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A high-resolution marine $^{187}Os/^{188}Os$ record for the late Maastrichtian: Distinguishing the chemical fingerprints of Deccan volcanism and the KP impact event

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ABSTRACT

A composite late Maastrichtian (65.5 to 68.5 Ma) marine osmium (Os) isotope record, based on samples from the Southern Ocean (ODP Site 690), the Tropical Pacific Ocean (DSDP Site 577), the South Atlantic (DSDP Site 525) and the paleo-Tethys Ocean demonstrates that subaerially exposed pelagic carbonates can record seawater Os isotope variations with a fidelity comparable to sediments recovered from the seafloor. New results provide robust evidence of a 20% decline in seawater $^{187}Os/^{188}Os$ over a period of about 200 kyr early in magnetochron C29r well below the Cretaceous–Paleogene Boundary (KPB), confirming previously reported low-resolution data from the South Atlantic Ocean. New results also confirm a second more rapid decline in $^{187}Os/^{188}Os$ associated with the KPB that is accompanied by a significant increase in Os concentrations. Complementary platinum (Pt) and iridium (Ir) concentration data indicate that the length scale of diagenetic remobilization of platinum group elements from the KPB is less than 1 m and does not obscure the pre-KPB decline in $^{187}Os/^{188}Os$. Increases in bulk sediment Ir concentrations and decreases in bulk carbonate content that coincide with the Os isotope shift suggest that carbonate burial flux may have been lower during the initial decline in $^{187}Os/^{188}Os$. We speculate that diminished carbonate burial rate may have been the result of ocean acidification caused by Deccan volcanism.

1. Introduction

There is substantial evidence the late Maastrichtian was punctuated by a transient warming event at ~66 Ma that terminated 100–200 kyr prior to the KPB, which some workers have attributed to the influence of Deccan volcanism (Barrera and Savin, 1999; Li and Keller, 1999; Wilf et al., 2003). Reconstructions of Maastrichtian CO_2 levels based on paleosol data indicate abrupt increases in pCO_2 superimposed upon elevated background concentrations of 3–4 times present-day levels, and are interpreted in the context of the Deccan-induced warming hypothesis (Nordt et al., 2003). Ravizza and Peucker-Ehrenbrink (2003) show a decline in the marine $^{187}Os/^{188}Os$ record prior to that associated with the Cretaceous–Paleogene Boundary (KPB), which they attribute to Deccan volcanism. These initial results suggest that the marine osmium (Os) isotope record of the late Maastrichtian has a distinct and resolvable shape that can be used to determine the relative timing of rapid and transient changes in osmium input to the oceans, specifically those resulting from Deccan volcanism. Studies of ferromanganese crusts (Klemm et al., 2005; Burton, 2006) and pelagic clays (Peucker-Ehrenbrink et al., 1995; Pegram and Turekian, 1999; Ravizza, 2007) for the late Maastrichtian also record the decline to extremely unradiogenic, nearly chrondritic $^{187}Os/^{188}Os$ values ($\approx$0.127: Horan et al., 2003) at the KPB, but these records lack the temporal resolution and stratigraphic control needed to confirm or refute the seawater Os isotope evolution proposed by Ravizza and Peucker-Ehrenbrink (2003).

The motivation for this study is four-fold: (1) To better resolve the shape and timing of the late Maastrichtian decline in the marine $^{187}Os/^{188}Os$ record by comparing coeval records from sites distributed throughout the global ocean. (2) To explore the correlation between the structure of the marine Os isotope record and the transient warming event at ~66 Ma by comparing osmium isotope data with existing oxygen isotope analyses of well preserved foraminifera, and nannofosssil abundance patterns from the same cores. (3) To determine whether or not the marine osmium isotopic record of pelagic carbonates is adversely affected by uplift and exposure above sea level by comparing Os records obtained from the modern seafloor

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to a record obtained from the analyses of pelagic carbonate now exposed on land. (4) To critically evaluate the length scale of osmium mobility during diagenesis and its potential influence on the marine osmium isotope record using complementary platinum group element (PGE: Pt, Ir, Os) data.

2. Sample materials

The samples analyzed for this study are from the Deep Sea Drilling Program (DSDP) Site 525 on Walvis Ridge in the Atlantic (29°04.24′S, 2°59.12′E), DSDP Site 577 on Shatsky Rise in the Western Pacific (32°26.53′N, 157°43.39′E), the Ocean Drilling Program (ODP) Site 690 on Maud Rise in the Weddell Sea (65°9.629′S, 1°12.296′E), and the Scaglia Rossa Formation at Bottaccione in Gubbio, Italy (43°22′N, 12°35′E). Sample volumes from DSDP and ODP were typically 20 cm^3, while sample from the Gubbio section were approximately 50–100 cm^3. The high latitude ODP Site 690 was selected for comparison to two previously studied lower latitude sites (DSDP 525 and 577) to evaluate whether the Os isotopic signal recovered is global in its extent. Additional samples from DSDP Sites 525 and 577 were analyzed to increase the temporal resolution available and compare leachate and Re data between sites. Benthic and planktonic foraminiferal stable isotope data from ODP Site 690 (See Wilf et al., 2003 and references therein.) allow for a direct comparison of Os ratios to paleoclimate proxy records without the potential discrepancies in age models that might arise between sites. The Bottaccione section was chosen because as a rapidly accumulating pelagic limestone with well-developed age constraints it is well suited for a high-resolution comparison to the submarine records generated for this period. DSDP Sites 525, 577 and ODP Site 690 are submarine pelagic carbonate sections (calcareous nannofossil oozes). Over the interval studied DSDP Site 525 varies between 42.1 and 83.8 wt.% $CaCO_3$ (Kucera et al., 1997), DSDP Site 577 sediments are generally >90 wt.% $CaCO_3$ (Zachos et al., 1985), and ODP Site 690 varies from 77 to 92 wt.% $CaCO_3$ (this study). The Scaglia Rossa section of Bottaccione (Premoli Silva and Sliter, 1995) is a pink to reddish-brown bedded limestone that varies from 91.6 to 97.2 wt.% $CaCO_3$ (Crocket et al., 1988; Alvarez et al., 1990; Rocchia et al., 1990).

3. Age models

We elected to use magnetostratigraphy and the KPB as the sole basis for an integrated timescale in order to correlate temporally between different sites. Although this approach limits the number of age datums available for use in constructing the age models, we argue this approach is preferable when correlating such widely distributed sites because geomagnetic reversals and the KPB are very nearly globally synchronous, while other biostratigraphic datums may be slightly diachronous. The age models for DSDP Site 525, DSDP Site 577 and ODP Site 690 are based on linear interpolation between age datums given by magnetostratigraphy and the KPB (Supp. Table s1). Note that we have retained the 65.5 Ma date for the KPB from Hicks et al. (2002), rather than the more recent date of 66.0 Ma based on 405 kyr eccentricity cycles (Kuiper et al., 2008). This is because there is no comparable orbitally tuned age assignment for the base of C29r, placed at 65.843 Ma by Hicks et al. (2002), and thus adopting the 66.0 Ma KPB age in isolation would create a negative duration for the Cretaceous portion of C29r. For ODP Site 690 stratigraphic control is derived from the magnetostratigraphy of Hamilton (1990) and the depth of the KPB iridium (Ir) anomaly from Michel et al. (1990). It should be noted that in ODP Site 690 the C29r/C30n magnetic reversal is located at the break between cores 15 and 16. The break between cores 16 and 17 includes an estimated 4 m of unrecovered section and occurs within chron C30r. Hamilton (1990) does not assign a depth for the C30r/C30n reversal boundary, so we selected 255.0 mbsf (meters below seafloor) based on the inclination data given (Fig. 5 from Hamilton (1990)). The C30r/C31n reversal boundary is not used as a datum for ODP Site 690. At DSDP Sites 525 and 577 stratigraphic control is based on integrated magnetobiostratigraphy using the same datums as in Ravizza and Peucker-Ehrenbrink (2003). Previous work establishes the magnitude and location of the KPB Ir anomalies at DSDP Site 577 (Michel et al., 1985). In the Bottaccione section we use the integrated magnetobiostratigraphy of Coccioni et al. (2004), with the previously established location of the KPB anomaly from Alvarez et al. (1990). Using these age models the average temporal resolution of the new Os isotope records reported here is ≈85 kyr for ODP 690, ≈100 kyr for DSDP 577, and ≈40 kyr for the Bottaccione section. In time intervals of special interest samples were analyzed at temporal resolution as high as one sample each 15 kyr.

4. Methods

Os isotope ratios and PGE concentrations were measured by isotope dilution using the nickel sulfide (NiS) fire assay preconcentration method followed by isotope ratio measurements using an Element2 ICP-MS (Ravizza and Pyle, 1997; Hassler et al., 2000). DSDP Site 577 and ODP Site 690 samples were hand-ground using a Pyrex mortar and pestle. Bottaccione samples were coarse crushed in a rock crusher with care taken that metal surfaces did not come in contact with the sample material by covering the surfaces of the jaw crusher with disposable plastic sheets. The resulting coarse crush was then fine ground in a Rocklabs ceramic zirconia mill. For NiS fire assay preconcentration a 1:1.5 sample to flux ratio was utilized, with 10 g of the sample used except when not enough sample was available. Procedural fusion blanks accounted for approximately 1 in 6 analyses performed. Procedural gas blanks were analyzed between every five samples to monitor the amount of Os cross contamination which may come from carry-over in the Teflon vials used in sparging (Hassler et al., 2000). In cases where gas blanks accounted for more than 10% of the ^{188}Os signal intensity due to low count rates, results were not used. Procedural blanks accounted for 1–2% of Os concentration measured in the Bottaccione Section, and 0.2%–2% in ODP 690 and DSDP 577 samples. An in house Os standard prepared from a concentrated Johnson–Matthey standard solution was analyzed between every 5 samples, with a measured $^{187}Os/^{188}Os$ value of 0.1085 ± 0.0020 (2 SD).

In order to better constrain the likely contribution of lithogenic Os to the sediment budget, a subset of samples from Site 690 was analyzed by XRF at Washington University in St. Louis, Missouri, for major and minor elements (supplemental Table s2). In order to better evaluate whether fluctuations in PGE concentrations resulted from differences in dilution, a subset of samples from ODP Site 690 was analyzed for bulk $CaCO_3$ content by elemental analyzer (EA) at the University of Hawaii. Bulk $CaCO_3$ content for selected samples from DSDP Site 577 were conducted at Woods Hole Oceanographic Institution (supplemental Table s3).

To further assess the potential influence of non-hydrogenous Os on bulk sediment Os concentrations, leachable rhenium (Re) and Os were measured in separate powder splits in a subset of samples (8 from ODP Site 690, 5 from Bottaccione, and 4 from DSDP Site 525) using a modification of the method described in Ravizza (2007). One gram of sediment was allowed to react with a leach solution of ~5.3 N HNO_3 and 0.8% H_2O_2 for about an hour, and then spiked with an enriched ^{190}Os and ^{185}Re isotope spike, prior to separation of the solution and sediment by centrifugation. After Os was measured, Re was separated from residual sample solutions using anion exchange columns prior to ICP-MS analysis (Peucker-Ehrenbrink et al., 1995). A general outline of the methods used in our lab for Re analysis by ICP-MS can be found in Ravizza and Paquay (2008).