The U-series toolbox for paleoceanography

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1. Introduction

The geochemistry of marine sediments is a major source of information about the past environment. Of the many measurements that provide such information, those of the U-series nuclides are unusual in that they inform us about the rate and timescales of processes. Oceanic processes such as sedimentation, productivity, and circulation, typically occur on timescales too short to be assessed using parent-daughter isotope systems such as Rb-Sr or Sm-Nd. So the only radioactive clocks that we can turn to are those provided by cosmogenic nuclides (principally $^{14}$C) or the U-series nuclides. This makes the U-series nuclides powerful allies in the quest to understand the past ocean-climate system and has led to their widespread application over the last decade.

As in other applications of the U-series, those in paleoceanography rely on fractionation of the nuclides away from secular equilibrium. In the oceanic setting, this fractionation is generally due to differences in the solubility of the various nuclides. The general behavior of the U-series nuclides in the oceans was widely researched in the middle decades of the twentieth century. This work established knowledge of the concentrations of the nuclides in the various compartments of the ocean system, and of their fluxes between these compartments. Such understanding was comprehensively summarized in the Ivanovich and Harmon U-series volume (Ivanovich and Harmon, 1992), particularly by Cochran (1992). Understanding of the basic behavior of the U-series nuclides has not advanced very dramatically in the decade since that summary but a major theme of research has been the use of this geochemical understanding to develop the U-series tools which are now used to assess the past environment (Table 1).

This chapter summarizes the use of U-series nuclides in paleoceanography. It starts with a brief summary of the oceanic U budget and an introduction to important features of the behavior of U-series nuclides in the marine realm. It then discusses the various U-series tools which have proved useful for paleoceanography, starting at $^{238}$U (and $^{235}$U) and progressing down the decay chain towards Pb. One tool that will not be discussed is U/Th dating of marine carbonates which has seen sufficient application to merit a chapter on its own (Edwards et al., 2003). The use of U-series nuclides to assess rates of processes in the modern ocean will also not be discussed in depth here but are dealt with elsewhere in this volume (Cochran and Masque, 2003).

2. U-series isotopes in the ocean environment

2.1 The ocean uranium budget

Uranium has a reasonably constant seawater concentration in both space and time, varying only in line with changes in salinity (Ku et al. 1977) (Table 1). This feature simplifies the use of many proxies making, for instance, the supply rate of Th and Pa isotopes constant. The ocean U budget was summarized by Cochran (1992) and, despite work in several areas since then, does not need dramatic revision. There remains, however, significant uncertainty about the sizes of some of the fluxes in the budget.

The dominant supply of U to the oceans is from the continents by river runoff. Palmer and Edmond (1993) measured dissolved U concentrations in a number of rivers and summarized existing literature to arrive at a total flux close to that of Cochran (1992) of $11 \times 10^9$ g/year. This flux is uncertain by about 35% due to inadequate sampling of rivers with large seasonal cycles (Palmer and Edmond, 1993).

Additional uncertainty about the size of the riverine flux arises from the behavior of U in the estuarine zone. The Amazon is one of the few major world rivers where estuarine U behavior has been studied. Early work suggested that significant U was released from Amazon shelf-sediments as salinity approached its open-ocean value during mixing. From the Amazon alone, this release would represent an additional source of U of up to 15% of the global riverine flux and the flux would obviously be larger if U behaves in a similar fashion in other estuaries. Further work, however, has demonstrated that U is removed from Amazon waters by colloidal coagulation at salinities of $<10$ psu (Swarzenski et al., 1995) and by reducing conditions in the underlying sediments (Barnes and Cochran, 1993). This removal may balance the release of U at greater salinity so that the Amazon provides neither a net sink nor input of U to the oceans. Other rivers, notably the Ganges-Brahmatuptra, appear to act as a net sink of U (Carroll and...
Moore, 1993). The behavior of U in estuaries clearly varies depending on river chemistry and the style of mixing and is fully summarized elsewhere in this volume (Swarzenski and Porcelli, 2003). At this stage, the poor knowledge of U behavior in estuaries represents a large uncertainty in the ocean U budget.

Additional sources of U to the oceans are dissolution of wind-blown dust and groundwater discharge. The former is unlikely to be significant and a 10% release of U from dust would amount to only about 3% of the riverine U flux. Groundwater may introduce a more significant flux of U but this is extremely difficult to estimate as both the total flux of groundwater to the ocean and the average U concentration of such waters are poorly known (Dunk et al., 2002).

U is removed from the oceans principally into marine sediments and by alteration of ocean basalts (Table 2). The removal into marine sediments is dominated by reducing sediments where pore-water U concentrations are lowered as U becomes insoluble. This lowering leads to a diffusion gradient which draws more seawater U into the pore-waters to be removed (Barnes and Cochran, 1990; Klinkhammer and Palmer, 1991). Recent estimates for each of the removal terms are given in Table 2, but significant uncertainty remains over most of these fluxes (Dunk et al. 2002). It is probably fair to say that the total removal flux may be incorrect by a factor of 2 and, at such a level of uncertainty, the U budget is in balance. This budget, together with the seawater U concentration of 3.3ppb (Chen et al., 1986a), indicates an oceanic residence time for U of ≈400 kyr.

This long residence time suggests that changes in seawater U concentration during the 100 kyr glacial-interglacial cycle are unlikely. Calculations using the expected area of reducing sediments during glacials also suggest that seawater U concentration does not change during the cycle (Rosenthal et al., 1995a). One caveat, however, was the assumption that U incorporated in anoxic sediments during glacial periods is not released to the ocean during interglacials when the deep sea is more oxygenated. This release was suggested (Emerson and Huested, 1991) but is now thought to be unlikely as U mobilized by re-oxygenation tends to move downward to be immobilized in reducing sediment at greater depth (Rosenthal et al., 1995b; Thomson et al., 1998).

2.2 Chemical behavior of U-series nuclides in the oceans

The chemical behavior of U and its daughter nuclides in the ocean environment was extensively studied in the 1960s and 1970s and has been well summarized (Cochran, 1992). The most important mechanism by which nuclides are separated from one another to create disequilibrium is their differing solubility. For U, this solubility is in turn influenced by the redox state. The process of alpha-recoil can also play an important role in producing disequilibrium.

In oxidizing aqueous conditions, such as those found in most seawater, U forms the soluble uranyl-carbonate species. In anoxic or suboxic conditions, however, U is reduced from its hexavalent to its tetravalent state and becomes insoluble. This process is not instantaneous and does not occur in anoxic deep-waters of, for instance, the Black Sea (Anderson et al., 1989). Reduction to the tetravalent state does, however, frequently occur in marine sediments which act as one of the principal sinks for U from the oceans (Barnes and Cochran, 1990; Klinkhammer and Palmer, 1991). Indeed, the removal of U into reducing sediments has been used as a proxy for both bottom-water oxygen concentrations (Francois et al. 1997, Frank et al., 2000) and past productivity (Kumar et al., 1995). These proxies rely on the fact that the redox state of sediment is controlled by the competition between the supply of oxygen from deep water, and the supply of organic material which consumes oxygen during its decay. Authigenic U concentrations are therefore high when deep-water oxygen concentrations are low, or organic material supply is high. The delivery of organic matter to the sea bed at any particular site depends both on the productivity-driven flux of particulate organic matter sinking from surface waters above, and on the lateral redistribution of particles by deep-sea currents. Discriminating among the factors controlling authigenic U formation can be difficult but the spatial pattern of authigenic U deposition over a wide region can sometimes be used to infer the relative importance of surface productivity and bottom-water oxygen levels (Chase et al., 2001).

Thorium generally exists as a neutral hydroxide species in the oceans and is highly insoluble. Its behavior is dominated by a tendency to become incorporated in colloids and/or
adhere to the surfaces of existing particles (Cochran, 1992). Because ocean particles settle from the water column on the timescale of years, Th isotopes are removed rapidly and have an average residence time of ≈20 years (Fig. 1). This insoluble behavior has led to the common assertion that Th is always immobile in aqueous conditions. While this is generally true in seawater, there are examples of Th being complexed as a carbonate (e.g. Mono Lake waters, Anderson et al., 1982; Simpson et al., 1982) in which form it is soluble.

As with 230Th, 231Pa is produced by decay of U in the water column. While decay of 234U produces 2.52x10^8 dpm m^-3 yr^-1 of 230Th, decay of 235U produces 2.33x10^9 dpm m^-3 yr^-1 of 231Pa leading to a production activity ratio of (235Pa/230Th) = 0.093 (note that here, and throughout this chapter, round brackets are used to denote an activity or activity ratio rather than an atom ratio). Like 230Th, 231Pa is removed from the water column by sorbtion to the surfaces of settling particles. However, Pa is slightly less insoluble than Th leading to a longer residence time than 230Th of ≈130 years (Fig. 1; Table 1). This can lead to the spatial separation of 231Pa and 230Th after their production in the water column and before their burial in sediments. This is reflected by (231Pa/230Th) ratios in recent modern sediments ranging from 0.03 to 0.3.

Radium, like most other group II metals, is soluble in seawater. Formation of 226Ra and 228Ra by decay of Th in marine sediments leads to release of these nuclides from the sediment into the deep ocean. Lead, in contrast, is insoluble. It is found as a carbonate or dichloride species in seawater (Byrne, 1981) and adheres to settling particles to be removed to the seafloor.

The energy involved in the α-decay of some nuclides within the decay chain leads to the largely physical fractionation process of α-recoil (Osmond and Ivanovich, 1992). As the α particle is ejected, the daughter nuclide recoils in the opposite direction and moves a distance of ≈550 angstroms in a typical mineral (Kigoshi, 1971). This recoil causes a fraction of the daughter nuclide produced during α decay to be ejected from the host mineral into the surrounding medium. An additional fraction of the daughter is left residing in damaged crystallographic sites within the mineral, from where it can be more readily mobilized. α-recoil therefore gives daughter nuclides of α-decay a tendency to leave their host mineral by a process which is independent of their chemistry. Alpha-recoil is most important in preferentially releasing 234U from minerals over 238U, but also plays a role in mobilizing other nuclides.

3. History of weathering - (234U/238U)

Seawater (234U/238U) is higher than secular equilibrium due to α-recoil on the continents and in marine sediments. The history of seawater (234U/238U) may provide information about the history of weathering during the Pleistocene.

Decay of 234U on the continents causes α-recoil of the immediate daughter, 234Th, which quickly decays to 234U. This process leads to (234U/238U) above the secular equilibrium value of 1.0 in most continental surface waters. Rivers, for example, have (234U/238U) values which range from 0.9 to 3.0 and the average riverine U flux to the oceans has a (234U/238U) lying somewhere close to 1.25 (Chabaux et al., 2003). Given the long residence time of U in the oceans (≈400 kyr) there is time for a portion of the excess 234U which enters the oceans to decay before U is again removed from the oceans. A simple calculation suggests that, if rivers were the only source of excess 234U, the oceans would have a (234U/238U) value of ≈1.08. Observed values are higher than this at 1.146±0.002 (Chen et al. 1986a, Cheng et al. 2000, Robinson et al. Press). This difference requires there to be an additional source of 234U to the oceans, probably related to α-recoil in marine sediments (Ku, 1965). Alpha-recoil leads to high (234U/238U) in marine pore waters (Cochran and Krishnaswami, 1980; Henderson et al., 1999c; Russell et al., 1994) and thus to diffusion of 234U into bottom waters. This process operates in addition to the net flux of seawater U into reducing sediments so that, although both 234U and 238U are removed from seawater, some 234U is also returned by diffusion from pore-waters. Although the size of the bottom-water 234U flux has not yet been independently assessed, the mismatch between riverine inputs of excess 234U and observed seawater (234U/238U) suggest that it must be of approximately equal importance to riverine inputs in supporting the high (234U/238U) values observed in seawater (Henderson, 2002a).

Changes in seawater (234U/238U) with time are most likely to be induced by changes in the riverine input and may therefore provide information about past continental weathering. In
particular, riverine \((^{234}\text{U}/^{238}\text{U})\) is thought to be increased by physical weathering (Kronfeld and Vogel, 1991) because the grinding of rocks increases the surface area from which \(^{234}\text{U}\) can be directly recoiled, and releases \(^{234}\text{U}\) held in damaged sites within mineral grains.

The history of seawater \((^{234}\text{U}/^{238}\text{U})\) was initially investigated in order to assess the reliability of U/Th ages of corals (Gallup et al., 1995; Henderson et al., 1993) and found to be within error of its present value during the last two interglacials. Further work has indicated constant interglacial values for the last 400 kyr (Henderson, 2002a) (Fig. 2). This suggests that the rate of physical weathering on the continents, averaged over a glacial-interglacial cycle, has not varied during the last 400 kyr.

The presence of changes in seawater \((^{234}\text{U}/^{238}\text{U})\) within a single glacial to interglacial cycle has been suggested based on compilations of coral data (Esat and Yokoyama, 1999; Yokoyama et al., 2001). Last glacial corals have \((^{234}\text{U}/^{238}\text{U})\) up to 0.020 lower than Holocene corals and the history of change mimics the history of sealevel. It is possible that these changes reflect differential diagenesis of corals, dependant on when they grew within the sealevel cycle and therefore their duration of subaerial versus submarine exposure. If such diagenesis could be discounted, however, the glacial-interglacial changes in seawater \((^{234}\text{U}/^{238}\text{U})\) would require dramatic changes in the U budget related to climate or sealevel. The increase in \((^{234}\text{U}/^{238}\text{U})\) from the glacial to the Holocene would require a very large pulse of high \(^{234}\text{U}\) (Fig. 3). The possibility of such glacial-interglacial changes in seawater \((^{234}\text{U}/^{238}\text{U})\) remains controversial and is an active area of research.

4. Sedimentation Rate - \(^{230}\text{Th}_{as}\)

4.1 The downward flux of \(^{230}\text{Th}\)

\(^{230}\text{Th}\) is extremely insoluble and adheres to the surface of particles in the ocean soon after it forms from the decay of \(^{234}\text{U}\). Because these particles continuously settle from the water column, \(^{230}\text{Th}\) is rapidly removed from the oceans to the seafloor. The combined process of surface adsorption, followed by particle settling, is termed scavenging. Measurement of the very low \(^{230}\text{Th}\) concentrations in seawater that result from this scavenging are challenging but were successfully performed in the particulate phase (Krishnaswami et al., 1976; Krishnaswami et al., 1981) and in total seawater (Moore, 1981; Moore and Sackett, 1964; Nozaki et al., 1981). Those studies showed a broadly linear increase in \(^{230}\text{Th}\) concentration with water depth, and total concentrations \(\approx 10\) times the particulate concentration. These features of the \(^{230}\text{Th}\) profile are best explained by a reversible scavenging model in which \(^{230}\text{Th}\) on the surface of settling particles continues to exchange with dissolved \(^{230}\text{Th}\) as the particles settle through the water column (Bacon and Anderson, 1982; Nozaki et al., 1987). The tendency for \(^{230}\text{Th}\) to adhere to the surface, rather than remain dissolved, can be described by the use of a distribution coefficient, \(K_{d}\), defined as the concentration of \(^{230}\text{Th}\) per mass of particles divided by the concentration of \(^{230}\text{Th}\) per mass of water. The \(K_{d}\) for \(^{230}\text{Th}\) in the open ocean is typically \(10\), indicating the extreme insolubility of thorium (Fig 3).

This low solubility leads to the theoretical expectation that \(^{230}\text{Th}\) should be removed to the seafloor as soon as it forms because there is insufficient time for advection or diffusion to occur (Bacon and Anderson, 1982; Bacon and Rosholt, 1982). This would make the \(^{230}\text{Th}\) flux to the seafloor dependant only on the depth of overlying water and on the concentration of \(^{234}\text{U}\) in that water. In numerical terms, the production rate of \(^{230}\text{Th}\) within a column of water, in dpm m\(^{-2}\) yr\(^{-1}\) is given by:

\[
P_{\text{Th}} = Z \cdot \left(^{234}\text{U}\right) \cdot \lambda_{^{230}} \quad (1)
\]

Where \(Z\) is the water depth in meters, \((^{234}\text{U})\) is the activity of \(^{234}\text{U}\) in seawater (=2750 dpm m\(^{-3}\)) and \(\lambda_{^{230}}\) is the decay constant of \(^{230}\text{Th}\). If the assumption of immediate removal is correct then the downward flux of \(^{230}\text{Th}\), \(V_{\text{Th}}\), is equal to \(P_{\text{Th}}\), and \(V_{\text{Th}}/P_{\text{Th}} = 1\).

It is worth mentioning at this stage that the actual downward flux of \(^{230}\text{Th}\) in the water column consists of not only the \(^{230}\text{Th}\) derived from \(^{234}\text{U}\) decay in the water column, but also a small component of \(^{230}\text{Th}\) contained in detrital material and supported by decay of \(^{234}\text{U}\). Measured \(^{230}\text{Th}\) values must therefore be corrected for this small portion of detrital \(^{230}\text{Th}\) to
assess $^{230}\text{Th}_{\text{ss}}$, i.e. the unsupported $^{230}\text{Th}$ derived directly from water-column $^{234}\text{U}$ decay (see Appendix 1).

If $V_{Th}/P_{Th} = 1$ then the accumulation of $^{230}\text{Th}_{\text{ss}}$ in marine sediments would provide an assessment of their sedimentation rate. For instance, if $P_{Th}$ is $N$ dpm m$^{-2}$ yr$^{-1}$ and $N$ dpm are found in the upper 1 cm of 1m$^{-2}$ of seafloor, then the sedimentation rate must be 1 cm yr$^{-1}$. Sedimentation rate is an important variable in paleoceanographic reconstruction as it provides the timescale for the continuous record of environmental change recorded in marine sediments. Sedimentation rate is also a key geochemical variable as sediments are the major sink for most chemical species in the ocean. A tool allowing assessment of past sedimentation rates is therefore an appealing prospect.

The use of $^{230}\text{Th}_{\text{ss}}$ to assess sedimentation rate relies on the assumption that the downward flux of $^{230}\text{Th}_{\text{ss}}$, $V_{Th}$, equals the production of $^{230}\text{Th}_{\text{ss}}$, $P_{Th}$. The simple fact that $^{230}\text{Th}$ exists in the water column at all (Fig. 1) suggests that some advection must occur and that $V_{Th}$ may not always exactly equal $P_{Th}$. Similarly, the spatial variability in $^{230}\text{Th}$ concentration in the water column (Henderson et al., 1999a) indicates that its rate of removal is not uniform and therefore that advection of $^{230}\text{Th}$ is not a constant. A good example of $^{230}\text{Th}$ advection has been the recognition that unusually low $^{230}\text{Th}$ concentrations found in deep waters of the North Atlantic reflect movement of surface waters into the deep ocean by North Atlantic Deep Water (NADW) formation (Moran et al., 1997; Moran et al., 1995; Vogler et al., 1998). Similarly, the high $^{230}\text{Th}$ observed in intermediate-depth waters of the Weddell Sea partially reflects upward advection of high $^{230}\text{Th}$ deep waters (Rutgers van der Loeff and Berger, 1993). It is important to assess the degree to which such advection invalidates the assumption that $V_{Th} = P_{Th}$. Such an assessment has been made using two approaches - sediment-trap measurements and modeling.

Using sediment traps to estimate the downward flux of $^{230}\text{Th}_{\text{ss}}$ through the water column is made difficult by the problems of incomplete or over-efficient trapping of falling material. Sediment traps in the open ocean frequently collect less $^{230}\text{Th}_{\text{ss}}$ than is produced in the water overlying them (Anderson et al., 1983b; Bacon et al., 1985; Colley et al., 1995; Taguchi et al., 1989). These low fluxes may be explained by either incomplete trapping of $^{230}\text{Th}_{\text{ss}}$-bearing material as it falls through the water column, or by advection of $^{230}\text{Th}_{\text{ss}}$ away from the production site before it adheres to particles. This question can be investigated by measurement and modeling of shorter lived U-series nuclides, particularly $^{234}\text{Th}$ (Cochran and Masqué, 2003). Such studies indicate that traps frequently do not capture the entire downward particle flux, particularly when they are situated in the upper ocean (Buesseler, 1991; Clegg and Whitfield, 1993). Unless the degree of undertrapping can be accurately assessed, the question of whether $V_{Th} = P_{Th}$ cannot be answered with trap studies. In fact, some studies have turned the question around and, by assuming that $V_{Th} = P_{Th}$, have used $^{230}\text{Th}_{\text{ss}}$ fluxes to assess sediment trap efficiency (Brewer et al., 1980). While such an approach can be useful to correct sediment-trap particle fluxes, it obviously precludes the use of sediment traps to assess the underlying assumption that $V_{Th} = P_{Th}$.

An accurate assessment of sediment trap efficiencies can be provided by coupling $^{230}\text{Th}_{\text{ss}}$ measurements with those of $^{231}\text{Pa}_{\text{ss}}$ - a nuclide with a similar formation and chemistry in the oceans. This approach was suggested by Anderson et al. (1983a) who used it to compare downward $^{230}\text{Th}$ fluxes in the open ocean with those at the ocean margin. It was also used by Bacon et al. (1985) to assess trapping efficiency of a single trap near Bermuda and has more recently been used to assess trap efficiency in a wide range of oceanographic settings (Scholten et al., 2001; Yu et al., 2001a; Yu et al., 2001b). In this approach, only an assumption about the ratio of $^{231}\text{Pa}_{\text{ss}}$ to $^{230}\text{Th}_{\text{ss}}$ in seawater is required in order to assess sediment-trap efficiency. The downward flux of $^{230}\text{Th}_{\text{ss}}$ is equal to the production of $^{230}\text{Th}_{\text{ss}}$ plus the net horizontal flux of $^{230}\text{Th}_{\text{ss}}$ (Scholten et al., 2001):

$$V_{Th} = P_{Th} + H_{Th}$$  \hspace{1cm} (2)

Where $H_{Th}$ is the net horizontal flux of $^{230}\text{Th}_{\text{ss}}$. Similarly:

$$V_{Pa} = P_{Pa} + H_{Pa}$$  \hspace{1cm} (3)

The vertical flux ratio of the radionuclides, $R_{xs}$, is measured in the trap:
\[ R_v = \frac{V_{Th}}{V_{Pa}} \]  

And the ratio of the nuclides in the net horizontally transported portion is assumed to equal that observed in the water column:

\[ R_h = \frac{H_{Th}}{H_{Pa}} \]  

The four equations 2 to 5 therefore include only four unknowns \( V_{Th}, V_{Pa}, H_{Th}, H_{Pa} \) and can be solved for \( V_{Th} \) (Yu et al., 2001b):

\[ V_{Th} = \frac{(P_{Pa} - R_{h} \cdot P_{pa}) \cdot R_{v}}{R_{v} - R_{h}} \]  

\( V_{Th} \) can then be compared to \( P_{Th} \) to assess the magnitude of lateral \(^{230}\text{Th}_{xs}\) advection, or with the measured sediment-trap \(^{230}\text{Th}_{xs}\) flux to assess the trapping efficiency.

Making an assumption about the \( \left( ^{231}\text{Pa}_{xs}/^{230}\text{Th}_{xs} \right) \) ratio in the horizontal component is not entirely straightforward as the value varies significantly in seawater both with depth and from region to region. Unfortunately, seawater measurements are also presently rather sparse so this pattern of variability is not particularly well constrained, limiting the ability to assess sediment trap efficiencies. There is also a question as to whether the seawater ratio is really an appropriate ratio to use. If advection transports the nuclides, then they will be transported at their seawater ratio. But if they are transported by diffusive processes then the concentration gradient of the two nuclides will control their rate of transport independently of one another and the seawater ratio may not be appropriate. A sensitivity analysis which addresses some of these issues indicated that sediment-trap efficiency can be assessed reasonably precisely in much of the open ocean, although the ocean margins and Southern Ocean are more problematic (Yu et al., 2001b). Efficiencies assessed with \( \left( ^{231}\text{Pa}_{xs}/^{230}\text{Th}_{xs} \right) \) in this way were found to be close to 100% in the deep ocean (>1200m) but are less good in the shallow ocean (Yu et al., 2001b). This is not simply related to currents, but probably related to changes in the size, density, and cohesiveness of particles with depth in the water column (Yu et al., 2001b).

Such sediment-trap studies indicate, \( V_{Th}/P_{Th} \) slightly below 1 for much of the open oceans (0.90±0.06), suggesting slight lateral advection of \(^{230}\text{Th}\) from these regions. In regions of high particle flux, \( V_{Th}/P_{Th} \) is slightly greater than 1 (e.g. 1.2 in the Panama basin) demonstrating horizontal addition of \(^{230}\text{Th}\) to these regions (Yu et al., 2001a). Deviations from the assumption that \( V_{Th}/P_{Th} = 1 \) are therefore reasonably small, supporting the use of sedimentary \(^{230}\text{Th}_{xs}\) concentrations to calculate sedimentation rates.

An alternative method of assessing the spatial and temporal variability of \( V_{Th}/P_{Th} \) for \(^{230}\text{Th}_{xs}\) is to introduce the nuclide into an ocean general circulation model (OGCM). By incorporating a single class of particles settling at 3 m day\(^{-1}\) into an existing OGCM, Henderson et al., (1999a) demonstrated that ocean particle concentrations could be well reproduced. Important features such as the typical particle concentration, the near-surface particle maximum, and the greater particle concentrations in equatorial and high-latitude regions were all successfully mimicked by the model. Decay of \(^{234}\text{U}\) was then incorporated into the model and the resulting \(^{230}\text{Th}_{xs}\) allowed to scavenge reversibly to the particles. The distribution coefficient for \(^{230}\text{Th}\) was tuned to give a good fit between the model \(^{230}\text{Th}_{xs}\) and the \( \approx 900 \) literature measurements of water column \(^{230}\text{Th}_{xs}\) concentration. A distribution coefficient within error of that constrained by observations provided a good fit to the data, except in the Southern Ocean, and enabled the rate and pattern of \(^{230}\text{Th}_{xs}\) removal from most of the world’s oceans to be assessed. This model demonstrated that \( \approx 70\% \) of the ocean floor is expected to have \( V_{Th}/P_{Th} \) within 30\% of 1.0 (Fig. 4). The model results compare well with sediment-trap measurements of \( V_{Th}/P_{Th} \) being within error in all but 1 of the 14 traps investigated by Yu et al. (2001a).

Such OGCM modeling also suggests the importance of ice-cover in controlling the amount of \(^{230}\text{Th}_{xs}\) advection (Henderson et al., 1999a). Low particle fluxes beneath sea-ice may lead to low scavenging rates in these areas, particularly where ice cover is permanent. In these areas, \(^{230}\text{Th}_{xs}\) may be advected to the edge of the ice sheet where it is scavenged by the higher particle fluxes. OGCM modeling may allow the correction of \( V_{Th} \) in these areas, and elsewhere where \( V_{Th} \) is not equal to \( P_{Th} \), so that the use of \(^{230}\text{Th}\) to assess sedimentation rates can be extended.
In summary, sediment trap and modeling studies have now constrained reasonably well the precision and limitations of the assumption that \( ^{230}\text{Th}_{xs} \) is removed to the seafloor immediately where it forms. In much of the open ocean, the assumption is good to better than 30% and the flux of \( ^{230}\text{Th}_{xs} \) to the sediment is close to its production in the overlying water column. This result supports the use of \( ^{230}\text{Th}_{xs} \) to assess sedimentation rates in ocean sediments for these regions. More care is needed in using \( ^{230}\text{Th}_{xs} \) to assess sedimentation rates at ocean margins, and in regions close to permanent sea-ice either now or in the past. More care may also be needed in regions underlying hydrothermal plumes as Mn-Fe oxyhydroxide particles have been shown to be particularly good scavengers of \( ^{230}\text{Th} \) (Shimmield and Price 1988).

4.2 Seafloor sediments

The predictable flux of \( ^{230}\text{Th}_{xs} \) to the seafloor means that the flux of other components into marine sediments can be assessed by simply measuring their concentration relative to that of \( ^{230}\text{Th} \) (Fig. 5). This approach, termed \( ^{230}\text{Th}_{xs} \) profiling, has seen widespread use in the last decade and has become a standard technique for measuring accumulation rates of many chemical species and sedimentary components. \( ^{230}\text{Th}_{xs} \) provides possibly the best constraint on such accumulation rates for late Pleistocene sediments and is therefore an important tool. It is the best constrained of the "constant flux proxies" which include other chemical species such as Ti (Murray et al., 2000) and \(^{3}\text{He} \) (Marcantonio et al., 1995). As with these other proxies, \( ^{230}\text{Th}_{xs} \) is not mobilized during sediment dissolution because of its extreme insolubility so that \( ^{230}\text{Th}_{xs} \) profiling assesses the final sedimentary burial flux, rather than the flux that initially arrives at the seafloor.

In downcore records, measured \( ^{230}\text{Th} \) requires correction not just for the presence of supported \( ^{230}\text{Th} \) but also for ingrowth of \( ^{230}\text{Th} \) from authigenic U incorporated in the sediment, and for decay of excess \( ^{230}\text{Th} \) with time (see Appendix 1 for details). These corrections require the measurement of \( ^{232}\text{Th} \) and \( ^{234}\text{U} \) in the sediment, and some knowledge of the age-to-depth relationship for the core being studied. Because the half life of \( ^{230}\text{Th} \) is 76 kyr, ingrowth and decay of \( ^{230}\text{Th} \) are relatively slow compared to the sedimentological or oceanographic processes being investigated which occur on timescales of thousands of years. The age-to-depth model therefore does not need to be particularly precise and sufficient precision is provided by stratigraphic markers such as changing species assemblages or oxygen-isotope stratigraphy. \( ^{230}\text{Th} \) measurements corrected for detrital \( ^{230}\text{Th} \), ingrown \( ^{230}\text{Th} \), and the decay of excess \( ^{230}\text{Th} \) are denoted \( ^{230}\text{Th}_{xs}^{0} \).

Having corrected measured \( ^{230}\text{Th} \) to derive \( ^{230}\text{Th}_{xs}^{0} \), the flux of a component, i, into the sediment is given by (Bacon, 1984; Suman and Bacon, 1989):

\[
F_{i} = Z \cdot \left( ^{234}\text{U} \right) \cdot \lambda^{230} \cdot f_{i} / ^{230}\text{Th}_{xs}^{0} \tag{7}
\]

Where \( F_{i} \) is the normalized flux of i to the sediment in g.yr\(^{-1}\).m\(^{-2}\); Z is the water depth at the core location in meters, \( f_{i} \) is the weight fraction of i in the sediment, \( ^{234}\text{U} \) is the seawater activity of \( ^{234}\text{U} \) in dpm.m\(^{-3}\), and \( ^{230}\text{Th}_{xs}^{0} \) is the \( ^{230}\text{Th} \) activity of the sediment in dpm.g\(^{-1}\).

Since accumulation rates of \( ^{230}\text{Th} \) were first assessed (Bacon and Rosholt, 1982; Ku, 1965) \( ^{230}\text{Th} \) profiling has seen many applications. One of the first uses was to ascertain the cause of regular cycles in carbonate concentration in North Atlantic sediments during the Pleistocene (Bacon, 1984). These changes might have been caused by changes in the detrital flux while the carbonate flux remained constant, or by changes in the carbonate flux while the detrital flux remained constant. Only by assessing the flux of one or both of these components to the sediment can this question be answered. Through the use of \( ^{230}\text{Th} \) profiling, Bacon concluded that the major cause of the cycles was changes in the supply rate of detrital material which varied by a factor of 2-5 while changes in calcite accumulation changed by less than a factor of 2.

This work was pursued by Francois et al. (1990) who assessed both spatial and temporal changes in calcite deposition rates in the tropical Atlantic and demonstrated a rapid increase in carbonate preservation at the onset of the last deglaciation, followed by an increase in carbonate dissolution as deglaciation continued. Only through the use of a precise accumulation tool such as \( ^{230}\text{Th} \) could this level of resolution be achieved and the rapid change in carbonate burial be recognized. Previous attempts to assess sedimentation rate had relied on recognition
of marine oxygen isotope stages, or on multiple $^{14}$C ages, neither of which can provide the high time resolution of $^{230}$Th. For instance, the use of $\delta^{18}$O curves can assess average sedimentation rates over a marine isotope stage (10-20 kyr), but over shorter periods runs into problems due to the uncertainty in the timescale of the SPECMAP $\delta^{18}$O curve and in the precise identification of marine isotope stages in the core of interest.

Another application of $^{230}$Th$_{xs}$ profiling has been to assess sedimentation rates during Heinrich events (Francois and Bacon, 1994; Thomson et al., 1995) (Fig. 5). Abrupt increases in the coarse detrital content of North Atlantic sediments during Heinrich events might be caused by a lowering of biogenic particle flux to the seafloor, or by an increase in the flux of ice-rafted detrital material. By measuring $^{230}$Th$_{xs}$ concentrations, the sedimentation rate was found to be up to 7 times higher during Heinrich layers, indicating an increase in the supply of ice-rafted detritus (Thomson et al., 1995). $^{230}$Th$_{xs}$ profiling has been used more recently to assess the duration of each Heinrich layer in Labrador Sea sediments (Veiga-Pires and Hillaire-Marcel, 1999) and has indicated typical durations of $\approx$1.2 kyr.

Several studies have also used $^{230}$Th$_{xs}$ to identify and quantify the redistribution of sediments on the seafloor by bottom currents. This has become an important field as paleoclimatologists seek to increase the resolution of marine climate records. To achieve high resolution, many climate records have been measured on "drift" deposits in which fine-grained sediment has been transported and deposited by deep-ocean circulation. Suman and Bacon (1989) first recognized that $^{230}$Th$_{xs}$ profiling enabled the past vertical flux of sediment from the water column to be assessed even in areas where horizontal redeposition dominates sediment supply. They applied the term "sediment focusing" for such areas where redeposition causes sediment, together with its complement of $^{230}$Th, to accumulate rapidly. Because the $^{230}$Th removed by the downward sediment flux remains with the sediment as it is redistributed, the $^{230}$Th concentration of the sediment still provides information about the downward fluxes. And, if an independent age model is available from, say, $\delta^{18}$O stratigraphy, then the accumulation rate of $^{230}$Th$_{xs}$ provides information about the extent of sediment focusing. $^{230}$Th$_{xs}$ has, for instance, been used to quantify sedimentary accumulation of opal and biogenic Ba up to 10 times their vertical rain rate in the Subantarctic zone of the Indian Ocean (Francois et al., 1993, 1997); in the Weddell Sea (Frank et al. 1995); and in the Atlantic sector of the Southern Ocean (Asmus et al., 1999; Frank et al., 1996, 1999). Similarly, sedimentation rates up to 4 times the vertical rain-rates were assessed on the Iberian margin (Hall and McCave, 2000; Thomson et al., 1999). And systematic changes in sediment focusing with climate change have been recognized for the Equatorial Pacific (Marcantonio et al., 2001b).

Other applications of $^{230}$Th$_{xs}$ profiling to assess accumulation rates of sedimentary components include carbonate accumulation in the Western Equatorial Atlantic (Rühlemann et al., 1996); biogenic and terrigenous particle accumulation on the Australian continental margin (Veeh et al., 2000); sedimentation rates in the North East Atlantic (McManus et al., 1998; Thomson et al., 1993) (Fig. 5); sedimentation rates during key changes in thermohaline circulation (Adkins et al., 1997); the constancy of the micrometeroritic $^{7}$Be flux to sediments during the Pleistocene (Marcantonio et al., 1999); and the rate of $^{10}$Be deposition as a guide to past variations in cosmonogenic radionuclide production (Frank et al. 1997). The $^{230}$Th approach has also frequently been used to normalize $^{231}$Pa fluxes in order to assess ocean productivity or circulation as discussed in sections 5 and 6.

4.3 Mn Crusts

$^{230}$Th incorporation has also been used to assess the growth rates and ages of Mn crusts and nodules growing on the seafloor (Chabaux et al., 1995; Krishnaswami et al., 1982; Ku and Broecker, 1969). These deposits have proved useful for the long-term records of marine geochemistry and paleoceanography that they contain (Frank, 2002) but have proved difficult to date. Unlike marine sediments, Mn deposits cannot be assumed to collect the entire flux of $^{230}$Th from the water column above them and the incorporation rate of $^{230}$Th is therefore generally poorly known. This limits the accuracy of the technique, although assuming a constant incorporation rate of $^{230}$Th$_{xs}$ with time seems appropriate in at least some crusts because they contain exponential decreases in $^{230}$Th$_{xs}$ with depth (Chabaux et al., 1995; Henderson and Burton, 1999; Ku et al., 1979) (Fig. 6). Some workers have preferred to normalize $^{230}$Th against $^{232}$Th on the assumption that seawater $^{230}$Th/$^{232}$Th is less likely to vary
with time than is the rate of $^{230}$Th$_{inc}$ incorporation (Chabaux et al., 1995; Neff et al., 1999). Variation in past ocean $^{232}$Th/$^{230}$Th is to be expected, however, due to climate-related changes in dust input of $^{232}$Th with time (Henderson et al., 2001). The isotope ratio approach is therefore not necessarily any more reliable than the assumption of a constant $^{230}$Th$_{inc}$ incorporation rate, although using the two approaches together can at least serve to improve confidence in resulting growth rates (Krishnaswami et al., 1982, Claude-Ivanaj et al. 2001) (Fig. 6).

Additional concern has been raised about the possibility of diffusion of Th isotopes within the Mn deposits (Ku et al., 1979; Mangini et al., 1986). This seemed possible given the very slow growth rate of such material (typically millimeters per million years) and therefore the small length scales required for diffusion to perturb $^{230}$Th chronology. Agreement between $^{230}$Th$_{inc}$ and $^{10}$Be chronologies argue against the importance of diffusion, however (Krishnaswami et al., 1982, Claude-Ivanaj et al. 2001). Diffusion of U within Mn crusts has, been observed in several studies (Henderson and Burton 1999, Neff et al. 1999). This diffusion prevents the use of $^{234}$U$_{inc}$ to date such crusts but allows an assessment of the diffusion rates of other elements in crusts (Henderson and Burton, 1999). This approach confirms that Th diffusion is too slow to perturb Mn crust chronology, due largely to its extremely high concentration in crusts relative to its concentration in seawater.

Despite the uncertainty about the rate of incorporation of $^{230}$Th$_{inc}$ into Mn deposits, Th chronology can still provide some useful information about their growth rates. For instance, $^{230}$Th$_{inc}$ has been used to suggest short-term changes in growth rates of Mn crusts (Eisenhauer et al., 1992) and to check the $^{10}$Be chronologies of crusts used to reconstruct the radiogenic isotope history of seawater (Abouchami et al., 1997; Frank, 2002).

5. Past Export Productivity - ($^{231}$Pa$_{inc}$/$^{230}$Th$_{inc}$)

Paleoceanographers have long sought to reconstruct past changes in the biological productivity of the ocean. Much of the motivation for this work has come from two related objectives: (1) understanding the sensitivity of ocean ecosystems to perturbation by climate change and, (2) establishing the role of the ocean’s biological pump in regulating the partitioning of carbon dioxide, a potent greenhouse gas, between the atmosphere and the deep sea. Reconstructing past changes in biological productivity of the oceans is difficult because biogenic phases that would provide the most direct measure of ocean productivity (e.g. organic carbon) are poorly preserved in marine sediments. Preservation of these phases is also highly variable and cannot be estimated from first principles. Consequently, a suite of indirect approaches have been developed to evaluate past changes in ocean productivity including barite or Ba accumulation, authigenic U concentrations, and ($^{231}$Pa$_{inc}$/$^{230}$Th$_{inc}$) (Henderson 2002b, Lochte et al., in press).

A correlation exists between the flux of particles collected by sediment traps and the ($^{231}$Pa$_{inc}$/$^{230}$Th$_{inc}$) of these particles (Kumar et al., 1995). In pelagic regions, particulate material settling through the deep sea is almost entirely of biogenic origin. A geochemical proxy that records particle flux, such as ($^{231}$Pa$_{inc}$/$^{230}$Th$_{inc}$), might therefore serve as a valuable measure of past changes in biological productivity. In this section we review the rationale for using ($^{231}$Pa$_{inc}$/$^{230}$Th$_{inc}$) as such a productivity proxy, together with more recent information that leads to a somewhat different view of the factors regulating particulate ($^{231}$Pa$_{inc}$/$^{230}$Th$_{inc}$) in the ocean.

5.1 Chemical Fractionation and Boundary Scavenging

Early studies demonstrated that ($^{231}$Pa$_{inc}$/$^{230}$Th$_{inc}$) in particulate material caught in sediment traps (Anderson et al., 1983a, b) and in marine sediments (Shimmield et al., 1986; Yang et al., 1986) deviated from the production ratio (0.093), with lower values found in open-ocean sediments and higher values found in nearshore sediments. These observations were interpreted to reflect the combined effects of chemical fractionation during scavenging of $^{230}$Th and $^{231}$Pa by open-ocean particles and the intensified scavenging of particle-reactive substances that occurs near ocean margins. The tendency for insoluble nuclides such as $^{231}$Pa (together with $^{10}$Be, $^{26}$Al, $^{210}$Pb, etc.) to be removed at the margins of the ocean basins has been termed boundary scavenging (Spencer et al., 1981). Boundary scavenging must also influence the spatial pattern of $^{230}$Th burial in marine sediments to some extent but the effect is believed to be small because $^{230}$Th is removed from the open ocean too quickly to permit significant lateral redistribution (see section 4.1). There are several causes for the increased scavenging in the
near-shore environment, including the supply of particles eroded from nearby continents, the enhanced production of biogenic particles due to upwelling, and the greater redox cycling of Fe and Mn (Cochran, 1992).

The differential removal of $^{230}$Th and $^{231}$Pa from the open ocean can be expressed in terms of a fractionation factor (Anderson et al., 1983b), $F$(Th/Pa), where:

$$F$(Th/Pa) = ($^{230}$Th$_{xs}$/$^{231}$Pa$_{xs}$)$_{particles}$ / ($^{230}$Th$_{xs}$/$^{231}$Pa$_{xs}$)$_{dissolved}$ = $K_a$(Th)/$K_a$(Pa) \hspace{1cm} (8)$$

Particles in open-ocean regions have an affinity for Th that is roughly an order of magnitude greater than their affinity for Pa; i.e. $F$(Th/Pa) $\approx 10$. Preferential removal of $^{230}$Th therefore leads to dissolved ($^{231}$Pa/$^{230}$Th) in open-ocean seawaters of $\approx 0.3$ to $0.4$ (i.e. higher than the production ratio of 0.093). Such $^{230}$Th removal also leads to a correspondingly low ($^{231}$Pa/$^{230}$Th)$_{xs}$ of $\approx 0.03$ to $0.04$ in the sediments underlying open-ocean seawaters (Anderson et al., 1983b; Nozaki and Yang, 1987).

The intensified scavenging that occurs at ocean boundaries lowers the concentrations of dissolved $^{230}$Th and $^{231}$Pa in deep waters several-fold relative to those found in open-ocean regions (Anderson et al., 1983b). Consequently, eddy diffusion and advection of deep waters from the open ocean toward ocean margins causes a net supply of dissolved $^{231}$Pa and $^{230}$Th at a ($^{231}$Pa/$^{230}$Th)$_{xs}$ much greater than 0.093, and potentially as high as the dissolved ($^{231}$Pa/$^{230}$Th)$_{xs}$ ratio in open-ocean waters (0.3 to 0.4). Early studies concluded that the intense scavenging at ocean margins of $^{231}$Pa and $^{230}$Th supplied by lateral transport, with a dissolved ($^{231}$Pa/$^{230}$Th)$_{xs}$ typical of open-ocean deep water, was responsible for the high ($^{231}$Pa/$^{230}$Th)$_{xs}$ ratios found in ocean-margin sediments (Anderson et al., 1983a; Nozaki and Yang, 1987).

5.2 ($^{231}$Pa/$^{230}$Th)$_{xs}$ ratios as a paleoproductivity proxy

The principles of boundary scavenging were later invoked to explain the empirical correlation between ($^{231}$Pa/$^{230}$Th)$_{xs}$ and the annual mass flux of particles collected by sediment traps (Kumar et al., 1995; Yu, 1994). Whereas $^{230}$Th is scavenged so intensely that its flux to the sea bed is everywhere nearly in balance with its production in the overlying water column (Section 4), the residence time of dissolved $^{231}$Pa is sufficiently long to permit substantial lateral redistribution, by eddy diffusion or advection, from regions of low particle flux (low productivity) to regions of high particle flux (Fig. 7). Early assessments of ($^{231}$Pa/$^{230}$Th)$_{xs}$ as a paleo flux (productivity) proxy seemed to support this view, in that sedimentary ($^{231}$Pa/$^{230}$Th)$_{xs}$ was found to be well correlated with $^{230}$Th-normalized accumulation rates of biogenic opal at sites in the Southern Ocean (Francois et al., 1993; Kumar et al., 1993; Kumar et al., 1995). As diatoms are a primary component of the phytoplankton in the Southern Ocean, the good correlation between ($^{231}$Pa/$^{230}$Th)$_{xs}$ ratios and opal accumulation rate seemed to support the basis for using ($^{231}$Pa/$^{230}$Th)$_{xs}$ as a paleoproductivity proxy. The use of ($^{231}$Pa/$^{230}$Th)$_{xs}$ as a paleoproductivity proxy has the disadvantage that the relationship between ($^{231}$Pa/$^{230}$Th)$_{xs}$ and particle flux observed in the modern ocean is influenced by factors other than the flux of particles at the site studied. Rates of lateral transport (advection and mixing) as well as fluxes of particles in surrounding regions also influence the ($^{231}$Pa/$^{230}$Th)$_{xs}$. However, ($^{231}$Pa/$^{230}$Th)$_{xs}$ has an advantage over biogenic phases as a paleoproductivity proxy in that ($^{231}$Pa/$^{230}$Th)$_{xs}$ is insensitive to dissolution of biogenic phases during early diagenesis (i.e., the ratio is insensitive to the degree of preservation of biogenic material).

The Southern Ocean has been a particular focus for the application of ($^{231}$Pa/$^{230}$Th)$_{xs}$ as a paleoproductivity proxy. This region is believed to play a critical role in climate change because it serves as the “window” through which deep waters of the world's oceans exchange gases, including the greenhouse gas CO$_2$, with the atmosphere. Furthermore, the nutrients upwelled in the Southern Ocean today are used inefficiently by phytoplankton. Greater nutrient utilization efficiency in the past may have contributed to the lower atmospheric CO$_2$ levels that existed during glacial times. For these reasons, a substantial body of paleoceanographic research has been devoted to understanding past changes in biological productivity, circulation, and nutrient utilization efficiency of the Southern Ocean (see reviews by Elderfield and Rickaby, 2000; Sigman and Boyle, 2000; Anderson et al., 2002).

($^{231}$Pa/$^{230}$Th)$_{xs}$ has contributed to the view that the zone of maximum biological productivity in the Southern Ocean was located equatorward of its present position during
5.3 The role of particle composition

Compared to Holocene conditions, Kumar et al. found \((231\text{Th}/230\text{Th})^0\) and \((231\text{Pa}/230\text{Th})^0\) ratios have also been used to assess changes in productivity in the Arabian Sea in response to changing monsoon strength (Marcantonio et al., 2001a). Abrupt changes in \((231\text{Pa}/230\text{Th})^0\) were found to coincide with climate events such as the Younger Dryas which are normally associated with changes in the North Atlantic region. Sediments from the glacial and Younger Dryas exhibited low \((231\text{Pa}/230\text{Th})^0\) while those from the Bolling Allerod and Holocene had high \((231\text{Pa}/230\text{Th})^0\). The increased productivity indicated by high \((231\text{Pa}/230\text{Th})^0\) were assumed to reflect greater monsoon intensity and hence increased upwelling during warm periods.

5.3.1 The role of particle composition

Early views of boundary scavenging relied on differential scavenging rates coupled with lateral mixing to drive the net flux of \(231\text{Pa}\) from the open ocean to ocean margins (Bacon, 1988). It was recognized that manganese oxides scavenged \(231\text{Pa}\) and \(230\text{Th}\) without detectable fractionation (i.e. at \(F(\text{Th}/\text{Pa})=1\)) (Anderson et al., 1983a, b), and that the redox cycling of Fe and Mn, which generates oxide-rich particles in ocean-margin waters, might contribute to the boundary scavenging of dissolved nuclides (Anderson et al., 1983a; Cochran, 1992). These phases were, however, ignored in the interpretation of open-ocean results because it was assumed that the Fe and Mn oxides would settle out of the water column near their source. Early studies did not consider that variability in \(F(\text{Th}/\text{Pa})\) might contribute significantly to the spatial pattern of \((231\text{Pa}/230\text{Th})^0\) in marine sediments.

Evidence for regional variability in \(F(\text{Th}/\text{Pa})\), even in the open ocean, began to mount as investigators examined the scavenging of \(230\text{Th}\) and \(231\text{Pa}\) in different regions. Taguchi et al. (1989) noted that particulate \((231\text{Pa}/230\text{Th})^0\) in North Pacific sediment-trap samples increased with increasing opal content of the samples. Subsequent studies showed that \(F(\text{Th}/\text{Pa})\) in the Atlantic sector of the Southern Ocean decreases southwards and is close to 1.0 south of 60°S (Rutgers van der Loeff and Berger, 1993; Walter et al., 1997). These results led to the hypothesis that biogenic opal scavenges \(230\text{Th}\) and \(231\text{Pa}\) without significant fractionation. That hypothesis was confirmed by the recent comparison of \(231\text{Pa}\) and \(230\text{Th}\) concentrations in sediment trap samples with the corresponding concentrations of \(230\text{Th}\) and \(231\text{Pa}\) in the surrounding water column (Chase et al. in press-b). Effective \(K_d\) values computed from these results (Fig. 8) demonstrated for the first time that the affinity of marine particles for \(231\text{Pa}\) increases with increasing opal content of particles, and that this change controls the previously observed decrease in \(F(\text{Th}/\text{Pa})\) for opal-rich particles. Consequently, particle composition, as well as particle flux, influences the \((231\text{Pa}/230\text{Th})^0\) of marine sediments.

A surprising feature of the particle reactivity of \(230\text{Th}\) is that its \(K_d\) decreases with increasing opal content of particles (Fig. 8). The underlying chemical cause for this decrease in \(K_d(\text{Th})\) is not known, but it is consistent with laboratory studies. Osthols (1995) found that Th...
sorbs weakly to amorphous silica and lab experiments by Guéguen and Guo (2002) are qualitatively consistent with the results of Chase et al., in showing that Th preferentially sorbs on CaCO₃ surfaces, whereas Pa preferentially sorbs on opal. The decrease of Kₐ(Th) contributes as much to the absence of fractionation during scavenging by opal-rich particles as does the increase of Kₐ(Pa). Another surprise is that the Kₐ(Th) of the calcite-rich end member reaches values as large as observed anywhere in the ocean, including ocean-margin environments (~1x10⁻³). This result precludes the possibility that lithogenic phases have Kₐ(Th) orders of magnitude greater than Kₐ(Pa) of biogenic phases, as had previously been suggested by Luo and Ku (1999). Because open-ocean particles with less than 1% lithogenic content have as high a Kₐ(Th) as ocean-margin particles containing more than 50% lithogenic material, preferential scavenging of ²³⁰Th onto lithogenic material cannot occur (Chase et al., In press-b).

Much of the geographic variability in sedimentary (²³¹Pa/²³⁰Th) observed in modern sediments may be explained by variability in the composition of biogenic particles arising from variability in the structure of the planktonic ecosystem. This can be inferred from the composition-dependence of F(Th/Pa) (Fig. 8), and is shown explicitly by the relationship between sediment trap (²³¹Pa/²³⁰Th) and the opal/calcite ratio of the trapped particles (Fig. 9). Sediment trap (²³¹Pa/²³⁰Th) also exhibits a positive relationship with the mass flux of particles, but the correlation is poorer than that with particle composition (Fig. 9). Indeed, the relationship between particulate (²³¹Pa/²³⁰Th) and particle flux is partly due to pelagic systems with high particle flux also tending to have abundant diatoms and therefore a high opal content in the resulting particles (Buesseler, 1998).

5.4 Prospects for future use

The recognition that particle composition is of prime importance in controlling fractionation of ²³¹Pa from ²³⁰Th during scavenging casts doubt over the use of (²³¹Pa/²³⁰Th) to assess past productivity. Certainly, previous results must be reconsidered in the light of this knowledge (Chase et al., In press-c). The good news, though, is that (²³¹Pa/²³⁰Th) may provide information about the composition of settling particles in the past and therefore about the nature of the past phytoplankton communities (Chase et al., In press-b).

Sedimentary (²³¹Pa/²³⁰Th) can also be used to interpret downcore records of ²³⁰Th-normalized opal accumulation rates. Opal accumulation depends both on production and on preservation, which is in turn variable and difficult to evaluate (Sayles et al., 2001). By combining opal accumulation rates with (²³¹Pa/²³⁰Th) and with other paleoproductivity proxies such as excess barium, however, it is possible to discriminate between a production control and a preservation control when interpreting ²³⁰Th-normalized opal accumulation rates. Such a use is illustrated by the strong similarities between the downcore pattern of opal burial and the corresponding records of excess barium accumulation and (²³¹Pa/²³⁰Th) in sediments from a site in the SW Pacific sector of the Southern Ocean (Fig. 10). Excess barium is widely used as a proxy for export production because fluxes of excess barium collected by sediment traps have been shown to correlate with fluxes of organic carbon (Dymond et al., 1992; Francois et al., 1995). Whereas all three proxies are similarly responsive to changes in diatom production, they have distinct differences in their sensitivity to regeneration at the sea bed, with (²³¹Pa/²³⁰Th) ratios being completely insensitive to regeneration of biogenic phases (Chase et al., In press-c). Consequently, the strong similarity among the three proxy records provides robust evidence that the pattern of opal burial at this site reflects climate-related changes in diatom production rather than regeneration. A similar use for (²³¹Pa/²³⁰Th) was suggested in the Atlantic sector of the Southern Ocean where low opal accumulation rates are coincident with low (²³¹Pa/²³⁰Th) confirming that the low opal values are a reflection of low opal productivity rather than low opal preservation (Frank et al. 2000). When combined with complementary proxies, and used with an awareness of the particle composition-dependent fractionation between ²³⁰Th and ²³¹Pa, sediment (²³¹Pa/²³⁰Th) will continue to provide valuable information about past changes in ocean productivity.

6. Rates of past ocean circulation - (²³¹Pa/²³⁰Th)

The oceanic fractionation of ²³¹Pa from ²³⁰Th has also been used to assess the rate of past deep-ocean circulation. Such ocean circulation is fundamental to climate, transporting heat and greenhouse gases around the globe. There are several tools with which to assess past
circulation, but the most commonly used of these (δ\(^{13}\)C and Cd/Ca) assess the distribution of water masses in the past, rather than the rate of flow. While the distribution of water masses is significant, it is their rate of flow which ultimately controls heat transport and is therefore of critical importance. Four proxies have been used to reconstruct past flow rates: surface versus deep water \(^{14}\)C analyses (Adkins and Boyle, 1997); stable-isotope geostrophy (Lynch-Stieglitz et al., 1999); the grain-size of deep-sea sediments (McCave et al., 1995); and sedimentary (\(^{231}\)Pa, \(^{230}\)Th)\(^0\) (Yu et al., 1996).

The use of (\(^{231}\)Pa, \(^{230}\)Th)\(^0\) to assess circulation rates again relies on the difference in solubility of \(^{230}\)Th and \(^{231}\)Pa (Fig. 7). When these nuclides form from U decay, the short residence time of \(^{230}\)Th (≈20 years) does not allow it to be advected far before it is removed to the sediment. The longer residence time of \(^{231}\)Pa (≈130 years), on the other hand, allows it to be advected so that, if the water mass is moving, \(^{231}\)Pa may be transported downstream to be removed in regions of high particle flux. Sediments underlying waters with a low scavenging efficiency for \(^{231}\)Pa and with active transport of dissolved \(^{231}\)Pa by ocean currents are therefore expected to have (\(^{231}\)Pa, \(^{230}\)Th)\(^0\) below the seawater production ratio. The degree of lowering below the production ratio will be proportional to the speed of the current (Marchal et al. 2000). Sediments down-stream of such areas, particularly in regions of high particle flux, are expected to have (\(^{231}\)Pa, \(^{230}\)Th)\(^0\) correspondingly higher than the production ratio.

This approach has been applied to the Atlantic to assess changes in the flow rate of NADW between the last glacial and the Holocene (Yu et al., 1996). Holocene sediments from 68 cores situated north of the Southern-Ocean opal belt had (\(^{231}\)Pa, \(^{230}\)Th)\(^0\) below the production ratio at 0.060±0.004, indicating net advection of \(^{231}\)Pa out of the Atlantic. Holocene sediments in the Southern-Ocean opal belt had corresponding high (\(^{231}\)Pa, \(^{230}\)Th)\(^0\) of 0.17±0.04 and clearly act as the sink for the advected \(^{231}\)Pa. Glacial-age sediments from the same cores showed a similar pattern with (\(^{231}\)Pa, \(^{230}\)Th)\(^0\) of 0.059±0.007 in most of the Atlantic, and of 0.15±0.02 in the opal belt. The similar distribution of (\(^{231}\)Pa, \(^{230}\)Th)\(^0\) between the glacial and the Holocene strongly suggests that there was no change in the rate of NADW flow between these periods. This result came as a surprise because previous water-mass studies had demonstrated that less of the Atlantic region was influenced by NADW during the glacial (e.g. δ\(^{13}\)C (Duplessy et al., 1988) and Cd/Ca (Boyle and Keigwin, 1982)).

The suggestion that glacial and Holocene NADW flow rates were similar has been sufficiently controversial that the use of (\(^{231}\)Pa, \(^{230}\)Th)\(^0\) to assess the flow rate has been carefully assessed. The recognition that opal was an effective scavenger of \(^{231}\)Pa (Walter et al., 1997; Section 5.3) suggested that Southern Ocean (\(^{231}\)Pa, \(^{230}\)Th)\(^0\) would be high due to the high opal productivity in the region, regardless of the rate of NADW flow. This suggestion has been confirmed by the discovery that sedimentary (\(^{231}\)Pa, \(^{230}\)Th)\(^0\) in the Pacific sector of the Southern Ocean, far removed from the inflow of NADW, are as high as those observed within the Atlantic sector of the Southern Ocean which does experience NADW flow (Chase et al., In press-c). It has also been demonstrated that, in the specific oceanographic regime of the Southern Ocean, scavenging from surface waters plays an unusually important role in the behavior of \(^{231}\)Pa and \(^{230}\)Th thereby reducing the ability to use (\(^{231}\)Pa, \(^{230}\)Th)\(^0\) in this area to assess deep-water flow out of the Atlantic. (Chase et al., In press-c; Walter et al., 2001). These Southern-Ocean problems of particle composition and regional oceanography do not exist for the rest of the Atlantic, however. A modeling study has indicated that existing (\(^{231}\)Pa, \(^{230}\)Th)\(^0\) data in the North Atlantic constrain the glacial NADW flow rate to be no more than 30% lower than that during the Holocene (Marchal et al., 2000).

Another suggested flaw with the use of (\(^{231}\)Pa, \(^{230}\)Th)\(^0\) to assess glacial rates of NADW flow is that the spatial coverage of cores in the Yu et al. study is not complete and may miss some important sink regions for \(^{231}\)Pa. Additional cores have been analyzed, particularly in the mid-latitude North Atlantic, but this region was not found to be a significant or changeable sink of \(^{231}\)Pa (Anderson et al., 2001) so that the conclusion of unchanged NADW flow appears robust.

One issue which has not yet been addressed is the depth at which the southward flow of deep water occurred in the past. It is possible, for instance, that true NADW did weaken at the LGM, as is suggested by the nutrient-like tracers of water masses, but that this decrease was largely compensated by increases in flow higher in the water column. This issue could be investigated using (\(^{231}\)Pa, \(^{230}\)Th)\(^0\) if cores from a variety of depths were analyzed.
The successful use of \( (^{231}\text{Pa}_{i}/^{230}\text{Th}_{i})^0 \) to assess glacial-interglacial changes in ocean circulation rates has led to its use to assess circulation changes across more rapid climate events. Early work has assessed the changes in circulation during Heinrich event H1 and the Younger Dryas (McManus et al., 2002). By working on cores at different water depths in the region close to deep-water formation, flow rates of both deep and intermediate waters were reconstructed and found to work in opposition. When deep circulation rates decreased, intermediate circulation rates increased, but not by the same magnitude. Net flow rates therefore varied and were found to be lower during cool periods - by \( \approx 50\% \) in the Younger Dryas, and by more than this during H1 (McManus et al., 2002).

The use of \( (^{231}\text{Pa}_{i}/^{230}\text{Th}_{i})^0 \) to assess past circulation rates only works well where the residence time of deep waters is low and advection therefore dominates over the removal of \(^{231}\text{Pa}\) by particle scavenging (Yu et al., 2001a). The Atlantic Ocean fits these criteria well but, in many other areas \( (^{231}\text{Pa}_{i}/^{230}\text{Th}_{i})^0 \) is more strongly influenced by particle flux and composition and the ratio is then better suited for assessing changes in past productivity or ecosystem structure (Yu et al., 2001a). Nevertheless, in regions which do have rapidly flowing deepwaters \( (^{231}\text{Pa}_{i}/^{230}\text{Th}_{i})^0 \) is a powerful tool which will doubtless see further application.

### 7. Holocene sediment chronology - \(^{226}\text{Ra}\)

\(^{226}\text{Ra}\) is soluble and therefore tends to be released to deep waters when it is formed by \(^{230}\text{Th}\) decay in marine sediments. Substrates which capture the resulting excess of \(^{226}\text{Ra}\) found in seawater can potentially be dated using the decay of \(^{226}\text{Ra}\) excess \( (^{226}\text{Ra}_{ex}) \). Unfortunately there is no stable isotope of Ra with which to normalize measured \(^{226}\text{Ra}\) values but the marine chemistry of Ba is sufficiently close to that of Ra that it can be used as a surrogate for a stable Ra isotope and seawater \(^{226}\text{Ra}/\text{Ba}\) ratios are constant throughout the oceans, except in the deep North Pacific (Chan et al. 1976). The half life of \(^{226}\text{Ra}\) is only 1600 years so \(^{226}\text{Ra}_{ex}/\text{Ba}\) chronology is limited to the Holocene but it nevertheless has potential for use in several regions.

Given the chemical similarity between Ra and Ba it is not surprising that \(^{226}\text{Ra}_{ex}\) is high in marine barites that form in the upper water column, particularly in regions of high productivity. Such barite forms a minor constituent of marine sediment but can be separated from other sediment components by dissolution because barite is extremely resistant to chemical attack. Barite separated in this way from two Pacific cores had \(^{226}\text{Ra}\) activities at least ten times higher than those of the parent \(^{230}\text{Th}\) and ranging up to 1400 dpm \(^{226}\text{Ra} \) g\(^{-1}\) (Paytan et al., 1996). \(^{226}\text{Ra}\) activities decreased exponentially with depth in the sediment at a rate consistent with \(^{14}\text{C}\)-derived sedimentation rates and were in secular equilibrium with \(^{230}\text{Th}\) at depths equivalent to \( > 8 \) kyr (Fig. 11). These observations suggest that such marine barite behaves as a closed system for \(^{226}\text{Ra}\) and initially incorporates \(^{226}\text{Ra}\) at a reasonably constant rate. Marine barite might therefore be used to assess the age of Holocene marine sediments. A more detailed study further demonstrated the suitability of the system for chronology by more accurately assessing the nature of supported and ingrown \(^{226}\text{Ra}\) within marine sediment (Van Beek and Reyss, 2001). The first application of this technique has been to marine barite from the Southern Ocean in order to assess the \(^{14}\text{C}\) reservoir age of surface waters in this region during the Holocene (van Beek et al. 2002). This work has indicated a reasonably constant reservoir age of 1100 years in the late Holocene, but a higher value of \( \approx 1900 \) years in the early Holocene.

\(^{226}\text{Ra}\) has also proved useful to date some Holocene Mn crusts (Liebetrau et al., 2002). Most Mn crusts grow extremely slowly and the distribution of \(^{226}\text{Ra}\) within them is dominated by diffusion - both out of the crust and inward from underlying sediments (Moore et al., 1981). Unusual crusts from the Baltic Sea, however, accumulate sufficiently quickly that the \(^{226}\text{Ra}_{ex}\) distribution is controlled by initial incorporation of \(^{226}\text{Ra}_{ex}\) and subsequent decay. Liebetrau et al. (2002) used the decrease of \(^{226}\text{Ra}_{ex}/\text{Ba}\) from the edge to the center of such fast-growing Baltic crusts to calculate growth rates ranging from 0.02 to 1 mm yr\(^{-1}\). They found \(^{226}\text{Ra}_{ex}/\text{Ba}\) values over an order of magnitude higher than those in Baltic seawater suggesting a dominant source of \(^{226}\text{Ra}\) from the underlying sediments. At the rapid growth rates observed, the effects of diffusion were deduced to be negligible and the initiation of crust growth found to coincide with the stabilization of sealevel at modern values. These nodules may provide a good archive to investigate changes in weathering inputs to the Baltic Sea during the Holocene, and of anthropogenic contamination of the area.
Marine carbonates may also prove datable using $^{226}$Ra/$^{138}$Ba. Modern Antarctic mollusks have been found to have $^{226}$Ra/Ba equal to that of seawater (Berkman et al., 1992) and a significant excess of $^{226}$Ra over $^{230}$Th. Turning this observation into a useable chronometer requires assessment of whether mollusks are closed systems for Ra and Ba; correction for ingrown and detrital $^{226}$Ra; and assumptions about the constancy of seawater $^{226}$Ra/Ba through time (Staubwasser et al., In press). Such a chronometer, however, would prove useful for assessing the Holocene history of sea surface $^{14}$C, particularly in upwelling regions where no other suitable dating tool presently exists.

8. Sediment mixing - $^{210}$Pb

Mixing of the upper surface of marine sediments by benthic animals limits the resolution at which past climate and oceanography is recorded by marine sediments. Typical marine sediments experience such mixing to a depth of 10±5 cm (Boudreau, 1994) and have sedimentation rates of only a few cm kyr$^{-1}$. Any climate event shorter than ≈1 kyr is, therefore, all but lost from the sediment record. Constraining the rate and depth of mixing in diverse oceanographic settings is therefore important as it allows the limits of paleoclimate resolution to be assessed, and allows inverse modeling to be performed to attempt reconstruction of the full amplitude of past climate events (Bard et al., 1987). The rate of mixing is also important in models of sediment diagenesis and geochemistry.

The $^{210}$Pb distribution in marine sediments provides a method of assessing this mixing. $^{210}$Pb is produced in the water column by decay of $^{226}$Ra, and is also added to the surface of the ocean by $^{222}$Rn decay in the atmosphere and subsequent rainout (Henderson and Maier-Reimer, 2002). Pb is insoluble in seawater so, once formed, $^{210}$Pb adheres to particles and is removed to the seafloor. $^{234}$Th is also removed in this way when it forms as the immediate daughter of $^{238}$U decay in seawater (Cochran and Masque, 2003). In the absence of mixing, these nuclides would only be found on the uppermost surface of the sediment because their half lives are short compared to typical sedimentation rates ($^{210}$Pb = 22 years; $^{234}$Th = 24 days). The presence of these nuclides at depth in the sediment therefore reflects their downward mixing by bioturbation. The depth and pattern of penetration of these isotopes into sediments has been used to assess sediment mixing rates in a large number of studies since the 1970s (e.g. Nozaki et al., 1977).

Because mixing consists of many small events which progressively move the sediment grains it is akin to diffusion and can be modeled as such following the mathematical approach of Guinasso and Schink (1975). $^{210}$Pb and $^{234}$Th decay as they are mixed downwards which leads to an activity profile in the sediment which decreases exponentially with depth (Fig. 12). The activity of the nuclide, A, is given by (Anderson et al., 1988):

$$A = A_0 e^{-\frac{(w^2+4D\lambda)}{2D}Z}$$

(9)

Where $A_0$ is the activity at the sediment surface, w is the sedimentation rate (cm kyr$^{-1}$), D is the mixing rate (cm$^2$ kyr$^{-1}$), $\lambda$ is the decay constant for the nuclide of interest (yr$^{-1}$); and Z is the depth in the sediment (cm). In some nearshore environments both sedimentation and bioturbation must be considered. But in most open marine environments the sedimentation rate is sufficiently slow that it can be ignored and the equation simplifies to:

$$A = A_0 e^{-\frac{(\lambda/D)^{0.5}Z}$$

(10)

D, the mixing rate, varies widely depending on environment. Boudreau (1994) comprehensively summarized measurements of D from some 36 papers including 22 using $^{210}$Pb and 7 using $^{234}$Th. These studies indicated mixing rates varying from 0.02 to 370 cm$^2$ yr$^{-1}$. Several environmental variables appear to be responsible for this large range in mixing rate and a recent thrust of research has been to establish general rules for mixing rate which enable it to be assessed for a new environment without direct measurement. Examples include that of Boudreau who, based on $^{210}$Pb data from over 130 sites, suggested a power-law relationship between mixing rate and sedimentation rate (Boudreau, 1994):
D = 15.7w^{0.69} \tag{11}

Where D is in cm$^2$ kyr$^{-1}$ and w in cm kyr$^{-1}$. Other studies have used $^{210}$Pb to demonstrate a relationship between D and water depth (Henderson et al., 1999b; Soetaert et al., 1996):

D = 6330Depth$^{-1.65} \tag{11}$

Where D is in cm$^2$ kyr$^{-1}$ and Depth in m. Although these two relationships explain some of the variability in D, it is clear that other environmental factors are also important, including sediment grain-size (Wheatcroft, 1992) and the organic carbon flux (Trauth et al., 1997).

The different half-lives of the nuclides that can be used to assess mixing indicate that mixing is more frequent close to the sediment-water interface. In the ≈100 days that $^{234}$Th survives before decay, it is only mixed a short distance into the sediment. Its profile suggests values of D higher than those calculated with $^{210}$Pb, which can survive for ≈100 years and is mixed to greater depth. This decrease in biological mixing rate probably reflects the greater supply of labile and nutritious organic matter close to the sediment surface (Fornes et al., 2001; Smith et al., 1993). The use of $^{233}$Th and other short-lived nuclides to assess mixing is also discussed in this volume by Cochran and Masque (2003).

In addition to the rate of mixing, these nuclides provide an indication of the depth of mixing (L) on various timescales. The ≈100 yrs required for $^{210}$Pb decay is sufficiently long to give a reasonable idea of the total depth of mixing that occurs before sediment is buried to sufficient depth to escape further disturbance. This makes $^{210}$Pb a particularly useful nuclide to constrain mixing depths for paleoceanographic studies, where the total depth of mixing is the key variable in the smoothing of climate records. $^{210}$Pb measurements of L in the deep sea range from 4 to 20 cm (Boudreau, 1994) but indicate deeper mixing in near shore environments (Henderson et al., 1999b; Kim and Burnett, 1988). Below this well-mixed zone, subsurface peaks in $^{210}$Pb concentration are sometimes observed and provide evidence for rapid injection of surface material to depth (Fig. 12). This process, referred to as “conveyor-belt” feeding (or mixing) has been modeled (Robbins, 1988; Smith et al., 1997) and incorporated into models of diagenesis (Sayles et al. 2001).

Short-lived U-series nuclides such as $^{210}$Pb and $^{234}$Th thus provide key information about the rate and depth of sediment mixing in marine records. This information is critical if the resolution of down-core paleoceanographic records are to be assessed.

9. Concluding Remarks

This chapter has outlined the uses of U-series nuclides to investigate the past ocean environment. The most widely used tools are presently $^{230}$Th$^\circ$ (to assess sedimentary fluxes and sediment focusing) and short-lived nuclides such as $^{210}$Pb (to assess sediment mixing rates). The fractionation of $^{231}$Pa from $^{230}$Th in seawater has also been widely investigated to assess past productivity and ocean circulation rates. The controls on sedimentary ($^{231}$Pa/$^{230}$Th)$^\circ$ are only now being fully understood, however, calling into question the conclusions reached in some early studies using this proxy. Armed with this better understanding of ($^{231}$Pa/$^{230}$Th)$^\circ$, this tool has significant promise for assessing circulation rates in areas of rapid flow such as the Atlantic, and for assessing particle fluxes and composition elsewhere. Seawater ($^{234}$U/$^{238}$U) has also been used to assess the past U budget of the oceans and the extent of physical weathering on the continents. And $^{226}$Ra$^\circ$/Ba dating has potential to improve chronologies for the Holocene in a variety of settings.

The U-series nuclides used in these tools range in half life from 4.5x10$^9$ yrs ($^{238}$U) to 22 yrs ($^{210}$Pb). The next longest-lived nuclides in the U and Th series are $^{227}$Ac (22yrs), $^{228}$Ra (5.8 yrs) and $^{228}$Th (1.9 yrs). While these nuclides provide information about modern ocean processes, their half lives are probably too short for use in paleoceanography. The range of U-series isotopes with which to investigate the past environment has therefore probably been exhausted. But there are doubtless new applications for these longer-lived nuclides which will go beyond the uses described above. Such new applications will continue to make use of the fact that, together with the cosmogenic nuclides, U-series isotopes provide quantitative estimates.
of the rates of past processes. This attribute will ensure that U-series geochemistry continues to be widely applied to questions of paleoceanography.

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Table 1: Summary of seawater data for U-series nuclides with paleoceanographic applications. S - soluble, I - insoluble. Full descriptions of the paleoceanographic uses and references are provided in the text. Further details of the half lives are in Bourdon et al. (2003).
Table 2: Known inputs and outputs of U to the oceans. Units are $10^9$ g yr$^{-1}$, or thousand tonnes per year. References are the most recent primary studies of that flux. Some other fluxes (e.g. groundwater input and input or removal at estuaries) are so poorly known that they cannot be realistically included. Significant uncertainty remains in most of the fluxes listed above so that, within these uncertainties, the U budget can be considered to be in balance.
Figure Captions

Figure 1  A summary of water-column measurements of $^{230}$Th and $^{231}$Pa. Most of this data was compiled by Henderson et al. (1999a) and a full list of references is contained therein. More recent data have been added from Edmonds et al., (1998), Moran et al. (2001) and Vogler et al., (1998). Averages and the total number of measurements are shown on each panel for the various types of data. The average $^{230}$Th concentration can be used to calculate the average ocean residence time for $^{230}$Th (Yu et al., 1996) using the equation $\tau_{th} = \left( ^{230}Th / \left( ^{234}U \right) \right) \times \left( 1 / \lambda_{230} \right)$ = 0.5/2750*1.09x10$^{7}$ = 20 years. Similarly $\tau_{p} = \left( ^{231}Pa / \left( ^{235}U \right) \right) \times \left( 1 / \lambda_{231} \right) = 0.3/108*4.61x10^{7}$ = 130 years. Average profiles are shown by black lines and were calculated by averaging nuclide measurements and depth data in 9 layers (0-100m, 100-500m, 500m layers to 2km, and 1km layers to 6km).

Figure 2  The history of seawater ($^{234}U$/$^{238}U$) for the last 500 kyr. Data shown in black are from studies specifically investigating the U isotope history of seawater and demonstrate that ($^{234}U$/$^{238}U$) has remained close to the modern value of 1.146 (shown by black line) for at least the last 400 kyr. Data is mostly from the Bahamas slope sediment (Henderson, 2002) and is supplemented by similar sediment from the Nicaragua slope (Gallup et al., 1995) and by two coral studies which focused on unaltered corals (Gallup et al., 1994; Henderson et al., 1993). Other corals have frequently suffered alteration, as shown by their high initial ($^{234}U$/$^{238}U$) values (gray circles).

Figure 3  Distribution coefficient ($K_d$) versus particle concentration for Th. Note that, for typical open-ocean particle concentrations, Th is about 10' times more likely to adhere to a mass of particles than to remain in the same mass of water. This tendency to be found in the particulate phase decreases with particle concentration, probably due to the presence of a larger number of colloids which, because they pass through filters, appear to be in the dissolved phase (Honeyman et al., 1988). Grey squares are $^{234}$Th data from Honeyman et al., (1988); gray triangles are $^{234}$Th data from the continental shelf from McKee et al.(1986) and black circles are a compilation of open ocean $^{230}$Th data from Henderson et al.(1999a).

Figure 4  A model of the $^{230}$Th flux to the sediment normalized to its production in the water column (Henderson et al., 1999a). Values less than 1 signify that $^{230}$Th is advected away from that region prior to removal to the sediment, and those greater than 1 that $^{230}$Th is advected into that region to be removed. This model result is in agreement with 13 of 14 sediment trap measurements of the downward $^{230}$Th flux (Yu et al., 2001a). These observations and modeling suggest that the $^{230}$Th flux to the seafloor is within 30% of its production in the overlying water column over about 70% of the area of the open ocean.

Figure 5  An example of the use of $^{230}$Th concentrations to assess changes in sediment mass accumulation taken from McManus et al. (1998). The upper panel shows the measured $^{230}$Th, calculated from measured $^{230}$Th concentrations by correction for detrital $^{230}$Th, and for the effects of age using $\delta^{18}O$ stratigraphy (see appendix). Because the supply of $^{230}$Th to the sediment is a constant, low $^{230}$Th represent times of rapid sediment mass accumulation. The calculated mass flux is shown in the lower panel. Dramatic increases in mass flux are observed during all but one of the Heinrich events, shown by the gray bands.

Figure 6  An example of the use of $^{230}$Th to assess the growth rate of Mn nodules taken from Krishnaswami et al.(1982). Both panels show the same $^{230}$Th data from nodule R/V Vitiaz from the Southern Indian Ocean. Errors on the activities are within symbol size. The lower panel shows the $^{230}$Th activity, while the upper panel shows the same data normalized to the $^{232}$Th activity. Note that both profiles show a general exponential decrease which can be used to assess the growth rate using the relationship that $^{230}$Th$_{\text{now}} = \text{^{230}Th}_{\text{initial}} \times e^{-\lambda_{230} t}$. Curves shown on both panels are for a steady growth rate of 1.15 mm/Myr. Note, however, that this calculation involves an assumption that either the $^{230}$Th$_{\text{now}}$ and/or the $\text{^{230}Th}_{\text{initial}} / \text{^{232}Th}$ remains constant at the outer surface of the nodule throughout its growth. That this is not exactly true is shown by the fact that the growth rate history for the crust is not identical using the two
chronometers. For instance, the outermost \( ^{230}\text{Th}_{\infty} \) data imply a slow growth rate, while the same three points, when normalized to \( ^{232}\text{Th} \), imply a rapid growth rate. The problem of variable initial conditions limits the usefulness of \( ^{230}\text{Th}_{\infty} \) dating of Mn nodules and crusts.

**Figure 7** Schematic of \( ^{231}\text{Pa} - ^{230}\text{Th} \) fractionation in the oceans. Both nuclides are formed from decay of U throughout the water column. The length of gray arrows represents the size of the fluxes illustrating that \( ^{230}\text{Th} \) is rapidly scavenged everywhere, while \( ^{231}\text{Pa} \) can be advected or transported by diffusion (not shown) from areas of low to high productivity. Sedimentary \( ^{231}\text{Pa} / ^{230}\text{Th} \) is therefore a function of both the productivity and the net lateral transport of \( ^{231}\text{Pa} \) by ocean circulation.

**Figure 8** Partition coefficients (\( K_d \)) for Th and Pa and the fractionation factor (F) between Th and Pa plotted as a function of the opal and calcium carbonate percentage in settling particulate material. Note the tendency for the \( K_d \) for Th to increase with increasing carbonate fraction and decrease with increasing opal fraction. Pa shows the opposite behavior so that F increases with low opal fraction or high carbonate fraction. This plot is modified from Chase et al. (In press-b) but excludes the continental margin data also shown in that study and instead focuses exclusively on open-ocean sites.

**Figure 9** A log-log plot of the annual average \( (^{231}\text{Pa}_{\infty} / ^{230}\text{Th}_{\infty}) \) as a function of sediment trap particle composition, and as a function of total mass flux. Note the importance of particle composition on the \( (^{231}\text{Pa}_{\infty} / ^{230}\text{Th}_{\infty}) \) of trapped material, with a high opal fraction leading to higher ratios. Note also the poor relationship between \( (^{231}\text{Pa}_{\infty} / ^{230}\text{Th}_{\infty}) \) and mass flux. This data was compiled by Chase et al. (In press-b) and includes data from that study, as well as from Lao et al. (1993), Scholten et al. (2001), and Yu et al. (2001a).

**Figure 10** An example of the use of \( (^{231}\text{Pa}_{\infty} / ^{230}\text{Th}_{\infty}) \) to reconstruct past productivity taken from Chase et al. (In press-a). Data is from a core in the Southern Pacific (AESOPS Station 6 at 61° 52.5’S, 169° 58.3’W). The downcore record of \( (^{231}\text{Pa} / ^{230}\text{Th})_{\infty} \) indicates an increase in opal productivity centered at 15 ka. This productivity increase is also seen in the records of two other productivity proxies - the opal accumulation and Ba accumulation rates. Downcore records of these sediment constituents are also shown and have been converted from concentrations to accumulation fluxes by normalizing to the known \( ^{230}\text{Th}_{\infty} \) flux.

**Figure 11** \( ^{226}\text{Ra} \) in barite and bulk sediment from Core MC82 in the equatorial Pacific (Paytan et al., 1996). Note the considerably higher \( ^{226}\text{Ra} \) concentration in the barite, and the general exponential decrease in barite \( ^{226}\text{Ra} \) with depth. This decrease allows barite \( ^{226}\text{Ra} \) to be used to provide Holocene chronology in sediments devoid of carbonates for \( ^{14}\text{C} \) dating.

**Figure 12** An example of use of \( ^{210}\text{Pb} \) to assess the rate and depth of sediment mixing from a core on the slopes of the Bahamas (Henderson et al., 1999b). The exponential decrease in \( ^{210}\text{Pb} \), seen in the upper 6 cm of the sediment reflects decay of \( ^{210}\text{Pb} \) as it is mixed downward. The diffusional model of mixing described in the text indicates a mixing rate, \( D \), of 51 cm\(^2\) kyr\(^{-1}\) for this core. The two circled points at greater depth reflect rapid injection of surface material to depth in a process known as “conveyor-belt” feeding (Robbins, 1988; Smith et al., 1997).
Appendix 1

Measured concentrations of $^{230}\text{Th}$ and $^{231}\text{Pa}$ in marine sediments consist of three components: that scavenged from seawater; that supported by U contained within lithogenic minerals; and that produced by radioactive decay of authigenic U. Most of the proxies described in this paper make use of only the scavenged component. Measured $^{230}\text{Th}$ and $^{231}\text{Pa}$ must therefore first be corrected for the presence of the other two components. To make this correction to the measured $^{230}\text{Th}$ or $^{231}\text{Pa}$, it is generally assumed that the U decay series are in secular equilibrium in lithogenic phases, and that the formation of authigenic U is contemporary with the deposition of the sediments. Accepting those assumptions, unsupported (scavenged from seawater) $^{230}\text{Th}$ is calculated from its measured value as:

$$
^{230}\text{Th}_{\text{xs}} = ^{230}\text{Th}_{\text{meas}} - \left\{ (0.6\pm0.1) \times ^{232}\text{Th}_{\text{meas}} \right\} -
\left\{ ^{238}\text{U}_{\text{meas}} - (0.6\pm0.1) \times ^{232}\text{Th}_{\text{meas}} \right\} \times \left[ (1-e^{-\lambda_{230}t}) + \frac{\lambda_{230}}{\lambda_{230} - \lambda_{234}} \times (e^{-\lambda_{234}t} - e^{-\lambda_{230}t}) \times \left( \frac{^{234}\text{U}}{^{238}\text{U}} \right)_{\text{init}} - 1 \right]\}
$$

and unsupported $^{231}\text{Pa}$ as:

$$
^{231}\text{Pa}_{\text{xs}} = ^{231}\text{Pa}_{\text{meas}} - \left\{ 0.046 \times (0.6\pm0.1) \times ^{232}\text{Th}_{\text{meas}} \right\} -
\left\{ 0.046 \times ^{238}\text{U}_{\text{meas}} - (0.6\pm0.1) \times ^{232}\text{Th}_{\text{meas}} \right\} \times \left[ (1-e^{-\lambda_{231}t}) \right]
$$

In both expressions, the first term in curly brackets corrects for $^{230}\text{Th}$ (or $^{231}\text{Pa}$) supported by U in lithogenic material, and the second term in curly brackets corrects for $^{230}\text{Th}$ (or $^{231}\text{Pa}$) ingrown from authigenic U. For samples that are known to be young, such as sediment trap or core-top samples, $t=0$ and this second term equals zero reflecting the lack of time for decay of authigenic U in such samples.

The concentration of lithogenic $^{238}\text{U}$ (or $^{235}\text{U}$) is estimated from the measured concentration of $^{232}\text{Th}$, which is entirely of lithogenic origin (Brewer et al., 1980), together with an appropriate lithogenic $^{238}\text{U}/^{232}\text{Th}$ (or $^{235}\text{U}/^{232}\text{Th}$) ratio. Although there has never been a formal compilation of lithogenic U/Th ratios in marine sediments, based on our own experience as well as results reported in the literature (e.g. Walter et al., 1997), appropriate lithogenic $^{238}\text{U}/^{232}\text{Th}$ ratios (expressed as activity ratios) are 0.6±0.1 for the Atlantic Ocean, 0.7±0.1 for the Pacific Ocean, and 0.4±0.1 for regions south of the Antarctic Polar Front in the Southern Ocean. In the equations above, 0.6±0.1 represents the applied lithogenic $^{238}\text{U}/^{232}\text{Th}$ activity ratio, and 0.046 is the natural $^{235}\text{U}/^{238}\text{U}$ activity ratio.

Authigenic U is precipitated within chemically-reducing marine sediments (Klinkhammer and Palmer, 1991). Particulate non-lithogenic U is also formed in surface ocean waters (Anderson, 1982). Although much of this particulate non-lithogenic U is regenerated prior to burial in pelagic sediments (Anderson, 1982), a substantial fraction (tens of percent) survives to be buried in ocean-margin sediments, particularly in regions where an intense oxygen minimum zone impinges on the sediments (Zheng et al., 2002). Authigenic U is assumed to have an initial $^{234}\text{U}/^{238}\text{U}$ ratio equivalent to that of U dissolved in seawater (=1.146). To correct for ingrowth from U using the above equations, an estimate of the age of the sediment, $t$, is required. This is generally derived from stratigraphy (e.g. $\delta^{18}\text{O}$) and by assuming the SPECMAP timescale (Imbrie et al., 1984).

Age correction is also generally required in order to correct for the decay of excess $^{230}\text{Th}$ (or $^{231}\text{Pa}$) since the formation of the sediment. Only by such a correction can the conditions at the time of sediment formation be determined. For $^{230}\text{Th}_{\text{xs}}$, this correction is given by:

$$
^{230}\text{Th}_{\text{xs}} = ^{230}\text{Th}_{\text{xs}} \times e^{\lambda_{230}t}
$$

(C)
And for $^{231}\text{Pa}_{ss}$, by:

$$^{231}\text{Pa}_{ss}^0 = ^{231}\text{Pa}_{ss} \cdot e^{231t}$$  \hspace{1cm} (D)

Again, a stratigraphic estimate of the age of the sediment is used to give $t$ in both equations. The ratio of age-corrected excess $^{230}\text{Th}$ to $^{231}\text{Pa}$, denoted $(^{231}\text{Pa}_{ss}/^{230}\text{Th}_{ss})^0$ is that most widely used to investigate the past environment.
Figure 1

- **Particulate $^{230}$Th**
  - Average: 0.09
  - N: 276

- **Dissolved $^{230}$Th**
  - Average: 0.52
  - N: 382

- **Total $^{230}$Th**
  - Average: 0.41
  - N: 381

- **Particulate $^{231}$Pa**
  - Average: 0.02
  - N: 92

- **Dissolved $^{231}$Pa**
  - Average: 0.29
  - N: 136

- **Total $^{231}$Pa**
  - Average: 0.31
  - N: 86
Other coral data
Bahamas sediments (Henderson 2002)
Nicaragua Rise sediments (Gallup et al. 1995)
Hateruma corals (Henderson et al. 1993)
Select Barbados corals (Gallup et al. 1994)
Other coral data

Figure 2
Figure 3
Figure 5
Figure 6

Mn Crust

\[
\left( \frac{^{230}\text{Th}_{xs}}{^{232}\text{Th}} \right) \text{ (Activity Ratio)}
\]

Mn Crust

\[
\left( \frac{^{230}\text{Th}_{xs}}{^{232}\text{Th}} \right) \text{ (dpm/g)}
\]

Depth in crust (mm)
Advection

\[
\frac{^{231}\text{Pa}}{^{230}\text{Th}} = 0.093
\]

Figure 7
Figure 8
Figure 9
Figure 10
Figure 11
Figure 12