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New age for ferromanganese crust 109D-C and implications for isotopic records of lead, neodymium, hafnium, and thallium in the Pliocene Indian Ocean

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[1] This study presents a high-resolution record of osmium and thallium isotopes in a ferro-manganese (Fe-Mn) crust from the Indian Ocean, Antipode 109D-C. These results, when combined with additional new Os isotope data from ODP Hole 756B in the southeast Indian Ocean, define a new best estimate for the age at the base of this crust of ~6.5 Ma, which is significantly different from a previous estimate of ~15 Ma based on Co-flux modeling. The Tl isotope record obtained for the Indian Ocean resembles that for the Pacific Ocean with a small but well-defined increase occurring over the last ~5 Myr. This contrasts with two records from the Atlantic Ocean which do not have resolvable variations. Ocean basin-scale Tl isotope variation may be inconsistent with the inferred modern marine residence time for Tl of ~20 kyr but could be explained by an increase in ocean crust production rates in the Pacific and Indian oceans since ~10 Ma. The improved age model for 109D-C reveals that the Hf isotope composition of Indian Ocean bottom waters has remained homogenous over the last ~6 Myr. Thus, this isotope system does not bear any evidence that the influence of North Atlantic Deep Water in the formation of Indian Ocean bottom waters has changed during that time. However, because of the lack of knowledge about Hf isotopes as a tracer of ocean circulation, we cannot conclude that export of NADW decreased over the last 6 Myr.

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1. Introduction

[2] With the advent of new analytical techniques, mainly multiple collector inductively coupled plasma mass spectrometry (MC-ICPMS), a host of new isotope paleoceanographic proxy tools have been developed over the last 15 years. These include, to mention just a few, hafnium, iron, molybdenum, neodymium, osmium, and thallium [Lee *et al.*, 1999; Livasseur *et al.*, 2004; Nielsen *et al.*, 2009; Peucker-Ehrenbrink *et al.*, 1995; Piotrowski *et al.*, 2000; Rehkämper *et al.*, 2004; Siebert *et al.*, 2003; van de Flierdt *et al.*, 2002, 2004a, 2004c]. This particular group of elements have the common trait that they all occur in concentrations sufficiently high to be examined in hydrogenetic ferromanganese (Fe-Mn) crusts, which are chemical precipitates from seawater that grow slowly in areas of little or no other sedimentation. Due to the slow growth rate, a thickness of 15 cm may represent as much as 80 million years of precipitation

from seawater [e.g., Frank, 2002] making Fe-Mn crusts a unique archive for monitoring long-term changes in Cenozoic ocean chemistry.

[3] In theory, isotopic records in Fe-Mn crusts have the potential to produce a four-dimensional view of ocean circulation when it is assumed that water masses retain their isotope characteristics over long time periods. However, it should be kept in mind that for most of these recently developed paleoceanographic tracers we do not even know how water masses are fingerprinted in the modern ocean. Thus, it is at present tenuous to utilize these isotope tracers indiscriminately as, for example, proxies of ocean circulation when it cannot be asserted if the isotope composition of the water mass that was sampled by the Fe-Mn crust changed due to other processes such as local input fluxes. Currently, the most advanced of the new proxies is Nd isotopes where efforts in the last few years have significantly progressed our understanding of this isotope system as an ocean circulation tracer [Jones *et al.*, 2008; Siddall *et al.*, 2008]. But for the remaining new isotope proxies much work is needed before they are equipped to yield unambiguous information about paleoceanographic processes. Still, the temporal data generated over the last few decades on these new isotope tracers in Fe-Mn crusts and

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other sedimentary archives clearly have some utility and when interpreted carefully may reveal interesting information already at this early stage in our understanding of the processes governing variation for each system in the oceans.

[4] Apart from the difficulty of interpreting the paleoceanographic significance of isotopic records in Fe-Mn crusts, one of the most challenging aspects of Fe-Mn crust studies is the determination of accurate and precise ages for sections older than ~10 Ma. Younger sections can be dated by measuring cosmogenic ^{10}Be abundances or U-series isotopes, whereas older sections conventionally have been dated by a combination of extrapolating growth rates measured from ^{10}Be in the upper sections [Segl *et al.*, 1984] and assuming a constant flux of Co into the crust [Halbach *et al.*, 1983]. Both these methods, however, are unreliable because they cannot detect hiatuses in crust growth. Additionally, it is questionable whether the assumptions of constant growth rate and Co flux are valid, further hampering the use of these methods. This is clearly a major problem because large inaccuracies in the age of Fe-Mn crusts will lead to incorrect interpretations of the isotope or elemental records obtained as they are placed into an incorrect time frame. Recently, Os isotope stratigraphy was developed as a new means of age determination in Fe-Mn crusts [Fu *et al.*, 2005; Klemm *et al.*, 2005]. This method is analogous to Sr isotope stratigraphy [Depaolo and Ingram, 1985; Jones and Jenkyns, 2001], where the isotopic composition of a sample is compared with an independently determined seawater curve, yielding an age calibration for the sample. The Os isotope seawater curve is not well defined through the entire Cenozoic, but it has sufficient diagnostic features to provide a significant advance in the accuracy of Fe-Mn crust ages.

[5] It is well known that the residence time of an individual element will play a significant role in how variations in isotope compositions may be interpreted. Here we study the element thallium (Tl), which is estimated to possess a residence time between 5 and 50 ka [Flegal *et al.*, 1989; Rehkämper and Nielsen, 2004]. The upper end of this range could result in virtually homogeneous oceans whereas the lower end might lead to measurable differences occurring between water masses or ocean basins.

[6] The marine isotope geochemistry of Tl is of interest because it appears to respond to important changes in ocean chemistry such as cycling of Fe and Mn as well as marine organic carbon burial [Baker *et al.*, 2009; Nielsen *et al.*, 2009]. Thallium has two isotopes, ^{203}Tl and ^{205}Tl , that are both stable and the seawater isotope composition is most likely solely determined by the ratio between the two marine output fluxes [Nielsen *et al.*, 2009], which display highly fractionated and contrasting Tl isotope compositions [Nielsen *et al.*, 2006; Rehkämper *et al.*, 2002, 2004]. These output fluxes are scavenging by the authigenic phases of pelagic clays and uptake of Tl during low temperature alteration of oceanic crust. Thallium is supplied to the oceans by rivers, hydrothermal fluids, volcanic emanations, mineral aerosols, and pore water fluxes from continental margin sediments, all of which show essentially identical and relatively unfractionated Tl isotope compositions [Baker *et al.*, 2009; Nielsen *et al.*, 2005, 2006, 2009] and are therefore unlikely to drive significant seawater Tl isotope

changes [Nielsen *et al.*, 2009]. However, very little is actually known about seawater Tl isotope evolution over the Cenozoic (i.e., the past 65 Myr). Although the Tl isotope composition of seawater is fractionated from that of modern Fe-Mn crusts by $\alpha \sim 1.002$ [Rehkämper *et al.*, 2002, 2004] these have, by assuming a time-independent isotope fractionation factor, thus far been our best tool in reconstruction of seawater Tl isotopes. In a recent study, two detailed Fe-Mn crust records from the Pacific indicated that despite large temporal Tl isotope variation, this ocean basin remained homogeneous throughout the Cenozoic [Nielsen *et al.*, 2009], which is consistent with the current best estimate of the marine Tl residence time of ~20 ka [Rehkämper and Nielsen, 2004]. However, the remaining temporal Tl isotope data for seawater is from Fe-Mn crusts that are either too poorly dated or not sampled at sufficiently high resolution [Rehkämper *et al.*, 2004] to provide constraints on the overall homogeneity of Tl isotopes in seawater through the Cenozoic.

[7] In this study we determined a high-resolution Tl isotope profile through the hydrogenetic Fe-Mn crust Antipode 109D-C (hereafter 109D-C). This crust, which is from the Madagascar Rise in the Southwest Indian Ocean (27°58'S, 60°48'E), was recovered from a water depth of 5689–5178 m. It has previously been dated with a combination of Be isotopes and Co flux modeling [Frank *et al.*, 1999; O'Nions *et al.*, 1998] and it was estimated that the base of the crust has an age of ~15 Ma [Frank *et al.*, 1999]. In addition, 109D-C has also been investigated for Nd, Pb and Hf isotopes [O'Nions *et al.*, 1998; Piotrowski *et al.*, 2000]. We have also obtained Os isotopes for splits of the same samples to obtain a more accurate age model for this crust and in addition we determine Os isotope compositions of well-dated sediments from ODP leg 121 Site 756B from the Ninetyeast Ridge in the southeastern Indian Ocean in order to compare with the Os isotopes determined in 109D-C.

[8] The aim of this study is to relate the isotopic evolution of Tl in the Indian Ocean with those determined already for the Pacific and Atlantic Oceans [Nielsen *et al.*, 2009; Rehkämper *et al.*, 2004], and thereby obtain information about the large-scale heterogeneity of seawater for Tl over the age range of 109D-C. We also use the new age information obtained from Os isotopes to reevaluate the interpretations previously made for the Nd, Hf, and Pb isotope records preserved by this crust.

2. Sampling, Sample Preparation, and Isotopic Analyses

[9] The piece of 109D-C studied here has a total thickness of ~36 mm. It was sampled at 1 mm intervals with a dental drill connected to a manual stage yielding a total of 36 samples. For each sample several mg of sample was extracted in order to have sufficient material to carry out Tl and Os isotope composition measurements on aliquots of the same powder. This was achieved by dissolving each sample in 1 M HCl on a hotplate overnight and taking out a minor split of the dissolved sample (~5%) for Tl isotope analysis. The remainder of the sample was used for Os isotope analysis.

[10] The sediments from Site 756 studied here dominantly comprise pelagic carbonate (nanofossil ooze) usually between 93 and 95% CaCO_3 [Peirce *et al.*, 1989]. Recent work has

Table 1. Os and Tl Isotope Data in 109D-C^a

Depth (mm)	[Os] (ppt)	[Re] (ppt)	¹⁸⁷ Os/ ¹⁸⁸ Os	ε ²⁰⁵ Tl
1	2036	105	1.011	15.3
2	2278	195	1.002	15.3
3	1860	158	0.982	15.4
4	2019	212	0.974	14.9
5	1702	na	0.985	14.7
6	1750	217	0.880	13.5
7	1402	189	0.921	13.2
8	1185	213	0.943	12.6
9	1794	139	0.860	12.4
10	1501	77	0.900	12.1
11	1440	253	0.896	11.5
12	1831	172	0.892	na
13	2263	202	0.889	11.5
14	2721	173	0.788	11.6
15	2046	75	0.867	11.7
16	1971	180	0.866	11.8
17	1698	143	0.771	11.4
18	1734	139	0.868	11.8
19	1797	147	0.871	na
20	2045	141	0.869	11.7
21	1595	197	0.867	na
22	1867	119	0.866	11.7
23	1826	166	0.843	na
24	1913	142	0.848	11.3
25	2000	85	0.853	na
26	1786	152	0.796	11.8
27	1500	125	0.850	na
28	1427	160	0.861	11.4
29	1335	136	0.845	na
30	1552	181	0.763	11.2
31	1579	173	0.758	na
32	1281	200	0.868	10.9
33	1103	168	0.873	na
34	1087	156	0.863	11.3
35	1063	154	0.866	na
36	955	288	0.882	11.3

^aThe entries marked “na” were not analyzed.

shown that bulk dissolution of such carbonates yields a dominantly hydrogenous Os isotope signal [Dalai and Ravizza, 2006] even when carbonate contents are much lower [Burton et al., 2010]. Consequently, the bulk sediments studied here were simply powdered and dissolved in 3 N HCl, and insoluble silicates were removed by centrifugation prior to chemical separation of Re and Os.

[11] Techniques for the chemical separation of Tl and Os from sample matrix are identical to those employed in a previous study [Nielsen et al., 2009], which are based on procedures developed elsewhere [Birck et al., 1997; Nielsen et al., 2004; Rehkämper and Halliday, 1999].

[12] The Tl isotope compositions were determined at University of Oxford on a Nu Plasma HR-MC-ICPMS. Previously described techniques that utilize both external normalization to NIST SRM 981 Pb and standard-sample bracketing were applied for mass bias correction [Nielsen et al., 2004; Rehkämper and Halliday, 1999]. Thallium isotope compositions are reported relative to the NIST SRM 997 Tl standard in parts per 10,000 such that

$$\varepsilon^{205}\text{Tl} = 10,000 \times \left(\frac{{}^{205}\text{Tl}/{}^{203}\text{Tl}_{\text{sample}}}{{}^{205}\text{Tl}/{}^{203}\text{Tl}_{\text{SRM 997}}} - 1 \right) \quad (1)$$

The uncertainty of the Tl isotope measurements is estimated to be ~0.4 ε²⁰⁵Tl units. Thallium procedural blanks were <3 pg throughout this study, which is insignificant compared to the amounts of Tl processed (>5 ng).

[13] Osmium isotopes were measured at University of Oxford (Fe-Mn crusts) and Clermont-Ferrand (sediments) with a Thermo-Finnigan TRITON[®] thermal ionization mass spectrometer on high-purity Pt filaments using the ion counting electron multiplier. Rhenium concentrations for the Fe-Mn crusts were determined on the Nu Plasma HR-MC-ICPMS at the Oxford University using Ir for mass fractionation correction [Klemm et al., 2005].

[14] Two and three osmium blanks were run in Oxford and Clermont-Ferrand, respectively, as part of this study. The blanks in Oxford exhibited ¹⁸⁷Os/¹⁸⁸Os = 0.481 and [Os] = 0.020 pg and ¹⁸⁷Os/¹⁸⁸Os of 0.384 and [Os] = 0.039 pg. The blanks in Clermont-Ferrand possessed ¹⁸⁷Os/¹⁸⁸Os = 0.480 and [Os] = 0.030 pg; ¹⁸⁷Os/¹⁸⁸Os = 0.421 and [Os] = 0.032 pg; and ¹⁸⁷Os/¹⁸⁸Os = 0.325 and [Os] = 0.022 pg. The blank corrections were between 0.1% and 0.4%. The mean ¹⁸⁷Os/¹⁸⁸Os ratio for 35 pg JM standard yielded 0.17424 ± 0.00033 (2 sd, n = 6).

3. Results and Data Outliers

[15] The measured Os and Tl isotope data for 109D-C and Os isotope data from ODP Site 756B are shown in Tables 1 and 2 and are plotted against the sampling depth in Figures 1 (top), 1 (bottom), and 2. Both isotope systems display steadily decreasing values from the top of the crust to a depth of ~12 mm after which they are both largely invariant. Our Tl isotope data differ slightly (by ~1–2 ε²⁰⁵Tl unit) from two out of three previous analyses in 109D-C [Rehkämper et al., 2004]. However, due to the much larger and systematic data set presented here and because the previous analyses are almost within error, we will consider only the measurements made in this study.

[16] For the Os isotope ratios, seven samples from 109D-C and sample 5H-3-W 100-105 display “excursions” toward more unradiogenic values (Figures 1 (top) and 2). These can be explained either by changes in the isotope composition of seawater or some form of contamination. Previous studies have reported short intervals of marked change in the Os isotope composition of seawater as a response to short-term changes in weathering, volcanic activity, or meteorite impacts [Oxburgh, 1998; Oxburgh et al., 2007; Paquay et al., 2008;

Table 2. Osmium Isotope Data From ODP Site 756B^a

Core ID	Depth (mbsf)	Age (Ma)	¹⁸⁷ Os/ ¹⁸⁸ Os	[Os] (ppt)
1H-2-W 100-105	2.5	2.0	1.014	5.23
3H-2-W 100-105	20.6	5.6	0.856	7.21
3H-4-W 100-105	23.6	6.3	0.833	11.6
3H-6-W 100-105	26.6	6.9	0.804	7.23
4H-2-W 100-105	30.2	7.7	0.821	7.12
4H-4-W 100-105	33.2	8.4	0.799	8.93
5H-1-W 100-105	38.3	10.2	0.783	6.28
5H-3-W 100-105	41.3	11.8	0.321	22.14
5H-4-W 100-105	42.8	12.6	0.762	6.53
5H-5-W 100-105	44.3	13.5	0.857	7.47
6H-2-W 100-105	49.4	15.4	0.622	5.73

^aAges based on biostratigraphy as outlined by Peirce et al. [1989].

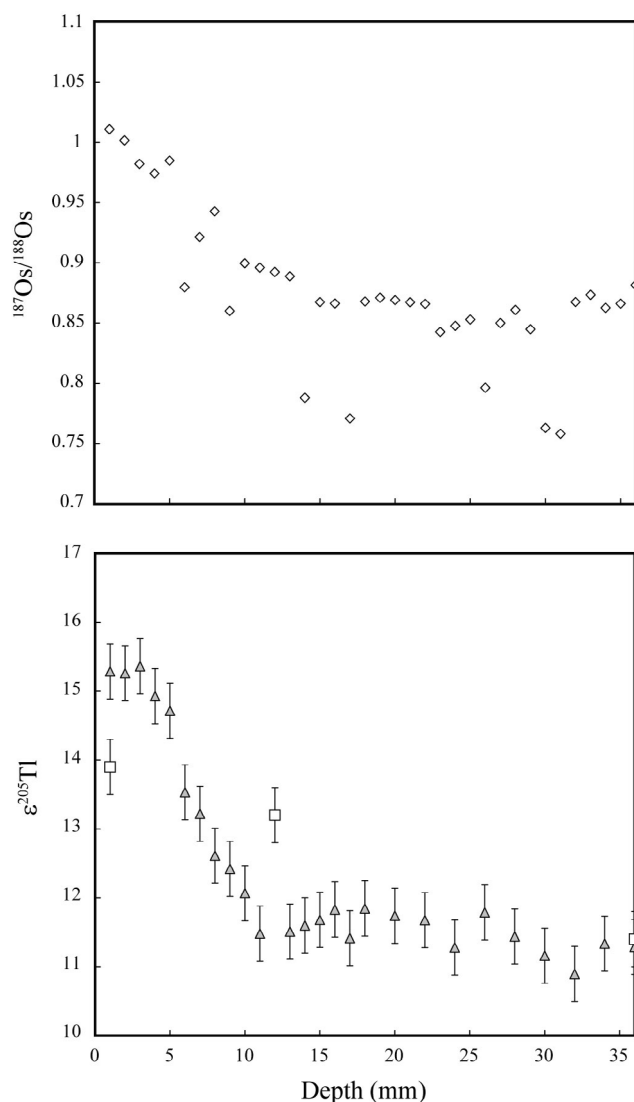


Figure 1. (top) Osmium and (bottom) thallium isotope compositions plotted against depth in crust 109D-C. The squares in Figure 1 (bottom) are previously published analyses from the same crust [Rehkämper *et al.*, 2004].

Ravizza *et al.*, 2001; Ravizza and Peucker-Ehrenbrink, 2003]. The anomalies observed here could be explained in such a way, but no previous study of the marine Os isotope record has identified similar excursions to have occurred over the past ~15 Ma [Klemm *et al.*, 2005, 2008; Pegram and Turekian, 1999; Peucker-Ehrenbrink *et al.*, 1995; Ravizza, 1993], which is the current best age estimate for 109D-C [Frank *et al.*, 1999]. Alternatively, these anomalies may reflect the presence of micro meteorites in the Fe-Mn crust and sediment. Meteorite contamination corrections are often applied for bulk sediments [Esser and Turekian, 1988; Pegram and Turekian, 1999] and considering the anomalously high [Os] observed in 5H-3-W 100-105 there is little doubt that the unradiogenic isotope signature of this sample is caused by such contamination. Though extraterrestrial material is clearly present in Fe-Mn crusts [Basu *et al.*, 2006], it is not normally considered likely to perturb the overall Os budget, because of the

high Os concentrations, low amounts of detrital material, and therefore low trapping efficiency of extraterrestrial material [Basu *et al.*, 2006; Peucker-Ehrenbrink and Ravizza, 2000]. However, it has previously been suggested that extraterrestrial material could account for a significant fraction of the Os in some Fe-Mn crusts [Burton *et al.*, 1999a; Palmer *et al.*, 1988]. Additionally, 109D-C has an unusually high abundance of detritus [Frank *et al.*, 1999] implying that the likelihood of trapping a micrometeorite might be higher, especially at sample depths >14 mm, which is also where the majority of the Os isotope anomalies occur (Figure 1, top). We can estimate how much meteoritic material is required to produce the observed anomalies by using the average concentration and isotope composition of Os in chondritic meteorites of [Os] ~ 600 ng/g and $^{187}\text{Os}/^{188}\text{Os} \sim 0.128$ [Walker *et al.*, 2002]. Assuming a spherical meteorite and a density of 3 g/cm³ each excursion observed can be produced by the addition of one micrometeorite with a diameter of 10–15 μm . We therefore conclude that the Os isotope anomalies in sediment sample 5H-3-W 100-105 and crust 109D-C most likely originate from the addition of very small amounts of cosmic dust and do not reflect the isotope composition of seawater.

[17] The apparent higher occurrence of micro meteorites in the Fe-Mn crust compared with the sediments from ODP Site 756B (Figures 1 (top) and 2) is most likely due to the fact that we have sampled the entire crust continuously, whereas we only cover ~1% of the depth of the ODP Site 756B sediment core. The different coverage in combination with the random nature of encountering a single micrometeorite makes it impossible to assess the relative accumulation of extraterrestrial material at the two sites.

[18] These small amounts of cosmic dust would not affect the Tl isotope composition of 109D-C because the Tl concentrations in chondrites are at least 3 orders of magnitude lower than in Fe-Mn crusts [Baker *et al.*, 2010; Hein *et al.*, 2000; Rehkämper *et al.*, 2002; Wasson and Kallemeyn, 1988]. In addition, the Tl isotope compositions of chon-

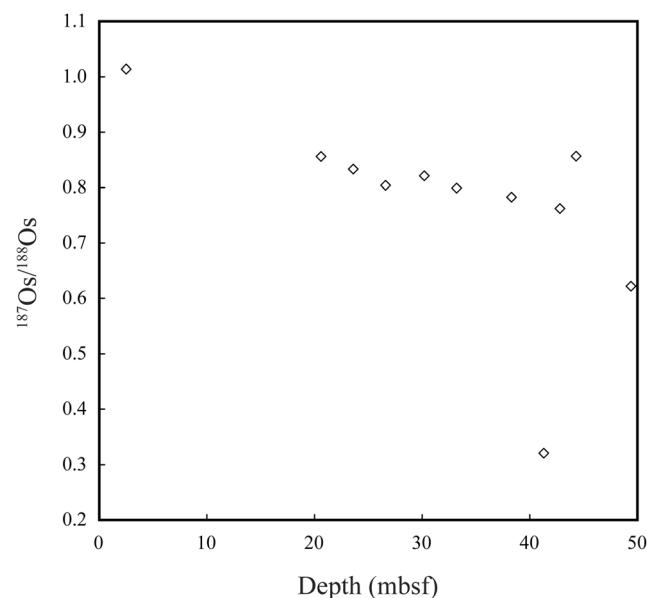


Figure 2. Osmium isotope compositions in nanofossil ooze samples from ODP Hole 756B plotted against depth.

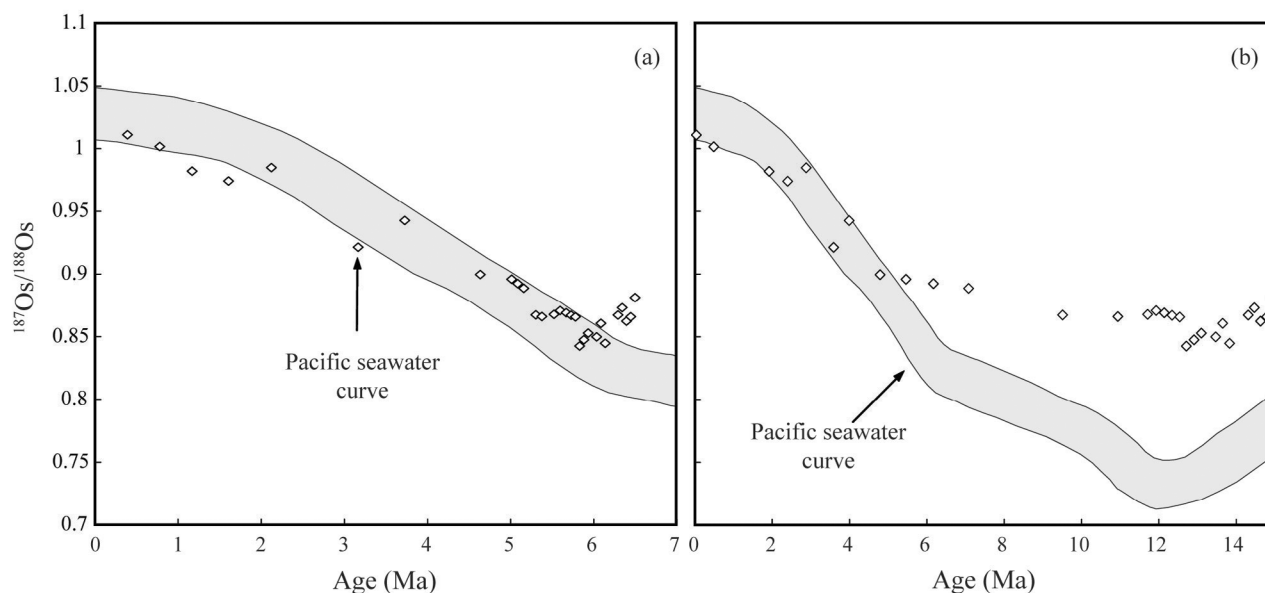


Figure 3. Osmium isotopes in 109D-C plotted versus (a) age model using Os isotope stratigraphy and ^{10}Be ages (b) age model using combined Co-flux and ^{10}Be ages. Grey areas denote the curves (including error envelope) observed in the Pacific Ocean. Samples that have been identified as contaminated with meteorite Os have been filtered out.

drites differ by $<0.2\%$ compared to Fe-Mn crusts [Baker *et al.*, 2010; Rehkämper *et al.*, 2002].

4. Age of 109D-C

[19] Two studies have published age models for 109D-C [Frank *et al.*, 1999; O’Nions *et al.*, 1998]. Based purely on ^{10}Be measurements O’Nions *et al.* [1998] concluded that the base of 109D-C had an age of ~ 25 Ma, though one analysis at a depth of ~ 17 mm suggested that the growth rate in the bottom half of the crust may be significantly higher than the upper part. Subsequently, Frank *et al.* [1999] presented a more detailed age model that combined the older ^{10}Be data with Co-flux modeling, which confirmed that the growth rate in the lower section of the crust is higher and derived a revised estimate of the age at the base of ~ 15 Ma.

[20] In recent years, several studies have utilized Os isotopes as a new method of Fe-Mn crust dating by comparing the crust Os isotope stratigraphy to an age calibrated seawater curve [Burton, 2006; Fu *et al.*, 2005; Klemm *et al.*, 2005, 2008]. As such, the new Os isotope data presented here can be applied in a similar manner to obtain an independent measure of the growth history of 109D-C. Figure 3a shows the Os isotope data plotted using the age model that provides the best fit between the Pacific osmium isotope seawater curve and the 109D-C data while still being consistent with previous ^{10}Be data [O’Nions *et al.*, 1998]. With this age model the bottom of the crust has an age of ~ 6.5 Ma and has a growth history where the lowermost ~ 27 mm grew in ~ 1.5 Ma, which corresponds to an average growth rate of ~ 18 mm/Myr. This is more than ten times faster than the most recent layers and about a factor of three faster than the growth rates inferred for the bottom half of 109D-C from Co flux modeling [Frank *et al.*, 1999]. Growth rates for deepwater hydrogenetic

Fe-Mn crusts are usually <5 mm/Myr [Claude-Ivanaj *et al.*, 2001; Eisenhauer *et al.*, 1992; Henderson and Burton, 1999; Segl *et al.*, 1989], but examples of growth rates up to ~ 20 mm/Myr have been documented [Segl *et al.*, 1989], but some of those may have a hydrothermal component. Though the Co-flux model carries significant uncertainties and can be somewhat inaccurate [Klemm *et al.*, 2008; Nielsen *et al.*, 2009] it is surprising that it would produce errors as large as those implied by the Os isotope stratigraphy in 109D-C (Figures 3a and 3b). Furthermore, there is a significant correlation between the Os concentration data and the growth rates determined by Frank *et al.* [1999] (Figure 4a), whereas there is no correlation between Os concentrations and the growth rates produced by the ^{10}Be -Os isotope stratigraphy age model. In fact, the sample with the highest Os abundance is situated in the section of the crust that according to the ^{10}Be -Os isotope stratigraphy age model has a growth rate of ~ 14 mm/Myr (Figure 4b). High growth rates of hydrogenetic Fe-Mn crusts are expected to produce significantly diluted trace element concentrations. This is because it is assumed that the short residence times of Fe and Mn allow for local supply rates of these elements to dictate the crust growth rate whereas elements with significantly longer residence times (e.g., Os and Co) are presumed to be supplied at a constant rate. Using this line of argument the relatively high Os concentrations observed in the lower section of 109D-C appear inconsistent with the extreme growth rates inferred from Os isotope stratigraphy. High growth rates are commonly observed in Fe-Mn deposits of hydrothermal origin and it may therefore be suspected that the lower sections of 109D-C have a hydrothermal component. However, neither major elements (Fe/Mn does not change significantly [Frank *et al.*, 1999]) nor radiogenic Pb or Hf isotopes [O’Nions *et al.*, 1998; Piotrowski *et al.*, 2000] would imply input from a hydrothermal source.

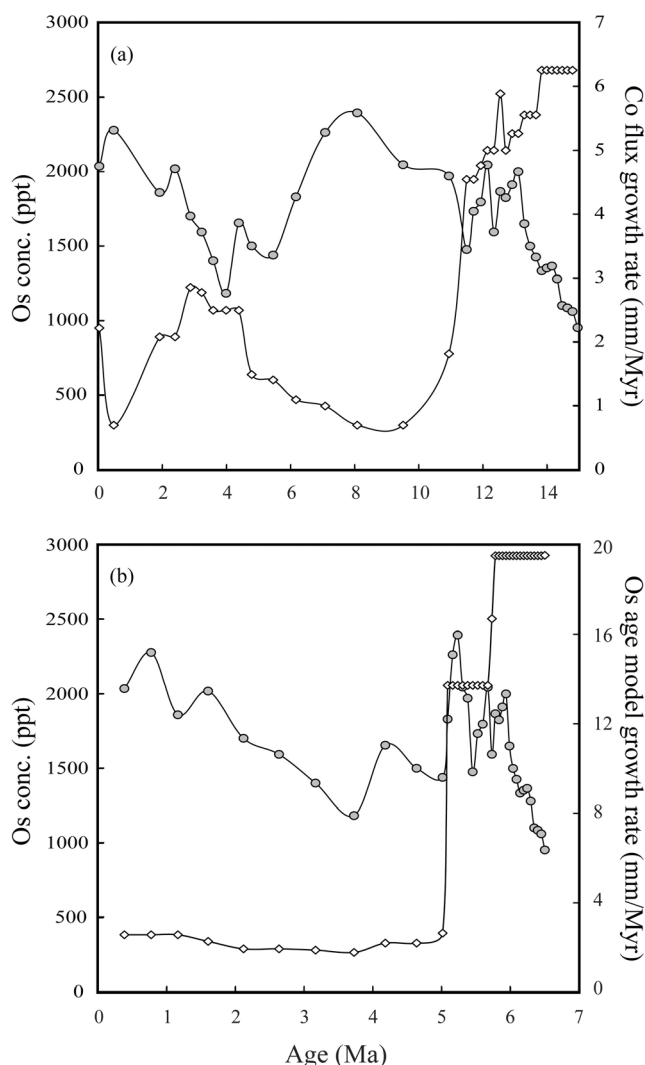


Figure 4. Osmium concentrations (filled grey circles) and crust growth rates (open diamonds) plotted against age. (a) The age model used is that of Frank *et al.* [1999], and it can be seen that there is a reasonable inverse correlation between Os concentration and growth rate. (b) The age model used is that obtained via Os isotope stratigraphy as shown in Figure 3. Osmium concentrations have been corrected for their meteorite component by assuming uncontaminated sample displayed Os isotope composition between adjacent samples.

[21] Alternatively, it could be argued that the combined Be and Co-flux age model gives the most accurate growth history for crust 109D-C and hence the base has an age of ~15 Ma. It can be seen that this age model results in a significantly more radiogenic Os isotope composition for the Indian Ocean than the Pacific during the interval ~6–15 Ma (Figure 3b), which is not expected considering the long residence time of Os and largely uniform isotope composition of the modern oceans [Levasseur *et al.*, 1999; Sharma *et al.*, 1997]. In order to constrain the Os isotope composition of the Indian Ocean over the last 15 Myr we determined $^{187}\text{Os}/^{188}\text{Os}$ for a number of nannofossil ooze samples from the ODP Hole 756B on the Ninetyeast Ridge

in the southeastern Indian Ocean. The ages of these samples are determined using biostratigraphy [Peirce *et al.*, 1989] and are therefore considerably more accurate than age models for Fe-Mn crusts. It is evident that $^{187}\text{Os}/^{188}\text{Os}$ ratios in the southeastern Indian Ocean since 15 Ma are indistinguishable from records obtained in the Pacific (Figure 5). The data from ODP Site 756B are also consistent with Os isotope measurements for carbonate ooze samples from ODP Site 758 [Klemm *et al.*, 2005], which strongly suggests that the Os isotope composition of the Indian Ocean (or at least the eastern part) has not been significantly different to that of the Pacific since 15 Ma. In the absence of evidence that the western Indian Ocean could have been almost isolated from the eastern Indian Ocean between 15 and 6 Myr ago, it is most reasonable to infer that the base of 109D-C has an age of 6.5 Ma. This age estimate is still consistent with ^{10}Be dating of 109D-C [O'Nions *et al.*, 1998] as a single data point in the middle of the crust, which was originally ignored as it was thought to be altered from its true value, yielded an age in agreement with the Os age model.

[22] It should be noted that the Os isotope composition of 109D-C in the bottom 5 mm appears to record a slight increase, which is contrary to the decline of the Pacific seawater curve (Figure 3a). This offset is relatively small and might not be significant with respect to data uncertainty. Alternatively, it is possible that 109D-C grew in two directions during the earliest stages of crust growth. Since 109D-C was dredged from the seafloor and recovered without a substrate it is not possible to rule out this possibility. Additionally, all other isotope records (Hf, Nd, Pb and Tl) display no variation in the affected depth interval [O'Nions *et al.*, 1998; Piotrowski *et al.*, 2000], and hence these isotope systems could be consistent with a slightly younger maximum age. A similar interpretation has also previously been used for some Atlantic crusts [Reynolds *et al.*, 1999]. For 109D-C this would not alter the inferred age substantially as the oldest point in the crust would have an age of ~6 Ma (instead of 6.5 Ma).

[23] There are several consequences of the young age obtained for 109D-C. First, it is evident that Co-flux models may produce much more inaccurate ages than was previously thought. The direct conclusion must be that the assumption of a constant Co flux into Fe-Mn crusts almost independent of growth rate is not correct. The data for 109D-C suggest that at least in some cases there may be a strong coupling between Fe-Mn crust growth rate and amount of Co supplied from the water column. Considering the clear relationship between [Os] and Co-derived growth rates (Figure 4a) it might also be inferred that this applies to other trace metals and that trace element concentrations in Fe-Mn crusts in general are not necessarily indicative of growth rate. This, of course, does not mean that Co-flux modeling will always produce erroneous results but based on the data presented here it will be very difficult to distinguish the cases where Co dating is accurate from those that are not. Second, the large age difference between the Co-based and Os isotope-based ages implies that some of the interpretations previously made on records of Hf, Nd, and Pb isotopes in 109D-C [O'Nions *et al.*, 1998; Piotrowski *et al.*, 2000] are no longer valid. In particular, it is clear that we can no longer use the isotopic records of

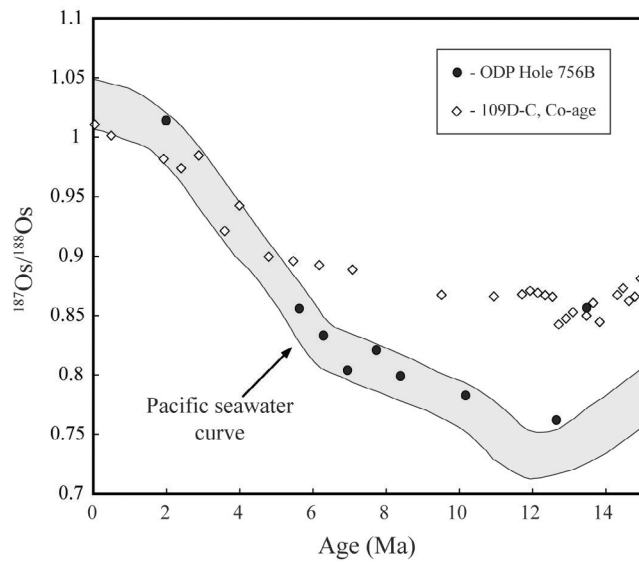


Figure 5. Osmium isotope composition of ODP Hole 756B sediments plotted versus age. Also shown are Os isotopes in 109D-C using Co-flux age model and Os isotope curve from the Pacific Ocean (grey band). It is evident that Os isotopes in the Indian Ocean do not appear to have been significantly different to the Pacific Ocean over the last ~15 Ma, rendering the Co-flux age model highly unlikely.

109D-C to infer the long-term isotopic evolution of the Southern Indian Ocean [Frank and O’Nions, 1998; Gourlan *et al.*, 2008; Piotrowski *et al.*, 2000; van de Flierdt *et al.*, 2004c]. Below we will first compare the Tl isotope record of 109D-C with those obtained in the Pacific and Atlantic Oceans and then discuss the implications of the younger age of 109D-C on the Hf, Nd, and Pb isotope records previously published.

5. Thallium Isotope Records in Fe-Mn Crusts

5.1. Comparison of Ocean Basins and Implications for Tl Isotopes in Seawater

[24] Using the Os isotope age model we can construct the temporal Tl isotope variability in 109D-C (Figure 6). The most notable feature of the Tl isotope record presented here for 109D-C is the strong resemblance to the records obtained in the Pacific (Figure 6). There is a small offset from the Pacific record at 2–0 Ma and 7–5 Ma, but these are only just outside analytical reproducibility. It is possible to explain the offset at 7–5 Ma with small inaccuracies in the applied age models caused by differential growth rates of the Fe-Mn crusts [Nielsen *et al.*, 2009]. Last, it should also be kept in mind that the Tl isotope composition of modern Fe-Mn crusts from the Pacific and Indian Oceans vary by ~2 $\epsilon^{205}\text{Tl}$ units [Rehkämper *et al.*, 2002] and thus it is not realistic to infer isotopic differences between ocean basins based on the smaller temporal offsets observed between 109D-C and the Pacific crusts. Assuming that the isotope fractionation factor between seawater and Fe-Mn crusts has remained relatively constant, we can infer that the Indian and Pacific Oceans have remained well mixed and homogeneous with respect to Tl isotopes over the last ~6.5 Myr. Two

Fe-Mn crust records from the Atlantic (samples BM1969.05 and ALV539) show slightly disparate temporal Tl isotope patterns (Figure 6), with modern values about 2–3 $\epsilon^{205}\text{Tl}$ units lower than the Indian and Pacific Oceans followed by convergence toward the values of the Indian and Pacific Oceans at ~5 Ma [Rehkämper *et al.*, 2004]. Even though these crusts may have experienced periods of disturbance or large changes in crust growth [Frank *et al.*, 1999; Klemm *et al.*, 2008] there is little evidence to suggest that the younger sections (<10 Ma) were affected by such processes [Frank *et al.*, 1999; O’Nions *et al.*, 1998]. A more definitive Fe-Mn crust Tl isotope curve for the Atlantic Ocean might be obtained by analyses of crust ROM46 from the central Atlantic, which appears to have a relatively simple growth history for the last ~15 Ma [Klemm *et al.*, 2008].

[25] In general, the Tl isotope compositions of Fe-Mn crust surfaces are ~2 $\epsilon^{205}\text{Tl}$ units lower in the North Atlantic compared with the Pacific and Indian Oceans [Rehkämper *et al.*, 2002] supporting the suggestion of a temporal difference between Atlantic and Indian/Pacific Fe-Mn crusts (Figure 6). Assuming that the Tl isotope fractionation factor between seawater and Fe-Mn crusts is currently invariant, and has been for the last ~7 Ma [Nielsen *et al.*, 2009], then this would suggest that the Tl isotope composition of the Atlantic Ocean is presently not identical to the Pacific and Indian Oceans. Four seawater samples from a depth profile in the Pacific yield very homogenous values of $\epsilon^{205}\text{Tl} = -6$ [Nielsen *et al.*, 2006]. If the Tl isotope fractionation factor between Fe-Mn crusts and seawater is constant throughout the oceans, the Atlantic Ocean should thus display $\epsilon^{205}\text{Tl} \sim -8$. To date only two coastal Atlantic seawater samples have been analyzed for Tl isotopes yielding values of $\epsilon^{205}\text{Tl} = -5.5$ and -9.0 [Nielsen *et al.*, 2004] and it is therefore unclear if the oceans today are completely homogenous. Ocean basin–

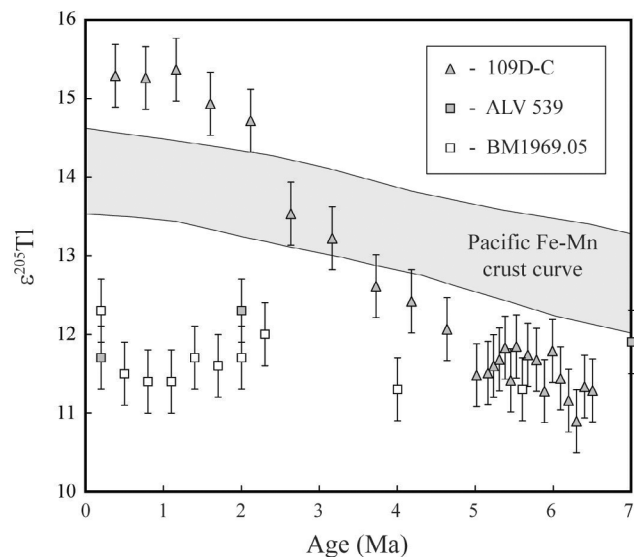


Figure 6. Thallium isotope compositions in 109D-C plotted against the Os isotope stratigraphy age. The Pacific Ocean curve is denoted with a grey band [Nielsen *et al.*, 2009]. Also shown are two records from the Atlantic Ocean [Rehkämper *et al.*, 2004], which display an invariant curve since 7 Ma.

scale differences in Tl isotopes are not expected due to the inferred residence time for Tl of ~ 20 ka [Baker *et al.*, 2009; Nielsen *et al.*, 2009; Rehkämper and Nielsen, 2004], but only further investigations of Tl isotopes in seawater and Fe-Mn crusts from different ocean basins will reveal the extent of Tl isotope homogeneity in the oceans and enable more exact models of Tl isotope cycling in the marine environment today and over the last 5–10 Ma.

5.2. Causes of Tl Isotope Variations in Fe-Mn Crusts Over the Last ~ 7 Myr

[26] Following the conclusions of previous investigations of Tl isotopes in Fe-Mn crusts [Nielsen *et al.*, 2009; Rehkämper *et al.*, 2004], the small increase in $\epsilon^{205}\text{Tl}$ observed in crusts from the Indian and Pacific Oceans from ~ 6 Ma to today (Figure 6) appears to be a consequence of a similar change in the Tl isotope composition of seawater. Though the crusts from the Atlantic may imply that seawater is not entirely homogenous, we can qualitatively infer that this shift happened on a semiglobal scale as the Pacific and Indian Oceans account for the majority of the total ocean volume. Previous studies have argued that such changes are most likely caused by altering the ratio of the two principal marine Tl output fluxes. These are scavenging by the authigenic phases of pelagic clays and uptake of Tl during low temperature alteration of oceanic crust, and these fluxes display $\epsilon^{205}\text{Tl}$ values higher and lower than seawater, respectively [Nielsen *et al.*, 2006; Rehkämper *et al.*, 2002]. Assuming that the isotope fractionation factors for the output fluxes have remained constant [Nielsen *et al.*, 2009], we can calculate how much the ratio between the two output fluxes has changed since ~ 7 Ma by using the steady state equation derived by Nielsen *et al.* [2009]:

$$\epsilon_{\text{SW}} = \epsilon_{\text{IN}} - \Delta_{\text{AU}} + (\Delta_{\text{AU}} - \Delta_{\text{AB}})/((F_{\text{AU}}/F_{\text{AB}}) + 1), \quad (2)$$

where F_{AU} , and F_{AB} are the authigenic and altered basalt output fluxes, respectively; ϵ_{SW} and ϵ_{IN} are the isotope compositions of seawater and the total input fluxes, respectively; and Δ_{AU} and Δ_{AB} are the isotopic differences between seawater and authigenic phases and seawater and altered basalts, respectively. It should be noted that Δ_{AU} is not identical to the isotope fractionation factor between seawater and Fe-Mn crusts as pelagic sediments and other types of Fe-Mn deposits than hydrogenetic crusts display somewhat lower and variable $\epsilon^{205}\text{Tl}$ [Rehkämper *et al.*, 2002, 2004]. Equation (2) also assumes that the oceans are at steady state and homogenous, which considering the Fe-Mn crust records from the Atlantic Ocean may not be the case. However, a general increase in the Tl isotope composition of seawater would be consistent with a concomitant decrease in $F_{\text{AU}}/F_{\text{AB}}$.

[27] Recently, Nielsen *et al.* [2009] proposed that the Tl isotope composition of seawater in the early Eocene was mainly controlled by changes in the rate of Fe-Mn precipitation (i.e., F_{AU}). This could in turn be driven by the degree to which Fe and Mn are utilized biologically and buried with organic carbon, such that high rates of organic carbon burial suppress inorganic Fe-Mn precipitation. This hypothesis is supported by the strong covariation observed for Tl and sulfur (S) isotopes in the early Cenozoic because the S cycle

is known to be strongly dependent on changes in marine organic carbon burial. The small Tl isotope increase observed in the record for ~ 7 Ma to today (Figure 6) could in principle be explained in the same way, hence implying that marine organic carbon burial rates have increased since the late Miocene, at least in the Indian and Pacific Oceans. However, this is in stark contrast to carbon burial rates calculated based on the marine C isotope record, which display a decrease over the last ~ 5 Ma [Kurtz *et al.*, 2003]. Additionally, the Tl and S isotope records have diverged for the last 5–8 Ma [Nielsen *et al.*, 2009; Paytan *et al.*, 1998] as seawater $\delta^{34}\text{S}$ has decreased by $\sim 0.8\%$. Hence, the strong coupling of the Tl and S cycles in the early Cenozoic appears to have been reversed since the late Miocene thus arguing against organic carbon burial as an explanation for the Pliocene Tl isotope shift observed in Fe-Mn crusts.

[28] Alternatively, the Tl isotope shift could have been caused by increased hydrothermal deposition of Tl in the oceanic crust. This parameter is most likely controlled by the magnitude of hydrothermal circulation, which in turn must be dictated by the rate of ocean crust production. Reconstructions of ocean crust production can often diverge significantly from each other [Cogné and Humler, 2004, 2006; Kaiho and Saito, 1994; Larson, 1991; Rowley, 2002; Xu *et al.*, 2006], but a few of the more recent studies appear to agree that the last 10 Ma has seen an increase in crust production of ~ 30 – 40% [Cogné and Humler, 2004, 2006; Kaiho and Saito, 1994]. In addition, it was shown by Cogné and Humler [2006] that the increased ocean crust production occurred mainly in the Indian and Pacific Oceans, whereas the Atlantic has remained constant over the last ~ 20 Ma. If this is correct, it could potentially explain the observed Tl isotope shift and it may also be consistent with the isotopic divergence that might have occurred between the Indian/Pacific and Atlantic Oceans. In addition, the increased ocean crust production might also account for the small S isotope dip seen in the Pliocene [Paytan *et al.*, 1998] because of the resulting increase in the supply of isotopically light S to the oceans. However, our conclusion will remain tentative until further studies on Tl isotopes have determined the extent of Tl isotope homogeneity in the oceans today and in the past.

6. Implications of the Young Age of 109D-C for Hf, Nd, and Pb Isotope Records

6.1. Hafnium Isotopes

[29] Based on the Hf isotope records of 109D-C and the Central Indian Ocean Fe-Mn crust SS663, it was concluded that the Indian Ocean bottom waters displayed a Hf isotope gradient in the Miocene, which was inferred to have been caused by incomplete mixing of unradiogenic North Atlantic deep water (NADW) and radiogenic Pacific waters flowing through the Indonesian seaway [Piotrowski *et al.*, 2000]. However, with the new chronology of 109D-C it is evident that there is no discernible difference between the two crusts over the last 7 Myr (Figure 7a). The Fe-Mn crust records would imply that the majority of the abyssal Indian Ocean was homogenous with respect to Hf isotopes during this time and hence there is no evidence that the Hf isotope composition of the Indian Ocean was controlled by variable export of NADW. As outlined in the introduction, our limited knowledge of the behavior of isotope tracers such as

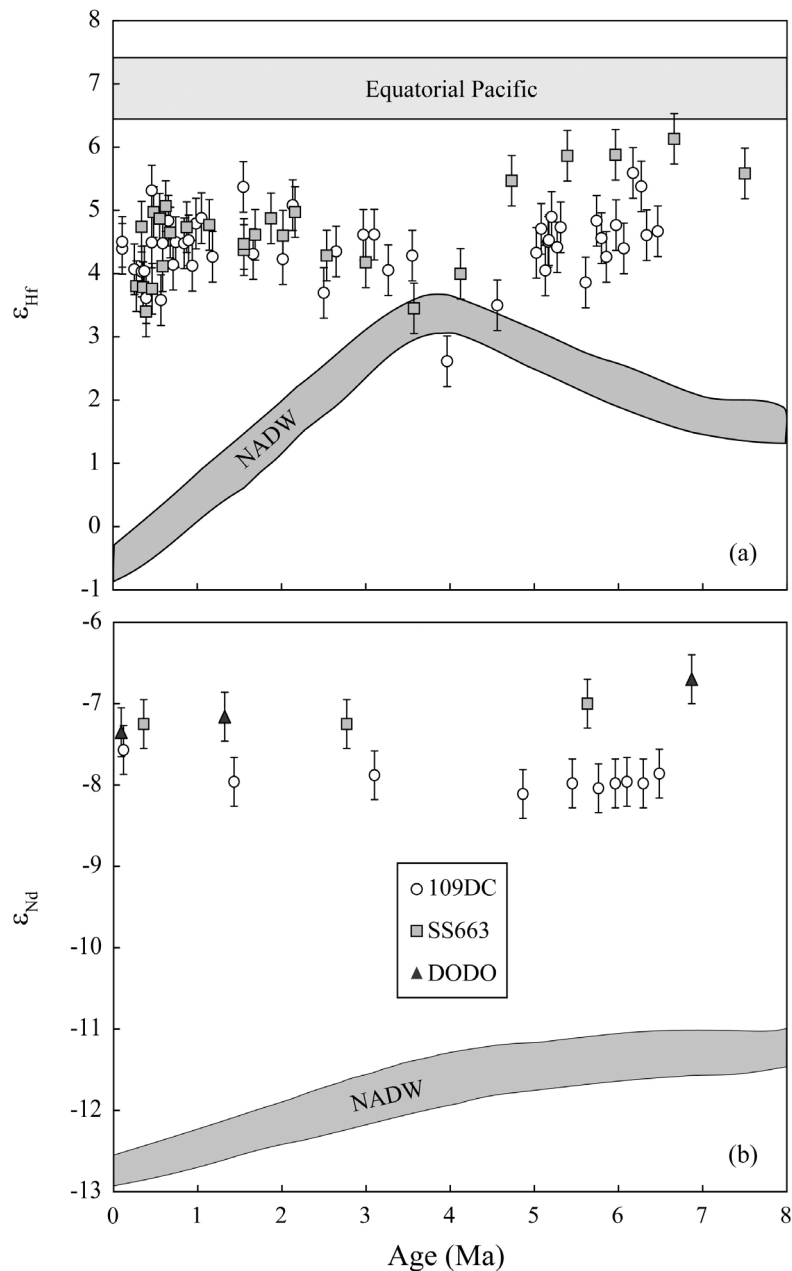


Figure 7. Previously published (a) Hf and (b) Nd isotope curves in 109D-C [O’Nions *et al.*, 1998; Piotrowski *et al.*, 2000] plotted using the new Os isotope age model. Also plotted are data from two additional Fe-Mn crusts from the North (SS663) and East (DODO) Indian Ocean [Frank *et al.*, 2006; O’Nions *et al.*, 1998; Piotrowski *et al.*, 2000]. Also shown are North Atlantic Deep Water compositions [Burton *et al.*, 1997, 1999b; O’Nions *et al.*, 1998; Piotrowski *et al.*, 2000] and equatorial Pacific for Hf isotopes [Lee *et al.*, 1999].

Hf complicates the current utility of these proxies. For example, the largely invariant Hf isotopes in the Indian Ocean are in stark contrast to the strong decrease observed in North Atlantic Fe-Mn crusts over the last 4–5 Myr (Figure 7a). This divergence could be due to a waning influence of NADW in the Indian Ocean bottom waters (IOBW) [Frank *et al.*, 2002]. However, equally, this lack of NADW signature might also be explained by the recently inferred short marine residence time of Hf [Rickli *et al.*,

2009, 2010; Zimmermann *et al.*, 2009], which may prevent the preservation of distinct isotope signatures in water masses over large distances. It is therefore, currently, not possible to use the observed Hf isotope variations as a proxy for ocean circulation. If the Hf isotope composition of the abyssal Indian Ocean is not controlled by changes in ocean circulation then an alternative explanation for the observed Hf isotope variations must be sought. Since proximal hydrothermal sources do not impose distinct Hf isotope

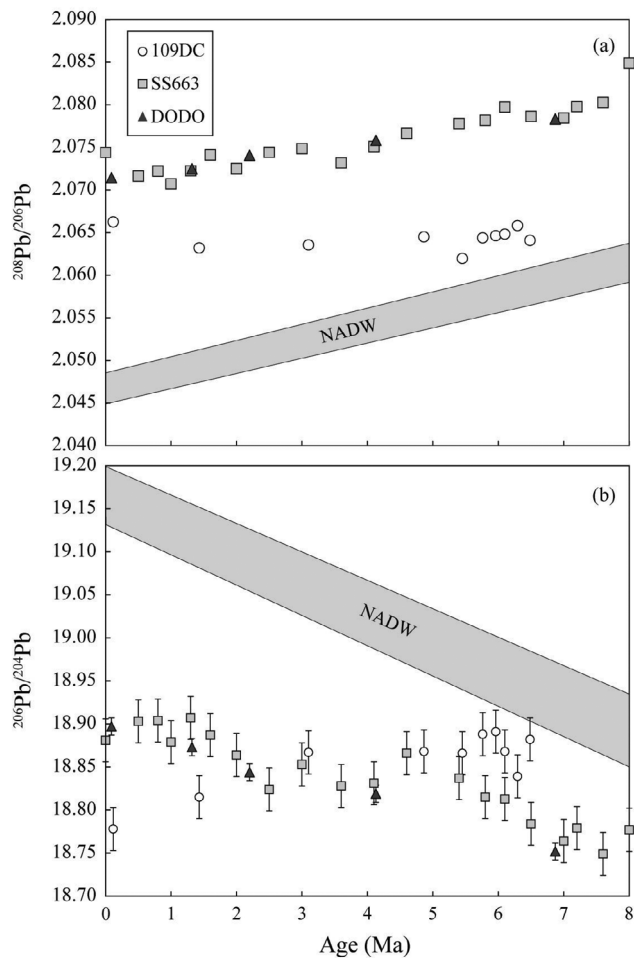


Figure 8. (a) The $^{208}\text{Pb}/^{206}\text{Pb}$ and (b) $^{206}\text{Pb}/^{204}\text{Pb}$ isotope compositions of 109D-C [O’Nions *et al.*, 1998] plotted using the new Os isotope age model. Also plotted are data from two additional Fe–Mn crusts from the North (SS663) and East (DODO) Indian Ocean [Frank and O’Nions, 1998; Frank *et al.*, 2006] as well as NADW [Burton *et al.*, 1997; O’Nions *et al.*, 1998].

signals in Fe–Mn crusts [van de Flierdt *et al.*, 2004b], it appears that changing weathering regimes or sources to the Indian Ocean are the most likely candidates to explain the striking change in Hf isotopes in IOBW ~4 Myr ago [Piotrowski *et al.*, 2000].

6.2. Neodymium and Lead Isotopes

[30] The Nd isotope composition of the deep Indian Ocean has often been considered to be dominated by influx of Southern Ocean waters [Albarède *et al.*, 1997; O’Nions *et al.*, 1998]. Using the previous chronology for 109D-C there appeared to be little or no Nd isotope gradient in the bottom waters of the Indian Ocean over the last ~15 Myr [Frank *et al.*, 1999, 2006; O’Nions *et al.*, 1998]. Application of the Os isotope age to the 109D-C Nd isotope data raises the possibility that southern IOBW was slightly less radiogenic than east and central IOBW over the last 7 Myr (Figure 7b). The records for 109D-C, SS663, and the eastern Indian Ocean crust DODO (4100 m water depth) are still

very similar and it is conceivable that the application of more conservative errors would produce no significant difference among all three records. Assuming that the Nd isotope gradient inferred for IOBW is real, this could be interpreted as reflecting the variable importance of Nd eroded from the Himalayas. However, as Himalayan sediments display $\epsilon_{\text{Nd}} \sim -15$ [France-Lanord and Michard, 1993; Galy *et al.*, 2010] and the least radiogenic Fe–Mn crust is located furthest to the south, this interpretation seems unlikely, particularly because Pb isotopes in SS663 and DODO appear to have a strong influence from Himalayan erosion whereas 109D-C does not [Frank *et al.*, 2006; O’Nions *et al.*, 1998]. Perhaps a more likely possibility is that SS663 and DODO have been influenced by minor contributions of Pacific deep waters [Albarède *et al.*, 1997] or radiogenic Nd from erosion of the Indonesian Island Arcs [Frank *et al.*, 2006], which is not registered in 109D-C as it is located much further away from these sources. This is consistent with the pattern observed in the modern Indian Ocean for Fe–Mn crusts and nodules where western samples are slightly less radiogenic than eastern samples [Albarède *et al.*, 1997].

[31] With respect to the effect of the new chronology for 109D-C on Pb isotopes, it does not significantly change the relative differences observed between the Southern and Northeastern IOBW over the last 7 Myr (Figure 8). It has been suggested that the Pb isotopes in 109D-C have been affected by export of NADW into the Indian Ocean [Frank and O’Nions, 1998]. However, with a marine residence time for Pb of less than 200 years [Cochran *et al.*, 1990] it is less likely that large-scale ocean circulation can be deduced with this isotope system. More realistically, local weathering sources are the main control of the Pb isotope composition of different portions of the Indian Ocean [Frank *et al.*, 2002].

7. Conclusions

[32] We have conducted the first high resolution Os and Tl isotope study of a Fe–Mn crust (Antipode 109D-C) from the Indian Ocean. We conclude the following.

[33] We use the Os isotope data for 109D-C and well-dated sediments from ODP Hole 756B to obtain a best estimate for the age at the base of this crust of ~6.5 Ma. This is significantly younger than previous estimates based on extrapolation of ^{10}Be growth rates and Co-flux modeling [Frank *et al.*, 1999; O’Nions *et al.*, 1998].

[34] The Tl isotope record obtained for the Indian Ocean is similar to those recently published for the Pacific Ocean [Nielsen *et al.*, 2009] but shows a systematic offset compared with two time series from Atlantic Ocean Fe–Mn crusts [Rehkämper *et al.*, 2004]. The offset would imply that the present-day Atlantic Ocean is ~2–3 $\epsilon^{205}\text{Tl}$ units lighter than the Pacific Ocean and may call into question the current best estimate for the marine residence time of Tl of ~20 kyr [Baker *et al.*, 2009; Rehkämper and Nielsen, 2004]. Assuming that the inferred offset is correct, it could be explained by increased ocean crust production in the Indian and Pacific Ocean basins while Atlantic Ocean crust production remained constant over the last ~10 Myr [Cogné and Humler, 2006; Kaiho and Saito, 1994]. However, such

interpretations must await systematic investigations of seawater Tl isotope ratios in all the Ocean basins.

[35] The improved age model for 109D-C reveals that the Hf isotope composition of Indian Ocean bottom waters as recorded by 109D-C and a crust from the North Indian Ocean [Piotrowski et al., 2000] has remained homogenous during the last ~6 Myr. Thus, Hf isotopes cannot be used to infer that NADW was a major source for Indian Ocean Bottom waters during this time. However, because of the lack of knowledge about Hf isotopes as a tracer of ocean circulation, we cannot conclude that export of NADW decreased since 6 Ma.

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