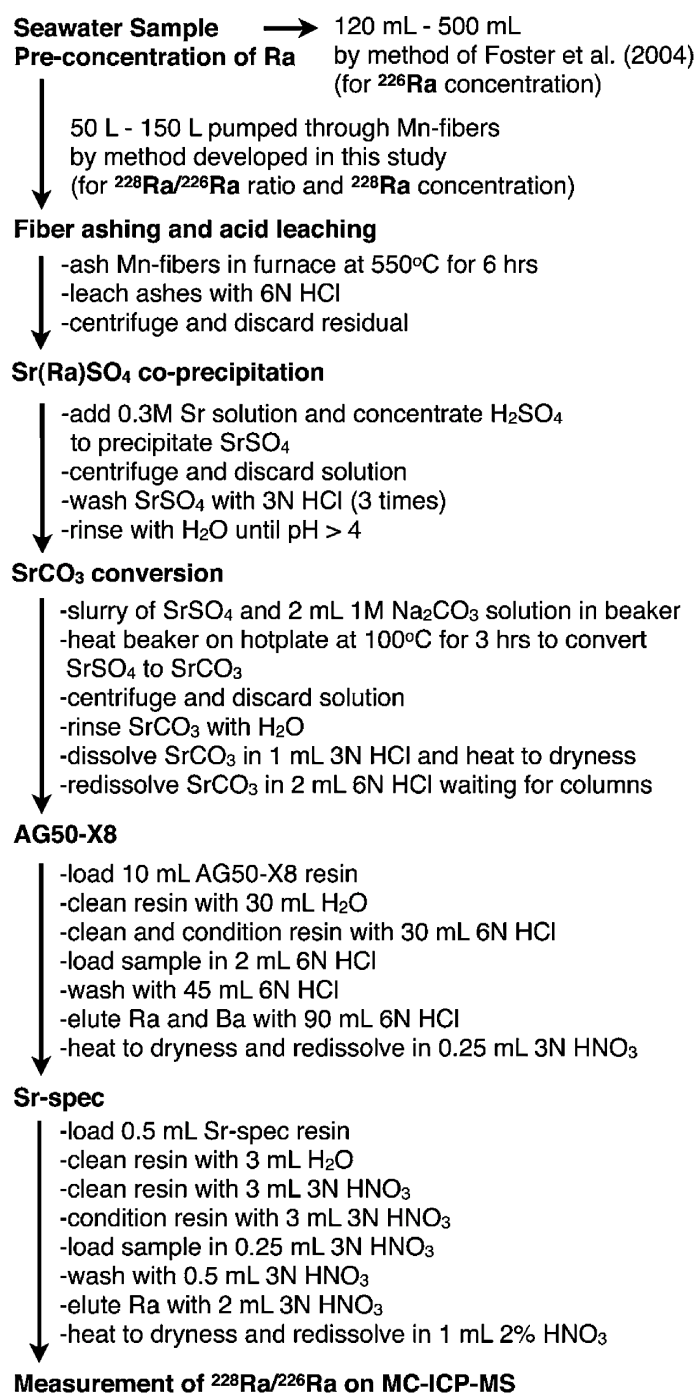


Figure 3.1 The chemical procedure for seawater Ra pre-concentration and separation for ^{228}Ra and ^{226}Ra analysis.

3.5.2 Pre-concentration of Ra from seawater on Mn-fibres

Acrylic fibres impregnated by MnO_2 were used to pre-concentrate Ra from large volumes of seawater samples following published techniques (Moore et al., 1985; Moore and Reid, 1973). A high efficiency of Ra recovery ($\sim 100\%$) with Mn-fibres is achieved if seawater is pumped through the Mn cartridge at flow rates of 2 L/min or less (Moore et al., 1985; Bourquin et al., 2008). In this study, seawater samples of 50 to 150 L were pumped through Mn-fibres at 1 L/min for measurement of $^{228}\text{Ra}/^{226}\text{Ra}$ ratios. In addition, following the published protocol of Foster et al. (2004), 120 to 500 mL samples of the same seawater were collected in prewashed HDPE bottles for measurement of ^{226}Ra concentrations. Mn-fibres were subsequently ashed in a furnace at 550°C for 6 hours to reduce the volume of the fibres by $\sim 90\%$ (Dulaiova and Burnett, 2004; Charette et al., 2001). This step allows the use of significantly less 6 N HCl for the subsequent leaching. The ashing process liberates cyanide gas and must be performed in a fume hood or similar evacuated environment. Resulting ash was leached with 30 mL 6 N HCl and heated on a hotplate at 120°C for ~ 2 hours to ensure dissolution of Ra into the acid solution by reduction of Mn^{4+}O_2 to Mn^{2+} . The solution was then centrifuged and the residual solid discarded before co-precipitation of Ra from the liquid. This Mn-fibre method could be readily adapted to pre-concentrate other U and Th series nuclides (e.g. ^{228}Th , ^{230}Th and ^{227}Ac) or other ultra-trace elements and their isotopes (e.g. Hf and Nd).

3.5.3 Co-precipitation of radium

The Mn-fibre cartridge provides an efficient method to pre-concentrate Ra from large volumes of seawater, but results in a large amount of Mn^{2+} matrix, which must be removed prior to analysis by MC-ICP-MS. Separation of Ra from Mn is therefore required and is achieved by precipitation of Ra with SrSO_4 . BaSO_4 has been used in previous studies to co-precipitate Ra prior to measurements by decay-counting techniques (Moore et al., 1985; Reyss et al., 1995). For ICP-MS analysis, however, SrSO_4 is preferred as the precipitate rather than BaSO_4 , because Ba can produce molecular interferences in the Ra spectrum during analysis (Foster et al., 2004). 0.4 mL of a 0.3 M Sr-solution (SrCl_2) was added to the 6 N HCl used to leach the Mn-fibres solution to provide enough Sr^{2+} for precipitation. 5 mL of concentrated H_2SO_4 was then gradually added and the resulting white precipitate of $\text{Sr}(\text{Ra})\text{SO}_4$

allowed to settle for several hours. The solution was then centrifuged and $\text{Sr}(\text{Ra})\text{SO}_4$ was transferred to a smaller centrifuge tube (2 mL) for cleaning. The precipitate was rinsed with 2 mL of 3 N HCl three times to remove residual Mn and repeatedly washed with H_2O until $\text{pH} > 4$.

Strontium sulphate is largely insoluble in water or acid. Conversion of $\text{Sr}(\text{Ra})\text{SO}_4$ to an acid-soluble $\text{Sr}(\text{Ra})\text{CO}_3$ allows for dissolution, however. This conversion was performed using a procedure from Cohen and O'Nions (1991) according to the classical Curie-Debiegne method (Curie and Debiegne, 1910). The precipitate of $\text{Sr}(\text{Ra})\text{SO}_4$ was mixed with 2 mL of 1 M Na_2CO_3 solution in a tightly capped 7 mL PFA Teflon beaker. The beaker and its contents were heated on a hotplate at 100 °C for 3 hours resulting in conversion of $\text{Sr}(\text{Ra})\text{SO}_4$ to $\text{Sr}(\text{Ra})\text{CO}_3$. After the conversion, $\text{Sr}(\text{Ra})\text{CO}_3$ was centrifuged and rinsed with H_2O , and then dissolved in 1 mL of 3 N HCl. The solution was then evaporated to dryness and re-dissolved in 2 mL of 6 N HCl for column purification. The chemical recovery of the entire precipitation and sulphate-to-carbonate conversion process was assessed, using a ^{228}Ra tracer, as between 70% to 90%. To achieve this relatively high yield requires considerable care in handling the precipitate during the procedure, because a careless pretreatment will cause a major sample loss especially during the processes of ashing the fibres and rinsing precipitates.

3.5.4 Column purification of radium

We have adapted chromatographic methods described in previous studies for the purification of Ra (Ghaleb et al., 2004; Foster et al., 2004; Chabaux et al., 1994) (Fig. 3.1). A first column of AG50-X8 (200-400 mesh) exchange resin is used to purify Ra (and Ba) from other elements (e.g. Ca, Sr, Th and any residual Mn). We used a custom-made column consisting of a 10 mL Eppendorf pipette tip and a 120 mL plastic funnel reservoir to provide a thin and long column to produce effective peak separation. The column length is 195 mm and the diameter is 8.2 mm. The column elution curve of AG50-X8 was calibrated using 6 N HCl as the elutant (Fig. 3.2 (a)). Ca, Sr and any residual Mn were washed from the column before collection of Ra (and Ba). Thorium remained on the column due to the strong affinity of Th for AG50-X8 resin in strong HCl. This is important because it separates ^{228}Th from the Ra portion, which would otherwise interfere with ^{228}Ra during mass spectrometry.

The second column, using Eichrom Sr-spec resin (50-100 mesh), was used for separation of Ra from Ba. The column length is 27 mm and the diameter is 2.8 mm. The elution curve for Sr-spec during elution of 3 N HNO_3 is shown in Fig. 3.2 (b). Radium was separated from Ba due to their different distribution coefficients on Sr-spec under these conditions. The chemical recovery of Ra, as assessed using a ^{228}Ra yield tracer, throughout the overall column chemistry is ~95%. The final elutant was dried and dissolved in 1 mL 2% HNO_3 ready for analysis by MC-ICP-MS. Resins were not reused to avoid any inter-sample contamination. This method of Ra purification could be readily modified for separation of Ra from the direct precipitation of MnO_2 from seawater.

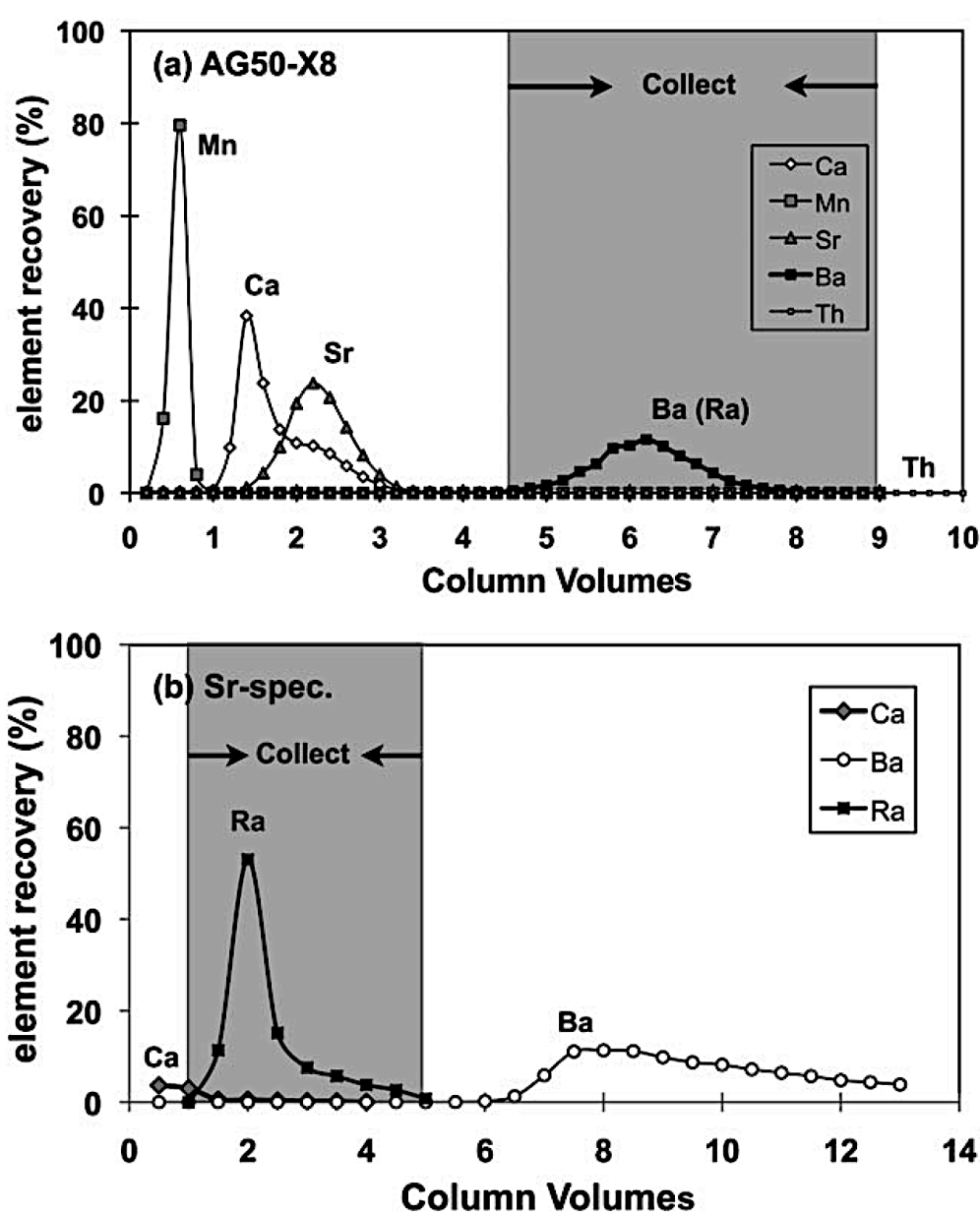


Figure 3.2 Elution curves for Ra and other elements (Mn, Ca, Sr, Ba and Th) on the first column (10 mL AG50-X8) and second column (0.5 mL Sr-spec) using 6 N HCl and 3 N HNO_3 , respectively.

Samples cannot be stored for too long between column separation and mass spectrometry due to ingrowth of ^{228}Th which will interfere with ^{228}Ra during analysis. Such ingrowth of ^{228}Th will represent $\sim 1\%$ of the ^{228}Ra beam after one month and starts to become significant. To reduce this effect, ^{228}Ra measurements in this study were completed within 10 days of chemistry, limiting the ingrowth of ^{228}Th to less than 0.3% of ^{228}Ra (comfortably within the error of the analytical precision). Samples left for longer than one month would require an additional column pass (e.g. AG1-X8 as described in Foster et al., 2004) before the analysis to remove ingrown ^{228}Th .

3.5.5 Blank and detection limit

The chemical blank of the total chemical procedure was measured regularly. For the entire Mn-fibre procedure including leaching, precipitation, and column chemistry, the overall chemical blank is 0.14 ± 0.02 pg ^{226}Ra (1 S.D., $n = 4$), which is ~ 1 to 2% of the ^{226}Ra contained in 150 L seawater. Ra-228 blanks are immeasurably small but, on the assumption that they are at a similar ratio to ^{226}Ra blanks as the $^{228}\text{Ra}/^{226}\text{Ra}$ of samples, are likely to be 0.03 fg. The detection limit of ^{228}Ra in seawater is 0.09 fg, based on 3 times the overall chemical blank. The procedural blank for the ^{226}Ra concentration measurements, performed following the technique of Foster et al. (2004) was 0.2 fg, less than 1% of the ^{226}Ra in the 500 mL samples. Chemical blanks can be reliably and precisely corrected because it largely comes from the various reagents and is therefore rather consistent.

3.6 Mass spectrometry

A Nu Instruments multi-collector ICP-MS at the Department of Earth Sciences, University of Oxford, was used for the determination of seawater Ra concentrations and $^{228}\text{Ra}/^{226}\text{Ra}$ ratios. Standard and sample solutions were aspirated at an approximate uptake rate of 60 $\mu\text{L}/\text{min}$ into a DSN-100 desolvation nebuliser system. The ion yield from introduction to detection is $\sim 2.5\%$ (equivalent to a 1 fg/g Ra solution yielding ~ 60 cps of Ra signal). The Nu Instrument MC-ICP-MS has 11 Faraday collectors and 3 ion counters and its general design (Belshaw et al., 1998) and performance for U-series measurements (Mason and Henderson, 2010) have been described previously (Table 3.1).

Table 3.1 The measurement configurations for U standard and Ra sample

Detector	H1	AXIAL	L1	L2	IC0	L3	IC1
Uranium							
<i>step 1</i>	^{238}U			^{235}U	^{234}U		
<i>step 2</i>			^{238}U			^{235}U	^{234}U
Radium					^{228}Ra		^{226}Ra

Two-step U measurement is conducted before and after every Ra analysis to assess instrument mass bias and ion counter gains.

The analytical protocol is adapted from Foster et al. (2004). ^{228}Ra and ^{226}Ra were simultaneously measured in two ion-counters situated 3 and 5 mass units below the axial Faraday (Fig. 3.3). The relative gain of the two ion counters and the mass bias of the instrument were measured simultaneously by analysing CRM-145, a uranium standard with well-known isotopic compositions of $^{238}\text{U}/^{235}\text{U}=137.88$ and $^{235}\text{U}/^{234}\text{U}=137.19$ (Robinson et al., 2002), before and after each Ra sample. The $^{238}\text{U}/^{235}\text{U}$ ratio was measured on two Faradays and the deviation of the measured ratio from the known ratio used to calculate a mass bias which was typically close to 0.8% per amu. This mass bias was extrapolated to correct the $^{228}\text{Ra}/^{226}\text{Ra}$ ratio assuming a simple linear mass bias law. The choice of mass bias law makes no difference at the percent level of precision at which the Ra isotope ratios are measured.

U-234 was analysed sequentially in the two ion counters and the measured $^{235}\text{U}/^{234}\text{U}$ ratio first corrected for mass bias, as above, and then used to calculate the gains of the ion counters relative to the Faradays. Measured ion counter gains were always in the range 75 – 90%, with the relative gain of the two ion counters used for $^{228}\text{Ra}/^{226}\text{Ra}$ measurement stable at close to 90%. Uncertainty in the gain ratio is ~0.5% for any measurement run and is propagated directly into final measurement uncertainty, although it is small compared to the final uncertainty.

Backgrounds on the two ion counters were measured before each Ra analysis. The instrumental background and Ra memory is typically about 0.4 count per second (cps) if the system is clean and without Ba molecular interferences. The analytical detection limit is 0.016 fg Ra, based on 3 times instrument background (3×0.4 cps) and a required solution volume of ~0.8 mL used for a

measurement. This is significantly smaller than the chemical detection limit, implying that is the blank contribution that sets the detection limit for this technique of ≈ 0.1 fg Ra.

Analysis of Ra standards were conducted on ~ 1 mL 2% HNO_3 solution containing ~ 0.1 pg/g ^{226}Ra , yielding count rates of 5800 cps of ^{226}Ra and 17 cps of ^{228}Ra (Fig. 3.3). A single measurement consisted of 80 integrations of 800 seconds and, including uptake, prior wash out, the U standard run and background measurement, took ~ 20 minutes. The total number of collected ^{228}Ra ions in an analysis suggests a maximum possible precision, based on counting statistics, of 1.7% (2 S.E.) Measured internal repeatability of the 80 $^{226}\text{Ra}/^{228}\text{Ra}$ ratios is 1.7% (2 S.E.) and is therefore dominated by counting statistics. Reproducibility of 10 separate standard runs demonstrates an external precision of 2% (2 S.D.) (Fig. 3.4). Samples were run in similar conditions to these standards and produced similar analytical performance.

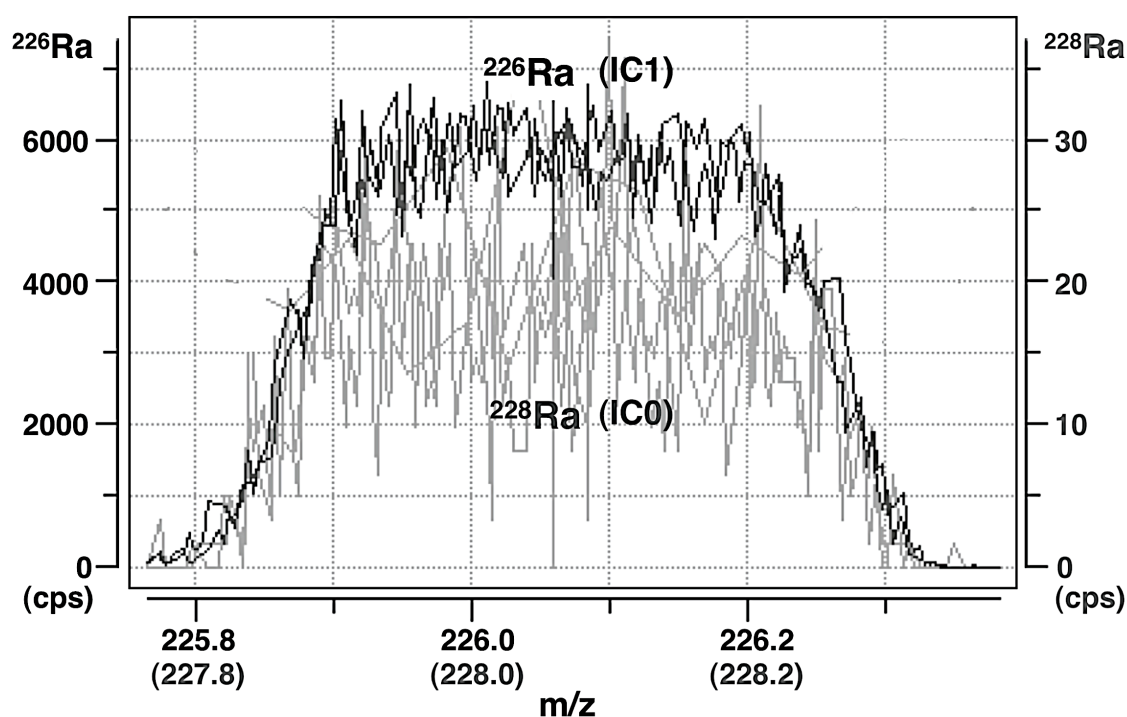


Figure 3.3 Peak shapes of ^{228}Ra and ^{226}Ra simultaneously collected in two scans across the two ion counters. The scanned solution is an in-house Ra standard with the $^{228}\text{Ra}/^{226}\text{Ra}$ ratio of 0.0029, close to the ratio of open ocean seawater. The figure was constructed while aspirating a 1 pg per g ^{226}Ra solution to give ~ 5800 cps for ^{226}Ra .

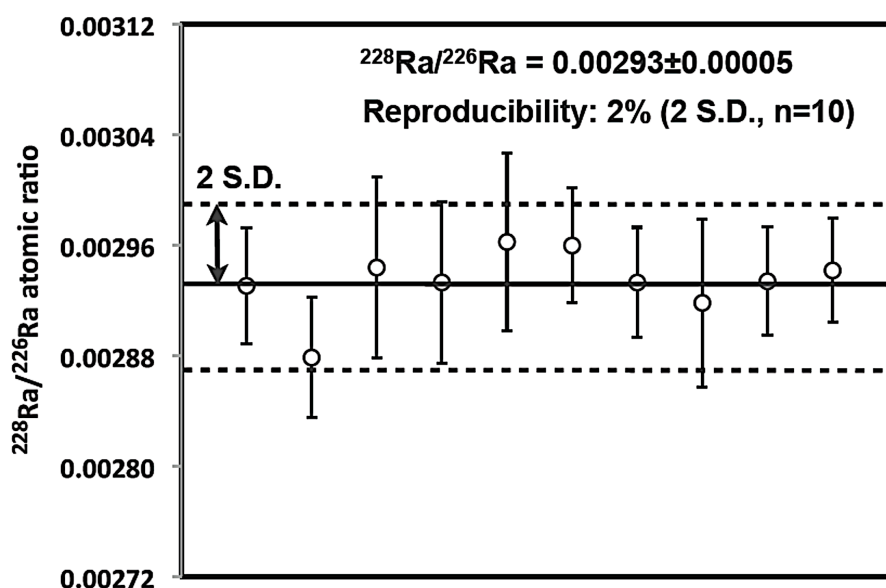


Figure 3.4 Replicate measurement of $^{228}\text{Ra}/^{226}\text{Ra}$ in an in-house Ra standard by MC-ICP-MS. The error bar on each point represents the internal measurement at ± 2 S.E. The dashed lines represent the external reproducibility of 2% (2 S.D., $n = 10$) based on the repeatability of these ten measurements.

3.7 Application to seawater samples

3.7.1 Southampton Dock seawater

Four Mn-fibre cartridge samples and five accompanying bottle samples were collected in Southampton Dock at the National Oceanography Centre, specifically to test the analytical protocol. A rotary peristaltic pump was used to pump 100 L of seawater through Mn cartridges at a flow rate of 1 L/min. Seawater samples, of 120 mL each, were collected before and after each Mn-fibre sampling for measurement of the ^{226}Ra concentrations. An average of the two ^{226}Ra measurements – before and after each Mn-fibre sample – were used to assess the ^{226}Ra and, with the measured $^{228}\text{Ra}/^{226}\text{Ra}$ ratio, to derive the ^{228}Ra concentration.

The mean value of the $^{228}\text{Ra}/^{226}\text{Ra}$ atomic ratio of the Southampton Dock seawater is 0.0074 ± 0.0002 (Table 3.2 and Fig. 3.5). The external reproducibility of 2% (2 S.D., $n=4$) provides a good assessment of the uncertainty of the analytical technique including chemical procedures and spectrometric measurements and is similar to the external reproducibility of the standard measurements. The internal error for each sample is about 1.5% (2 S.E.), included the errors of counting statistics, ion-counter gain, mass bias and blank corrections.

The concentrations of ^{226}Ra , collected at different times on the same day, are shown in Fig. 3.6 (a). The internal uncertainty of each sample is $\approx 3\%$ (2 S.E.) Seawater concentrations of ^{228}Ra , calculated from measured $^{228}\text{Ra}/^{226}\text{Ra}$ ratios and from an average of the two closest ^{226}Ra concentration measurements, are shown in Fig. 3.6 (b) and have an external reproducibility of 2% (2 S.D., $n=4$). These Southampton dock samples demonstrate the success of the protocol for measurement of $^{228}\text{Ra}/^{226}\text{Ra}$ and ^{228}Ra concentrations on real seawater samples.

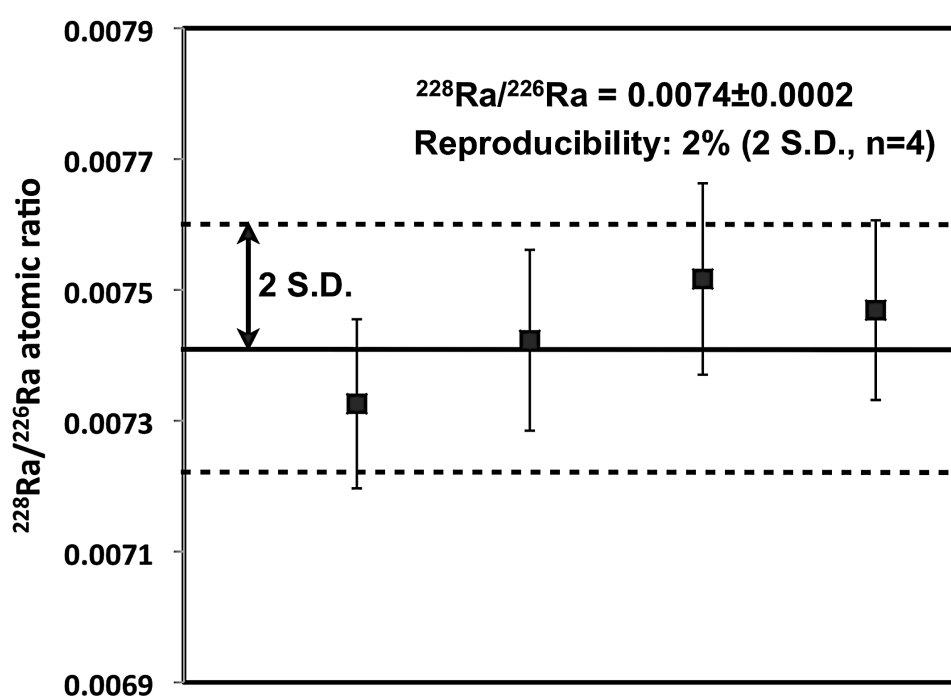


Figure 3.5 Replicate measurement of $^{228}\text{Ra}/^{226}\text{Ra}$ in Southampton Dock seawater by MC-ICP-MS. The error bar on each point represents the internal measurement uncertainty at ± 2 S.E. The dashed lines represent the external reproducibility of 2% (2 S.D., $n = 4$).

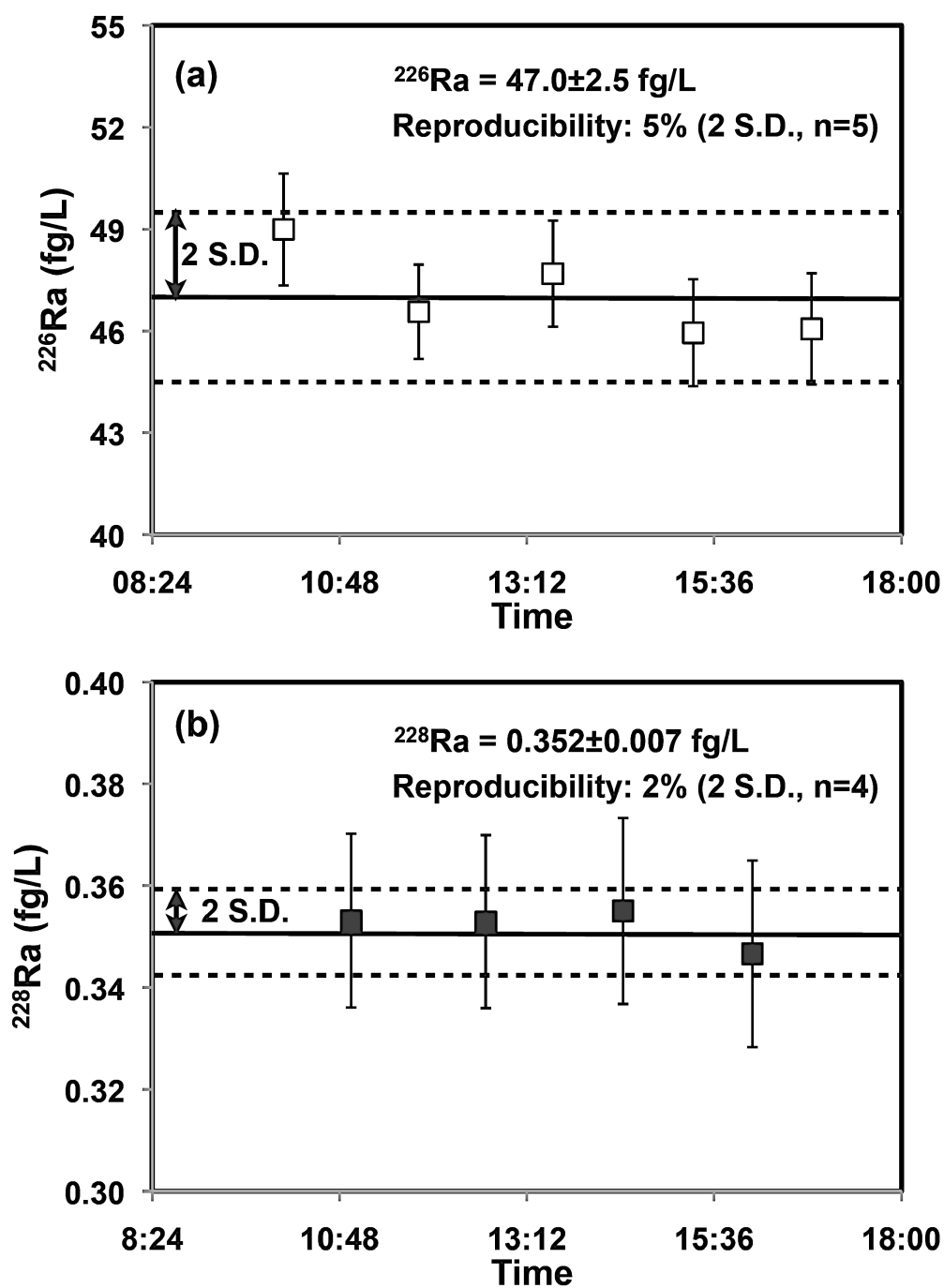


Figure 3.6 Variation of (a) ^{226}Ra and (b) ^{228}Ra concentrations for waters collected over 8 hours in Southampton Dock. Error bars are 2 S.E. internal errors in each case.

Table 3.2 ^{226}Ra and ^{228}Ra concentrations and $^{228}\text{Ra}/^{226}\text{Ra}$ ratios in seawater samples^{a,b}

Sample	Date	Salinity (‰)	T (°C)	^{226}Ra (fg/L)	^{226}Ra (dpm/100 L)	^{228}Ra (fg/L)	^{228}Ra (dpm/100 L)	$^{228}\text{Ra}/^{226}\text{Ra}$ (atomic ratio)	$^{228}\text{Ra}/^{226}\text{Ra}$ (activity ratio)
Southampton Dock seawater									
SA-W1	24/11/2009	30.3	11.7	49 ± 3	10.7 ± 0.6				
SA-W2	24/11/2009	30.5	11.8	47 ± 2	10.2 ± 0.5				
SA-W3	24/11/2009	30.2	12.0	48 ± 3	10.5 ± 0.6				
SA-W4	24/11/2009	30.5	11.9	46 ± 2	10.1 ± 0.5				
SA-W5	24/11/2009	30.9	12.0	46 ± 2	10.1 ± 0.5				
SA-M1	24/11/2009	30.4	11.7			0.353 ± 0.016	21.4 ± 1.0	0.0073 ± 0.0001	2.03 ± 0.04
SA-M2	24/11/2009	30.3	11.9			0.333 ± 0.016	21.4 ± 1.0	0.0074 ± 0.0001	2.06 ± 0.04
SA-M3	24/11/2009	30.4	11.9			0.355 ± 0.018	21.5 ± 1.1	0.0075 ± 0.0001	2.09 ± 0.04
SA-M4	24/11/2009	30.7	12.0			0.347 ± 0.018	21.0 ± 1.1	0.0075 ± 0.0001	2.07 ± 0.04
GEOTRACES Ra intercalibration									
S1C	01/07/2008			37 ± 2	8.0 ± 0.4				
S2C	10/07/2008			46 ± 2	10.2 ± 0.5				
S3C	12/07/2008			63 ± 3	13.8 ± 0.6				
S4C	13/10/2008			59 ± 3	13.1 ± 0.6				
S1A	01/07/2008					0.056 ± 0.003	3.4 ± 0.2	0.00152 ± 0.00003	0.42 ± 0.01
S2A	10/07/2008					0.288 ± 0.013	17.4 ± 0.8	0.00613 ± 0.00008	1.70 ± 0.02
S3A	12/07/2008					0.636 ± 0.028	38.4 ± 1.7	0.01006 ± 0.00012	2.79 ± 0.03
S4A	13/10/2008					0.965 ± 0.043	58.3 ± 2.6	0.01609 ± 0.00013	4.47 ± 0.04

^a All errors are given at the 95% confidence interval (±2 S.E.)^b Activity calculations use the half-lives of ^{226}Ra and ^{228}Ra of 1600 years and 5.75 years, respectively.

3.7.2 GEOTRACES intercalibration samples

Four Mn-fibre samples and four seawater samples have been analysed using the protocols presented here as part of the GEOTRACES intercalibration. As preparation for the International GEOTRACES programme, two US-led cruises collected a wide range of samples for distribution to labs internationally to assess the level to which measurements could be compared from lab to lab and to improve measurement protocols. For radium isotopes, samples were collected during the first of these two cruises, conducted in the North Atlantic. These samples were from the Bermuda Atlantic Time Series (BATS) site (denoted S1); from the Gulf Stream shelf break (denoted S2) and from inner shelf stations (denoted S3 and S4). $^{228}\text{Ra}/^{226}\text{Ra}$ ratios and ^{228}Ra , ^{226}Ra concentrations have been measured using the protocols outlined here and are reported in Table 3.2, and compared with the consensus value from these seawaters in Fig. 3.7. There are no certified values for these seawater samples, but the consensus value represents the average of measurements made by the 16 laboratories world-wide who had measured identical seawater samples by April 2010. All of these laboratories use decay counting rather than mass spectrometric approaches (except one lab that reports mass spectrometry values for ^{226}Ra concentration only). Our measurement of these GEOTRACES intercalibration samples therefore provides an ideal point of comparison between the new protocol described here and well-established decay counting techniques.

The concentrations of ^{226}Ra in these samples increase from 37 to 63 fg/L from the open ocean to near-shore, while ^{228}Ra concentrations increase from 8.0 to 13.7 fg/L. These increases indicate a Ra origin at the coast particularly for ^{228}Ra , and offer a wide range of typical seawater $^{228}\text{Ra}/^{226}\text{Ra}$ ratios with which to test the new protocol described in this measurement.

The concentrations of ^{226}Ra and ^{228}Ra measured by MC-ICP-MS show good agreement with the consensus numbers from other labs for all stations, except that we measure slightly lower concentrations of ^{226}Ra in the inner-shelf S3 and S4 samples. The large uncertainty of the consensus ^{226}Ra value, however, allows for the possibility of agreement even for these samples. For ^{228}Ra concentrations, there are no obvious differences between our technique and the well-established decay counting approaches. This demonstrates the accuracy of the new MC-ICP-MS approach.

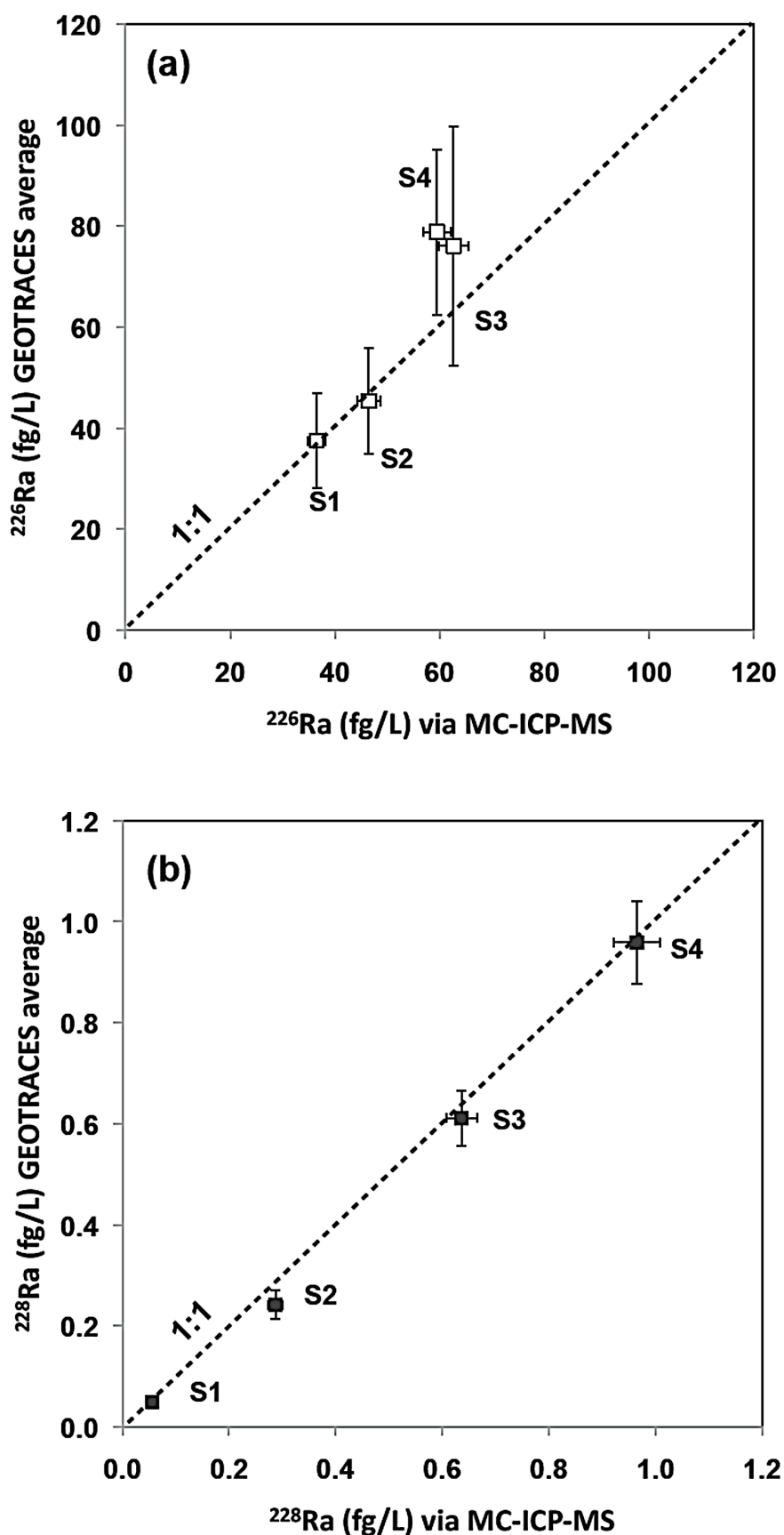


Figure 3.7 Comparison of (a) ^{226}Ra and (b) ^{228}Ra measurements by the MC-ICP-MS protocol described in this paper with other measurements from the GEOTRACES Ra intercalibration. The dashed line defines agreement between data measured by MC-ICP-MS and the intercalibration consensus values.

3.8 Comparison with existing analytical techniques

Previous measurements of seawater Ra concentrations have typically relied on decay counting techniques. Here, we compare our method with previous techniques including those of alpha counting (Jia et al., 2006), gamma counting (Moore, 1984; Reyss et al., 1995; van Beek et al., 2007; van Beek et al., 2010; Bourquin et al., 2008) and TIMS (Cohen and O’Nions, 1991; Ollivier et al., 2008; Yokoyama and Nakamura, 2004). Comparisons are made for detection limit, pretreatment time, counting time and uncertainty for measured seawater ^{228}Ra concentrations.

Detection limit is important because it sets the lowest volume of seawater that can be analysed. Ra-228 concentrations can be very low in the open ocean and, even with the Mn-cartridge approach, volumes of seawater are generally limited so that analytical detection limits control the ability to make meaningful ^{228}Ra measurements.

Detection limits for ^{228}Ra measurement with the MC-ICP-MS approach outlined here are as low as those of any previous technique. Detection limits relative to blank and mass-spectrometric background are ≈ 0.1 fg, similar to those for alpha spectrometry (Moore, 1969; Moore et al., 1985) and for TIMS (Smith et al., 2007). Gamma spectrometry has higher detection limits. Even using underground facilities, detection limits are ≈ 0.76 fg, whereas more typical facilities have detection limits of 10 fg or higher.

The efficiency of data production is determined by any delay awaiting in-growth of daughters, by chemical pretreatment time, and by counting time for each technique. Gamma spectrometry requires 3 to 4 weeks for in-growth of daughters before analysis, while alpha spectrometry requires 5 to 20 months to wait for ^{228}Th in-growth. For mass spectrometry, no waiting time for equilibrium is required, but a labor-intensive chemical pretreatment is necessary to purify Ra from Ba, Th and other elements. In the protocol presented here, chemical separation of a batch of 8 samples takes about 4 days. This length of pretreatment is similar to that for TIMS analysis. Alpha spectrometry also requires chemical pretreatment to purify Ra and Th, but this process is somewhat less time consuming. Pretreatment for gamma spectrometry is minimal and Mn-fibre samples can rapidly be ashed ready for counting. In terms of time required for the actual analysis, MC-ICP-MS is the fastest of the techniques,

returning values in ≈ 20 minutes per sample, compared to ≈ 1 hour for TIMS, and much longer periods for decay counting techniques (generally more than a day per sample).

The precision of the MC-ICP-MS technique for ^{228}Ra concentration presented here surpasses that of published techniques, particularly those relying on decay counting techniques. Alpha spectrometry has a precision of $\sim 10\%$ (2 S.E.) (Moore et al., 1985), while gamma spectrometry can achieve precision as high as 6% (2 S.E.) (van Beek et al., 2010) in specialised underground laboratories, but is often less precise. Published mass spectrometric approaches report $^{228}\text{Ra}/^{226}\text{Ra}$ ratio uncertainty of 2% (2 S.E.) (Ollivier et al., 2008; Sharabi et al., 2010), but rather poorer ^{228}Ra external precision ($\approx 10\%$) due to uncertainty in the accompanying ^{226}Ra measurements. In the protocol described here, we achieve uncertainty on the $^{228}\text{Ra}/^{226}\text{Ra}$ of 2% (2 S. D., $n = 4$) and, though use of a ^{228}Ra isotope dilution method for ^{226}Ra concentration measurements, a precision of 2% for measurements of seawater ^{228}Ra concentrations.

In summary, the analytical protocol described in this paper is somewhat more labour intensive than decay-counting approaches during sample pretreatment, but its rapid analytical phase does not impose any analytical bottle-neck as can be generated by long decay-counting times. Most importantly, the MC-ICP-MS approach described here allows significantly lower detection limits than commonly used gamma-counting techniques, and provides precisions that are significantly improved. This approach therefore offers the potential to study ^{228}Ra distributions in the ocean interior where concentrations are low, and to distinguish variations not previously observable.

3.9 Conclusions

We have developed a method to precisely measure seawater $^{228}\text{Ra}/^{226}\text{Ra}$ ratios and ^{228}Ra and ^{226}Ra concentrations by MC-ICP-MS. This method provides a low detection limit of ≈ 0.1 fg ^{228}Ra , high analytical precision of 2% (2 S.D.) on ^{228}Ra concentration, and a short analysis time of 20 minutes per measurement. Although the preconcentration required for this new technique is more time-consuming than commonly applied gamma-counting techniques, its low detection limits and high precision offers it significant advantages in situations where ^{228}Ra concentrations are low, such as much of the ocean interior. We have demonstrated the new analytical approach on waters from Southampton Dock and on

samples collected as part of the GEOTRACES Programme intercalibration effort. For the latter, agreement of values measured by the new MC-ICP-MS approach with decay-counted measurements in other laboratories provides confidence in the accuracy of the technique.

In the future, this method will enable extension of the use of ^{228}Ra analysis to understand oceanic mixing and trace elements fluxes in the ocean, even in regions with low ^{228}Ra concentrations.

Chapter 4

Using the radium quartet (^{228}Ra , ^{226}Ra , ^{224}Ra and ^{223}Ra) to estimate water mixing and radium inputs in Loch Etive, Scotland

4.1 Abstract

Fjords, a special type of estuarine environments, provide strong physical and chemical gradients from river water to seawater, and are an important coastal environment. Measurement of water mixing and chemical fluxes in the fjord system are important to understand both the local environment, and the fjordic influence on global oceanic chemical and biological cycles. In this study, the radium quartet (^{228}Ra , ^{226}Ra , ^{224}Ra and ^{223}Ra) has been investigated in Loch Etive, a Scottish fjord, to provide new constraints on water mixing rates and on the inputs of Ra from sediments in the fjord system. Surface-water transport rates are determined from $^{223}\text{Ra}_{\text{ex}}$ and indicate a transport rate of seawater of $2.4 \pm 0.2 \text{ cm s}^{-1}$ so that it takes 17 ± 2 days to travel from the mouth to the head of the loch. Shelf sediments around the head of the loch provide inputs of ^{224}Ra and ^{228}Ra to the surface water, which alter the activity ratio of $^{228}\text{Ra}/^{226}\text{Ra}$ in the surface water by about 11 ~ 19%. Periodic overturning circulation plays an important role in resetting chemical cycles in the isolated deep basin of the inner loch. Sediment in this deep-basin provides the major input of ^{228}Ra to the isolated deep water such that the accumulation of ^{228}Ra in deep-waters allows an assessment of sedimentary fluxes of ^{228}Ra , an important unknown in the ^{228}Ra input to the global ocean. The calculated sedimentary ^{228}Ra flux is $5.5 \pm 0.3 (\times 10^9) \text{ atoms m}^{-2} \text{ yr}^{-1}$ in the inner deep basin, which is comparable with previous measurements of sedimentary ^{228}Ra inputs from shelf sediments.

4.2 Introduction

Estuaries play an important role in the transformation of river water to seawater, showing strong physical and chemical gradients. Estuarine environments provide inputs of trace elements and nutrients to the ocean, and can act as a significant filter between the land and open ocean (Howe et al. 2010). Understanding the physical mixing and advection of waters in these environments is an important

aspect of understanding the chemical cycles of estuaries and their role in controlling chemical fluxes to the open ocean.

Since fish farming started in the 1970s, fjords have been increasingly used for aquaculture. The fish farm industry has been found to have negative impacts on the fjord ecosystem, such as the spreading of infectious diseases, waste pollution and marine eutrophication (Cloern, 2001). Studies have focused on assessing and modeling the environmental effects of fish farming in fjords (Karakassis et al., 2000; Skogen et al., 2009). However, the fjord environment is a very complex system in terms of water circulation and chemical exchange (Howe et al., 2010). Thus, understanding the physical and chemical environment in fjords would improve the assessment of the environmental effects of fish farming in fjords, which also has a societal and economic value.

Fjords usually have glacially over-deepened and semi-enclosed marine basins which provide a particular style of estuarine environment and generate distinct water circulation to control chemical and physical transitions from terrestrial to marine environments (Howe et al., 2010). Fjord circulation systems have also been shown to influence global ocean circulation by regulating glacial runoff and the water exchange between estuarine and coastal environments (Straneo et al., 2011). Despite their importance, water mixing rates and chemical fluxes are not well quantified in the fjord system.

Radium has four naturally occurring isotopes (^{226}Ra , $T_{1/2} = 1600$ years; ^{228}Ra , $T_{1/2} = 5.75$ years; ^{223}Ra , $T_{1/2} = 11.4$ days; ^{224}Ra , $T_{1/2} = 3.66$ days), the so-called radium quartet. These have been used as powerful tracers for estimating chemical fluxes to the ocean, including: riverine inputs (Li and Chan, 1979); sediment inputs (Hancock et al., 2000); and submarine groundwater discharge (SGD) (Moore et al., 2008)). Radium isotopes are produced by the radioactive decay of thorium isotopes, typically in sediments. They are dissolved in pore-water and released from sediments into seawater. Ra is therefore a useful tracer for studying chemical interaction at the sediment-water interface. In addition, Ra behaves conservatively (except for its known radioactive decay) once released into seawater. Ra isotopes have therefore also been widely applied to the study of a variety of oceanographic processes and chemical fluxes to the ocean, such as diffusion (Kadko et al., 1987), large scale ocean mixing (Chung, 1980; Kaufman et al., 1973; Ku and Luo, 1994), horizontal and vertical eddy mixing (Broecker et al., 1967; Sarmiento et al., 1976; van Beek et al., 2008), shelf water and coastal ocean mixing (Moore, 1998;

Moore 2000; Rutgers van der Loeff et al., 1995), water-mass and particulate residence time (Broecker et al., 1973), pore-water exchanges (Cochran and Krishnaswami, 1980; Webster et al., 1994) and sediment benthic fluxes (Bollinger and Moore, 1984; Hammond et al., 1990; Hancock et al., 2000).

An example of the power of Ra isotopes in seawater is provided by their use to assess global SGD fluxes to the oceans. The inventory of ^{228}Ra in the surface Atlantic Ocean constrains the total SGD input to the ocean (Moore et al., 2008) provided that other important fluxes, from rivers and sediments, are known. This approach has demonstrated that SGD provides significant input of nutrients and other dissolved species to the ocean, potentially higher than that for riverine discharge. Confirming the use of open-ocean ^{228}Ra to assess SGD fluxes requires firm knowledge of the flux of ^{228}Ra from its other major source – marine sediments. Fjords with periodically isolated deep-water in contact with marine sediment, provide natural ocean laboratories to assess this sedimentary ^{228}Ra flux.

This study has provided new constraints on the Ra cycle in the fjord system with a set of analyses on Loch Etive, a Scottish fjord. It also discusses the influence of the water mixing and overturn circulations to the Ra cycle in the fjord system. The resulting understanding of Ra cycles in Loch Etive provides information about the physical mixing and circulation of the loch, and about sedimentary fluxes of ^{228}Ra .

4.3 Methods

4.3.1 Study area

Loch Etive is a sea-loch located on the west coast of Scotland (Edwards and Sharples, 1985) (Fig. 4.1). The loch hosts a number of mussel farms, and is used for occasional recreational boating. Details of the bathymetry and sedimentology of the loch have been investigated in a high-resolution seismic and gravity-coring survey (Howe et al., 2001; Howe et al., 2002). The loch is separated into an inner (inland) (145 m maximum depth) and outer (seaward) (70 m maximum depth) basin by a sill of 13 m depth at Bonawe. The geological setting is a mixture of igneous and metamorphic rocks, mostly granite, which restricts groundwater penetrating through this area. Tide flow drives seawater in and out of the loch. Seawater is mixed with freshwater from River Awe and River Etive from the large catchment area

of 1400 km² in this area (Wood et al., 1973). The mean freshwater discharge is $3037.5 \times 10^6 \text{ m}^3 \text{ yr}^{-1}$ (Edwards and Sharples, 1986).

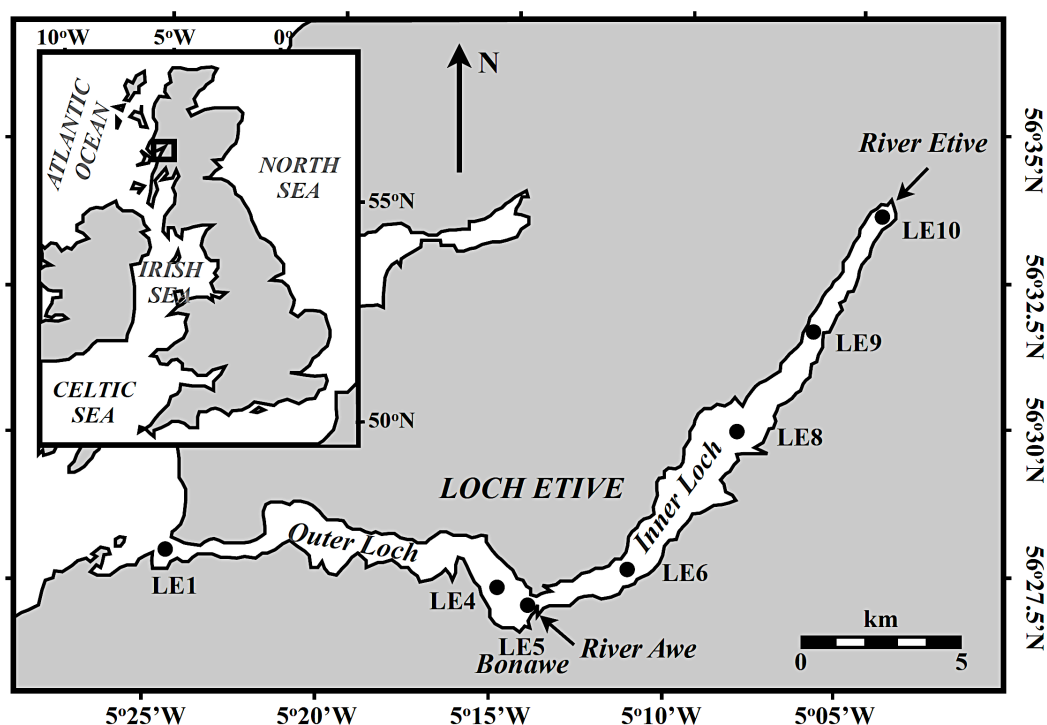


Figure 4.1 Map of Loch Etive with location of sampling sites. The loch is divided into inner loch and outer loch by Bonawe sill at station LE5. River Etive and River Awe provide freshwater input into the loch.

The hydrology and water circulation of Loch Etive have been well studied (Edwards and Edelsten, 1977) (Fig. 4.2a). In the surface layer, seawater is mixed efficiently with freshwater in the outer loch, which reduces the salinity of seawater and prohibits flow of waters to depth in the inner deep basin. Circulation in the inner deep basin is therefore usually restricted to the surface 40 – 70 m and deep water is isolated for extended periods. After a particularly dry period and when temperatures are cold during winter, mixing with freshwater is reduced, and high salinity dense seawater can flow over the Bonawe sill and sink into the deep inner basin to cause an overturn circulation. The average period of overturn circulation is about 16 months (Edwards and Edelsten, 1977) but there is no regular cycle to this overturning

Dissolved oxygen is constantly consumed and therefore decreases in the isolated deep-water, so that the level of oxygen in deep-waters can be used as an index to monitor overturning events. For

example, dissolved oxygen suddenly increased from 0.9 to 9.5 mg L⁻¹ during an overturn event in May 2000 and then gradually decreased with time to semi-anoxic levels in the deep inner basin (Austin and Inall, 2002). The change of dissolved oxygen also significantly controls other aspects of the chemistry of the loch, such as the manganese cycle (Overnell et al., 2002; Statham et al., 2005).

The distribution of Ra isotopes in Loch Etive is dominated by seawater, river and sediment inputs (Fig. 4.2a). The concentration of Ra isotopes in the isolated deep water of the inner basin is reset by overturn events. Between such overturns, ²²⁸Ra, ²²⁴Ra and ²²³Ra concentrations can decrease due to radioactive decay or increase due to addition from the sediment. Measurement of changing Ra concentrations in the deep-waters therefore has potential to be used to assess the rates of sedimentary Ra input to seawater.

4.3.2 Sampling methods

Water samples were collected aboard the *R. V. Calanus* during a two-day cruise on the 3rd and 4th August 2010 in Loch Etive. Surface water samples were collected from seven stations from the mouth of the loch (LE1), the outer loch (LE4 and LE5), the inner loch (LE6, LE8 and LE9) and the head of the loch (LE10) (Fig. 4.1). Deep water samples were collected from three stations at LE4, LE6 and LE8. Station LE6 was reoccupied ten months later on the 8th June 2011 to assess the temporal evolution of Ra in the deep loch.

Each sample consisted of water from twelve 5 L Niskin bottles mounted on a conductivity-temperature-depth (CTD) rosette. Resulting 60 L samples were stored briefly in cubitainers before ship-board pre-concentration of Ra. Samples were passed through a column of MnO₂-coated acrylic fibre, so-called “Mn-fibre”, by gravity at a flow rate < 2 L min⁻¹ to concentrate the Ra (Moore et al., 1985). After filtration, Mn-fibres were rinsed three times with Milli-Q water to remove adhering salt and squeezed to reduce liquid content. A sub-sample of 250 mL was also collected from each location and depth for a separate measurement of ²²⁶Ra concentration (Foster et al., 2004).

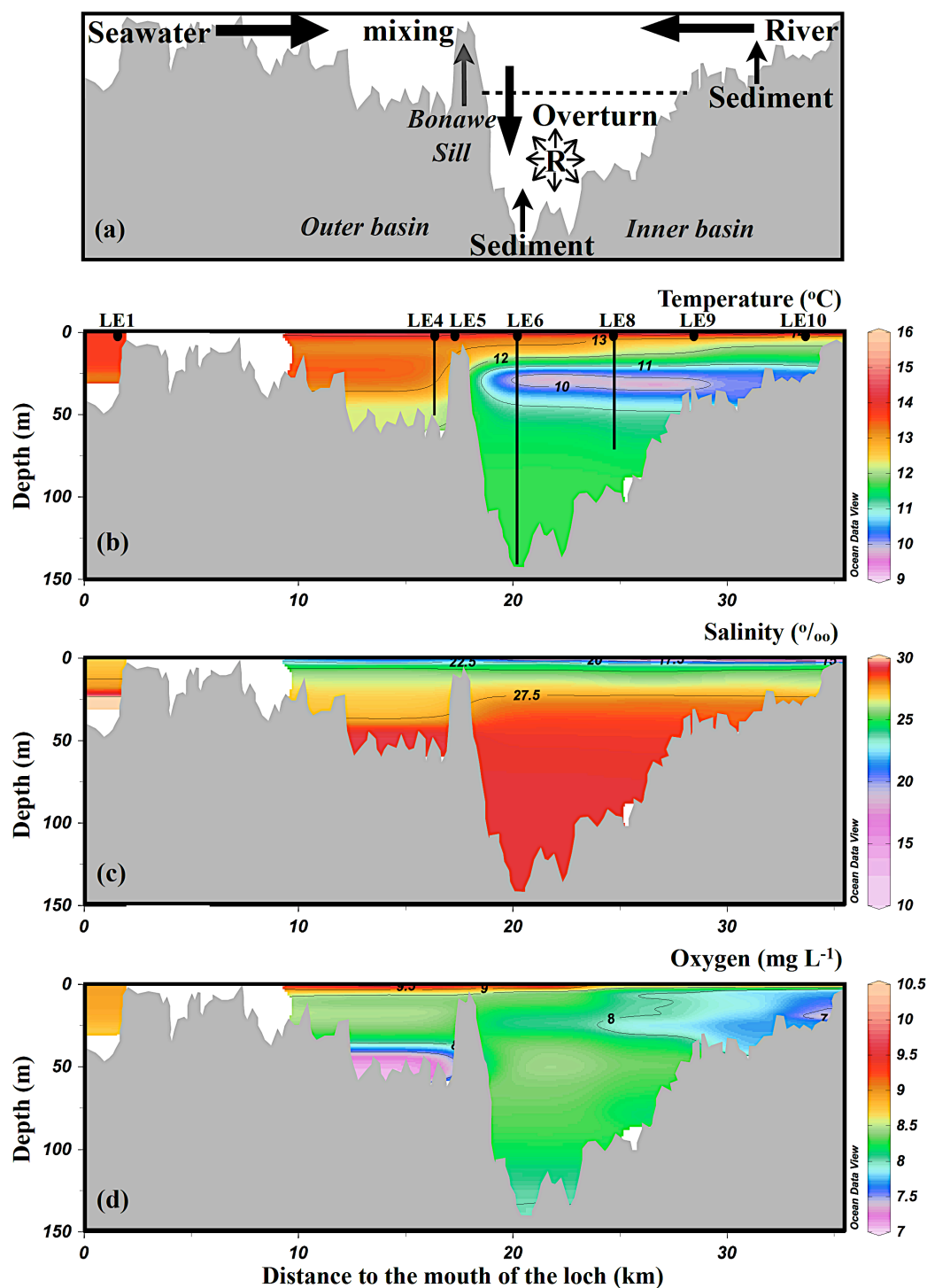


Figure 4.2 (a) Schematic of hydrography and Ra cycles in Loch Etive. The dashed line indicates the inner loch water stratification between mixed surface layer and isolated deep water. In the surface layer, two horizontal arrows indicate water mixing from seawater and river inputs. The arrow across the dashed line presents the inner loch overturning circulation which happens periodically. Two upward arrows indicate sedimentary Ra input. R is the radioactive decay of Ra. CTD data of (b) temperature (°C) (c) salinity (‰) and (d) oxygen (mg L⁻¹) in Loch Etive on the 3rd and 4th August 2010. The locations of station are shown in black dots. Samples were collected from the surface at all stations (black dots in (b)), and from three depth profiles at LE4 (54 m), LE6 (136 m) and LE8 (70 m) respectively (solid lines in (b)).

4.3.3 Measurements

Seawater ^{224}Ra and ^{223}Ra by RaDeCC

Mn-fibre samples were first counted using a 4-channel radium delayed coincidence counting system (RaDeCC) for ^{224}Ra and ^{223}Ra activities (Moore and Arnold, 1996). Fibres were then stored for several weeks before a second count on the same device to determine how much of the ^{224}Ra was supported by ^{228}Th . After 2 months, a third and final count was performed to assess how much of the ^{223}Ra was supported by ^{227}Ac (Geibert and Voge, 2008). Supported ^{223}Ra and ^{224}Ra activities, as measured on the second and third counts, were subtracted to give the excesses of ^{223}Ra and ^{224}Ra ($^{223}\text{Ra}_{\text{ex}}$ and $^{224}\text{Ra}_{\text{ex}}$) in each sample. The RaDeCC was calibrated regularly with two standard samples from the parent nuclides of short-lived Ra, ^{227}Ac and ^{232}Th , which had been obtained from IAEA-MEL Monaco in 2009 (Scholten et al., 2010). The overall uncertainties of ^{224}Ra and ^{223}Ra are 10 to 40% (2 S.E).

Seawater ^{228}Ra and ^{226}Ra by MC-ICP-MS

The long-lived Ra isotopes (^{226}Ra and ^{228}Ra) were measured using a newly developed technique which makes use of Multi-Collector ICP mass spectrometry (MC-ICP-MS) (Chapter 3, this thesis). After RaDeCC counting, Mn-fibres were ashed in a furnace and then leached with HCl for the purification of Ra. Ra was precipitated by $\text{Sr}(\text{Ra})\text{SO}_4$ in the leaching solution, and then converted to $\text{Sr}(\text{Ra})\text{CO}_3$ for dissolution (Cohen and Onions, 1991) before ion-exchange column chemistry (AG50-X8 and Sr-spec). For measurement of ^{226}Ra concentrations, water samples (250 ml) were spiked with an enriched ^{228}Ra spike following the procedure described in Foster et al. (2004). In short, Ra is precipitated with CaCO_3 in seawater and then purified by ion exchange columns (AG1-X8, AG50-X8 and Sr-Spec) before analysis. The pure Ra aliquot was analysed by MC-ICP-MS, with ^{228}Ra and ^{226}Ra simultaneously measured in two ion counters. Bracketing measurements of a uranium standard (CRM-145) were used to assess and correct for mass bias and ion counter gain between each sample. Chemical blanks were monitored for the whole procedure and are less than 1% of ^{226}Ra of the sample and not detectable for ^{228}Ra . The machine memory was also monitored and corrected between each measurement. The overall uncertainties of ^{226}Ra and ^{228}Ra are 3 to 4% (2 S.E), which is more precise than the uncertainties (> 10%, 2 S.E.) commonly obtained using decay-counting techniques (e.g. gamma and alpha counters).

The improved analytical precision allows us to more precisely calculate water mixing and Ra fluxes in Loch Etive.

4.4 Results

4.4.1 Temperature, salinity and oxygen data

Temperature, salinity and oxygen data are presented in Fig. 4.2. In the surface layer, the temperature is ~ 15 °C and salinity varies between 2 and 18‰ with a high dissolved oxygen of ~ 9.5 mg L⁻¹. At depth, the inner loch had a homogeneous water mass below 30 m with temperatures of 11 – 12 °C, salinity of 28 – 29 ‰ and dissolved oxygen of 7.5 – 8.5 mg L⁻¹ during the August 2010 cruise. A colder water layer with temperature < 10 °C and lower dissolved oxygen of ~ 8 mg L⁻¹ covers the whole inner loch between 20 and 30 m. In the outer loch, deep water shows oxygen depletion (~ 7 mg L⁻¹) below 42 m. Time-series oxygen data collected by the HYPOX project (Stahl, 2011) from December 2009 to April 2011 at 124 m at the inner-loch deep-basin observatory suggest that deep water in the inner loch had overturned just before our sampling in June 2010.

During the 2nd cruise (June 2011), CTD and time-series oxygen data both suggest that the deep-water of the inner basin had remained isolated since the overturn event in late June 2010.

4.4.2 Radium isotopes

Concentrations of $^{223}\text{Ra}_{\text{ex}}$ and $^{224}\text{Ra}_{\text{ex}}$ range from below the detection limit to 2.1 dpm 100 L⁻¹ and 9.7 dpm 100 L⁻¹ respectively (Table 4.1). In the water column of the inner basin (Fig. 4.3d and e), $^{223}\text{Ra}_{\text{ex}}$ and $^{224}\text{Ra}_{\text{ex}}$ show higher activities in the surface layer (0.54 and 3.05 dpm 100 L⁻¹ respectively), no measureable activity at mid-depths, and then an increase towards the basin floor (0.44 and 1.67 dpm 100 L⁻¹ respectively). However, $^{223}\text{Ra}_{\text{ex}}$ and $^{224}\text{Ra}_{\text{ex}}$ from the second cruise at LE6 are both below the detection limit in the inner basin. In the surface layer (Fig. 4.4b and c), $^{223}\text{Ra}_{\text{ex}}$ and $^{224}\text{Ra}_{\text{ex}}$ are both found to decrease with distance away from the mouth of the loch (from 0.65 to 0.26 dpm 100 L⁻¹ and from 6.0 to 1.8 dpm 100 L⁻¹ respectively).

The activities of ^{226}Ra and ^{228}Ra in the water samples range from 4.3 to 8.5 dpm 100 L⁻¹ and from 17.7 to 24.4 dpm 100 L⁻¹ respectively. The activity ratios of $^{228}\text{Ra}/^{226}\text{Ra}$ show a wide range from

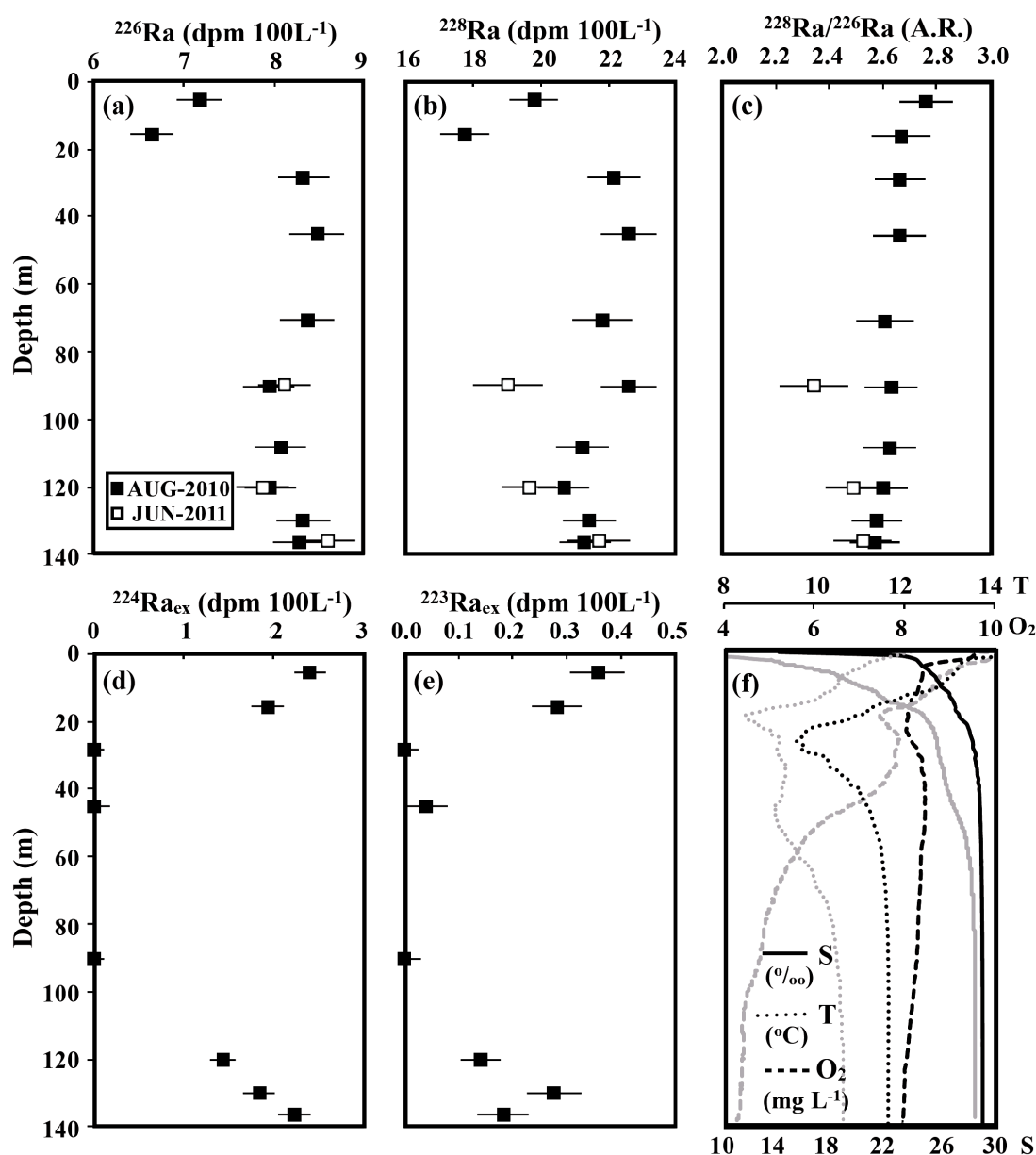


Figure 4.3 Water column profiles of (a) ^{226}Ra , (b) ^{228}Ra , (c) $^{228}\text{Ra}/^{226}\text{Ra}$, (d) $^{224}\text{Ra}_{\text{ex}}$, (e) $^{223}\text{Ra}_{\text{ex}}$ (dpm 100 L⁻¹) and (f) salinity, temperature and oxygen in the inner basin of Loch Etive. Data is from Station LE6 with the black line and filled squares representing data from 3rd of August 2010 and the gray line and open squares that from 8th of June 2011).

2.5 to 4.4 (Table 4.1). In the inner basin (Fig. 4.3a), ^{226}Ra activity shows a constant distribution (8.2 ± 0.4 dpm 100 L⁻¹) below 30 m during the first and second cruises. However, ^{228}Ra activity only shows a constant distribution (21.8 ± 1.4 dpm 100 L⁻¹) in the first cruise, but significantly decreases from 22.6 to 19.0 dpm 100 L⁻¹ at 90 m from the second cruise results (Fig. 4.3b). In the outer basin, the water column shows an oxygen depletion layer below 42 m, with constant salinity and temperature. In this layer, ^{226}Ra and ^{228}Ra both show the highest values of 8.3 and 23.5 dpm 100 L⁻¹ respectively in the water column. In the surface layer, ^{226}Ra activities are relatively constant between 7.1 and 7.5 dpm 100

L^{-1} (Fig. 4.4d) but ^{228}Ra activities increase from 18.4 to 24.4 dpm 100 L^{-1} (Fig. 4.4e) toward the head of the loch.

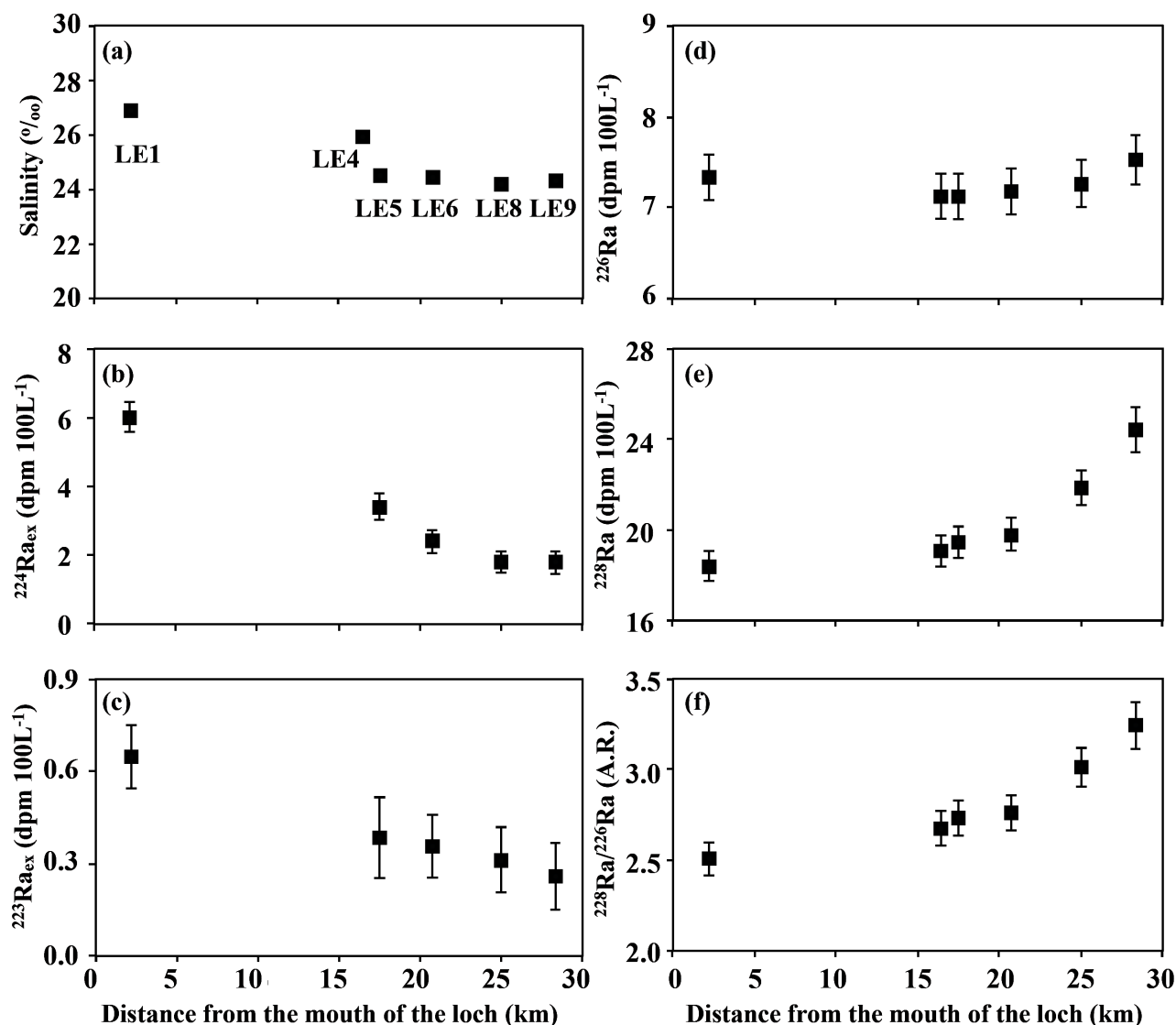


Figure 4.4 Surface profiles of (a) salinity (‰), (b) $^{224}\text{Ra}_{\text{ex}}$, (c) $^{223}\text{Ra}_{\text{ex}}$, (d) ^{226}Ra , (e) ^{228}Ra (dpm 100 L^{-1}) and (f) $^{228}\text{Ra}/^{226}\text{Ra}$ activity ratio at 5 m (except LE4 at 10 m) in Loch Etive plotted with the distance from the mouth of the loch. Note the relatively slight change in salinity within the loch, relative to the larger and generally systematic changes of Ra concentration with distance from the mouth of the loch.

able 4.1 Radium isotopic data in Loch Etive

Sample Station	Date	Depth (m)	Salinity (ppt)	T (°C)	Oxygen (mg L ⁻¹)	²²⁶ Ra (dpm 100L ⁻¹)	²²⁸ Ra (dpm 100L ⁻¹)	²²⁸ Ra/ ²²⁶ Ra (activity ratio)	²²³ Ra _{ex} (dpm 100L ⁻¹)	²²⁴ Ra _{ex} (dpm 100L ⁻¹)
LE1	4 Aug 2010	5	26.9	13.8	8.9	7.3 ± 0.3	18.4 ± 0.7	2.5 ± 0.1	0.7 ± 0.1	6.0 ± 0.4
LE4	3 Aug 2010	1	18.1	15.1	10.1	6.1 ± 0.2	18.9 ± 0.7	3.1 ± 0.1	0.4 ± 0.1	3.6 ± 0.5
		10	25.9	13.1	8.4	7.1 ± 0.2	19.1 ± 0.7	2.7 ± 0.1	0.0 ± 0.1	0.6 ± 0.4
		23	26.8	13.5	8.5	7.6 ± 0.3	19.6 ± 0.7	2.6 ± 0.1	B.D.	B.D.
LE5	3 Aug 2010	54	29.2	12.2	7.0	8.3 ± 0.3	23.5 ± 0.9	2.8 ± 0.1	0.3 ± 0.1	3.9 ± 0.5
		5	24.5	13.3	8.5	7.1 ± 0.3	19.5 ± 0.7	2.7 ± 0.1	0.4 ± 0.1	3.4 ± 0.4
LE6	3 Aug 2010	5	24.5	13.2	8.3	7.2 ± 0.3	19.8 ± 0.7	2.8 ± 0.1	0.4 ± 0.1	2.4 ± 0.3
		15	26.3	12.4	8.1	6.7 ± 0.2	17.7 ± 0.7	2.7 ± 0.1	0.3 ± 0.1	1.9 ± 0.4
		28	28.1	9.5	8.4	8.3 ± 0.3	22.2 ± 0.8	2.7 ± 0.1	B.D.	B.D.
		45	28.8	11.0	8.3	8.5 ± 0.3	22.6 ± 0.8	2.7 ± 0.1	0.0 ± 0.1	B.D.
		70	29.0	11.6	8.3	8.4 ± 0.3	21.8 ± 0.9	2.6 ± 0.1	B.D.	B.D.
		90	29.0	11.6	8.2	7.9 ± 0.3	22.6 ± 0.8	2.6 ± 0.1	B.D.	B.D.
		108	29.0	11.6	8.2	8.1 ± 0.3	21.2 ± 0.8	2.6 ± 0.1	B.D.	B.D.
8 Jun 2011		120	29.0	11.6	8.0	8.0 ± 0.3	20.7 ± 0.8	2.6 ± 0.1	0.1 ± 0.1	1.4 ± 0.3
		130	29.1	11.6	8.0	8.3 ± 0.3	21.4 ± 0.8	2.6 ± 0.1	0.3 ± 0.1	1.8 ± 0.3
		136	29.1	11.6	8.0	8.3 ± 0.3	21.3 ± 0.8	2.6 ± 0.1	0.2 ± 0.1	2.2 ± 0.4
		90	28.5	10.5	4.8	8.1 ± 0.3	19.0 ± 1.0	2.3 ± 0.1	B.D.	B.D.
		120	28.5	10.6	4.4	7.9 ± 0.3	19.6 ± 0.8	2.5 ± 0.1	B.D.	B.D.
		136	28.5	10.6	4.3	8.6 ± 0.3	21.7 ± 0.9	2.5 ± 0.1	B.D.	B.D.
LE8	4 Aug 2010	5	24.2	12.7	7.9	7.3 ± 0.3	21.9 ± 0.8	3.0 ± 0.1	0.3 ± 0.1	1.8 ± 0.3
		33	28.3	9.9	8.2	8.3 ± 0.3	21.9 ± 0.8	2.7 ± 0.1	B.D.	B.D.
		70	28.9	11.4	8.2	8.3 ± 0.3	21.8 ± 0.9	2.6 ± 0.1	B.D.	B.D.
LE9	4 Aug 2010	5	24.3	12.4	7.7	7.5 ± 0.3	24.4 ± 1.0	3.2 ± 0.1	0.3 ± 0.1	1.8 ± 0.3
LE10	4 Aug 2010	1	4.1	14.7	9.8	4.3 ± 0.2	18.8 ± 0.8	4.4 ± 0.2	2.0 ± 0.2	12.2 ± 0.6

All errors are given at ±2 S.E. B.D. means below detection limit.

4.5 Discussion

4.5.1 Surface water mixing in Loch Etive

The short-lived Ra isotopes, ^{223}Ra and ^{224}Ra , enable an assessment of horizontal mixing in the surface water of the loch and the transport rate of seawater from the mouth to the head of the loch. In the surface layer, the mixing of seawater and freshwater results in salinity that changes from 26.9 to 24.3‰ (Fig. 4.4a) towards the head of the loch. Activities of $^{223}\text{Ra}_{\text{ex}}$ and $^{224}\text{Ra}_{\text{ex}}$ decrease in concert with this salinity change (Fig. 4.4b and c). The decrease in activity of $^{223}\text{Ra}_{\text{ex}}$ and $^{224}\text{Ra}_{\text{ex}}$ with distance (x) can most readily be explained by the radioactive decay of Ra entering the loch in seawater as that water is transported towards the head of the loch by mixing or by advection. The magnitude of the salinity change is insignificant (Fig. 4.4a), so seawater is not mixing significantly with fresh water as it travels at the 5 m surface layer. Thus, the decreases in $^{223}\text{Ra}_{\text{ex}}$ and $^{224}\text{Ra}_{\text{ex}}$ are mainly controlled by radioactive decay and seawater advection. Assuming such a situation, the distribution of $^{223}\text{Ra}_{\text{ex}}$ and $^{224}\text{Ra}_{\text{ex}}$ in the surface layer can be expressed by the following equation:

$$w \partial A / \partial x = \lambda A \quad (4.1)$$

where w is the mean water transport rate; x is the distance from the mouth of Loch Etive; A is $^{223}\text{Ra}_{\text{ex}}$ or $^{224}\text{Ra}_{\text{ex}}$ activity; λ is the decay constant for ^{223}Ra (0.0608 d⁻¹) or ^{224}Ra (0.189 d⁻¹).

The solution for w is then given by:

$$w = \lambda x / \ln(A_i / A) = X_{1/2} / T_{1/2} \quad (4.2)$$

where A_i is the initial activity of $^{223}\text{Ra}_{\text{ex}}$ and $^{224}\text{Ra}_{\text{ex}}$ at LE1; $X_{1/2}$ is the distance at which $A = 0.5A_i$; $T_{1/2}$ is the half life of ^{223}Ra or ^{224}Ra . The water transport time between the initial and observed Ra activities. Based on the data in Fig. 4.4b and c, we obtain water transport rates of 6.1 and 2.4 cm s⁻¹ by $^{224}\text{Ra}_{\text{ex}}$ and $^{223}\text{Ra}_{\text{ex}}$ respectively. For comparison, previous measurements made by current meters show that the water transport rates are usually below their detection limit of 5 cm s⁻¹ in the water 40 m below the surface in Loch Etive (Edwards and Edelsten, 1977). Inall et al. (2004) found an average speed of 20 cm s⁻¹ using a current meter around the Bonawe sill during spring tides. In terms of depth, distance and timescale, the Ra-derived water transport rates appear to reflect a long-term (days to weeks) average

water transport throughout the surface layer, which is more suitable for assessing long-term average chemical fluxes but not for short-term (minutes to hours) variability.

The water transport rate calculated by $^{224}\text{Ra}_{\text{ex}}$ is ≈ 2.5 times higher than the rate calculated by $^{223}\text{Ra}_{\text{ex}}$. Assuming that seawater inflow is the only input for $^{223}\text{Ra}_{\text{ex}}$ and $^{224}\text{Ra}_{\text{ex}}$ to the surface water, $^{223}\text{Ra}_{\text{ex}}$ should show a slower decay with distance than $^{224}\text{Ra}_{\text{ex}}$ due to its longer half-life. If the $^{223}\text{Ra}_{\text{ex}}$ derived mixing is $^{224}\text{Ra}_{\text{ex}}$ values should decrease rapidly in the loch to values significantly lower than were observed. This discrepancy can be explained if there is an additional input of $^{224}\text{Ra}_{\text{ex}}$ to the surface water (see discussion below). The slower transport rate, derived from $^{223}\text{Ra}_{\text{ex}}$, is more likely to be a true estimate of transport and suggests a rate of $2.4 \pm 0.2 \text{ cm s}^{-1}$, which is consistent with a previously estimated horizontal mixing transport rate of 3.5 cm s^{-1} in the inner-loch basin (Inall, 2009). This results in a seawater transport time from the mouth to the head of Loch Etive of 17 ± 2 days in the surface layer. If there is a source of ^{223}Ra within the loch, in addition to ^{224}Ra , then these transport rates would be lower, but such a source appears unlikely as discussed below.

4.5.2 Sedimentary inputs of ^{224}Ra and ^{228}Ra to the surface water

Based on the $^{223}\text{Ra}_{\text{ex}}$ -derived water transport rate (Fig. 4.5a) and the radioactive decay of ^{224}Ra , we can calculate a theoretical curve of $^{224}\text{Ra}_{\text{ex}}$ (solid line) in the surface water with distance from the mouth to the head of loch (Fig. 4.5b). If there was no additional input of ^{224}Ra to the surface water, the decrease of $^{224}\text{Ra}_{\text{ex}}$ activity should follow this theoretical curve, but observed activities fall above this expected decay curve.

The source of $^{224}\text{Ra}_{\text{ex}}$ to explain these higher values is likely to be the shelves of the loch, particularly around Bonawe where these shelves are pronounced and where strong cross-sill flow (Inall et al., 2004; Stashchuk et al., 2007) may enhance the release of Ra from the sill flat to surface water. $^{224}\text{Ra}_{\text{ex}}$ concentrations continue to decrease further into the loch beyond the Bonawe Sill, but this decrease is still not explained by simple exponential decay and a further source of ^{224}Ra is required at the head of the loch (see the gray area highlighted in Fig. 4.5b).

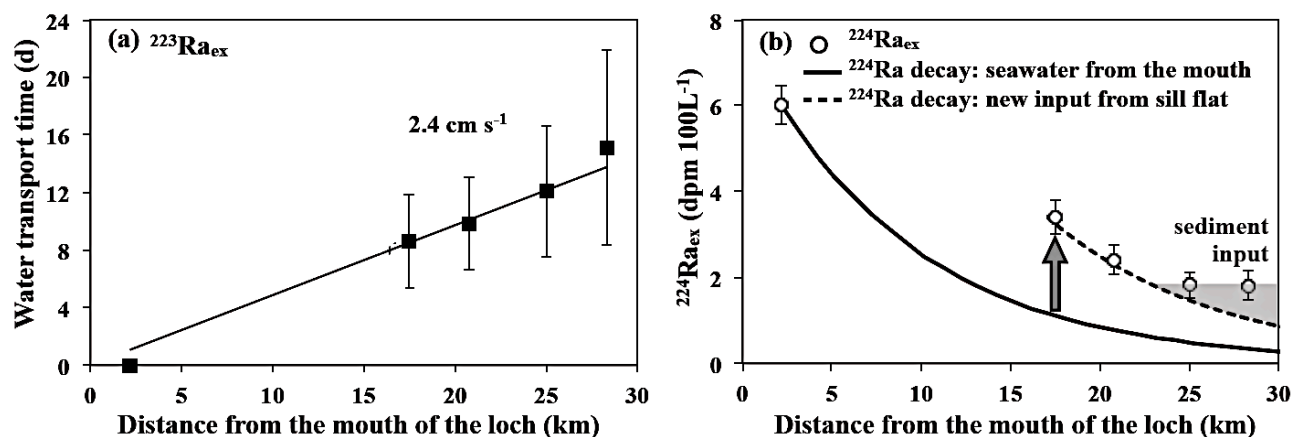


Figure 4.5 (a) Surface water transport time calculated from the radioactive decay of $^{223}\text{Ra}_{\text{ex}}$ with the distance from the mouth of the loch. (b) Predicted $^{224}\text{Ra}_{\text{ex}}$ decay curves based on the $^{223}\text{Ra}_{\text{ex}}$ -derived water transport rate: the solid line represents the expected change of ^{224}Ra if it is provided only from seawater outside the loch. The dashed line demonstrates the need for additional input of ^{224}Ra from sill flat at LE5 and is curved to represent expected mixing if there is no further source further into the loch. The gray shaded regions indicates additional offset of $^{224}\text{Ra}_{\text{ex}}$ from the decay curve due to the additional sediment input at the head of the loch.

This additional source of $^{224}\text{Ra}_{\text{ex}}$ at the head of the loch is associated with higher ^{228}Ra and $^{228}\text{Ra}/^{226}\text{Ra}$ ratios in surface waters (Fig. 4.4e and f). The increase of ^{228}Ra seen towards the head of the loch (Fig. 4.4e) in the surface water is not controlled by radioactive decay, as the half-life of ^{228}Ra is significantly longer than the surface water transport rate, so an input of ^{228}Ra is required. The small variation in salinity (24.5 to 24.3 ‰) in the surface layer at the head of the loch (Fig. 4.4a), indicates that the required input of ^{228}Ra and ^{224}Ra to the surface water are neither from freshwater or groundwater inputs. As at Bonawe in the middle of the loch, shelf sediments in the inner loch are likely to be the source of this ^{228}Ra and ^{224}Ra . The bathymetry of Loch Etive shows a large area of the shelf (with waters depths < 15 m) at the head of the loch (Howe et al., 2001) where riverine sediment depositions might be releasing ^{228}Ra and ^{224}Ra to surface water.

Surface-water Ra concentrations (at station LE9) enable the $^{224}\text{Ra}/^{228}\text{Ra}$ activity ratio of the sediment input to be calculated as 0.15 ± 0.02 . This is lower than the $^{224}\text{Ra}/^{228}\text{Ra}$ ratio of seawater outside the loch (0.33) and in River Etive (0.65). The $^{224}\text{Ra}_{\text{ex}}/^{228}\text{Ra}$ ratio observed at station LE8, ~ 10 km from the head of the loch, is consistent with the value seen at LE9 at the head of the loch and with

radioactive decay with the transport rate indicated by ^{223}Ra . This supports the idea that the shelf sediments at the head of the loch are the likely sources of $^{224}\text{Ra}_{\text{ex}}$ and ^{228}Ra in the inner loch.

Compared to ^{224}Ra and ^{228}Ra inputs, the input of ^{223}Ra from shelf sediments is insignificant in Loch Etive, because the bedrock of this region is granite, which usually has a lower content of U (^{235}U , grandparent of ^{223}Ra) than Th (^{232}Th , parent and grandparent of ^{228}Ra and ^{224}Ra respectively). For example, the granite in the Isle of Skye, Scotland, has an average U (^{238}U) concentration of 1.1 ppm and Th (^{232}Th) concentration of 7.3 ppm (Tammemagi 1976), and an average Th/U atomic ratio of 6.6. Based on the atomic ratios of $^{232}\text{Th}/^{238}\text{U}$ (6.6) and $^{238}\text{U}/^{235}\text{U}$ (137.88) in granite, the estimated input (or the production) of ^{223}Ra is about 9100 times smaller than ^{224}Ra and ^{228}Ra from the sediment or bedrock of Loch Etive.

Riverine inputs, seawater inflow and shelf sediments in the inner loch are the three major end-members for Ra in Loch Etive. Deviations from the mixing line between freshwater and seawater on the plots of ^{226}Ra and ^{228}Ra against salinity (Fig. 4.6) allow sedimentary inputs to be clearly identified. For ^{226}Ra (Fig. 4.6a), the trend shows two end-members mixing between seawater and river inputs. For ^{228}Ra (Fig. 4.6b), the mixing between seawater and river inputs is equal. However, the magnitude of these deviations from the two end-members mixing between the head and the mouth of the loch suggest that the sediment input could contribute 10 to 23% of the ^{228}Ra to the surface water.

4.5.3 Radium cycles and overturn circulation in the inner loch basin

Overturning circulation plays an important role in controlling Ra cycles in the isolated deep waters of the loch. In the inner basin, the vertical water profiles of ^{226}Ra and ^{228}Ra show uniform distributions with depth in the water column below 20 m. This can be interpreted as due to recent overturning of the loch waters, just one month prior to our sampling. This event reset the ^{226}Ra and ^{228}Ra activities in the water column (Fig. 4.3a and 4.3b) and may have lead to temporary perturbation of deep-water ^{223}Ra and ^{224}Ra due to sediment disturbance. The ^{228}Ra activity in inner loch water below 20 m is rather constant between 20.7 and 22.6 dpm 100-l (Fig. 4.3b), which is about 10 to 17% higher than the value of 18.7 dpm 100-l in the ^{228}Ra -salinity mixing relationship between seawater and freshwater in Fig. 4.6b. This suggests either that the mixing relationship was somewhat different at the time of the

last overturn, or that the additional input of ^{228}Ra from the loch shelf sediment also contributes new ^{228}Ra to the new deep waters during overturn. In this latter situation, surface waters incorporate additional ^{228}Ra from shelf sediments before and as they overturned and filled the deep loch.

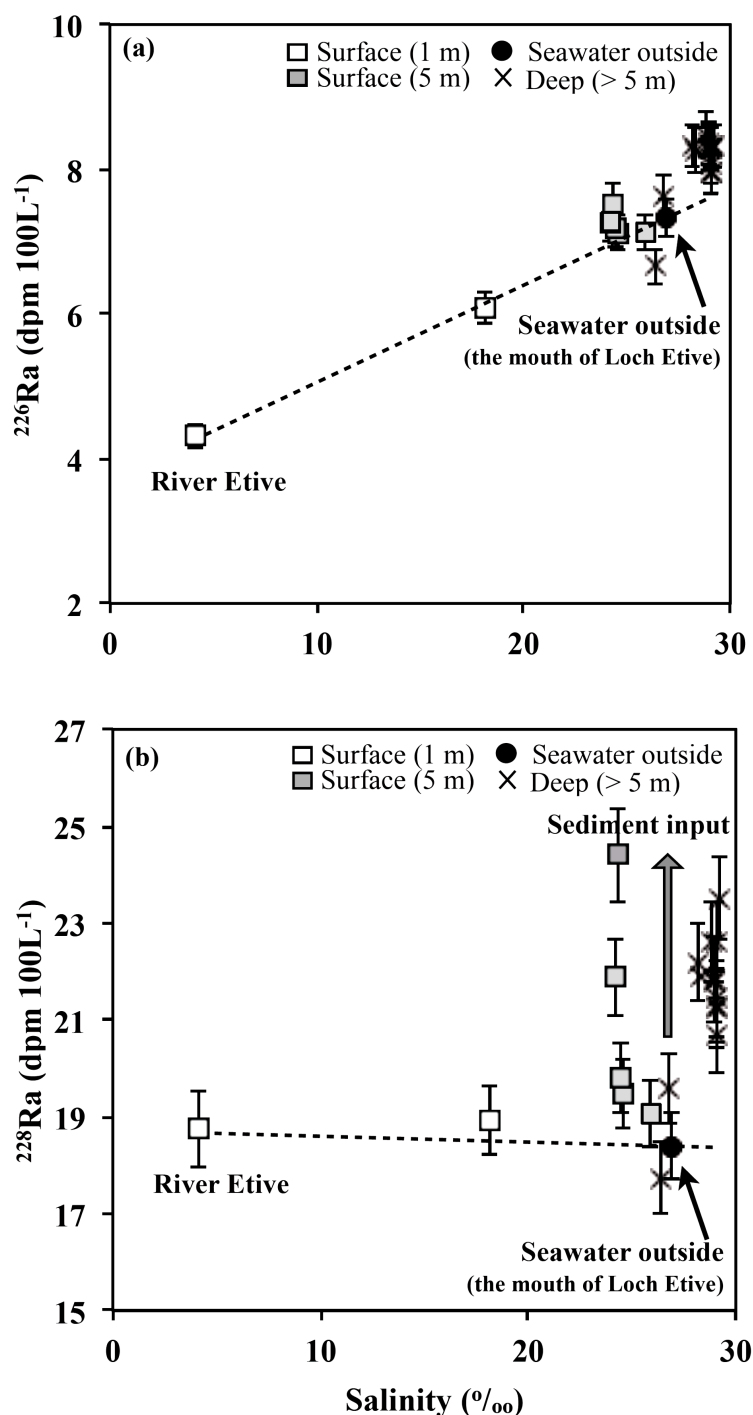


Figure 4.6 The activities of ^{226}Ra (a) and ^{228}Ra (b) plotted against salinity in Loch Etive. For these longer-lived Ra isotopes, there is insufficient time for significant changes in activity due to decay in the loch waters. A mixing curve is therefore expected between the waters of Rivers Etive and the seawater outside of the Loch. ^{226}Ra activities fall close to this mixing line, but ^{228}Ra activities show somewhat higher ^{228}Ra values, due to the addition of ^{228}Ra from sediments to water within the loch.

4.5.4 Sedimentary radium-228 flux in the inner loch basin

Following overturn, the deep water in the inner basin is isolated and addition of further ^{228}Ra can happen only from sediments below the loch. Addition of groundwater to the deep loch is not expected given the granite basement and there is no evidence for such flow from salinity measurements in this or other studies. $^{228}\text{Ra}/^{226}\text{Ra}$ ratios are therefore controlled only by the balance between radioactive decay and sedimentary inputs. Changes in ^{226}Ra are not expected because the half-life is long compared to the period between overturning events allowing insufficient time for decay, and little chance for alpha-recoil from sediments.

The sedimentary input flux of ^{228}Ra in the deep basin, can be calculated from data for Ra isotopes from two cruises in August 2010 and June 2011. Oxygen data suggest that deep-waters of the inner loch remain isolated between these dates and that there are no overturning events. The ^{226}Ra activity shows very consistent results between two cruises in the deep inner basin, which supports such isolation (Fig. 4.3a). However, the data for ^{228}Ra activity and $^{228}\text{Ra}/^{226}\text{Ra}$ ratio show a significant decrease at 90 m in the inner basin from August 2010 to June 2011 (Fig. 4.3b and c). This implies that the ^{228}Ra input from the deep basin sediment is not high enough to balance the output by radioactive decay in the water column.

A simple box model is used to calculate the average ^{228}Ra sediment flux in the inner basin (Fig. 4.7). At the time of the first cruise, the average activity ratio of $^{228}\text{Ra}/^{226}\text{Ra}$ (A_{R1}) in the deep water is constant (2.6 ± 0.1) because an overturn event has reset the value a month before sampling. Assuming no subsequent overturning and there is no sediment input, the activity ratio should decrease from 2.60 to 2.34 due to the radioactive decay of ^{228}Ra . At the time of the 2nd cruise, activity ratios higher than 2.34 demonstrate input of ^{228}Ra from deep basin sediments.

The total additional ^{228}Ra contributed to deep-waters is calculated from observed increase in $^{228}\text{Ra}/^{226}\text{Ra}$ above that expected from decay. The integrated increase of $^{228}\text{Ra}/^{226}\text{Ra}$ between 90 m (the depth of the top of deep-waters) and 136 m (the loch floor) during the period between the two cruises can be expressed by the following equations:

$$A_R = A_{R1} \times 2^{-t/T_{1/2}} \quad (4.3)$$

$$A_{R2}^* = \int_{z_2}^{z_1} (A_{R2} - A_R)(z) dz \quad (4.4)$$

where A_R is the activity ratio (2.34) estimated by the radioactive decay of ^{228}Ra ; t is the time between the two cruises (0.85 year); $T_{1/2}$ is the half-life of ^{228}Ra (5.75 years); A_{R2}^* is the integrated excess $^{228}\text{Ra}/^{226}\text{Ra}$ activity ratio (A_{R2}) subtracted from A_R in the water column between z_1 (90 m) and z_2 (136 m); z is the depth between z_1 and z_2 .

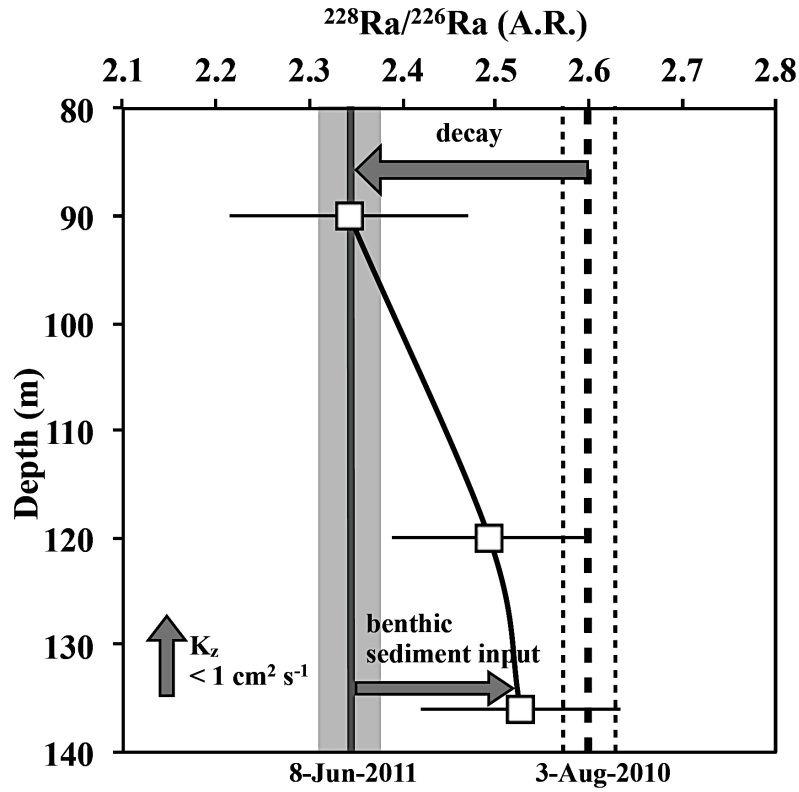


Figure 4.7 The activity ratios of $^{228}\text{Ra}/^{226}\text{Ra}$ in the inner deep basin on the 8th of June 2011. The dashed line is the initial $^{228}\text{Ra}/^{226}\text{Ra}$ on the 3rd of August 2010, calculated as the average of the four deepest samples and shown with 2 S.E. uncertainty. The gray line is the calculated $^{228}\text{Ra}/^{226}\text{Ra}$ ratio assuming radioactive decay from the 3rd of August 2010 to the 8th of June 2011. Note that the 90 m sample is well explained by this decay, while deeper samples have a higher $^{228}\text{Ra}/^{226}\text{Ra}$ value, implying addition of ^{228}Ra from sediments on the loch floor.

Based on the above equations, the sedimentary ^{228}Ra flux ($F_{sed}(^{228}\text{Ra})$) can be calculated by multiplying the integrated excess of the $^{228}\text{Ra}/^{226}\text{Ra}$ ratio (A_{R2}^*) by the constant ^{226}Ra activity in the deep basin ($A_{226\text{Ra}} = 8.2 \pm 0.2 \text{ dpm } 100 \text{ L}^{-1}$) in the following equation:

$$F_{sed}(^{228}\text{Ra}) = A_{R2}^* \times A_{226\text{Ra}} \times z / t \quad (4.5)$$

where $F_{sed}(^{228}\text{Ra})$ is the ^{228}Ra sedimentary flux ($\text{atoms m}^{-2} \text{ yr}^{-1}$). The calculated ^{228}Ra sedimentary flux is $5.5 \pm 0.3 (\times 10^9) \text{ atoms m}^{-2} \text{ yr}^{-1}$. This flux is based on the assumption that vertical mixing cannot remove ^{228}Ra from the deep-waters, which is justified given the very slow vertical mixing ($K_z \sim 2.5 \text{ cm}^2 \text{ s}^{-1}$) in the deep inner loch basin (Inall, 2009).

There are several factors controlling the sedimentary Ra flux in estuarine environments: sediment grain size, pore-water diffusive transport (porosity and partition coefficient K_d), bioturbation mixing, sedimentation rate, Ra production and decay (Cochran and Krishnaswami, 1980; Kadko et al., 1987). The new calculated sedimentary flux of $5.5 \pm 0.3 (\times 10^9) \text{ atoms m}^{-2} \text{ yr}^{-1}$ in the inner basin is lower than the average global sediment flux of $50 \pm 25 (\times 10^9) \text{ atoms m}^{-2} \text{ yr}^{-1}$ from the fine-grained shelf sediments seen in previous studies (e.g. Cochran, 1984; Hancock et al., 2000; Santschi, 1979) but higher than the flux of $1.0 \pm 0.5 (\times 10^9) \text{ atoms m}^{-2} \text{ yr}^{-1}$ from the coarse-grained shelf sediments (e.g. Hancock et al., 2006), as summarised in Moore et al. (2008). The global marine sedimentary ^{228}Ra fluxes have been discussed in Chapter 1 (this thesis). Sediments on the continental shelf generally have higher ^{228}Ra flux values, in the range 0.1 to $110 (\times 10^9) \text{ atoms m}^{-2} \text{ yr}^{-1}$, than those on the continental slope, which are in the range 5 to $11 (\times 10^9) \text{ atoms m}^{-2} \text{ yr}^{-1}$ (Hammond et al., 1990), or on the deep seafloor, which are in the range 1.4 to $4.3 (\times 10^9) \text{ atoms m}^{-2} \text{ yr}^{-1}$ (Cochran and Krishnaswami, 1980).

The grain size in the upper 0.60 m of sediment of the Loch Etive inner basin floor has a mean grain size range of $40 - 70 \mu\text{m}$ from coarse silt to very fine sand (Howe et al., 2002), which could explain the lower sedimentary ^{228}Ra flux in Loch Etive than the average flux from the fine-grained shelf sediments. The sedimentation rate in the inner loch basin of Loch Etive is relatively high, $\sim 0.89 \text{ cm yr}^{-1}$ (Ridgway and Price 1987), which may also restrict Ra sediment fluxes. Hancock et al. (2002) suggested that groundwater flow is important to enhance sedimentary Ra fluxes in the estuarine environments, but groundwater flow is insignificant in Loch Etive. The low sedimentary ^{228}Ra flux observed in this study are therefore perhaps not surprising, and are consistent with sedimentary fluxes calculated in other settings. They certainly do not indicate an unusually high ^{228}Ra sedimentary flux, and therefore support the assertion that ^{228}Ra inventories in the open ocean require significant input from global groundwater sources (Moore et al., 2008).

4.6 Conclusions

This study has used a suite of water-column measurements of the radium quartet to deduce seawater advection rates and sedimentary inputs of Ra in Loch Etive. The observed decrease of ^{223}Ra with distance from the mouth of the loch in surface waters is used to derive a maximum seawater advection rate into the loch of $2.4 \pm 0.2 \text{ cm s}^{-1}$. Addition of both ^{224}Ra and ^{228}Ra to this surface layer are required within the loch. These cannot come only from the river water of Rive Etive, at the head of the loch, but are instead likely to come largely from shelf sediments of the loch. Sedimentary input of ^{228}Ra is also indicated in deep-waters of the inner loch and a flux of $5.5 \pm 0.3 (\times 10^9) \text{ atoms m}^{-2} \text{ yr}^{-1}$ is calculated. This value falls at the low end of previous estimate of sedimentary ^{228}Ra fluxes, and therefore supports the assertion that open ocean ^{228}Ra inventories are not explained by sedimentary inputs and require significant input in groundwaters around the globe.

Chapter 5

Ra isotopes as tracers for ocean mixing and nutrient supply in the Cape Basin

5.1 Abstract

The Cape Basin is in an important location for dynamic inter-ocean exchange between the Atlantic Ocean and the Indian Ocean, in a transition region from the macronutrient-limited Subtropical Gyre to the micronutrient-limited Southern Ocean. Nutrients and micronutrients play important roles in marine productivity in the Cape Basin, but their sources and fluxes to this region remain unclear. In this study, the distribution of seawater ^{228}Ra and ^{226}Ra in the water column of the Cape Basin has been investigated to estimate lateral and vertical ocean mixing and nutrient supply in the surface ocean. A recently developed MC-ICP-MS technique (Chapter 3, this thesis) with improved analytical precision has been applied to measure seawater ^{228}Ra and ^{226}Ra in this study. Ra-228 profiles are used to determine the isopycnal and diapycnal mixing rates in the near-surface open ocean of the Cape Basin. Horizontal mixing (K_x) from the continental shelf to the open ocean is 3.8 ± 0.8 ($10^7 \text{ cm}^2 \text{ s}^{-1}$) and vertical mixing (K_z) in the upper 400 m layer is $0.9 - 2.1 \text{ cm}^2 \text{ s}^{-1}$. Ra-228-derived vertical mixing rates, combined with observed nitrate profiles are also used to estimate the supply of nitrate to the euphotic zone and to place an upper maximum on new production. Calculated upward nitrate fluxes are $0.4 - 0.5 \text{ mmol N m}^{-2} \text{ d}^{-1}$ leading to assumed downward organic carbon fluxes of $3.1 - 3.3 \text{ mmol C m}^{-2} \text{ d}^{-1}$ in the Cape Basin. There is no significant variation of nutrient supply in waters influenced by Agulhas waters relative to those in the Atlantic interior. The vertical mixing has also been applied to calculate phosphate fluxes of $0.03 \text{ mmol P m}^{-2} \text{ d}^{-1}$ and silicate fluxes of $0.14 - 0.33 \text{ mmol Si m}^{-2} \text{ d}^{-1}$ in this region. Compared to phosphate and silicate, the vertical nutrient fluxes in the euphotic zone suggest that ocean productivity in the Cape Basin is nitrogen-limited in early spring. For future comparisons, micronutrient inputs also need to be constrained to improve our understanding of micronutrient limitation in this region.

5.2 Introduction

The Cape Basin is an important location for the dynamic inter-ocean exchange between the Atlantic Ocean, the Indian Ocean and the Southern Ocean. It has been extensively studied in the past two decades to understand heat and water exchange through energetic eddies associated with Agulhas Current Leakage (ACL) (Beal et al., 2011), and is thought to play a central role for thermohaline ocean circulation and global heat transport. The Cape Basin is located in a transition region from the macronutrient-limited Subtropical Gyre to the micronutrient-limited Southern Ocean. Primary productivity is low ($< 1 \text{ mg C m}^{-2} \text{ d}^{-1}$) in this region (Joubert et al., 2011), and modelling results suggest that the region is typically nitrogen-limited (Moore et al., 2004). The input of nutrients and micronutrients to the region is however, not well constrained, but is the focus of significant study at present through cruises such as BONUS-GOODHOPE (Chever et al., 2010) and UK-GEOTRACES. Assessment of lateral and upward ocean mixing in the basin provides important information for such assessment, and the first assessment of upward nutrient supply into the photic zone in the region.

Vertical and horizontal oceanic mixing play an important role in nutrient supply to the euphotic zone (Oschlies, 2002). Geochemical tracers for ocean mixing can therefore also be used to indirectly estimate new production in the upper ocean, e.g. tritium- ^3He (Jenkins, 1988). Radium-228 has seen past use as a tracer to determine new production in the surface ocean (Cai et al., 2002; Ku et al., 1995; Nozaki and Yamamoto, 2001; Sarmiento et al., 1990).

The four naturally occurring radium isotopes cover a wide range of half-lives (^{226}Ra , $T_{1/2} = 1600$ years; ^{228}Ra , $T_{1/2} = 5.75$ years; ^{223}Ra , $T_{1/2} = 11.4$ days; ^{224}Ra , $T_{1/2} = 3.66$ days), which enables us to study oceanic processes at different time scales. In the surface ocean, ^{228}Ra is produced by the decay of ^{232}Th in shelf sediments and diffused into seawater then transported into the open ocean. The half-life of ^{228}Ra is much shorter than the estimated Ra residence time, due to particle removal, of 500 years (Moore and Dymond, 1991). The distribution of ^{228}Ra in the ocean is therefore mainly controlled by ocean mixing and radioactive decay. The distribution of ^{228}Ra can therefore be used to estimate lateral mixing from the coastal to the open ocean (Kaufman et al., 1973; Knauss et al., 1978; Yamada and Nozaki, 1986) and vertical mixing through the water column (Charette et al., 2007; Sarmiento et al., 1976; van Beek et al., 2008).

In this study, I investigate the distributions of ^{228}Ra , as well as ^{226}Ra , in the Cape Basin. A newly developed technique is used to precisely measure seawater ^{228}Ra and ^{226}Ra concentrations by MC-ICP-MS with improved detection limit and sensitivity (Chapter 3, this thesis). This is the first exploration of the vertical and horizontal ^{228}Ra distributions reported for the Cape Basin. In this study I aim to investigate the application of seawater ^{228}Ra as a tracer for vertical and horizontal mixing in the surface Cape Basin, which provides important estimates of the upward nutrient flux and new production in the nitrogen-limited euphotic zone.

5.3 Methods

5.3.1 Studying sites and sampling

Seawater samples were collected from 6 stations on the RRS Discovery during the UK-GEOTRACES cruise, GA-10E (D357), in the SE Atlantic from Cape Town to 40°S, 5°E between October and November 2010 (Fig. 5.1a). The cruise track crossed the French BONUS-GOODHOPE cruise track (MD166) as shown in Fig. 5.1a, along with stations from previous Ra studies around this region. The distribution of sea surface temperature (Fig. 5.1a) shows the pathway of a high-temperature water mass, the Agulhas Current Leakage (ACL), transporting warm water through the Cape Basin into the South Atlantic. Three major surface currents: the South Atlantic Current (SAC), the Benguela Current (BEC) and the Agulhas Return Current (ARC), interact in this region.

Under the surface layer (Fig. 5.1b and c), temperature and salinity show different deep water masses in the Cape Basin, which include the northward flowing Antarctic Intermediate Water (AAIW) at intermediate depth, Antarctic Bottom Water (AABW) in the deep water and the southward flowing North Atlantic Deep Water (NADW) enclosed in between. These water masses were also identified in the T-S diagram in Fig. 5.1d.

The ACL eddies transport a significant volume of warm and salty water ($14 \times 10^6 \text{ m}^3 \text{ s}^{-1}$) from the Indian Ocean to the Atlantic Ocean through the SE Atlantic (Gordon, 1985), and play an important role in the Atlantic meridional overturning circulation (Beal et al., 2011). A previous study showed that the ACL rings decay and lose much of their water in the Cape Basin (van Sebille et al.,

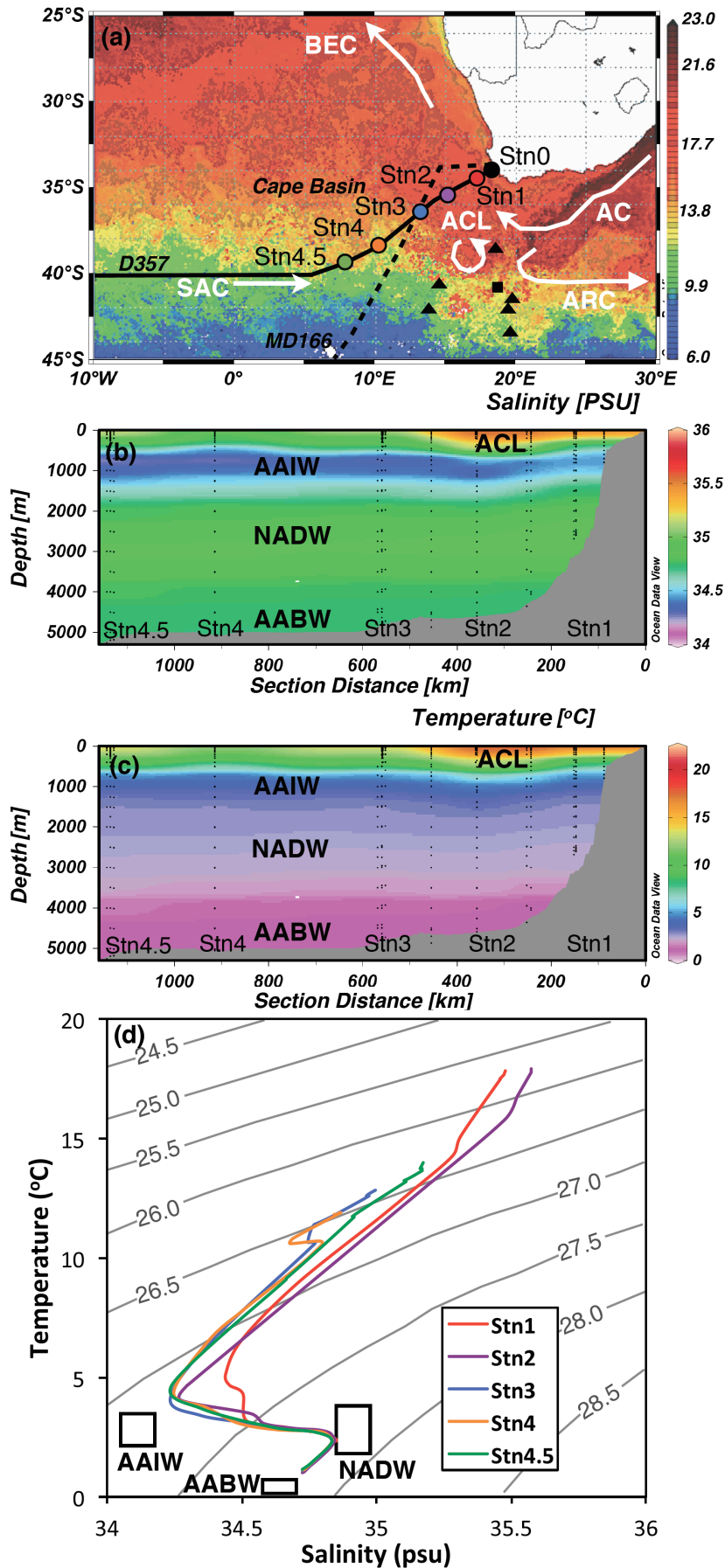


Figure 5.1 (a) Map of cruise track, station locations and surface currents with background of the October 2010 average sea surface temperature in the Cape Basin (data from MODIS_SST_4km, 11 micron day). Five stations are labelled with coloured circles, and the colour also repeated in T-S diagram (Fig. 5.1d) and ^{228}Ra and ^{226}Ra activity profiles (Fig. 5.2). The solid line is the UK-GEOTRACES GA10E cruise track (D357) and the dashed line is the French BONUS-GOODHOPE cruise track (MD166). Stations of previous Ra studies are labelled in solid square (Ku and Lin, 1976) and triangle (Hanfland, 2002). Surface currents are shown in arrows. (b) Salinity and (c) Temperature profiles along the cruise track of UK-GEOTRACES-GA10E. Water masses are labelled in respect to their characters of salinity and temperature. (d) Temperature-Salinity (T-S) diagram and hydrography. Water masses are identified in the black boxes in the diagram.

2010). In our study, the warm and salty water of the ACL was sampled in the surface 500 m water column at Stn2 (Fig. 5.1b and c).

A total of 35 samples were analysed for $^{228}\text{Ra}/^{226}\text{Ra}$ ratio, collected using three sampling techniques during the cruise. Surface seawater samples (80 – 100 L) at 5 m were collected via a clean seawater supply (fish) using an all-teflon pump and acid-cleaned tubing. Samples between 50 m and 400 m were collected using a standard CTD rosette, typically from four 20 litre Niskin bottles. These samples were stored briefly in LDPE cubitainers and filtered through Mn-fibre cartridges by gravity (flow rate $< 0.5 \text{ L min}^{-1}$) on-board for the extraction of radium isotopes from seawater (Moore et al., 1985; Reid et al., 1979). In addition, large-volume seawater sampling (300 – 600 L) was carried out using in-situ stand alone pump systems (SAPs), pumping sea water over Mn-fibre in polypropylene cartridges (van Beek et al., 2008) at flow rate of $2\text{--}5 \text{ L min}^{-1}$ in three selected water stations at Stn1, Stn3 and Stn4.5. All samples collected by these collection techniques (pump, CTD, SAP) were used for measurement of $^{228}\text{Ra}/^{226}\text{Ra}$ ratios and, by Walter Geibert using a delayed coincidence RaDeCC device, ^{224}Ra , ^{223}Ra , ^{228}Th , ^{227}Ac and ^{228}Ra activities. For most samples, a separate sample of 250 mL seawater was also collected for measurement of ^{226}Ra activities. Nutrient samples were collected from the CTD bottles and analysed on-board by Malcolm Woodward using the Bran and Luebbe 5-channel micro-molar segmented flow nutrient auto-analyser with standard analytical procedures established by the Plymouth Marine Laboratory (Krom et al., 2005). Sampling was carried using clean procedures and the samples analysed within 1-2 hours of collection.

5.3.2 Sample analysis

Mn-fibre samples were first counted on-board using a 4-channel radium delayed coincidence counting system (RaDeCC) for ^{224}Ra , ^{223}Ra , ^{228}Th and ^{227}Ac (Moore and Arnold, 1996). The data for ^{224}Ra , ^{223}Ra , ^{228}Th , and ^{227}Ac are not discussed in this thesis. After the counting, Ra was purified using the following procedure for precisely measuring $^{228}\text{Ra}/^{226}\text{Ra}$ ratios and ^{228}Ra concentrations by MC-ICP-MS (Chapter 3, this thesis). Mn-fibres were ashed at 550°C for 6 hours and then leached with distilled 6N HCl to remove Ra from the ashed fibres. Ra was then co-precipitated with $\text{Sr}(\text{Ra})\text{SO}_4$ in the leached solution, centrifuged and cleaned with 3N HCl and H_2O a few times until pH was > 4 . To

convert Sr(Ra)SO_4 to Sr(Ra)CO_3 , 2mL 1M Na_2CO_3 solution was added and then heated on a hotplate for 3 hours. After centrifuging and discarding the supernatant, Sr(Ra)CO_3 was finally dissolved in 2 ml 6N HCl for ion exchange column chemistry, AG50-X8 (to separate Ra and Ba from ^{228}Th and other matrix elements, e.g. Ca, Sr and Mn) and Sr-Spec (to separate Ra from Ba to avoid molecular interferences during MC-ICP-MS analysis).

Smaller seawater samples (250 mL) collected for ^{226}Ra were spiked with ^{228}Ra -spike (Chapter 3, this thesis) and Ra was purified by the precipitation of CaCO_3 and processing with ion exchange columns of AG1-X8, AG50-X8 and Sr-Spec for the measurement of ^{226}Ra concentrations by MC-ICP-MS (Foster et al., 2004). Overall chemical blanks were monitored throughout the whole chemistry, and contribute less than 1% of the sample's ^{226}Ra and were not detectable for ^{228}Ra .

Measurements of ^{228}Ra and ^{226}Ra were performed using a Nu Instrument MC-ICP-MS with the protocols described in Chapter 3. Ra-228 and ^{226}Ra were measured simultaneously on two ion counters. The uranium standard CRM-145, was used to bracket each sample for the mass bias and ion counter gain corrections. Instrumental memories of ^{228}Ra and ^{226}Ra were also detected on ion counters before each measurement. The machine memory was about 0.2 ± 0.1 cps (counts per second) ($n = 16$, 2σ). The memory correction was insignificant for ^{226}Ra , because the ratio of memory to sample signal is small ($< 10^{-4}$). However, the memory correction could be significant for samples with low ^{228}Ra activities and count rates. For instance, the count-rate during analysis of ^{228}Ra on the sample collected at 4741 m at Stn4.5 was only 0.5 cps. At this low count-rate, instrumental memory contributed ~40% of the signal to the sample ^{228}Ra signal and the uncertainty of memory correction becomes substantial (20%). In this study, most of the surface and deep waters in the Cape Basin were measured at count rates > 2 cps ^{228}Ra , which assures that the contribution of the instrumental memory uncertainty to the total uncertainty is $< 10\%$.

In this study, the total uncertainties of ^{226}Ra and ^{228}Ra measurements are typically about 3 – 4% and 5 – 10% (2σ), respectively. Compared to the precision ($> 10\%$, 2σ) obtained by more commonly used decay-counting techniques (e.g. gamma and alpha counters), the MC-ICP-MS technique therefore offers some improvement in the analytical precision of ^{228}Ra measurements.

5.4 Results

The results of ^{226}Ra and ^{228}Ra activities and the activity ratios of $^{228}\text{Ra}/^{226}\text{Ra}$ are presented in Table 5.1 (with $\pm 2\sigma$ errors). The vertical profile of ^{226}Ra shows good agreement with the data from the closest GEOSECS station to this region (Ku and Lin, 1976) (Fig. 5.2a). Ra-226 activities range from 8.2 to 22.4 dpm 100 L⁻¹. In the upper 400 m, the ^{226}Ra activities range from 8.2 to 11.6 dpm 100 L⁻¹, characteristic of Sub-Antarctic Surface Water (SASW) according to the classification by Ku and Lin (1976). Below 400 m, the ^{226}Ra activities of 13.4 to 16.6 dpm 100 L⁻¹ from 700 m to 1500 m reflect the AAIW signature, and the ^{226}Ra activities of 16.6 to 18.9 dpm 100 L⁻¹ between 2500 m and 4000 m reflect the characteristic of NADW. Below 4000 m, ^{226}Ra activities are constantly high (22.1 to 22.4 dpm 100 L⁻¹), which is the typical AABW signature, enriched with ^{226}Ra .

The activity ratios of $^{228}\text{Ra}/^{226}\text{Ra}$ range from 0.108 to 0.390 in the surface water and are comparable with the ratios from 0.080 to 0.497 observed in a previous study to the South East of this region (Hanfland, 2002). The vertical profiles of ^{228}Ra activity are shown in Fig. 5.2b. In the surface water, the activities of ^{228}Ra ranging from 0.99 to 3.22 dpm 100 L⁻¹ are also consistent with the observed values from 0.67 to 4.23 dpm 100 L⁻¹ from the previous Hanfland study (2002). Between 600 m and 4000 m, $^{228}\text{Ra}/^{226}\text{Ra}$ ratios decrease to 0.015 – 0.030 and the ^{228}Ra activities decrease to 0.29 – 0.32 dpm 100 L⁻¹. In the 100 m closest to the sea floor, the ratios of $^{228}\text{Ra}/^{226}\text{Ra}$ increase to 0.048 – 0.088 and the activities of ^{228}Ra also increase to 1.07 – 1.94 dpm 100 L⁻¹. This is the first dataset of seawater ^{228}Ra reported in the intermediate and deep waters in the Cape Basin. It shows higher ^{228}Ra values than those observed in intermediate (< 0.1 dpm 100 L⁻¹) and deep waters (0.22 – 0.28 dpm 100 L⁻¹) to the South in the Southern Ocean (Charette et al., 2007; van Beek et al., 2008). The vertical profiles of seawater ^{228}Ra in the Cape Basin are consistent, however, with expectations based on GEOSECS and TTO observations elsewhere in the Atlantic Ocean (Moore et al., 1985; Trier et al., 1972).

Near-surface vertical profiles of dissolved nitrate, silicate and phosphate are shown in Fig. 5.6, along with $\ln^{228}\text{Ra}$ profiles, and can be used to estimate the vertical nutrient fluxes to the euphotic zone. Nutrient concentrations are generally low in the surface mixed layer and increase with depth below the mixed layer. Nitrate concentrations range from 0.5 to 28.3 $\mu\text{mol L}^{-1}$ in the upper 400 m of

Cape Basin. Silicate and phosphate concentrations range from 1.58 to 0.52 and 0.19 to 1.61 $\mu\text{mol L}^{-1}$ respectively. Below the mixed layer, ACL waters (sampled at Stn2) show lower nutrients than other stations. At Stn0, the shelf water shows higher nitrate, silicate and phosphate concentrations of 3.81, 4.04 and 0.41 $\mu\text{mol L}^{-1}$, respectively, than the surface water in the open ocean of the Cape Basin.

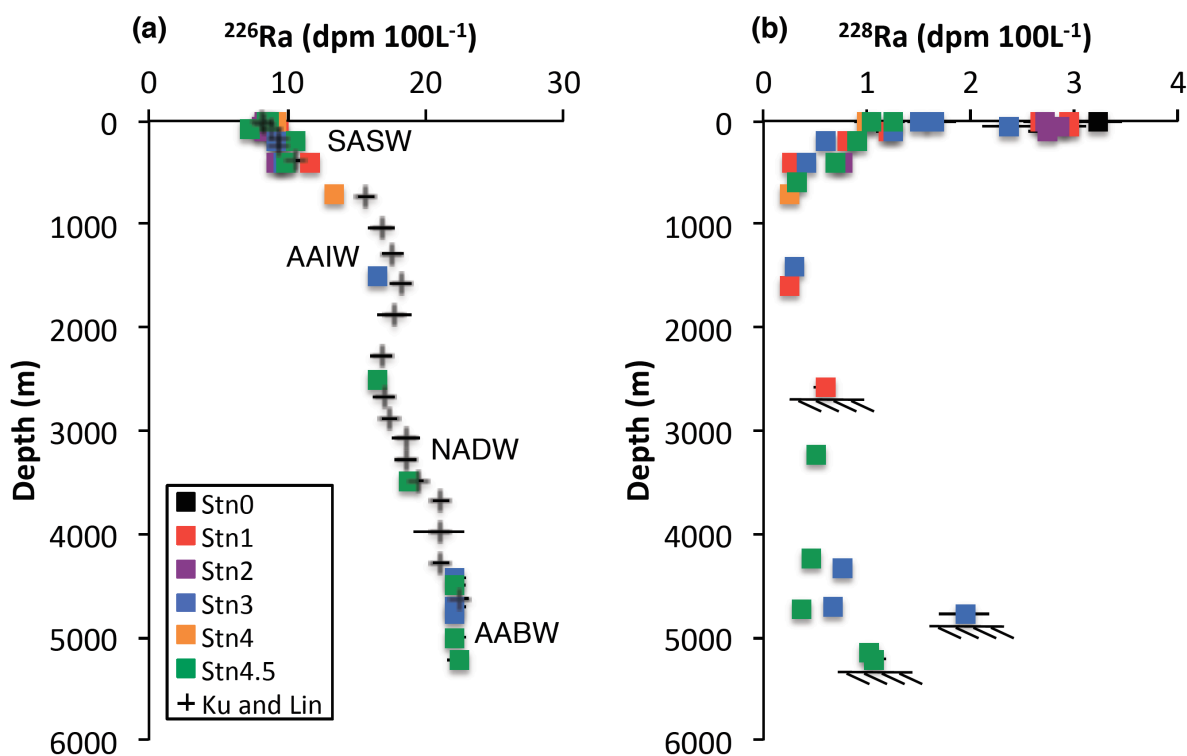


Figure 5.2 Depth profiles of (a) ^{226}Ra and (b) ^{228}Ra activities. The crossed symbols are data from the previous study (Ku and Lin, 1976) at the GEOSECS station ($41^{\circ}46.1'\text{S}$ $18^{\circ}27.2'\text{E}$). Different water masses are characterised in (a) ^{226}Ra profile (see details in text). Error bars are $\pm 2\text{S.E}$ (Error bars in all figures of this chapter are 2 standard errors).

Silicate data are used to assess the ^{226}Ra -Si relationship in this region (Fig. 5.3). The relationship between ^{226}Ra -Si is used to determine ^{226}Ra activities in the 12 cases where no subsamples were collected for separate ^{226}Ra analysis (such ^{226}Ra estimates are shown in brackets in Table 5.1). In Fig. 5.3, the regression line shows a slope of 0.125 dpm 100L⁻¹ of ^{226}Ra per $\mu\text{mol L}^{-1}$ of Si and an intercept of 8.6 dpm 100 L⁻¹, which is comparable with the average slope of 0.1 observed at the GEOSECS stations in the Atlantic (Broecker et al., 1976). The data of ^{226}Ra and silicate at the GEOSECS station around this region (Ku and Lin, 1976) are also plotted in Fig. 5.3, and show a very similar slope of 0.12 but a slightly higher intercept (9.4 dpm 100 L⁻¹).

Table 5.1 ^{226}Ra and ^{228}Ra activities and $^{228}\text{Ra}/^{226}\text{Ra}$ activity ratios

Station	Latitude Longitude	Depth (m)	Salinity (psu)	^{226}Ra (dpm 100L ⁻¹)	^{228}Ra (dpm 100L ⁻¹)	$^{228}\text{Ra}/^{226}\text{Ra}$ (AR)
Stn0	34°11' S 17°58' E	5	35.5	8.3 ± 0.3	3.22 ± 0.23	0.390 ± 0.028
Stn1	34°37' S 17°03' E	5	35.5	8.3 ± 0.3	2.94 ± 0.19	0.354 ± 0.023
		20	35.5	8.6 ± 0.3	2.68 ± 0.16	0.312 ± 0.019
		50	35.5	8.6 ± 0.3	2.94 ± 0.17	0.342 ± 0.020
		100	35.3	9.4 ± 0.4	1.19 ± 0.09	0.127 ± 0.010
		200	35.0	9.6 ± 0.4	0.80 ± 0.08	0.084 ± 0.008
		400	34.6	11.6 ± 0.4	0.29 ± 0.05	0.025 ± 0.005
		1600	34.8	(16.2 ± 0.7)	0.25 ± 0.06	0.015 ± 0.004
		2580	34.9	(15.7 ± 0.7)	0.59 ± 0.09	0.037 ± 0.006
Stn2	35°28' S 15°00' E	5	35.6	8.3 ± 0.3	2.71 ± 0.18	0.327 ± 0.021
		50	35.6	8.2 ± 0.3	2.85 ± 0.19	0.347 ± 0.023
		100	35.6	8.4 ± 0.3	2.73 ± 0.19	0.326 ± 0.022
		400	35.3	9.3 ± 0.3	0.76 ± 0.08	0.082 ± 0.008
Stn3	36°20' S 13°07' E	5	35.0	9.1 ± 0.3	1.52 ± 0.13	0.167 ± 0.014
		10	35.0	9.1 ± 0.3	1.65 ± 0.22	0.182 ± 0.024
		20	35.0	8.8 ± 0.3		
		50	35.0	(8.9 ± 0.4)	2.36 ± 0.25	0.264 ± 0.028
		100	34.8	9.2 ± 0.3	1.24 ± 0.09	0.135 ± 0.010
		200	34.7	9.3 ± 0.3	0.61 ± 0.05	0.065 ± 0.005
		400	34.5	9.7 ± 0.3	0.41 ± 0.04	0.042 ± 0.004
		1410	34.6	(16.5 ± 0.6)	0.29 ± 0.03	0.018 ± 0.002
		1500	34.6	16.6 ± 0.6		
		4335	34.7	(22.2 ± 0.7)	0.77 ± 0.07	0.035 ± 0.003
		4425	34.7	22.2 ± 0.7		
		4706	34.7	22.2 ± 0.8	0.67 ± 0.07	0.030 ± 0.003
		4776	34.7	22.1 ± 0.7	1.94 ± 0.24	0.088 ± 0.011
Stn4	38°24' S 10°24' E	5	34.6	9.2 ± 0.3	0.99 ± 0.11	0.108 ± 0.012
		700	34.3	13.4 ± 0.5	0.26 ± 0.03	0.019 ± 0.003
Stn4.5	39°13' S 07°48' E	5	35.2	8.6 ± 0.3	1.26 ± 0.10	0.146 ± 0.011
		10	35.2	(8.5 ± 0.3)	1.04 ± 0.08	0.121 ± 0.010
		20	35.2	8.6 ± 0.3		
		90	35.1	7.4 ± 0.3		
		200	34.9	10.6 ± 0.4	0.91 ± 0.07	0.086 ± 0.007
		400	34.7	10.0 ± 0.3	0.69 ± 0.10	0.069 ± 0.010
		600	34.3	(10.6 ± 0.4)	0.32 ± 0.03	0.030 ± 0.003
		2500	34.8	16.6 ± 0.6		
		3241	34.8	(18.3 ± 0.8)	0.50 ± 0.07	0.027 ± 0.004
		3500	34.8	18.9 ± 0.6		
		4241	34.7	(21.3 ± 0.9)	0.47 ± 0.06	0.022 ± 0.003
		4500	34.7	22.2 ± 0.8		
		4741	34.7	(22.2 ± 0.9)	0.37 ± 0.07	0.017 ± 0.003
		5000	34.7	22.2 ± 0.8		
		5141	34.7	(22.3 ± 0.9)	1.02 ± 0.10	0.046 ± 0.005
		5211	34.7	(22.4 ± 0.9)	1.07 ± 0.11	0.048 ± 0.005
		5231	34.7	22.4 ± 0.8		

^{226}Ra activity in bracket is extrapolated from the ^{226}Ra -silicate relationship in Fig. 5.3. ^{228}Ra activity is calculated from the activity ratio of $^{228}\text{Ra}/^{226}\text{Ra}$ multiplied by ^{226}Ra activity. All errors are 2 standard errors.

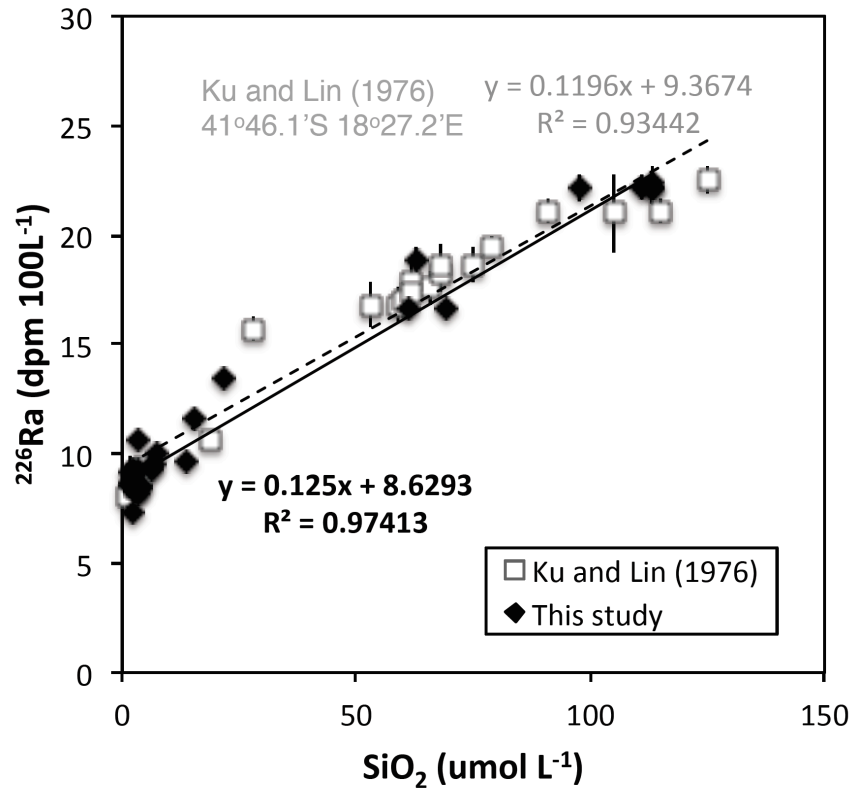


Figure 5.3 Relationships between ^{226}Ra activity and silicate concentration. Data of this study are plotted in closed diamonds and the linear relationship is in solid line. Data from Ku and Lin (1976) at the GEOSECS station ($41^{\circ}46.1'\text{S}$ $18^{\circ}27.2'\text{E}$) are plotted in open squares and dashed line for comparison.

5.5 Discussion

5.5.1 ^{228}Ra as a tracer of lateral mixing

The distribution of seawater ^{228}Ra in the surface ocean has been extensively used as a tracer for measuring mixing rates due to lateral eddy diffusion and advection on a basin-wide scale in the oceans (Cochran, 1992; Ku and Luo, 2008). Assuming the balance between mixing and ^{228}Ra radioactive decay is dominated by diffusion rather than advection, a simple one-dimensional diffusion model could be applied to the horizontal diffusion of ^{228}Ra as shown in Eqn. 1.12:

$$A = A_0 \exp \left[-x \sqrt{\frac{\lambda}{K}} \right] \quad (1.12)$$

The solution of K in Eqn. 1.12:

$$K = \left[\frac{x}{\ln(A_0/A)} \right]^2 \lambda \quad (5.1)$$

Thus, K can be calculated by using the ^{228}Ra decay constant ($\lambda^{228}\text{Ra}$) and the square of slope (m) from a plot of distance (x) (on the x-axis) to $\ln(^{228}\text{Ra})$ (on the y-axis) in Eqn. 5.1.

Ra-228 data from the surface transect in the Cape Basin are used to calculate the offshore horizontal eddy diffusion coefficient (K_x) for the basin. The ^{228}Ra activities and $\ln(^{228}\text{Ra})$ at 5 m water depth are plotted as a function of distance from the coast in Fig. 5.4a and b respectively. The best-fit slope (solid line) in Fig 5.4b is used to calculate a K_x of 3.8 ± 0.8 ($10^7 \text{ cm}^2 \text{ s}^{-1}$) in the surface layer of the Cape Basin (the error on K_x is based on the standard error of the slope in Fig 5.4b, which is 21%).

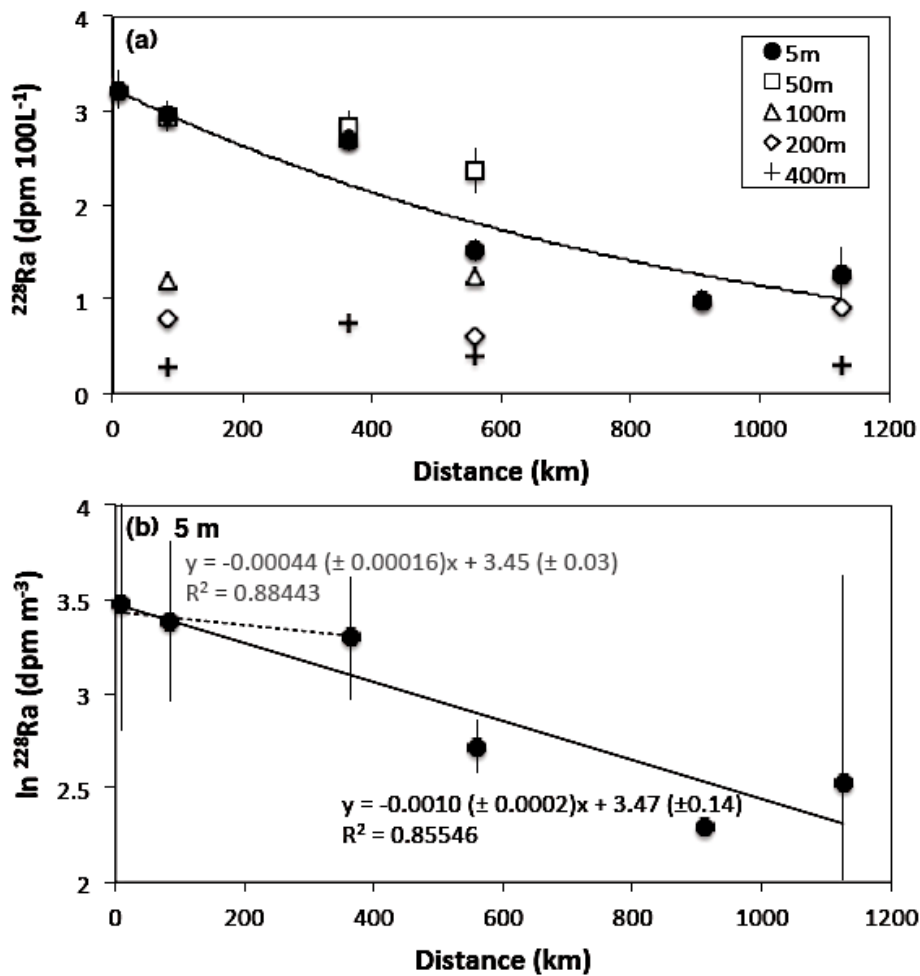


Figure 5.4 Plots of (a) ^{228}Ra activity at water depth 5, 50, 100, 200 and 400 m and (b) $\ln(^{228}\text{Ra})$ activity at water depth 5 m versus distance to the coast of Cape Town. The dashed and solid lines are liner regression lines through Stn0-Stn3 and Stn0-Stn4.5, respectively. The uncertainties of slope and intercept are ± 2 S.E.

The observed horizontal mixing is at the upper end of other estimations of K_x , which range from 10^5 to 10^8 $\text{cm}^2 \text{s}^{-1}$ in a variety of settings in the Atlantic and Pacific Oceans (Kaufman et al., 1972; Knauss et al., 1978; Yamada and Nozaki, 1986). This rapid mixing is not surprising in the Cape Basin, which is known as an ocean region of particularly high eddy activity. The spatial distribution of global ocean surface kinetic energy shows high energy (red) around the Cape Basin (Fig. 5.5) (Ferrari and Wunsch, 2009). The surface study of eddy kinetic energy reveals that the Cape Basin has the highest value of $3,650 \text{ cm}^2 \text{s}^{-2}$ in the vicinity of the Agulhas (Richardson, 2007), which is considerably higher than elsewhere in the Atlantic (e.g. the second highest observed value is $2,790 \text{ cm}^2 \text{s}^{-2}$ in the Gulf Stream (Fratantoni, 2001)).

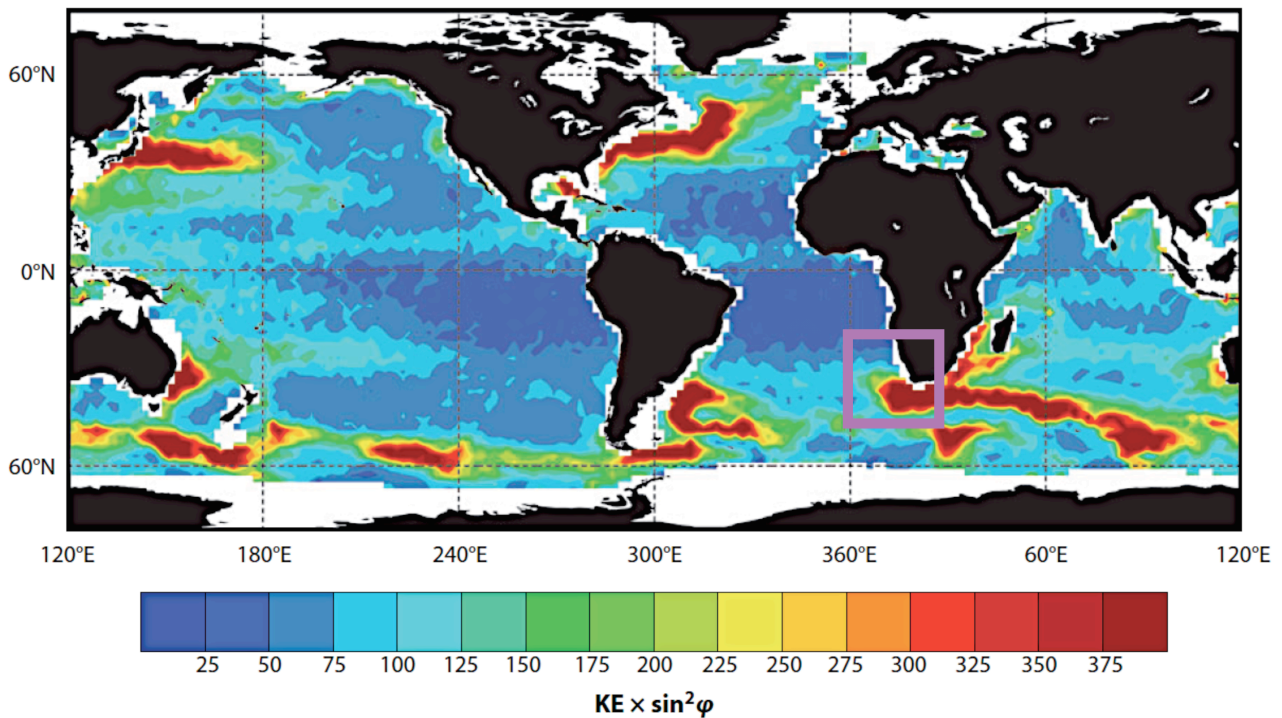


Figure 5.5 Global sea surface kinetic energy ($\text{cm}^2 \text{s}^{-2}$) distribution. The figure is modified from Ferrari and Wunsch (2009). To avoid the equatorial singularity, Ferrari and Wunsch (2009) present the data multiplied by $\sin^2\Phi$, where Φ is the latitude. The purple square indicates the location of the Cape Basin.

Indeed, mixing may be still higher in the 400 km closest to the coast. The value of ^{228}Ra at Stn2 (see Fig. 5.4b) is slightly above the best-fit slope, which may be due to the influence of more rapidly mixed ACL waters. A fit through only the three stations impacted by this water mass (see dashed line in Fig. 5.4b) yields a slope of 0.0004 km^{-1} and a K_x of 23.8 ± 8.5 ($10^7 \text{ cm}^2 \text{s}^{-1}$) within 400 km of the coast

(between Stn0 and Stn2). Although this is a region impacted by advection of waters in the ACL, this advection is along the coast and transport away from the coast still requires horizontal mixing. Such enhanced horizontal mixing in boundary current systems has been reported in some other settings, including the Peru and Kuroshio currents (Knauss et al., 1978; Yamada and Nozaki, 1986).

Alternatively, the higher ^{228}Ra near the shore may reflect non-steady state ^{228}Ra concentrations in coastal regions. Temporal variability of surface-water ^{228}Ra has been reported in Gulf Stream eddies in the Caribbean Sea (Reid, 1984) and in the South Atlantic Bight, USA (Moore, 1987), which suggests that the assumption of steady state ^{228}Ra is not always realistic in the dynamic coastal regions. Never-the-less, the exponential decrease of ^{228}Ra away from the shore in the Cape Basin does indicate its suitability to assess mixing rates at the basin scale, and support the conclusion of a horizontal mixing rate of 3.8 ± 0.8 ($10^7 \text{ cm}^2 \text{ s}^{-1}$) for use when considering fluxes of other properties in this region.

5.5.2 ^{228}Ra as a tracer of vertical mixing

Vertical profiles of $\ln ^{228}\text{Ra}$ in the upper 400 m surface ocean can also be used to calculate vertical eddy diffusion (K_z) in the near surface (Fig. 5.6a to d). The slope of $\ln(^{228}\text{Ra})$ to depth (z) below the surface mixed layer is used in the same 1-D diffusion model (Eqn. 5.1) to calculate vertical mixing K_z for the upper ≈ 400 m of the ocean.

This calculation is based on a situation in which ^{228}Ra is mixed horizontally away from the coast in the surface mixed layer, and then downwards into the subsurface. It therefore relies on the assumption that vertical gradients are not dominated by lateral input of ^{228}Ra at depths below the surface mixed layer. This assumption is supported by an inspection of horizontal ^{228}Ra gradients at depths below the mixed layer (Fig 5.4a) Unlike the exponential change seen in the surface layer, ^{228}Ra activities at 50 m and deeper do not show an increasing gradient towards the continental margin. This argues against lateral mixing away from shore and the major mechanism driving sub-surface ^{228}Ra concentrations. In addition, the distribution of ^{228}Ra on an isopycnal surface (σ_t of $\sim 26.6 \text{ kg m}^{-3}$; ≈ 200 m depth) is very constant and shows no lateral gradient. Although the possibility of lateral inputs cannot be entirely excluded, such arguments suggests that the vertical variation of ^{228}Ra below the

surface mixed layer is mainly dominated by radioactive decay and vertical mixing rather than lateral inputs.

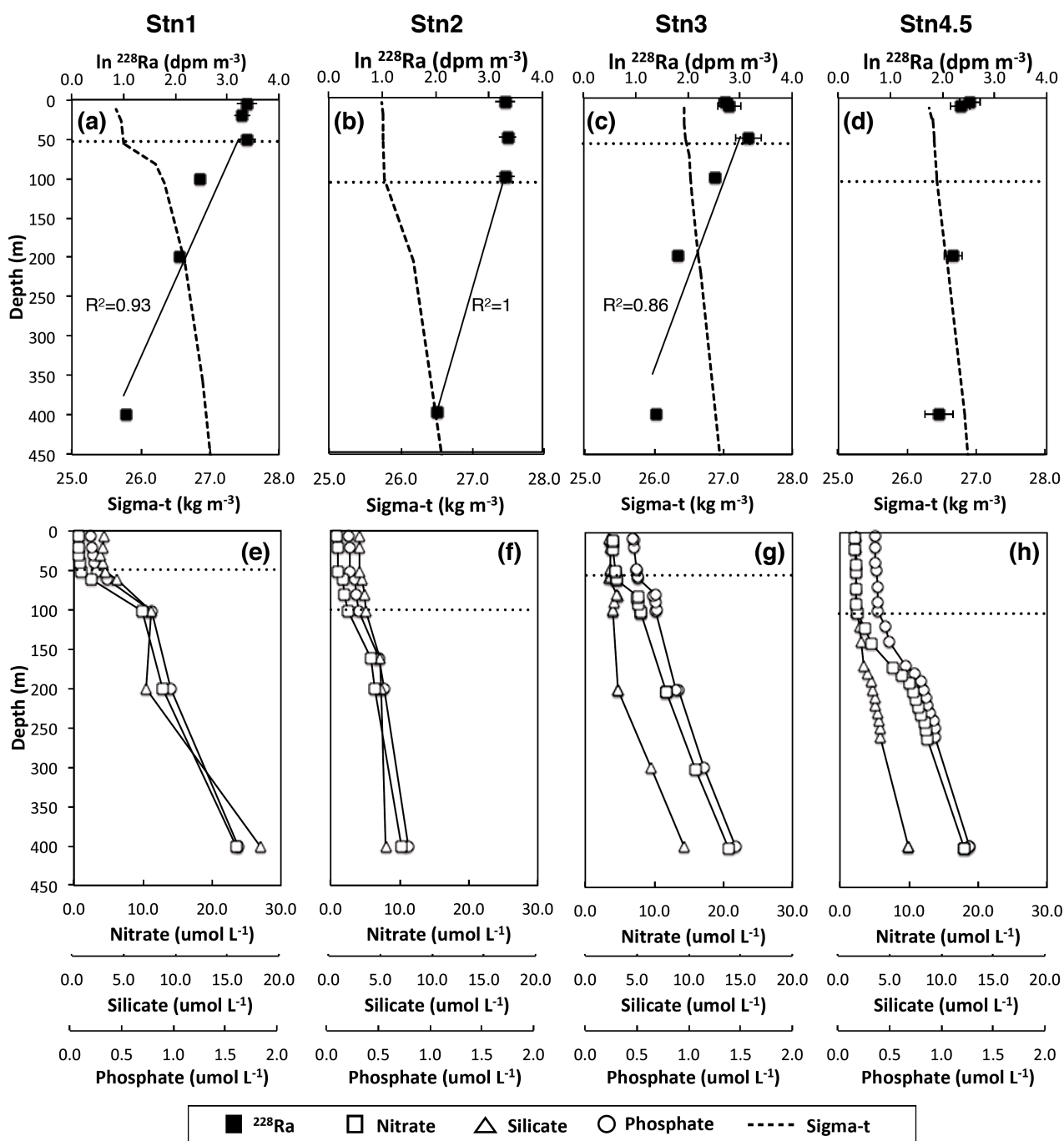


Figure 5.6 Depth profiles of (a) to (d) ln ^{228}Ra activity (dpm m $^{-3}$) and density (sigma-t), and (e) to (h) nitrate, silicate and phosphate concentrations at Stn1, 2, 3 and 4.5. Depths of mixed layer are labelled with the horizontal dashed lines. The linear regression lines of ln ^{228}Ra with depth below mixed layer are shown in the solid lines with the R square values.

Vertical diffusion coefficients (K_z), can be calculated at three stations in this study (Stn1, Stn2 and Stn3), where sufficient depth resolution of ^{228}Ra measurement is available. Resulting K_z values range from 0.9 to 2.1 $\text{cm}^2 \text{s}^{-1}$ at these three stations (Table 5.2), and are broadly comparable to the average K_z of 1.5 $\text{cm}^2 \text{s}^{-1}$ assessed from tritium measurements in the South Atlantic (Li et al., 1984). Station 2 (Stn2), which is influence by an ACL eddy and has a deeper mixed layer than other two stations, shows, unsurprisingly, the strongest vertical mixing of $2.1 \pm 0.4 \text{ cm}^2 \text{s}^{-1}$.

Table 5.2 Vertical diffusion coefficients and nutrient fluxes below the mixed layer

Station	Stn1	Stn2	Stn3
$K_z (\text{cm}^2 \text{s}^{-1})$	0.9 ± 0.2	2.1 ± 0.4	1.3 ± 0.3
Nitrate flux ($\text{mmol m}^{-2} \text{d}^{-1}$)	0.50 ± 0.12	0.46 ± 0.13	0.51 ± 0.13
Phosphate flux ($\text{mmol m}^{-2} \text{d}^{-1}$)	0.031 ± 0.007	0.029 ± 0.008	0.029 ± 0.007
Silicate flux ($\text{mmol m}^{-2} \text{d}^{-1}$)	0.33 ± 0.08	0.14 ± 0.04	0.23 ± 0.06
Organic C flux ($\text{mmol m}^{-2} \text{d}^{-1}$)	3.3 ± 0.8	3.1 ± 0.8	3.3 ± 0.8

All errors are ± 2 S.E.

The use of the vertical distribution of ^{228}Ra to constrain vertical mixing is not possible if the vertical gradient of ^{228}Ra is too small, as seen in the remote open ocean where surface concentrations are low. The vertical profile of $\ln ^{228}\text{Ra}$ at Stn 4.5 shows no gradient below the surface layer (Fig. 5.6d), due to the low ^{228}Ra activity at this station. This, and the lack of a data point from the base of the mixed layer, important to constrain the mixing rate, preclude the calculation of K_z at this setting.

The vertical profiles of ^{228}Ra in deep waters can also be used to calculate vertical mixing in the deep ocean. Many previous GEOSECS studies have used ^{228}Ra vertical profiles to determine vertical mixing in the deep oceans (Moore and Santschi, 1986; Sarmiento et al., 1976; Trier et al., 1972). Deep-sea sediments provide ^{228}Ra input into deep waters and ^{228}Ra diffuses with vertical mixing and decays with depth. Following the same logic discussed above, the slope of $\ln(^{228}\text{Ra})$ to depth (z) above the seafloor (Fig. 5.7) has been used in Eqn 5.1 to calculate the value of vertical mixing, K_z , in the deep sea, which is found to be $0.16 \pm 0.02 \text{ cm}^2 \text{s}^{-1}$ and $6.7 \pm 0.7 \text{ cm}^2 \text{s}^{-1}$ at Stn3 and Stn4.5 respectively. The calculation of vertical mixing in deep water at Stn3 excludes the data at 4330 m due to potential lateral

input. Overall, these values are found to be within the expected range of deep sea vertical mixing from 10^{-1} to $10^2 \text{ cm}^2 \text{ s}^{-1}$ (Polzin et al., 1997; Toole et al., 1994).

Lateral ^{228}Ra input from water masses contact with the bottom along the continental margins or slopes of basins and ridges may alter the vertical ^{228}Ra gradients. The ^{228}Ra distribution in the deep water column at Stn3 shows slightly higher ^{228}Ra activity at 4330 m than at 4706 m (Fig. 5.7a), which is not the same as expected, i.e. high activities in the bottom and decreasing away from the deep seafloor. Previous studies have also seen lateral input of ^{228}Ra around the continental margins (Hammond et al., 1990; Moore and Santschi, 1986). Such lateral input may cause an overestimate of vertical mixing in the deep ocean. Comparisons of ^{228}Ra with other radioactive nuclides (e.g. ^{227}Ac (Geibert et al., 2002; Nozaki, 1984) and ^{222}Rn (Chung and Craig, 1972)) may help to address this problem, because these nuclides have a more distinguished source in deep-sea sediments than elsewhere. Comparisons of ^{228}Ra and ^{227}Ac in the Cape Basin will be discussed in a forthcoming paper which is in preparation with a collaborator, Walter Geibert.

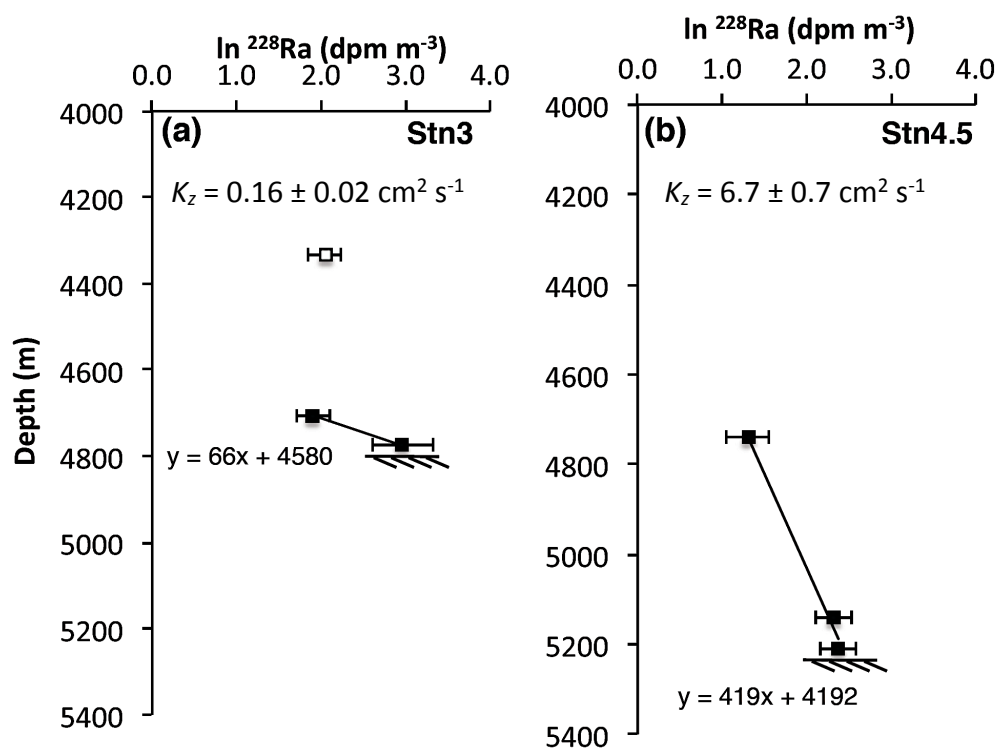


Figure 5.7 Depth profiles of $\ln(^{228}\text{Ra})$ activity in deep waters at (a) Stn3 and (b) Stn 4.5. The solid lines are linear regression lines. The open square data point is not used for linear regression.

5.5.3 ^{228}Ra -derived new production

New production in the euphotic zone is controlled by the supply of nitrate by vertical upward mixing upward across the thermocline. The vertical nitrate flux (F_{nitrate}) can be estimated by applying vertical diffusion coefficients (K_z) to Fick's first law of molecular diffusion in the following equation:

$$F_{\text{nitrate}} = K_z \left(\frac{\Delta \text{NO}_3^-}{\Delta z} \right) \quad (5.2)$$

where $\Delta \text{NO}_3^- / \Delta z$ is the gradient of nitrate concentration over the depth z below the mixed layer, which could be obtained from the linear regression of vertical nitrate profile below the surface mixed layer with uncertainty of 5 to 20% (Fig. 5.6). The vertical diffusion coefficients (K_z) can be determined by using microstructure measurements (Carr et al., 1992), tracer dispersion (Law et al., 2003) or ^{228}Ra vertical profiles (Cai et al., 2002; Ku et al., 1995; Sarmiento et al., 1990). In this study, we use the K_z obtained by the ^{228}Ra vertical profiles from Stn1, 2 and 3 (as discussed in Section 5.5.2) and the gradients of nitrate at the base of the mixed layer (Fig. 5.6e to h) to calculate the vertical nitrate flux (F_{nitrate}).

The ^{228}Ra -derived upward nitrate fluxes range from 0.46 to 0.51 mmol N m⁻² d⁻¹ at Stn1, 2 and 3 in the Cape Basin (Table 5.2). Interestingly, these stations show no significant variation of new production although they have different distances to the continental margin, which implies that the input of nitrate from the continental margin to the open ocean is limited in the Cape Basin. In a previous study, a nitrate flux of 1.01 ± 0.3 mmol N m⁻² d⁻¹ was estimated by using ^{15}N uptake incubation in the same region (34 – 41°S) during the BONUS-GOODHOPE cruise between February and March 2008 (the southern hemisphere summer) (Joubert et al., 2011), which is slightly higher than the ^{228}Ra estimations. This may be due to the seasonal variation. The sampling period of UK-GEOTRACES GA10E (October and November 2010) was early spring in the southern hemisphere, which is before the main phytoplankton bloom in this area. Never-the-less, both the ^{228}Ra -derived nitrate fluxes and the ^{15}N -derived nitrate fluxes suggest a low nitrate uptake in the subtropical region of the South Atlantic.

The nitrate flux can be converted to the organic carbon flux by assuming a Redfield C/N ratio of 6.6 (Redfield, 1934). The calculated total organic carbon fluxes are 3.1 to 3.3 mmol C m⁻² d⁻¹ in the Cape Basin (Table 5.2). In contrast, the estimations of ²³⁴Th-derived POC export is about 1.5 mmol C m⁻² d⁻¹ in the same region during the BONUS-GOODHOPE 2008 campaign (February – March) (Planchon et al., submitted), which is about 2 times lower than the ²²⁸Ra-derived new production. Joubert et al. (2011) have also found that the ²³⁴Th-derived POC export is 2 to 20 times lower than the ¹⁵N-derived new production in the South Ocean. The discrepancy of new production between chemical budgets and direct measurements of POC has been discovered in many previous studies in different regions as well (Cai et al., 2002; Ku et al., 1995; Luo et al., 1995; Murray et al., 1994).

Such discrepancy between chemical budgets (²²⁸Ra-based nitrate flux and ¹⁵N-nitrate uptake) and direct measurements (Th-derived POC and time-series sediment traps) may be due to different timescales of measurement and the size fraction of POC export. Due to the longer half-life of ²²⁸Ra than ²³⁴Th, the ²²⁸Ra-derived mixing is averaging a longer timescales than the ²³⁴Th responds. Additionally, the ²³⁴Th-derived POC is associated with particles larger than 20–50 µm. However, the sized-fractioned primary production in the South Atlantic suggests that about 44% to 84% of the total primary production is smaller than 2.0 µm in the Cape Basin (Froneman et al., 2001). To assess the timescale and size fraction issues, comparisons of ²²⁸Ra and ²³⁴Th (and ²³⁰Th) from the same sites and same seasons are required. The results of ²³⁴Th (obtained from Patrick Martin) and ²³⁰Th (obtained from Alex Thomas) from the UK-GEOTRACES GA10E cruise will be used in future for comparisons of ²³⁴Th-²³⁸U, ²³⁰Th-²³⁴U and ²²⁸Th-²²⁸Ra to discuss their spatial and temporal variations in another paper.

The assessment of the vertical fluxes can also be applied to phosphate and silicate. The vertical phosphate fluxes are very constant with 0.03 mmol P m⁻² d⁻¹ at Stn1, 2, and 3 (Table 5.2). The average ratio of the vertical nitrate to phosphate fluxes is 16.6 in this region, which is very consistent with the normal Redfield N/P ratio of 16. This result suggests that this region is not a P-limited system. The vertical silicate fluxes vary from 0.14 to 0.33 mmol Si m⁻² d⁻¹ at different stations (Table 5.2). However, the ratios of Si/N of 0.6 to 4.7 in the mixed layer are slightly higher than the Si/N ratio of 0.3 to 0.7 in

the upward nutrient fluxes. This implies that nitrogen is more likely to be limiting than silicon in this area. The Cape Basin is clearly not limited by silicon. It therefore seems to be in a similar state to the Southern Ocean, where diatom growth shows no difference between high and low silicic acid concentrations (Coale et al., 2004).

Compared to other macronutrients (P and Si), the low nutrient fluxes and the low primary productivity in the Cape Basin suggest that Cape Basin is nitrogen-limited in early spring of the southern hemisphere. The low new production in the surface ocean may be due to limited nutrient inputs from the continental margins. The ACL plays an important role to transport heat and salt into the Cape Basin, but it does not provide nutrients. The new production inside the ACL is not different from other stations, even though it has a stronger vertical mixing. Modelling results also suggest that this region is a nitrogen-limited area (Moore et al., 2004). However, micronutrient limitation has not been well studied in this region. Iron limitation is also important in the Southern Ocean (Martin et al., 1990). The forthcoming iron data from the UK-GEOTRACES GA10E cruise (obtained from Marten Klunder) will help to constrain the state of iron limitation in the Cape Basin.

5.6 Conclusions

The distribution of ^{228}Ra has been investigated to estimate ocean mixing and new production in the Cape Basin. The horizontal mixing (K_x) is 3.8 ± 0.8 ($10^7 \text{ cm}^2 \text{ s}^{-1}$) from the continental shelf to the open ocean and the vertical mixing (K_z) is $0.9 - 2.1 \text{ cm}^2 \text{ s}^{-1}$ in the upper 400 m layer. The ACL region shows slightly stronger mixing both vertically ($2.1 \pm 0.4 \text{ cm}^2 \text{ s}^{-1}$) and possibly laterally (23.8 ± 8.5 ($10^7 \text{ cm}^2 \text{ s}^{-1}$)). The ^{228}Ra -derived vertical mixing coefficients and the distribution of nitrate concentrations below the mixed layer are used to estimate new production in the euphotic zone. In this region, nitrate fluxes are $0.4 - 0.5 \text{ mmol N m}^{-2} \text{ d}^{-1}$ from below the surface mixed layer and the organic carbon fluxes are $3.1 - 3.3 \text{ mmol C m}^{-2} \text{ d}^{-1}$. The new production shows no significant variation in the surface ocean of the Cape Basin around the continental margin, which implies that the nitrate input from the continental margin to the open ocean is limited in the Cape Basin. The upward nutrient fluxes show no difference between the ACL eddy and other stations although the ACL vertical mixing is strong. The vertical mixing is also applied to calculate phosphate fluxes of $0.03 \text{ mmol P m}^{-2} \text{ d}^{-1}$ and silicate fluxes of $0.14 -$

0.33 mmol Si m⁻² d⁻¹ in this region. Compared to other macronutrients, low nitrate fluxes suggest that marine productivity in the Cape Basin is nitrogen-limited during early spring of the southern hemisphere. However, it still requires more micronutrient results from the same cruise to have a comprehensive comparison of micronutrient and macronutrient inputs and their limitations in the Cape Basin.

5.7 Future plans

This chapter demonstrates the use of ²²⁸Ra as a tracer for ocean mixing and hence as a means to estimate nutrient fluxes to the surface ocean. To better constrain the uncertainties of ²²⁸Ra-derived mixing rates and nutrient fluxes, comparisons of ²²⁸Ra and other methods are necessary. For future plans, the results of this chapter will be compared with other methods in several future publications: (1) ²²⁸Ra-derived mixing rates will be compared with VMP (vertical microstructure profiler) data to assess upwards mixing rates (Matthew Palmer); (2) the results for ²²⁸Ra and ²²⁷Ac will be combined together to provide comprehensive information on deep ocean mixing (Walter Geibert); (3) the results of short-lived Ra isotopes (²²³Ra and ²²⁴Ra) will be used to constrain ²²⁸Ra fluxes and coastal mixing on the continental shelf (Walter Geibert); (4) comparisons of ²³⁴Th-²³⁸U (Patrick Martin), ²²⁸Th-²²⁸Ra (Walter Geibert) and ²³⁰Th-²³⁴U (Alex Thomas) results will help to constrain downward fluxes and carbon export from the surface layer at different timescales.

Chapter 6

Conclusions

This thesis has applied Th and Ra isotopes as tracers to study ocean mixing and to quantify trace-metal nutrient inputs to the oceans from atmospheric dust, rivers, continental shelves and ocean sediments.

The outcomes from this thesis include:

- Investigation of seawater ^{232}Th and ^{230}Th to determine dust fluxes to the oceans.
- Analytical development of seawater ^{228}Ra and ^{226}Ra measurements by MC-ICP-MS.
- Applications of the Ra quartet (^{228}Ra , ^{226}Ra , ^{224}Ra and ^{223}Ra) to estimate ocean mixing and chemical fluxes in estuarine (Loch Etive) and open ocean (Cape Basin) environments.

6.1 Thesis summary

Using ^{232}Th and ^{230}Th as tracers to determine dust fluxes to the surface ocean

The use of Th isotopes as an improved tracer of dust inputs has been tested by measuring ^{232}Th and ^{230}Th concentrations of upper-ocean seawater at six stations along the AMT12 section that spans the Saharan dust plume. The highest ^{232}Th concentrations and $^{232}\text{Th}/^{230}\text{Th}$ ratios are observed at stations that are strongly influenced by Saharan dust deposition. In the surface water, the distribution of ^{232}Th concentration is in agreement with dissolved Al distributions and SeaWiFS aerosol imagery, supporting the use of ^{232}Th as a proxy for dust fluxes. Deeper in the water column, lateral input of ^{232}Th from Mediterranean Outflow Water is detected at 1000 m in the north Atlantic.

Surface-water Th residence times have been calculated separately from ^{230}Th and ^{234}Th using a simple scavenging model. In general, values from the two isotopes are consistent with one another. Despite the broad agreement in patterns of thorium removal assessed with ^{230}Th and ^{234}Th , there are differences in the absolute values calculated with the two nuclides at some locations. Longer residence times for ^{230}Th than ^{234}Th are observed in the North Atlantic subtropical gyre and equator due to upward mixing and particulate scavenging during seasonal bloom. Comparisons of ^{234}Th and ^{230}Th data suggest that ^{230}Th residence times appear to reflect the longer-term value, however, rather than exhibiting the strong seasonal influence seen for ^{234}Th .

Th residence times permit dust flux to the surface ocean to be calculated using the known concentration of Th in dust, and assumed values for the solubility of dust Th in seawater. Dust fluxes are calculated from measured ^{232}Th concentrations, ^{230}Th -derived removal rates, typical continental Th concentrations, and a dust Th solubility of 1 to 10%. The ^{232}Th estimated dust deposition shows good agreement with models of dust deposition if Th solubility is 1 to 5% in the north Atlantic (yielding fluxes of $0.4 - 19.2 \text{ g m}^{-2} \text{ yr}^{-1}$) and 5 to 10% in the south Atlantic (fluxes of $0.2 - 0.7 \text{ g m}^{-2} \text{ yr}^{-1}$). Despite the need for better constraints on the fractional solubility of dust Th, this study demonstrates the power of combining Th isotope measurements to constrain dust fluxes to the surface ocean.

Analytical development for measuring seawater ^{228}Ra and ^{226}Ra by MC-ICP-MS

A new technique for the precise measurement of $^{228}\text{Ra}/^{226}\text{Ra}$ ratios and ^{228}Ra and ^{226}Ra concentrations in seawater has been developed using MC-ICP-MS. Traditionally, the measurement of Ra isotopes has relied on decay-counting techniques with large-volume seawater samples. For the measurements of Ra isotopes using MC-ICP-MS, chemical separation is needed to purify Ra before analysis. Adapting pre-concentration approaches from previous studies, 50 to 150 L seawater samples are required to pump through Mn-fibre cartridges to pre-concentrate Ra. The Mn-fibres are ashed and then leached with 6N HCl to remove Ra which is then precipitated with SrSO_4 . The SrSO_4 is converted to SrCO_3 for dissolution, before purification of Ra using two ion-exchange columns – one with AG50-X8 resin and the other with Sr Spec resin. The resulting purified Ra aliquot from the Mn-fibre is used to assess the $^{228}\text{Ra}/^{226}\text{Ra}$ ratio of seawater. A separate sample (120 to 500 mL) of the same seawater is also collected and measured to assess ^{226}Ra concentrations by MC-ICP-MS, by applying isotope dilution with a ^{228}Ra spike. Seawater ^{228}Ra concentrations are calculated by multiplying $^{228}\text{Ra}/^{226}\text{Ra}$ ratios from the Mn-fibre by ^{226}Ra concentrations from the isotope dilution measurement.

Measurements of $^{228}\text{Ra}/^{226}\text{Ra}$ ratios on an in-house Ra standard demonstrate an internal precision of 1.7% (2 S.E.) and an external repeatability of 2% (2 S.D.) Similar external repeatability is demonstrated for four 100-litre seawater samples from Southampton Docks. The accuracy of this technique has been demonstrated by comparison of results with that of other labs as part of the GEOTRACES intercalibration. Compared to decay-counting approaches, the MC-ICP-MS technique

shows consistent results with other techniques, but with better analytical precision. Using comparable volumes of seawater to those for existing analytical techniques, MC-ICP-MS provides a lower detection limit ($\approx 0.1 \text{ fg } ^{228}\text{Ra}$), improved precision (2%) and a shorter counting time (20 minutes) for measurement of ^{228}Ra and ^{226}Ra concentrations (although it requires a longer pretreatment time for Ra purification). This method has been applied to studies in Loch Etive and the Cape Basin, which shows the advantage of measuring ^{228}Ra in the South Atlantic Ocean where ^{228}Ra concentrations are low. This method also extends the powerful use of ^{228}Ra to understand mixing and nutrient fluxes in the oceans.

Water mixing and Ra inputs in Loch Etive, Scotland

The Ra quartet (^{228}Ra , ^{226}Ra , ^{224}Ra and ^{223}Ra) has been investigated in Loch Etive, a Scottish fjord, to provide new constraints on water mixing and Ra cycles in the fjord system. Fjords play an important role in the transformation of river water to seawater, showing strong physical and chemical gradients. In addition, the glacially over-deepened and semi-enclosed marine basins usually provide a unique fjord water circulation as a buffer to control the exchange between terrestrial and marine environments. Precise estimates of water mixing and chemical fluxes in Loch Etive improve our understanding of the global oceanic chemical and biological cycles.

In the surface of Loch Etive, the water transport rate, determined by $^{223}\text{Ra}_{\text{ex}}$, is $2.4 \pm 0.2 \text{ cm s}^{-1}$. Based on the water transport rate, seawater traveling from the mouth to the head of the loch takes 17 ± 2 days. Shelf sediments around the head of the loch provides additional input ^{224}Ra and ^{228}Ra to the surface water, which alter the activity ratio of $^{228}\text{Ra}/^{226}\text{Ra}$ in the surface water by about 11 ~ 19%. Overturning circulation plays an important role in resetting Ra cycles in the isolated inner loch deep basin. The deep basin sediment provides ^{228}Ra to the isolated deep water. The sedimentary ^{228}Ra flux is $5.5 \pm 0.3 (\times 10^9 \text{ atoms m}^{-2} \text{ yr}^{-1})$ in the inner deep basin, which is comparable with the global range of sedimentary ^{228}Ra inputs from shelf sediments.

Ocean mixing and nutrient fluxes in the Cape Basin

The Cape Basin is in an important location for dynamic inter-ocean exchange between the Atlantic Ocean and the Indian Ocean, in a transition region from the macronutrient-limited Subtropical Gyre

to the micronutrient-limited Southern Ocean. Ocean mixing and nutrient fluxes are important to ocean circulation and marine productivity in the Cape Basin. Vertical and horizontal mixing rates have been investigated by studying ^{228}Ra and ^{226}Ra transects and depth profiles in the Cape Basin. Based on the ocean mixing rates and nutrient profiles, the results have also been used to extrapolate the upward nutrient flux and new production in the euphotic zone.

The study of horizontal and vertical ^{228}Ra profiles enables us to determine the diapycnal and isopycnal mixing rates in the surface open ocean of the Cape Basin. The horizontal mixing (K_x) from the continental shelf to the open ocean is $3.8 \pm 0.8 (\times 10^7 \text{ cm}^2 \text{ s}^{-1})$ and the vertical mixing (K_z) in the upper 400 m layer is $0.9 - 2.1 \text{ cm}^2 \text{ s}^{-1}$. The ^{228}Ra -derived vertical mixing and nitrate profiles are also used to estimate the new production in the euphotic zone. The upward nitrate fluxes in the Cape Basin are $0.4 - 0.5 \text{ mmol N m}^{-2} \text{ d}^{-1}$ and the organic carbon fluxes are $3.1 - 3.3 \text{ mmol C m}^{-2} \text{ d}^{-1}$. There is no significant variation of new production at different sampling stations. This vertical mixing has also been applied to calculate phosphate fluxes of $0.03 \text{ mmol P m}^{-2} \text{ d}^{-1}$ and silicate fluxes of $0.14 - 0.33 \text{ mmol Si m}^{-2} \text{ d}^{-1}$ in this region. Compared to silicate and phosphate fluxes, low nitrate fluxes suggest that marine productivity in the Cape Basin is nitrogen-limited during early spring of the southern hemisphere. However, it also requires micronutrient results to have a better constraint of micronutrient inputs and their limitations in the Cape Basin.

6.2 Future prospects

This study shows the advantages of using Th and Ra isotopes as tracers for estimating dust input, Th removal rates, water mixing and nutrient fluxes in the oceans. Several possible future studies have been mentioned in the discussion of each chapter. There are summarised here:

- The improved dust-input tracer, ^{232}Th combined with ^{230}Th , has been shown to have significant potential by work in this thesis. Such promise would undoubtedly be enhanced by research to better understand the solubility of Th, variations of mixed layer thickness and the possible magnitude of any lateral advection of ^{232}Th to the open ocean. These inquiries are important not only for Th, but also for Al as a dust tracer, and for other metals such as Fe that act as micronutrients

- A newly developed MC-ICP-MS technique provides high precision and low detection limit measurements of seawater ^{228}Ra concentration and $^{228}\text{Ra}/^{226}\text{Ra}$ ratio. This method would allow more applications of ^{228}Ra in the ocean interior where ^{228}Ra concentrations are low. However, this method is restricted by longer pretreatment time than gamma counting techniques. To address this problem, reducing seawater sample volume for ^{228}Ra is the key. Small sample volume would enable using MnO_2 precipitation for Ra preconcentration instead of Mn-fibres, which would shorten the preparation time. Higher sensitivity and lower background noise of mass spectrometer are required to improve this technique in future studies.
- Better knowledge of the sedimentary ^{228}Ra flux to the oceans is of great interest, because it plays an important role in the total ^{228}Ra inputs to the oceans. The use of ocean ^{228}Ra inventories to estimate SGD flux to the oceans also requires accurate estimate of ^{228}Ra fluxes from other sources, especially the sedimentary ^{228}Ra flux. However, this flux is not well constrained due to the complex system and different end-members of ^{228}Ra mixed in estuarine environments. In addition, sedimentary ^{228}Ra flux from the continental slopes is often ignored due to low ^{228}Ra activities in sub-surface waters, but this assumption may not be robust. Sedimentary ^{228}Ra fluxes in different marine environments should be further investigated in future studies.
- New production in the euphotic zone, estimated with different methods (e.g. ^{234}Th -POC, ^{15}N -incubation and ^{228}Ra -derived vertical mixing) often disagree with one another. Similarly, Th residence times in surface water differ depending on the isotope used for the calculation (e.g. ^{234}Th , ^{230}Th and ^{228}Th). Comparisons of different methods and isotopes at the same time and place would be helpful, and would enable us to understand the correlation between different methods and temporal variation.

To sum up, this thesis suggests new directions in research on Th and Ra isotopes in marine geochemistry oceanography. The use of U-Th series nuclides as tracers for ocean mixing and trace-metal inputs to the ocean shows great potential to extend our understanding of nutrient cycles and marine biogeochemistry in future studies. This would also enable us to investigate the key mechanism of micronutrient limitation to marine productivity in the oceans. In the next decade, the GEOTRACES

program will provide great opportunities for applications of the U-Th series nuclides in studying ocean mixing and tracing trace-metal nutrient inputs to the oceans. It is hoped that such work will reveal important information about the global nutrient and carbon cycles, along with ocean circulation and marine biological dynamics. Such information will enable us to better understand and predict ocean circulation and climate change.

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