INTERPRETING THE MARINE OSMIUM ISOTOPE RECORD

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Introduction

The osmium isotopic composition of sea water has increased throughout the Cenozoic from an $^{187}Os/^{188}Os$ of ~0.2 at the Cretaceous-Tertiary boundary to a ratio of 1.06 at present (Pegram et al., 1992; Ravizza, 1993; Peucker-Ehrenbrink et al., 1995; Pegram & Turekian, 1997). To first order this increase resembles the Cenozoic increase in the marine strontium isotope record. It is therefore tempting to interpret both records as to reflect increasing input of radiogenic continental material (average $^{187}Os/^{188}Os$ of upper continental crust ~1.2-1.3, Esser & Turekian, 1993; average $^{187}Os/^{188}Os$ of worldwide loess ~1.05, Peucker-Ehrenbrink & Jahn, 1999; average $^{187}Os/^{188}Os$ of world-wide run-off ~1.5, Levasseur et al., 1999) due to changes in the continental weathering intensity regulated by climatic/tectonic forcing. However, the sources of radiogenic osmium differ markedly from those dominating the marine strontium isotope system. Whereas the marine strontium isotope system is conventionally interpreted using multi-component (riverine, high-temperature hydrothermal, low-temperature hydrothermal, and diagenetic fluxes) isotope mass balances, variations in the marine osmium isotope record can be interpreted differently. Three characteristics unique to the marine Os isotope system are highlighted below.

1. Impact events

Large impacts are capable of "resetting" the marine Os isotope record to unradiogenic values characteristic of undifferentiated planetary matter ($^{187}Os/^{188}Os$ of ~0.13, e.g., Meisel et al., 1996). The most prominent excursion to unradiogenic marine Os isotope values coincides with the K-T boundary (core DSDP 596, Peucker-Ehrenbrink et al., 1995; core LL44-GPC3, Turekian & Pegram, 1997). Unpublished Os isotope data for K-T boundaries in cores DSDP 577 and DSDP 245 indicate that the marine Os isotope system recovered quickly (within a few 100 kyr at most) from $^{187}Os/^{188}Os$ of ~0.16 at the K-T boundary to $^{187}Os/^{188}Os$ values of ~0.4 in the early Danian. The quick recovery is consistent with a short residence time of Os, estimated at 10-100 kyr for the modern ocean (Richter & Turekian, 1993; Peucker-Ehrenbrink & Ravizza, 1996; Levasseur et al., 1998; Oxburg, 1998, Burton et al., 1999).

The LL44-GPC3 Os isotope record shows a second sharp excursion toward unradiogenic $^{187}Os/^{188}Os$ values of ~0.36 around 32-33 Myr (Turekian & Pegram, 1997). Analyses of the abundance of oxidized Ni-rich spinel, indicators of the presence of extraterrestrial material, demonstrate that this excursion at ~12 m core depth is bracketed by, but does not coincide with, major peaks in the abundance of Ni-rich spinel at 11.2 and 12.4 meters (Robin et al., 1999). It is therefore unlikely that this excursion toward unradiogenic sea water had an extraterrestrial cause. Turekian & Pegram (1997) noted that the Os isotope excursion coincides with high Th/Cr of up to 0.7, characteristic of acidic volcanic ash, and interpret this feature as reflecting enhanced input from ophiolite weathering at the suture formed at the site of the former Tethys. As this unradiogenic excursion so far only has been documented in LL44-GPC3, analytical artifacts caused by leaching unradiogenic volcanic sediment components have to be excluded through analyses of early Oligocene sections from other sediment cores.

2. Organic matter

Although only a minor fraction (~5%) of the crustal Os is bound to organic matter, this fraction disproportionately contributes to the mobile Os inventory of the crust. For instance, Peucker-Ehrenbrink & Hannigan (1999) demonstrate that black shales can loose 45-90% of their initial Os budget upon surficial weathering. Simple mass balance considerations show that release of Os due to weathering of one volume unit black shale is equivalent to mobilization of Os from ~1000 volume units of typical granitoid upper crustal rocks (Peucker-Ehrenbrink & Blum). The Re/Os of organic-rich sediments is sufficiently large that weathering of organic-rich sediments at a constant rate can lead to a steady increase in the osmium isotopic composition of sea water with time (Ravizza & Peucker-Ehrenbrink, 2000). In such a scenario trends towards more radiogenic Os isotope sea water values (e.g., the steady increase from a $^{187}Os/^{188}Os$ of ~0.7 at 16 Myr to a $^{187}Os/^{188}Os$ of ~0.95 at 2 Myr) are unrelated to increases in continental weathering intensity.

3. Short-periodic variations

The marine residence time of osmium is short enough to capture short-periodic (glacial-interglacial) fluctuations in the system that are inaccessible to the buffered marine strontium isotope system. This offers not only the opportunity to discriminate between high-frequency (climatic) and low-frequency (tectonic) forcing, but also increases the likelihood of the system reaching steady-state. Oxburg (1998) has reconstructed glacial-interglacial variations in the isotopic composition of sea water for the past 250 kyr. In general, sea water values fluctuate from less radiogenic $^{187}Os/^{188}Os$ values of ~0.97 in times of enhanced atmospheric dust input during glacial periods to more radiogenic $^{187}Os/^{188}Os$ values of ~1.03 during interglacial periods. The cause(s) for such fluctuations is (are) still a matter of debate. Oxburg (1998) favor reduced riverine flux during periods of enhanced dust input as the main cause for less radiogenic sea water. Peucker-Ehrenbrink & Blum (1998) argue that preferential release of radiogenic Os in the early stages of weathering following deglaciation leads to an "extra delivery" of radiogenic Os to sea water, speeding up recovery to more radiogenic Os isotope values. Rapid recovery from less radiogenic glacial to more radiogenic interglacial sea water isotopic compositions has been used by Oxburg (1998) to place constraints on the marine residence time of Os. The results, assuming a constant residence time, are consistent with the shortest residence time inferred for Os so far: ~6,000 ± 2,000 years. It should be noted, however, that the assumption of a constant residence time may be violated if the areal extent of anoxic marine sediments underwent significant fluctuations on glacial-interglacial time scales. Such sediments are important sinks for Os in sea water and temporal changes may affect the marine Os budget.

It should also be pointed out that short periodic fluctuations in the marine Os isotopic composition may not be unique to the late

Pleistocene. Reusch et al. (1998) have reconstructed oscillations in the marine Os isotope record during the middle Miocene with amplitudes in $^{187}Os/^{188}Os$ of 0.01-0.02 and periods of ~1 Myr or shorter. These oscillations appear to be negatively correlated with the bulk carbonate $\partial^{13}C$ and the benthic foraminiferal $\partial^{18}O$ records. Further analyses are needed to confirm the global nature of these marine Os isotope oscillations.

The Mesozoic marine Os isotope record

Reconstruction of the Mesozoic marine Os isotope record is at its infancy (Cohen et al., 1999; Ravizza et al., 1999; Cohen & Coe, 1999). Preliminary data indicate $^{187}Os/^{188}Os$ fluctuations from unradiogenic values ~0.2 during the upper Hettangian (~206 Myr) to radiogenic values of ~0.8 during the Toarcian (~183 Myr). Cohen & Coe (1999) also report a rapid drop in the isotopic composition of sea water following an anoxic event in the Toarcian. As noted above, the residence time of Os in sea water may be sensitive to the areal extent of anoxic sediments, allowing rapid fluctuations in the isotopic composition of sea water during and shortly after prominent anoxic events, potentially accompanied by Os isotope contrasts between ocean basins.

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