

# Long-term records of erosional change from marine ferromanganese crusts

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Ferromanganese crusts from the Atlantic, Indian and Pacific Oceans record the Nd and Pb isotope compositions of the water masses from which they form as hydrogenous precipitates. The  $^{10}\text{Be}/^9\text{Be}$ -calibrated time series for crusts are compared to estimates based on Co-contents, from which the equatorial Pacific crusts studied are inferred to have recorded ca. 60 Ma of Pacific deep water history.

Time series of  $\varepsilon_{\text{Nd}}$  show that the oceans have maintained a strong provinciality in Nd isotopic composition, determined by terrigenous inputs, over periods of up to 60 Ma. Superimposed on the distinct basin-specific signatures are variations in Nd and Pb isotope time series which have been particularly marked over the last 5 Ma.

It is shown that changes in erosional inputs, particularly associated with Himalayan uplift and the northern hemisphere glaciation have influenced Indian and Atlantic Ocean deep water isotopic compositions respectively. There is no evidence so far for an imprint of the final closure of the Panama Isthmus on the Pb and Nd isotopic composition in either Atlantic or Pacific deep water masses.

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## 1. Introduction

Tectonics and climate combine to influence the rates and mechanisms of rock weathering and erosion. However, details of their interrelationships are not well understood. Part of the problem is to identify records of the relevant changes that have taken place. Because a significant portion of the terrigenous products of continental weathering and erosion enter the oceans and leave an imprint on the chemical and isotopic composition of seawater much effort has been devoted to the recovery of marine records of seawater composition.

Of particular interest have been records of the abundance and isotopic composition of metals in seawater. These are controlled primarily by the nature of their terrigenous and hydrothermal sources on the one hand and their oceanic residence times on the other. As a consequence, different elements display quite different isotopic distribution patterns in the oceans. For example, despite the large variation in isotopic composition of the various Sr inputs into the ocean the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio of seawater is uniform

globally. This is because the oceanic residence time of Sr is ca. 2 Ma (1 Ma = 1 million years) and thus much longer than the ca. 1.5 ka ocean circulation time (1 ka = 1,000 years). In contrast, Nd has a residence time very similar to the circulation time of the ocean and consequently shows significant differences in isotopic composition between the main ocean basins and even different water masses (e.g. Piepgras *et al* 1979). Thus at any one time the isotopic distribution pattern of metals in the oceans is a result of the interplay between the advection of the dissolved metal input by the circulation and their removal into the marine sediments. In principle it should be possible to reconstruct details of any time-dependent changes in the isotopic distribution patterns arising from either changes in the inputs (erosion and hydrothermal) and the ocean circulation from the marine sedimentary record.

Considerable progress has been made in reconstructing the distribution of Nd and Pb isotopes in Atlantic, Indian and Pacific Ocean water masses from hydrogenous ferromanganese crusts (hereafter called

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crusts), in some cases as far back as 60 Ma ago (Goldstein and O’Nions 1981; Albarède and Goldstein 1992; Abouchami and Goldstein 1995; von Blanckenburg *et al* 1996a; b; Burton *et al* 1997; Christensen *et al* 1997; Albarède *et al* 1997; Ling *et al* 1997; Abouchami *et al* 1997; 1998). These metals have short oceanic residence times, similar to or shorter than the global circulation time, and therefore display a strong provinciality in their isotopic distribution. From these records it has been possible to assess the impact of changes in the balance of erosion products from different input sources to the oceans as well as changes in ocean circulation.

Crusts are widely distributed in the oceans and provide intact and often long-term records of Nd, Pb and Hf isotopes from which water mass characteristics have been derived. This reconstruction has been facilitated by successful dating of the crusts using cosmogenic  $^{10}\text{Be}$  (Segl *et al* 1984; Ling *et al* 1997; O’Nions *et al* 1998), which is introduced into the ocean after production in the upper atmosphere and scavenged from seawater by the Mn-Fe oxyhydroxides of which the crusts mainly consist.  $^{10}\text{Be}$  chronologies have a practical limit of around 10 Ma imposed by the 1.5 Ma half-life of  $^{10}\text{Be}$ . Linear extrapolation of the growth rates beyond 10 Ma has resulted in maximum ages up to 60 Ma (Ling *et al* 1997; O’Nions *et al* 1998) which has recently been supported by using a chronometer based on Co-contents (Frank *et al* 1999).

In this contribution the progress made in the use of well-dated crusts to reconstruct the Nd and Pb isotopic composition of ocean water masses over the last 10 to 60 Ma will be reviewed. The importance of the changing balance of terrigenous inputs into the ocean, particularly over the last 3 Ma is summarised together with evidence for the apparently very limited response of the Nd- and Pb-isotopic composition of deep water to the paleoceanographic changes related to the closure of the Panama Gateway over the last 10 Ma.

## 2. Chronology of ferromanganese crusts

The attempts to derive chronologies and growth rates for ferromanganese crusts have broadly been of three types based respectively upon *in situ* radioactive decay, Co-contents and  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios. The periods datable with the decay-based methods range from 300 ka for  $^{230}\text{Th}$  to approximately 10 Ma for  $^{10}\text{Be}$ . The approach based on Co-content assumes a constant and known flux of Co to the crust growth surface and has theoretically no age limitations whereas the third method is based upon matching  $^{87}\text{Sr}/^{86}\text{Sr}$  variations in the Mn-Fe-oxyhydroxide material of the crusts to the known global ocean  $^{87}\text{Sr}/^{86}\text{Sr}$  evolution. Of these the Sr isotope approach although the subject of much careful work has been the least successful due to

apparent isotope exchange (Burton *et al* 1997; Ling *et al* 1997; O’Nions *et al* 1998).

Hydrogenous ferromanganese crusts have growth rates typically in the range from 2 to 5 mm/Ma but occasionally up to 15 mm/Ma (cf. Segl *et al* 1984; Manheim 1986; Puteanus and Halbach 1988). Therefore the U-series based methods are useful only for the outer 1–2 mm of crusts but have been used widely (Segl *et al* 1984; Banakar and Borole 1991; Eisenhauer *et al* 1992; Chabaux *et al* 1995; 1997; Bollhöfer *et al* 1996; Abouchami *et al* 1997). Recent evidence for mobility of  $^{234}\text{U}$  suggests that  $^{230}\text{Th}$ -based approaches are more reliable than U-based ones (Neff *et al* 1998). Methods for determining growth rates based on the decay of  $^{10}\text{Be}$  have overall been the most successful for the period of the last 10 Ma (Segl *et al* 1984; McMurtry *et al* 1994). In the Oxford laboratory we have used profiles of direct and high precision measurements of the  $^{10}\text{Be}/^9\text{Be}$  ratio in crusts (Belshaw *et al* 1995) to determine their growth rates (Ling *et al* 1997; O’Nions *et al* 1998; Frank and O’Nions 1998). This method has the advantage of being independent of the amount of Be incorporated into the crust and succeeds because  $^{10}\text{Be}/^9\text{Be}$  ratios in the oceans appear to have varied little over the last 5 to 10 Ma.

The Co-method in many cases provides a check on the uniformity of crust growth over the  $^{10}\text{Be}$  dated intervals and the viability of extrapolated growth rates to deeper levels in the crust. The Co-method assumes a constant “rain rate” of Co to the growth surface of the crust and its concentration in the crust then depends upon the rate of addition of the other more abundant elements such as Fe and Mn. Thus as long as the “rain rate” has been constant the Co content will provide a reliable estimate of growth rate variations. The original calibration of the Co content as a chronometer was based on U-series dating of Co-rich crusts with Co contents >1% from the central equatorial Pacific (Halbach *et al* 1983; Puteanus and Halbach 1988). An alternative relationship between Co-content and growth rate which is supposed to be applicable over a wider range of genetically different ferromanganese crusts and nodules and even pelagic sediments was developed by Manheim (1986).

Some of these aspects of crust chronology are illustrated here. In figure 1 the age-depth relationships obtained for crust D11-1 from the central equatorial Pacific based on  $^{10}\text{Be}/^9\text{Be}$  ratios (Ling *et al* 1997) and Co contents (Frank *et al* 1999) are compared. The ages derived from the  $^{10}\text{Be}/^9\text{Be}$  ratios suggest an average growth rate of 1.4 mm/Ma between 7 Ma ago and present and 2.7 mm/Ma between 11 and 7 Ma ago. Extrapolation of the latter suggests an age of about 58 Ma at the base of the crust. The Co content measured by electron probe confirms that the growth rate has indeed deviated very little from the average growth rate of the uppermost 20 mm over the entire depth interval. The great value of the Co method is

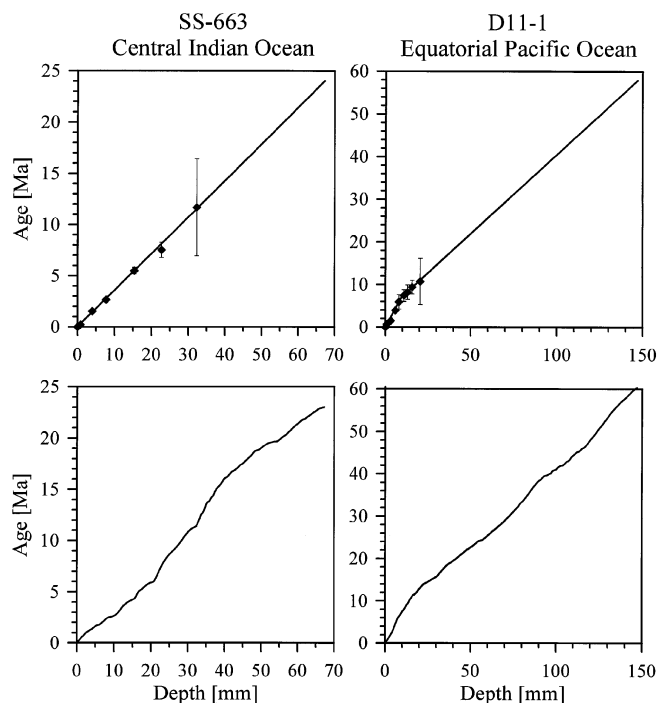


Figure 1. Comparison of age-depth relationships based on  $^{10}\text{Be}/^9\text{Be}$  and Co-content chronometers for crusts SS-663 and D11-1 from the Central Indian and Pacific Ocean respectively. The upper diagrams show ages calculated from  $^{10}\text{Be}/^9\text{Be}$  ratios assuming that the growth surfaces of the crusts have had the present day surface value during their growth and that the decrease in  $^{10}\text{Be}/^9\text{Be}$  ratio with depth is due to decay of  $^{10}\text{Be}$  (Ling *et al* 1997; O’Nions *et al* 1998). The lower diagrams show the age-depth relationships obtained from the Co-content chronometer (Frank *et al* 1999) using the relationships proposed by Manheim (1986) for SS-663 and by Puteanus and Halbach (1988) for D11-1. Note the excellent overall agreement between the two approaches and particularly the agreement between the Co-content age estimate and the extrapolated  $^{10}\text{Be}/^9\text{Be}$  age estimates for D11-1.

the support it provides for the  $^{10}\text{Be}/^9\text{Be}$  method and the justification for assuming that 60 Ma of equatorial Pacific deep water history is recorded by this crust.

It should be recalled that there is an element of circularity in these age estimates. In the case of  $^{10}\text{Be}/^9\text{Be}$  ratios the age estimates assume that the  $^{10}\text{Be}/^9\text{Be}$  ratio at the present-day growth surface is the same as that over the last 10 Ma. The self-consistent nature of the data supports this view but does not prove it. Similarly the claim of a uniform growth rate over the whole 150 mm of the crust assumes that the Co rain rate has been constant throughout and that there have been no hiatus which is apparently supported by the good correspondence between the two approaches.

Self-consistent results from the  $^{10}\text{Be}/^9\text{Be}$  ratio and Co-content chronometers as obtained for equatorial Pacific samples such as D11-1 (figure 1) are not found at all locations tested so far. The Co rain rate is not uniform everywhere in the ocean and appears to depend on the proximity to and intensity of the oxygen minimum layer; age models using the relationship of Puteanus and Halbach (1988) which were

developed for Co-rich central Pacific seamount crusts are not directly applicable to other parts of the oceans. For Co-poor crusts anywhere else in the ocean the relationship of Manheim (1986) appears to be more suitable to estimate changes in growth rate (Frank *et al* 1999). The results for crust SS-663 from the central Indian Ocean (figure 1) provide an example of the application of the Co chronometer as adapted for crusts with low Co contents (Manheim 1986). The  $^{10}\text{Be}/^9\text{Be}$  ratios obtained for SS-663 suggest a uniform growth rate for the crust over the outer 35-mm and an age at the base of the crust close to 25 Ma (Frank and O’Nions 1998). The Co-derived ages for this crust are in good agreement and also indicate an age between 20 and 25 Ma at the base (Frank *et al* 1999). At present these are the only methods which have any general applicability and there is considerable merit in applying them in a complementary manner.

### 3. Global pattern of Nd and Pb distribution

The isotopic composition of seawater Nd varies as a function of water depth and water mass in the modern oceans as illustrated by published profiles of seawater  $\epsilon_{\text{Nd}}$  from the Atlantic Ocean (figure 2). It also varies between ocean basins in a way that primarily reflects the age distribution pattern of the surrounding continental crust. At present seawater contains a large component of anthropogenic Pb but the pre-anthropogenic distribution also appears to reflect local provenance and residence time (von Blanckenburg *et al* 1996b). The surfaces of ferromanganese crusts and nodules from the Atlantic, Indian and Pacific Oceans have Nd isotope compositions, which obviously match those of the water masses in which they have grown (Albarède and Goldstein 1992; Abouchami and Goldstein 1995; Albarède *et al* 1997). They offer therefore the possibility that variations in the Nd and Pb isotope compositions of ocean water masses or changes in the pathways of water masses may be reconstructed from time series of ferromanganese crusts. In the case of the equatorial Pacific this may be back as far as 60 Ma (Ling *et al* 1997; Frank *et al* 1999).

In order to reconstruct the Nd and Pb isotope composition of deep water at a particular location back through time it is necessary to acquire Nd and Pb isotope profiles on accurately dated crusts which are unaffected by diagenesis on the scale sampled for analysis. These conditions are apparently met for seven crusts from the Atlantic, Indian and Pacific Oceans and the results of Nd and Pb isotope analyses are displayed in figures 3 and 4. These Nd and Pb isotope time series differ from those originally published (Ling *et al* 1997; Burton *et al* 1997; O’Nions *et al* 1998; Frank and O’Nions 1998) in that they use the modified age-depth relationships for three crusts (109D-C, BM1969.05, VA13-2) from Frank *et al* (1999).

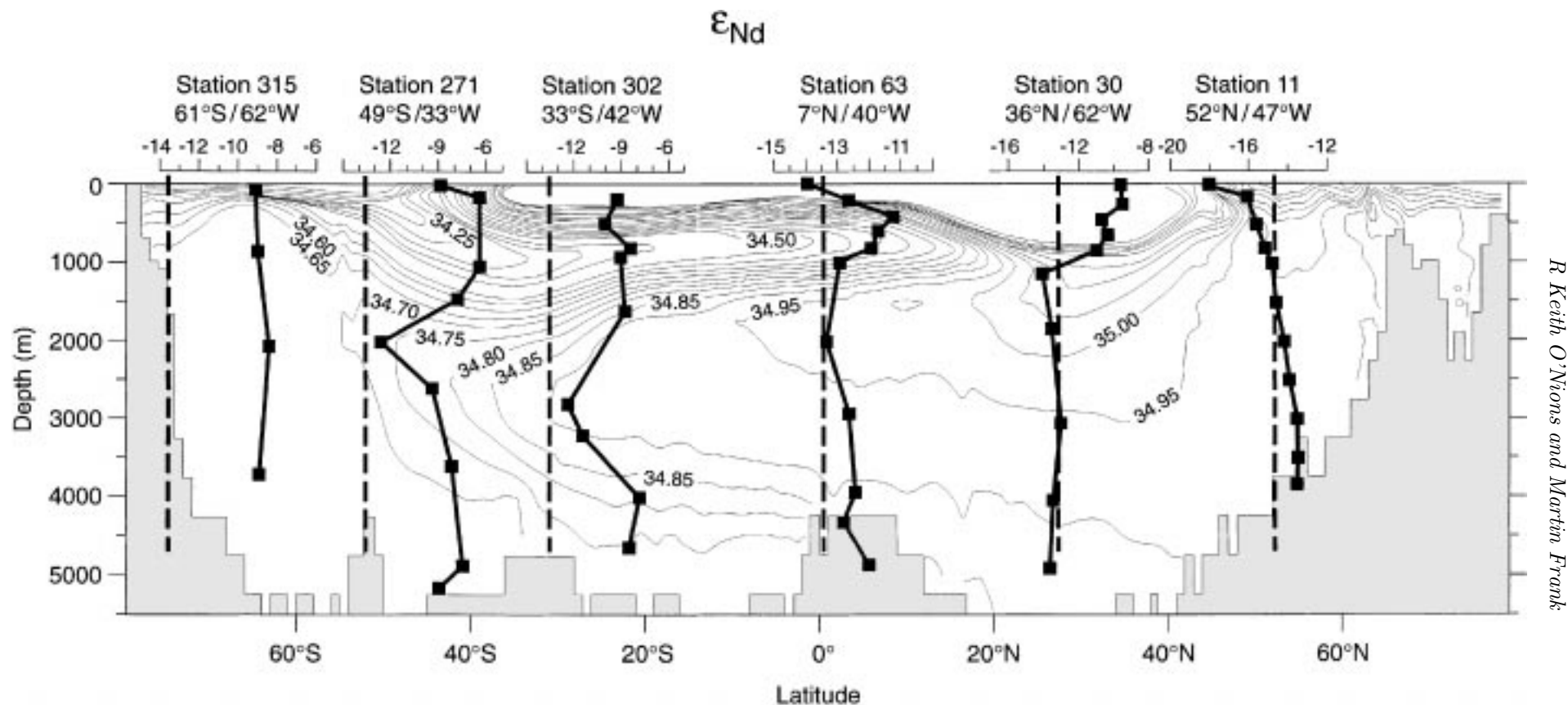


Figure 2. Depth profiles of Nd isotopes, expressed as  $\epsilon_{Nd}$  values, at 6 stations in the present day Atlantic (Piepgras and Wasserburg 1982, 1987; Jeandel 1993). These profiles are superimposed on contours of the present-day salinity in the Atlantic as observed along a north-south transect (Levitus 1982). The sea floor topography along the profile is shown in grey. North Atlantic deep water generated by sinking of saline water at a number of sites in the N. Atlantic is identified at mid-ocean depths by its high salinity core and is advected into the S. Atlantic where it is recognisable until about 50°S. The  $\epsilon_{Nd}$  value of NADW close to its formation in the N. Atlantic is close to  $-13.5$ , and thus several  $\epsilon_{Nd}$  units lower than Atlantic surface, intermediate or bottom waters such as Antarctic Intermediate Water or Antarctic Bottom Water which are derived in the S. Atlantic. NADW retains a characteristic  $\epsilon_{Nd}$  value of  $-13$  as far south as 49°S in the southern Atlantic and corresponds well with the water mass distribution defined by salinity.

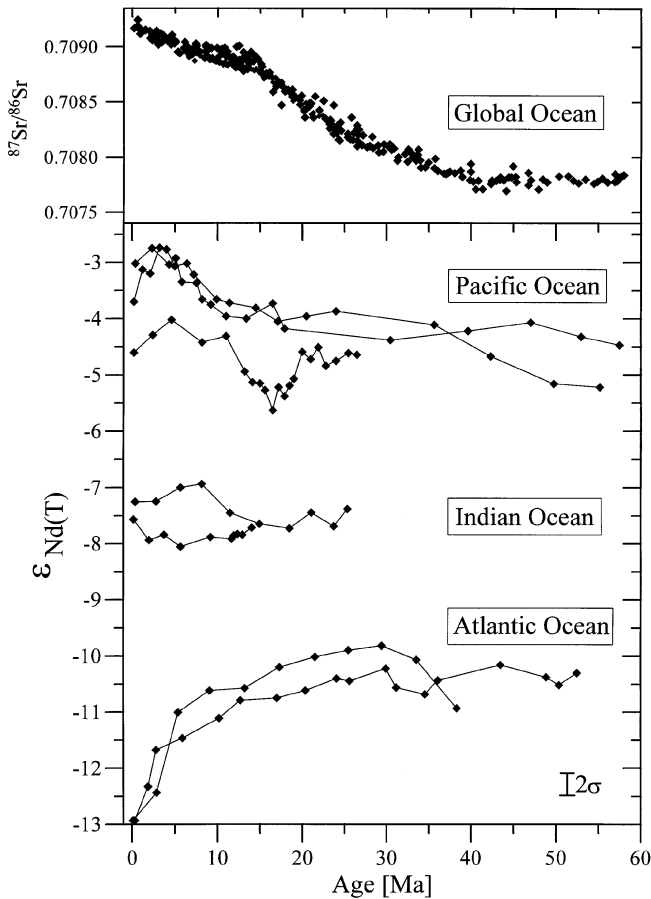


Figure 3. Comparison of  $\epsilon_{\text{Nd}}$  time series of ferromanganese crusts from the Atlantic, Indian and Pacific Oceans (Ling *et al* 1997; Burton *et al* 1997; O’Nions *et al* 1998) using the revised chronologies for SS-663, BM1969.05 and VA13/2 (Frank *et al* 1999). Note the strong inter-ocean provinciality of  $\epsilon_{\text{Nd}}$ , which is caused by the different overall  $\epsilon_{\text{Nd}}$  value of the terrigenous inputs into the ocean basins and the residence time of Nd which is similar to the ca. 1.5 ka global ocean circulation time. This is too short for efficient mixing of Nd between the major ocean basins. These  $\epsilon_{\text{Nd}}$  results are compared with the global ocean Sr isotope evolution derived from analyses of foraminifera (Koepnick *et al* 1985; DePaolo 1986; Hess *et al* 1986; Hodell *et al* 1991).

These authors have used Co-content profiles for each crust to identify changes in growth rate in those parts of the profiles which are beyond the range of  $^{10}\text{Be}/^9\text{Be}$  dating. The most significant change compared to the originally published age-depth relationships was found for VA13-2 from the central Pacific (Segl *et al* 1984; Ling *et al* 1997), for which the Co content profile reveals a change from high growth rates around 13 mm/Ma prior to 14 Ma ago to the lower rates of 3.75 and 2.3 mm/Ma determined by  $^{10}\text{Be}/^9\text{Be}$  afterwards.

The Nd isotope time series in figure 3 reveal some remarkable features as follows:

- Although the mechanically sampled growth surfaces of the crusts represent 100 ka or more of growth and integrate any variations in  $\epsilon_{\text{Nd}}$  over this interval they are indistinguishable from those in their ambient water masses at the present day.

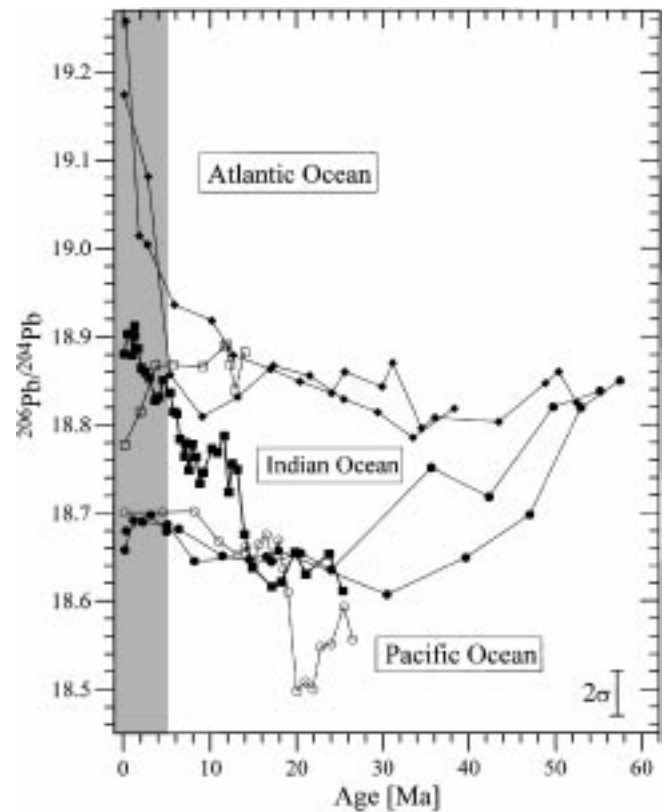


Figure 4. Comparison of  $^{206}\text{Pb}/^{204}\text{Pb}$  time series of the same crusts as in figure 3. The North Atlantic crusts are marked by diamond symbols (Burton *et al* 1997; O’Nions *et al* 1998), the southern Indian Ocean crust by open squares (Frank and O’Nions 1998), the central Indian Ocean one by closed squares (Frank and O’Nions 1998), the Pacific deep water crust by open circles (Ling *et al* 1997) and the two Pacific seamount crusts by closed circles (Ling *et al* 1997). The shaded area highlights the last 5 Ma over which separate Atlantic, Indian and Pacific Ocean signatures of the Pb isotopes in the deep water have apparently existed.

- For the last 20 Ma, and probably also the last 60 Ma, deep water masses in the Atlantic, Indian and Pacific Oceans have maintained separate identities in terms of  $\epsilon_{\text{Nd}}$  values. These different identities reflect the  $\epsilon_{\text{Nd}}$  values of the terrigenous inputs into the three ocean basins which in turn reflect the age patterns of the surrounding continental crust. Thus, the more negative  $\epsilon_{\text{Nd}}$  values in the Atlantic reflect the inputs from the old Precambrian cratons surrounding the N. Atlantic, whereas the much higher values in the Pacific have originated from the young volcanic arcs in the Pacific Ocean and its young continental margins.
- The equatorial Pacific deep water crust VA 13-2 was dredged from a depth of 4830 m compared with depths between 2400 and 1700 m for the other two Pacific seamount crusts. The  $\epsilon_{\text{Nd}}$  values of VA 13-2 are lower than the other two crusts for the entire 26 Ma record and suggest the long term presence of different water masses and stratification of Nd isotopes in the equatorial Pacific.

- In addition to the long-term provinciality of Nd in the oceans there are superimposed shorter-term variations of  $\varepsilon_{\text{Nd}}$  in each of the records. These are most evident for the samples from the NW Atlantic where  $\varepsilon_{\text{Nd}}$  has decreased by about two units to reach the present day NADW value over the last few Ma. The records from the equatorial Pacific display smaller (less than 1  $\varepsilon_{\text{Nd}}$  unit) but significant decreases over the same time period. In the two Indian Ocean crusts only small and barely significant variations in  $\varepsilon_{\text{Nd}}$  occurred; slight increases of 0.5–0.7  $\varepsilon_{\text{Nd}}$  units are recorded in the southern Indian Ocean during the last 1 Ma and in the central Indian Ocean at about 8 Ma ago.

In addition to  $\varepsilon_{\text{Nd}}$  time series, Pb isotopes are also presented for Atlantic, Pacific and Indian Ocean samples again using the revised chronology of Frank *et al* (1999). These are displayed as  $^{206}\text{Pb}/^{204}\text{Pb}$  ratios in figure 4. Because Pb has a residence time of 80–100 years in deep waters (Schaule and Patterson 1981) it is expected *a priori* to show a similar behaviour to that of Nd, at least if processes occur on the basin scale. A comparison of the time series in figures 3 and 4 indeed shows similarities but also reveals major differences between Pb and Nd.  $^{206}\text{Pb}/^{204}\text{Pb}$  ratios, like  $\varepsilon_{\text{Nd}}$  values, show an inter-ocean provinciality for the last few Ma, with well-resolved differences between the Atlantic, Indian and Pacific samples. Such differences have also existed for the other Pb-isotope ratios (Frank and O’Nions 1998). Unlike the  $\varepsilon_{\text{Nd}}$  time series, however,  $^{206}\text{Pb}/^{204}\text{Pb}$  ratios show much less provinciality further back in the past. This is particularly the case if the Atlantic and Pacific records are compared, which had a similar Pb isotope composition until about 50 Ma ago and then started to diverge. The highlighted area in figure 4 emphasises the pronounced divergence in Pb isotopes over the last 5 Ma, much of which, as in  $\varepsilon_{\text{Nd}}$ , is accounted for by variations in the N. Atlantic crusts.

#### 4. Records of continent erosion

Weathering and erosion of continental crust is the dominant source of Nd in the oceans: the contribution from submarine hydrothermal sources was shown to be negligibly small in terms of mass balance (Michard *et al* 1983; Piepgras and Wasserburg 1985). Thus ferromanganese crusts bear a record of dissolved Nd of terrigenous origin at their deep water growth sites over the last up to 60 Ma. The variations in  $\varepsilon_{\text{Nd}}$  at any particular site must reflect either changes in the  $\varepsilon_{\text{Nd}}$  of a particular input or its distribution by the ocean circulation. The effects of ocean circulation are at present substantial as evidenced by the advection of NADW with  $\varepsilon_{\text{Nd}} = -13.5$  from the sites of NADW generation in the North Atlantic into the southern Atlantic Ocean (figure 2).

The major part of pre-anthropogenic Pb in the oceans has also been terrigenous in origin. Although Pb has a shorter residence time than Nd it can obviously also be advected on the basin scale depending on the residence times of the respective water masses (Abouchami and Goldstein 1995; Abouchami *et al* 1998). This implies that Pb isotope time series in a particular crust, similar to Nd isotopes, reflect potential changes in input as well as in circulation. In this section those parts of the records which most clearly reflect changes in erosional inputs to the oceans and their significance will be reviewed.

#### 4.1 Neodymium

- Erosion of the continents and the input of the erosion products into the oceans, either as particulates (including atmospheric dust) or as part of the dissolved river load are the ultimate source of Nd present in the crusts.
- The most spectacular shifts in  $\varepsilon_{\text{Nd}}$  in any of the time series occurs in the two western N. Atlantic crusts (Burton *et al* 1997; O’Nions *et al* 1998). Over the last few Ma they have shifted from the long-term (50 Ma) characteristic  $\varepsilon_{\text{Nd}}$  value of the N. Atlantic of  $\sim -10$  by approximately 3  $\varepsilon_{\text{Nd}}$  units to  $\varepsilon_{\text{Nd}} = -13.5$ , which is the characteristic value for NADW in the present day Atlantic (e.g. Piepgras and Wasserburg 1987). The contribution which is responsible for this unradiogenic Nd isotope composition of NADW is known to be located in the Labrador Sea (Stordal and Wasserburg 1986; Piepgras and Wasserburg 1987). This is the only known source where water masses with  $\varepsilon_{\text{Nd}}$  values  $< -20$  are found.

There are two possibilities for the cause of the dramatic shift of  $\varepsilon_{\text{Nd}}$  in the western N. Atlantic. The first is that there was no change at all in the amount and composition of Nd delivered to the oceans by erosion over the last 5 to 10 Ma. In this case the shift in  $\varepsilon_{\text{Nd}}$  would be due to an intensification of deep water generation in the Labrador Sea and as a consequence an increased amount of Nd with a low  $\varepsilon_{\text{Nd}}$  value contributing to NADW (Burton *et al* 1997). The second possibility is that amount and composition of the Nd input did change in a way expected to have accompanied the onset of the Northern Hemisphere Glaciation. It has been shown that prior to ca. 3 Ma ago the amount of erosional input in the Labrador Sea region was small (Shackleton *et al* 1984; Raymo 1994) and it has also been suggested that deep water formation in the Labrador Sea region may have been much less important before about 3 Ma than afterwards (Burton *et al* 1997). Von Blanckenburg and O’Nions (1999) have argued that the constant  $^{10}\text{Be}/^9\text{Be}$  ratio in the N. Atlantic seawater over this time period requires that the balance between terrigenous  $^9\text{Be}$

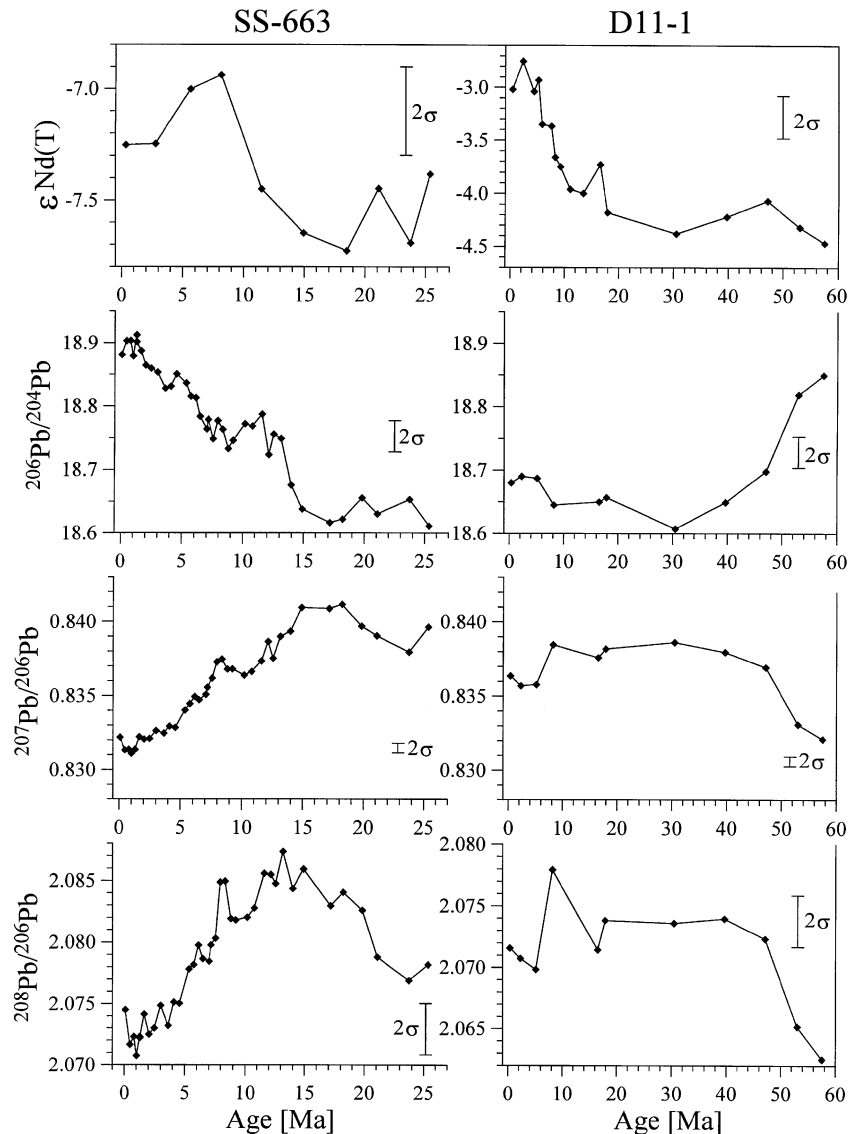


Figure 5. Comparison of  $\epsilon_{\text{Nd}}$  (age corrected) and Pb isotope time series for crusts SS-663 (O'Nions *et al* 1998; Frank and O'Nions, 1998) and D11-1 (Ling *et al* 1997) based on the  $^{10}\text{Be}/^9\text{Be}$  chronologies given in figure 1. Note the  $^{208}\text{Pb}/^{206}\text{Pb}$  structure in SS-663 which has been related to the uplift and erosion of the Himalayas (Frank and O'Nions 1998).

input and cosmogenic  $^{10}\text{Be}$  input into the N. Atlantic remained fixed in which case a change in the integrated  $\epsilon_{\text{Nd}}$  value of the terrigenous input into the N. Atlantic is more likely as a cause for the observed isotopic shifts than a change in circulation. Thus, there appears to be a close link between the Quaternary glaciation and the input of Nd with highly unradiogenic isotope composition in the area of the Labrador Sea. This is supported by results of Winter *et al* (1997) on ferromanganese micronodules from marine sediments in the Arctic Ocean which also show a major shift in  $\epsilon_{\text{Nd}}$  towards more negative values around 2 Ma ago.

A second point concerns the approximately contemporaneous shift in  $\epsilon_{\text{Nd}}$  towards more unradiogenic values evident in the time series of crusts from the Pacific. Although these effects are more subtle with  $\epsilon_{\text{Nd}}$  varying by only 1 unit or less they are nevertheless

significant (Ling *et al* 1997). It was initially suggested that the overall increase in  $\epsilon_{\text{Nd}}$  from 20 to around to 5 Ma ago in the Pacific crusts may have been arrested by an increased influx of water from the Antarctic Circumpolar Current (ACC) in combination with an intensification of NADW production which enhanced the transfer of unradiogenic Nd from the North Atlantic into the Pacific Ocean via the ACC (Ling *et al* 1997; Burton *et al* 1997). Later missing evidence for a trend towards more unradiogenic Nd in a crust that has grown from ACC water (O'Nions *et al* 1998) has suggested that this was not the case and that the unradiogenic trend in the Pacific crusts since about 3–5 Ma ago may have been caused by regional changes of Nd sources in the Pacific. This is also suggested by the approximately contemporaneous changes in Pb isotopes in the Pacific crusts which trend towards more Pacific-type values (Ling *et al*

1997; Christensen *et al* 1997) and can not be explained by any kind of contribution from the N. Atlantic.

#### 4.2 Lead

Pb is advected over shorter lengthscales than Nd in the oceans because it is more particle reactive. Nevertheless there is a very close correspondence between the Pb and Nd isotope time series in some crusts such as those from the western N. Atlantic. It is thus likely that there is a straightforward connection between these isotopic changes and a change in the source of terrigenous erosion products or a change in circulation. In the specific case of the western N. Atlantic crusts the isotope time series of both Nd and Pb apparently recorded changes in the erosional input into NADW.

Crust SS-663 from the central Indian Ocean provides another good illustration of the way in which the crusts record changes of erosion inputs into the ocean (O’Nions *et al* 1998; Frank and O’Nions 1998). The  $\epsilon_{Nd}$  and Pb isotope time series for SS-663 are compared in figure 5. The first point to note is that  $\epsilon_{Nd}$ , the variation of which is barely outside the assigned experimental error, shows a minimum between 19 and 15 Ma ago and a shift towards more positive values 8 Ma ago. The structure in the Pb isotope time series is much better resolved, particularly for  $^{207}Pb/^{206}Pb$  and  $^{208}Pb/^{206}Pb$  ratios. In the latter case the  $^{208}Pb/^{206}Pb$  ratios are the highest observed in the ocean so far and show a pronounced maximum between 20 and 15 Ma ago. Frank and O’Nions (1998) have suggested that the Pb with this unusual isotopic composition has been derived from the products of Himalayan erosion and that the maximum values correspond to the period of maximum uplift rate. If this interpretation is correct then it is perhaps surprising that the  $\epsilon_{Nd}$  signal is so damped in the record of SS-663, particularly given that the Himalayan erosion products as preserved in the Bengal Fan have a low and relatively uniform  $\epsilon_{Nd}$  of around  $-16 \pm 2$  (Derry and France-Lanord 1996). There may be three contributing factors responsible for this observation. The first is that no deep water has been generated in the northern Indian Ocean and, unlike the Labrador Sea area, there has not been a direct route for the transfer of an isotopic signal from surface waters to deep water in the northern Indian Ocean. The second factor is the low Pb/Nd ratio of seawater compared with the anticipated much higher ratio in particulates produced by erosion of the Himalayas: interaction between seawater and such particulates may have had a more profound effect on dissolved Pb than Nd (Frank and O’Nions 1998). The third factor may be that a Pb isotope signal from the Himalayas is scavenged more efficiently than Nd due to the higher particle reactivity of Pb and was thus recorded close to the source of input whereas an Nd signal may have been mixed and diluted.

### 5. Influence of gateway and circulation changes

The establishment of the Antarctic Circumpolar Current (ACC) following the opening of the Drake passage between Antarctica and South America about 23 Ma ago (Barker and Burrell 1977) was a key prerequisite on the way to the contemporary pattern of the global thermohaline circulation. The more recent closure of the Panama Gateway has been considered an important factor in further moderating this global circulation pattern. Modelling has suggested that unrestricted exchange of low salinity Pacific water masses with the Atlantic and the contemporaneous wind-forced flow of high salinity Atlantic surface waters into the Pacific prevented the formation of NADW deep water (Meier-Reimer *et al* 1990). Since 12 Ma ago the throughflow became increasingly restricted (Keller and Barron 1983; Duque-Caro 1990) with some indication for a transient landbridge as early as 9.3–8 Ma ago (Marshall 1985). The consequent redirection of the saline Caribbean Current to the north contributed to an increase of the strength of the Gulf Stream (Kaneps 1979) thus increasing the salinity and heat transfer to the North Atlantic. Cooling of this highly saline surface water enabled the production of deep water in the N. Atlantic to start, probably as early as 10 Ma ago (Woodruff and Savin 1989; Delaney 1990). Support for a further enhancement of NADW flow at 3–4 Ma was deduced from sediment accumulation patterns on drifts in the North Atlantic (Wold 1994) and Atlantic versus Pacific benthic foraminiferal carbon isotope gradients (Raymo *et al* 1990; Billups *et al* 1998). Final establishment of the modern circulation mode was suggested to have been in principle completed by 4.6 Ma (Haug and Tiedemann 1998; Driscoll and Haug 1998). The  $\epsilon_{Nd}$  and Pb-isotope records of ferromanganese crusts summarised above may provide some further insights into these effects.

The opening of the Drake Passage is not reflected by any shifts in the Nd or Pb isotope time series in the Atlantic and Pacific crusts analysed so far. Although none of the Atlantic and Pacific crusts available which cover the period of this event is located close to the Passage the observation is surprising given the large changes in ocean circulation that presumably occurred.

A similar conclusion arises for the effects of the closure of the Panama Gateway. Whereas final closure at about 3 Ma ago must have affected the exchange of surface and shallow waters between the Atlantic and Pacific Oceans, the complex archipelagic character of the Gateway and missing precise bathymetric data make it difficult to estimate how and when water mass exchange between the Atlantic and Pacific was affected. The marked change of the Pb and Nd isotope time series in the western N. Atlantic at about 3–4 Ma ago was suggested to be linked to the final closure

through an increase in production of deep water in the Labrador Sea (Burton *et al* 1997). However, the onset of northern hemisphere glaciation at about 3.2–2.6 Ma ago (Shackleton *et al* 1984; Raymo 1994) was responsible for a large increase in supply of unradiogenic Nd and radiogenic Pb at about the same time (O’Nions *et al* 1998; Frank and O’Nions 1998; von Blanckenburg and O’Nions 1999). In addition, it was shown that similar patterns in Nd and Pb isotope time series have occurred in the Arctic Ocean (Winter *et al* 1997) which suggests that the increased input of detrital material was the dominant process.

A trend towards more radiogenic Nd-isotopic composition starting around 12 Ma in the equatorial Pacific isotope records may have been caused by a decreasing supply of unradiogenic Nd from the Atlantic to the Pacific due to the shallowing of the Panama Gateway and the subsequent change of the trend towards more unradiogenic Nd may be related to the intensification of the global thermohaline circulation (Burton *et al* 1997). However, this change of the trend must have been caused by the transfer of a signal via the thermohaline circulation for which there is no evidence in crusts from the ACC and the central Indian Ocean (O’Nions *et al* 1998). It appears therefore that the closure of the Panama isthmus and the associated circulation changes have together left a surprisingly small imprint on the Nd and Pb isotopic composition of the deep water and that the change of provenance and supply of detrital material has been the dominating process controlling dissolved Nd and Pb in the deep ocean.

## 6. Concluding remarks

The Nd and Pb isotope time series of well-dated crusts from the Atlantic, Indian and Pacific Oceans have retained a remarkable record of deep water mass compositions in some cases back to 60 Ma. It is suggested that the Nd and Pb isotope record through time has been mainly controlled by variations of composition and amount of terrigenous inputs into the oceans and their dispersal by the ocean circulation. Major events suggested to be recorded in the isotope time series are Himalayan uplift and erosion and the Northern Hemisphere Glaciation. The records in the Atlantic and Pacific crusts show little unambiguous evidence for circulation changes which accompanied the opening of the Drake Passage and the start of the circum-Antarctic circulation as well as the closure of major oceanic gateways such as Panama.

The isotope records in the ferromanganese crusts are expected to provide further information on more subtle shifts in water mass distribution. Of particular interest will be crusts located over a range of depths at a particular locality, which will be sensitive to vertical shifts in the positions of different water masses.

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