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Osmium isotope stratigraphy of a marine ferromanganese crust

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Abstract

Ferromanganese crusts provide records of long term change in ocean circulation and continental weathering. However, calibrating their age prior to 10 Ma has been entirely based on empirical growth rate models using Co concentrations, which have inherently large uncertainties and fail to detect hiatuses and erosional events. We present a new method for dating these crusts by measuring their osmium (Os) isotope record and matching it to the well-known marine Os isotope evolution of the past 80 Ma. The well-characterised crust CD29-2 from the central Pacific, was believed to define a record of paleooceanographic change from 50 Ma. Previous growth rate estimates based on the Co method are consistent with the new Os isotope stratigraphy but the dating was grossly inaccurate due to long hiatuses that are now detectable. The new chronology shows that it in fact started growing prior to 70 Ma in the late Cretaceous and stopped growing or was eroded between 13.5 and 47 Ma. With this new technique it is now possible to exploit the full potential of the oceanographic and climatic records stored in Fe–Mn crusts.

Keywords: Fe–Mn crusts; osmium isotopes; stratigraphy; Central Pacific

1. Introduction

Changes in the Sr, Nd, Hf, Os and Pb isotopic compositions of seawater in time and space are recorded in chemical seawater precipitates such as carbonates, ferromanganese coatings of foraminifera or ferromanganese crusts. These records provide powerful insights into Earth's long-term history of climate, weathering and ocean circulation [1–14]. For

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some elements (e.g. Sr) the best archives are foraminifera recovered from marine sediments. However, long-term records of change in the Nd, Pb and Hf isotopic composition of seawater have mainly been extracted from ferromanganese crusts.

The biggest difficulty with ferromanganese crusts is that no reliable method has yet been found for dating those portions that are older than about 10 Ma, the limit of ^{10}Be chronology (e.g., [11]). The constant hydrogenous Co flux model, hereafter referred to as Co-model, can be applied to estimate changes in growth rates in the older sections [7,15–19]. This method is based on the relationship between Co content and growth rate determined in Fe–Mn crusts and nodules as well as pelagic sediments [17].

The Co incorporated into the crusts is of purely hydrogenous origin, as the detrital contributions are generally negligible.

The relationship between the growth rate and the [Co] for Co-rich Fe–Mn crusts from the central Pacific was developed by Halbach and Puteanus [15,16,19] by first determining their growth rates by decay profiles of radioactive ^{10}Be and $^{230}Th_{excess}$. The relationship between the growth rate and [Co] was then empirically derived:

$$\text{Growth rate } (mm/\text{Ma}) = \frac{1.28}{[\text{Co}] - 0.24}.$$

The flux of Co into Co-rich crusts was shown to be nearly constant with a value of ~3 μg/cm^2 kyr [15] and ~1.9 μg/cm^2 kyr for Co-poor crusts [7]. Thus the concentrations directly reflect dilution by varying growth rates.

This approach will, however, fail to account for any growth hiatus or intervals of crustal erosion in Fe–Mn crusts. Therefore the Co-method can only give minimum ages of a given crust layer and cannot be used as a reliable stand-alone dating tool.

Moreover there are also uncertainties regarding the constancy of the Co flux into crusts at a given location over the long periods of crust growth (up to 80 Myr). In order to be able to interpret records of radiogenic isotopes in ferromangnese crust sections correctly and to put them into paleoceanographic perspective, it is necessary to have a reliable method to date crusts older then 10 Ma.

Elements with long oceanic residence times such as strontium (Sr) and osmium (Os) are isotopically homogeneous, or nearly so, in the world's oceans. The evolution of their isotopic composition in seawater over time is known from other sedimentary records (e.g., [8,9]). For this reason Sr isotope stratigraphy has been developed as a very effective method for determining the ages of carbonate sediments [20]. However, attempts to date ferromanganese crusts with Sr isotopes failed due to alteration by exchange with ambient seawater. For example, Sr isotope ratios close to those of modern seawater were often measured in the inner parts of crusts [5,21–23].

In contrast, the rate of post-depositional exchange of Os is comparatively small. Following Henderson and Burton [24] an osmium diffusion coefficient (D_{eff}) of 3×10^{-8} cm^2/yr is calculated (not 3×10^{-5} as stated in Table 2 of their original paper). This is much lower than strontium ($D_{eff}=2 \times 10^{-5}$) and it is small enough that the Os isotope composition is not significantly altered by diffusion over the time span of the formation of these crusts. Thus it should be possible to fit the $^{187}Os/^{188}Os$ profiles of ferromanganese crusts to the established global evolution of seawater [9] and thereby determine the age of each crust layer. This approach has been applied to crust CD29-2 from the Central Pacific ocean, which has already been subject to radiogenic isotope studies [5,25–27], and high-resolution Co concentration chronometry [7].

2. Materials and methods

Studied crust CD29-2 grew on a basaltic hyaloclastite substrate and was collected during cruise F7-86-HW from a seamount (part of the Karin Ridge south of the Hawaiian Ridge) in the Central Pacific (16°42′N, 168°14′W) at a water depth between 2390 and 1970 m [26]. Extrapolating the average growth rate of 2.1 mm/Myr, determined by using $^{10}Be/^{9}Be$ ratios for the upper 21 mm, yields an age of 50 Ma for the base of the crust at 105 mm depth [5,7]. It has been shown [7] that there are no large deviations between the ages determined by extrapolation of the $^{10}Be/^{9}Be$-derived growth rate and by the Co-flux model [15,16,19]. Nevertheless, neither approach is capable of detecting growth hiatuses or erosion in the sections older than 10 Ma. The age of 50 Ma at the base of the crust thus represents a minimum age. The maximum age, on the other hand, cannot be higher than 81–86 Ma, which is the age of a seamount near the location of this crust [28]. The crust is phosphatized in the section below a depth of 52 mm [5,7], but this does not appear to have compromised the Nd and Pb isotope records [7,26].

The sampling of the crust for Os isotope analysis was carried out using a computer-controlled drilling device to obtain a continuous profile perpendicular to the growth layers at a spatial resolution of 1 mm throughout the entire crust. Applying the average growth rate of 2.1 mm/Ma [5,7] each analysed sample represents the Os isotopic composition of seawater averaged over roughly 500,000 yrs.

To determine the seawater $^{187}Os/^{188}Os$ ratio it was necessary to correct for ingrowth of ^{187}Os from decay of ^{187}Re within the crust over time. For this purpose the rhenium ([Re]) and osmium concentrations ([Os]) were determined by an isotope dilution technique closely following the method of Birck et al. [29] (see online supplement) and using an in-house ^{185}Re-^{190}Os mixed spike. Given that the crust had been embedded in epoxy resin, the concentrations determined are for some samples not the true concentrations of the crust but represent minimum values. The presence of resin mostly affects the concentrations in the uppermost centimetre of the crust whereas the samples below should not be influenced. However, the $[^{187}Re]/[^{188}Os]$ ratios necessary to correct for the internal decay of ^{187}Re is not affected by the presence of resin. Re and Os separation was achieved in a single step using a solvent-extraction technique [29]. The Os isotope ratios and [Os] were measured by negative thermal ionisation mass spectrometry (N-TIMS) [29–31]. [Re] was measured with a Nu Plasma multiple-collector inductively coupled plasma mass spectrometer (MC-ICPMS) at ETH Zürich. The internal ^{187}Re decay correction of the $^{187}Os/^{188}Os$ record ranges between 0.014% in the young part of the crust with a low [Re] and about 21% in old crust sections with high [Re] (see also online supplements).

3. Results and discussion

Fig. 1 shows the $^{187}Os/^{188}Os$ seawater curve obtained by combining different records from sediment cores from the Pacific and Atlantic Ocean [4,32–36] (grey band). The $^{187}Os/^{188}Os$ profile for crust CD29-2 is plotted as grey triangles applying the average growth rate of 2.1 mm/Myr obtained by the ^{10}Be and Co-constant flux dating methods for the entire crust [5,7] (Fig. 1, see also Table 1 in online supplement). The $^{187}Os/^{188}Os$ record starts at values around 0.6 at the base of the crust followed by a steep decrease to the minimum of the profile ($^{187}Os/^{188}Os = 0.188$). After this minimum the values continuously increase to ratios of up to 0.58 followed by another pronounced minimum ($^{187}Os/^{188}Os = 0.436$) and another steep increase ($^{187}Os/^{188}Os = 0.771$). After this step the ratios continuously increase to the surface values of $^{187}Os/^{188}Os$ between 0.992 and 1.015, which are very close to present day seawater ($^{187}Os/^{188}Os = 1.057 \pm 0.038$; [37,38]) and to surfaces of other hydrogenous crusts representing present day seawater ($^{187}Os/^{188}Os$ between 1.01 and 1.07; [6]).

The $^{187}Os/^{188}Os$ seawater evolution shows a very similar pattern and essentially the same amplitude of isotopic variability since 75 Ma but there is a clear mismatch in the timing between the record of CD29-2 and the seawater curve prior to about 3.5 Ma. This is most readily explained by a, previously unrecognised, change in growth rate of the crust. To match the seawater curve a growth rate as low as 0.5 mm/Myr in the sections of the crust representing the period between 11 and 40 Ma (22.5–37.5 mm depth) would be required, for which there is, however, no indication at all in the Co-derived growth rate record [7]. Thus the mismatch can be best explained by the occurrence of hiatuses or erosional events representing a total duration of 22 Myr in that part of the crust. With three such hiatuses, the data of CD29-2 can be matched almost perfectly with the existing $^{187}Os/^{188}Os$ seawater curve (black diamonds in Fig. 1B), leaving the growth rate fixed to 2.1 mm/Ma as determined by the Co method. The first hiatus of 15 Myr duration is assigned to the period between 13.5 and 29.5 Ma, a second one of 3 Myr to the period between 33 and 36 Ma and a last one of 4 Myr to the period between 43 and 47 Ma (dotted lines in Fig. 1B). There are, however, always uncertainties with placing the hiatuses, in particular if there is no distinct slope in the seawater curve as is the case between about 12 and 30 Ma. Therefore the first hiatus of 15 Myr duration could equally well have started at 25 Ma and have finished at 10 Ma. Unpublished data by Burton et al. of a Fe–Mn crust from

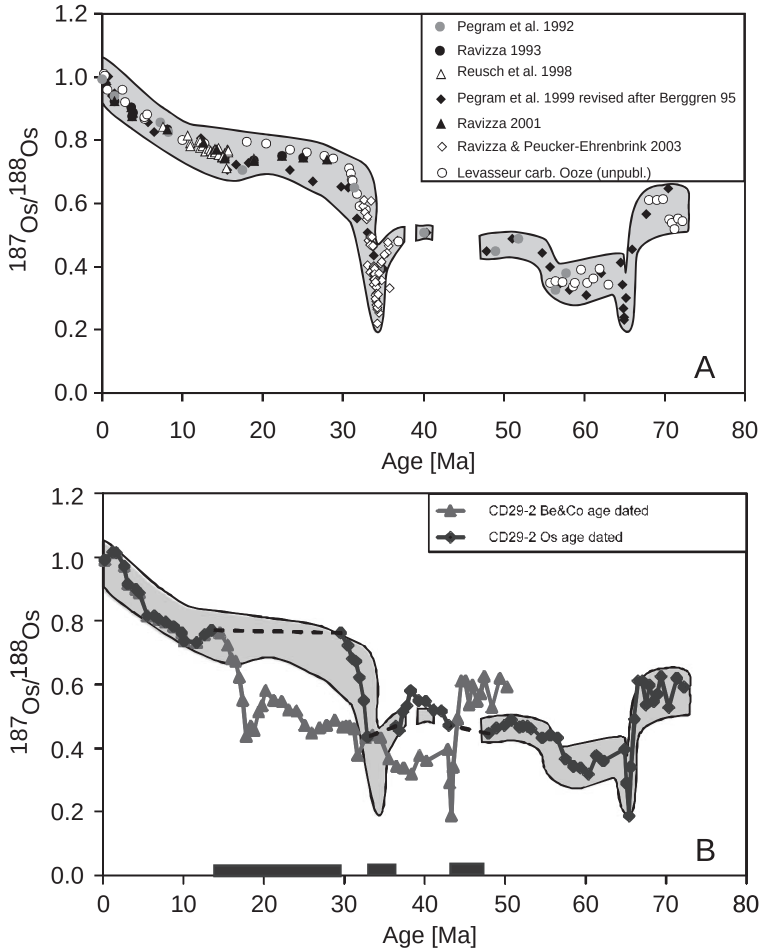

Fig. 1. A) represents the $^{187}Os/^{188}Os$ seawater curve determined from metalliferous pelagic clay sediments of the central North Pacific (LL44 GPC-3; [4,35]) and metalliferous carbonate sediments from the East Pacific Rise and the South East Pacific (Leg 92; [32,34]) as well as from the Mediterranean Sea, the Southern Atlantic and the Equatorial Pacific [36]. The grey band envelopes the data. B) is the match of the osmium isotope record of crust CD29-2 and global seawater for the past 72 Myr. The grey triangles show the $^{187}Os/^{188}Os$ ratios of CD29-2 corrected for internal Re decay assuming a constant growth rate of 2.1 mm/Myr as was determined by the Be method for the first 10 Ma and constant Co flux method for the whole crust. The $^{187}Os/^{188}Os$ record adjusted to the seawater curve is shown by the black diamonds. The dotted lines and the black boxes mark the inferred durations of the observed hiatuses or erosion periods of this crust.

the Central Pacific (personal communication) shows a similar kink in the data between 10 and 13 Ma as is observed in this crust, which was the reason for placing the required hiatus between 13.5 Ma and 29.5 rather then between 10 and 25 Ma. The time represented by the hiatuses and the anchor points given by the K/T boundary and the Eocene–Oligocene transition increase the age of the base of the crust from 50 to 72 Ma. As the seawater Os record from sediment cores terminates at 73 Ma (grey band in Fig. 1A), there are no other data available for correlation prior to this time, and the crust could thus be as old as the substrate (81–86 Ma, [28]) if further hiatuses occurred.

Osmium isotope studies of Fe–Mn nodules [39–43] and some Fe–Mn crusts grown on peridotites [44] often revealed excursions to high Os concentrations and low $^{187}Os/^{188}Os$ ratios, possibly indicating the presence of Os-rich extraterrestrial particles. The same is observed in marine sediments [4,45]. Therefore the presence of micrometeoritic material in sediments could also account for the unradiogenic values seen in Fe–Mn nodules, since those nodules actually grew on sediment [6].

If this is correct, ferromanganese crusts, which only grow in areas with negligible sedimentation, should not be affected. The work of Burton et al. [6] confirmed this although 20% of the crusts they studied have compositions lying on a mixing line between seawater and unradiogenic osmium sources (mantle peridotites or meteorites). The fact that our record fits the global seawater curve so well essentially excludes a significant influence of Os from extraterrestrial particles. Even if there are extraterrestrial particles present, our leaching technique (HBr 3 N, 20 °C, overnight) did not attack those to any significant extent.

Secondary phosphatization occurred in the crust below a depth of 52 mm (older than 47 Ma applying the revised chronology). The phosphorus concentration increases from 1% in the unphosphatized section to 2–8% in the phosphatized part of the crust [5]. Within uncertainties the Os isotopic signal in this part of the crust remains indistinguishable from seawater without any change in the amplitude of the pattern or indication of smoothing of the signatures. Whether or not phosphatization affected the Os isotope record at a level smaller than the uncertainties of the seawater curve cannot be decided from the currently available data. It is noted that the concentrations of Os in the phosphatized section are similar to those of the unphosphatized part. The higher Re concentrations observed are, except for two values, all located in a spike at the K/T boundary. Thus this increase does not seem to be related to phosphatisation but possibly to secular changes in the seawater Re concentration around that time.

The absence of noticeable effects on the Os isotopic compositions is in agreement with previous evidence that phosphatization in ferromanganese crusts did not affect Pb and Nd isotope records [26]. The essentially identical seawater curve recorded in the ferromanganese crust and marine sediments also shows that post-depositional exchange with seawater is negligible even in the oldest sections of the Os isotope time series of crust CD29-2. The Os isotope composition is thus considered a reliable dating tool for sections of ferromanganese crusts as far back in time as there is a continuous $^{187}Os/^{188}Os$ seawater record available (about 75 Ma).

The time series of crust CD29-2 is particularly important because it fills some of the gaps in the existing Os seawater curve which is poorly constrained between 38 Ma and 48 Ma. Fitting the Os record of a Fe–Mn crust to the known global seawater record and then inferring that this new record can now be used to fill previous gaps in the seawater record may appear to be a circular reasoning. However, there are some arguments in favour of this approach. First, the Co concentration is constant throughout the crust resulting in a constant growth rate. This allows us to fit our data to the seawater curve only by introducing hiatuses and still fully applying the Co model for growth rate determination. Secondly there are enough points to fit the Os isotopic signature of the crust (i.e. Eocene–Oligocene decline and the K/T boundary) to allow the inference that the data between these points represents a reliable and continuous Os isotope stratigraphy at each point. Therefore the time series of crust CD29-2 also provides a continuous seawater Os isotope record for the period between 48 and 72 Ma. The very good match between the record of the crust, which for this period is based on the Co-constant flux age model, and the existing sedimentary data essentially excludes any significant hiatuses. Thus, the time series of crust CD29-2 almost doubles the existing Os isotope data set for that period of time. It fully corroborates the previously observed pattern of the Os isotope evolution, which so far was mainly based on a deep sea core from the North Pacific (GPC-3 with a weak stratigraphic control) [35] and a core from the South Pacific (DSDP site 596) [33]. CD29-2 is thus the first ferromanganese crust that reliably recorded the Cretaceous–Tertiary boundary, which is represented by several data points and the pronounced $^{187}Os/^{188}Os$ minimum of 0.188, essentially identical to the $^{187}Os/^{188}Os$ minimum of 0.15 in core DSDP 577 from the Western Pacific [39]. This opens a new archive to study the marine geochemical changes of this key period in Earth's history. Ling et al. [25] also observed similarities in the Pb istope patterns from 6 different crusts from the Pacific, including CD29-2, with the deep sea core GPC-3, which however did not match in time. They concluded that hiatuses or erosional events are responsible for that mismatch but could not solve this obvious problem. Our data now confirms their hypothesis.

Finally, it is worth noting that crust CD29-2 was previously studied by Christensen et al. [26] who found that the changes in $^{207,208}Pb/^{206}Pb$ with time are positively correlated with the global deep water $\delta^{18}O$ over the past 55 Myr. With the revised chronology and after detection of the hiatuses in the crust this correlation is not existent any more. Rather it now appears that there was a negative correlation with the global deep water $\delta^{18}O$ evolution between 73 and 36 Ma and no correlation thereafter, which is most likely due to the fact that the deep water oxygen isotope signal has since then not been controlled by temperature alone anymore but also by ice volume.

4. Conclusions

Our results show that the Os isotope composition of Fe–Mn crusts is a reliable tool to date crusts back to the Cretaceous. Osmium isotope stratigraphy facilitates the detection of growth hiatuses within the crusts, which has not been possible with the only other available dating method based on Co constant flux. The results demonstrate that the Co constant flux method can provide realistic growth rate estimates but, due to the occurrence of significant hiatuses, can in the absence of other independent age constraints only give minimum ages for particular sections of crusts. The Os isotope stratigraphy is therefore currently the only reliable dating tool for crusts that are older then 10 Ma. It enables the reliable interpretation of radiogenic isotope records in crusts (Pb, Nd, Hf) as proxies for past continental weathering and ocean circulation.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.epsl.2005.07.016.

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