



Evidence for weathering and volcanism during the PETM from Arctic Ocean and Peri-Tethys osmium isotope records

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ABSTRACT

Sudden global warming during the Paleocene–Eocene Thermal Maximum (PETM, 55.9 Ma) occurred because of the rapid release of several thousand gigatonnes of isotopically light carbon into the oceans and atmosphere; however, the cause of this release is not well understood. Some studies have linked carbon injection to volcanic activity associated with the North Atlantic Igneous Province (NAIP), while others have emphasised carbon cycle feedbacks associated with orbital forcing. This study presents the osmium isotope compositions of mudrocks that were deposited during the PETM at four locations (one from the Arctic Ocean, and three from the Peri-Tethys). The Os-isotope records all exhibit a shift of similar magnitude towards relatively radiogenic values across the PETM. This observation confirms that there was a transient, global increase in the flux of radiogenic Os from the weathering of continental rocks in response to elevated temperatures at that time. The tectonic effects of NAIP volcanic emplacement near the onset of the PETM is recorded by anomalously radiogenic Os-isotope compositions of PETM-age Arctic Ocean samples, which indicate an interval of hydrographic restriction that can be linked tectonic uplift due to hotspot volcanism in the North Atlantic seaway. The Peri-Tethys data also document a transient, higher flux of unradiogenic osmium into the ocean near the beginning of the PETM, most likely from the weathering of young mafic rocks associated with the NAIP. These observations support the hypothesis that volcanism played a major role in triggering the cascade of environmental changes during the PETM, and highlight the influence of paleogeography on the Os isotope characteristics of marine water masses.

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1. Introduction

There is considerable debate surrounding the source of ^{13}C -depleted carbon that was released into the oceans and atmosphere at the onset of the PETM, as well as the triggering mechanisms that could have initiated this carbon-cycle perturbation. One possibility is that orbital forcing destabilised exchangeable sources of carbon on land and in the oceans through a series of Earth-system feedback mechanisms, such as ocean and atmospheric circulation (Lourens et al., 2005; Lunt et al., 2011; DeConto et al., 2012). This hypothesis is supported by the cyclostratigraphic tuning of data from marine sedimentary sections, which suggests that early Eocene hyperthermals occurred in phase with 100 kyr orbital eccentricity cycles (Westerhold et al., 2007). This suggestion is, however, inconsistent with the observation of a difference between the phasing of the PETM relative to the 400 kyr orbital eccentricity cycle, compared to subsequent early Eocene hyperthermal events

(Westerhold et al., 2007; Charles et al., 2011). An alternative hypothesis has linked the onset of the PETM to volcanic triggering associated with extensive volcanism in the North Atlantic Igneous Province (NAIP), which began ~60 Ma ago and culminated in rapid North Atlantic seafloor spreading near the Paleocene/Eocene boundary (Eldholm and Thomas, 1993; Storey et al., 2007a,b). Tectonic uplift caused by the emplacement of a NAIP mantle plume at the base of the lithosphere could have caused carbon release at the start of the PETM, by triggering the dissociation of marine gas hydrates through the depressurisation of uplifted marine sediments (MacLennan and Jones, 2006), or from intermediate-depth seawater warming triggered by tectonically-induced changes in ocean basin morphology (Bice and Marotzke, 2002; Roberts et al., 2009). A further theory suggests that the thermal alteration of organic-carbon rich marine sediments might have liberated substantial amounts of carbon by igneous intrusions during emplacement of the NAIP (Svensen et al., 2004, 2010). However, it is difficult to test hypotheses linking the emplacement of the NAIP to the PETM using radioisotopic ages alone because the uncertainties associated with the dating of many volcanic rocks in the late Paleocene are longer than the duration of the PETM itself (Storey et al., 2007a; Svensen et al., 2010, Supplementary material).

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The osmium (Os) isotope composition of seawater (expressed as $^{187}\text{Os}/^{188}\text{Os}$) reflects the mixing of radiogenic Os weathered from ancient continental crust ($^{187}\text{Os}/^{188}\text{Os} = \sim 1.4$ (Peucker-Ehrenbrink and Jahn, 2001)), and unradiogenic Os from mantle (hydrothermal) and extraterrestrial sources ($^{187}\text{Os}/^{188}\text{Os} = 0.12$ Peucker-Ehrenbrink and Ravizza, 2000). The residence time of Os in seawater is $\sim 10,000$ – $55,000$ years (Sharma et al., 1997; Burton et al., 1999; Levasseur et al., 1999; Peucker-Ehrenbrink and Ravizza, 2000), which is longer than the present-day mixing time of the oceans. Seawater $^{187}\text{Os}/^{188}\text{Os}$ is therefore able to track globally-averaged variations in the proportions of radiogenic Os delivered to the oceans by the weathering of old continental rocks, and unradiogenic Os delivered by the weathering and alteration of young mafic rocks emplaced subaerially and in submarine hydrothermal systems (Pegram et al., 1992; Cohen et al., 1999; Peucker-Ehrenbrink and Ravizza, 2000). Tracing variations in weathering fluxes using Os isotopes carries the assumptions that extra-terrestrial Os fluxes to the oceans are quantitatively insignificant or temporally constant, and also that the globally averaged $^{187}\text{Os}/^{188}\text{Os}$ of the radiogenic Os flux to the oceans from weathered continental rocks does not vary significantly on relatively short timescales. These assumptions are supported by previous reconstructions of global weathering fluxes using Os isotopes, which are reproducible at different locations (e.g. Cohen et al., 1999; Peucker-Ehrenbrink and Ravizza, 2000; Ravizza et al., 2001; Cohen and Coe, 2002; Cohen et al., 2004; Turgeon and Creaser, 2008; Bottini et al., 2012; Du Vivier et al., 2014). Furthermore, the relatively short seawater residence time of Os allows it to be utilised as an ocean circulation tracer in certain situations. If seawater mixing is limited in a basin or marginal seaway (for example due to topographic or hydrographic constraints), the residence time of Os in the basinal seawater may become shorter than the global seawater Os residence time. Since Os is typically associated with organic matter (Ravizza and Turekian, 1992; Cohen et al., 1999), enhanced organic carbon burial in restricted basins under low-oxygen conditions would favour depletion of the dissolved Os inventory in the basin seawater, which would be recorded as a decrease in sedimentary Os abundances. In such circumstances, $^{187}\text{Os}/^{188}\text{Os}$ may evolve locally to compositions that differ from the fully mixed global signal due to the greater relative importance of local Os input and output fluxes (e.g. Paquay and Ravizza, 2012).

The Os-isotope composition of seawater can be reconstructed from organic-rich mudrocks because of the high degree of enrichment of hydrogenous Os in these deposits that limits the proportional contribution from lithogenic Os (Ravizza and Turekian, 1992; Cohen et al., 1999). Recovery of the hydrogenous Os component of sediments can be assisted by acid-leaching organic-rich mudrocks using either inverse Aqua-Regia (Cohen and Waters, 1996), or CrO_3 – H_2SO_4 (Selby and Creaser, 2003). Previous studies of deep-marine metalliferous clays have demonstrated a radiogenic shift in the Os-isotope composition of seawater across the PETM (Ravizza et al., 2001; Ravizza and Peucker-Ehrenbrink, 2012), but these data have never been replicated in marine mudrocks. This study presents $^{187}\text{Os}/^{188}\text{Os}$ measurements of samples from four organic-carbon enriched marine sedimentary sections spanning the PETM; three of the sections are from the northern Peri-Tethys Ocean, and the fourth is from the Arctic Ocean (Fig. 1). The intention was to assess the impact of volcanic activity on seawater $^{187}\text{Os}/^{188}\text{Os}$ during the PETM, and to investigate whether the previously observed radiogenic Os-shift across the PETM was expressed globally in a range of different marine basins.

2. Methods

Re–Os preparation and analyses were carried out in metal-free conditions in a Picotrace© clean laboratory using the method of Cohen and Waters (1996). 0.25–1 g of finely ground sample powder was accurately weighed into an acid-cleaned glass Carius tube, to which an exact amount of a mixed ^{185}Re – ^{190}Os isotope spike and 8–12 ml of inverse Aqua Regia were added. Each sample tube was sealed with an oxygen

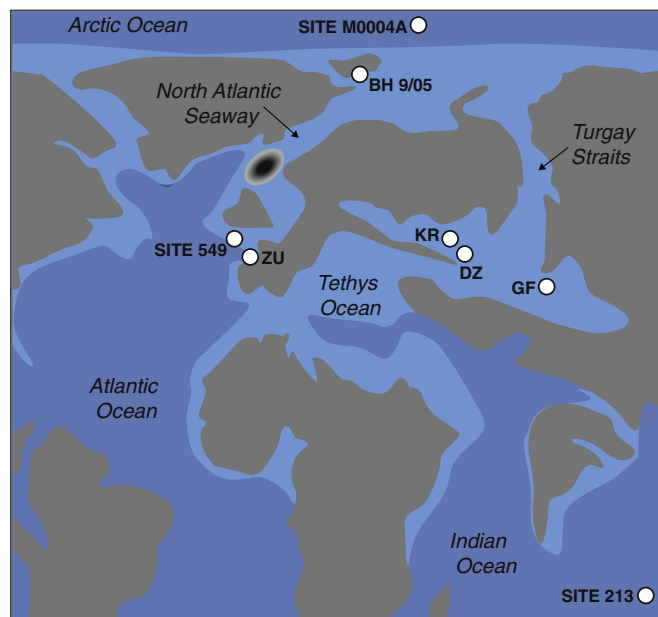


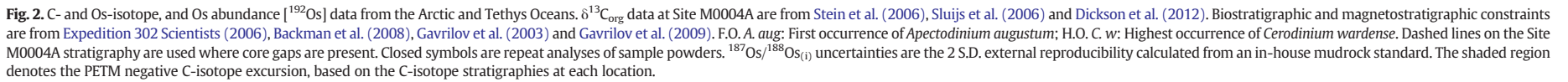
Fig. 1. Map of locations. KR: Kheu River, Karbardino-Balkaria; DZ: Dzhengutay, Dagestan; GF: Guru-Fatima, Tajikistan; ZU: Zumaya, Spain; site numbers refer to Deep Sea Drilling Program (Sites 213 and 549) and Integrated Ocean Drilling Program (Site M0004A) cores. The shaded ellipse represents the zone of transient uplift associated with the NAIP mantle plume in the North Atlantic seaway region modelled by MacLennan and Jones (2006). Base map modified from www.scotese.com.

and propane flame and placed into an oven at 180°C for 5 days. Os was extracted from the chilled acid digest with carbon tetrachloride (CCl_4), and subsequently back extracted from CCl_4 with hydrobromic acid. Following a micro-distillation step (Birck et al., 1997), sample residues were loaded onto clean, degassed Pt filaments for analysis by n-TIMS. Instrumental mass fractionation was corrected by internal normalisation to a $^{192}\text{Os}/^{188}\text{Os}$ ratio of 3.09202. Re concentrations were determined by isotope dilution from aliquots of the same acid digests analysed for Os. Re was extracted from the inverse Aqua-Regia using an iso-amylol liquid–liquid separation technique (Birck et al., 1997). Aliquots of the purified Re solutions were doped with Ir and analysed using a Thermo-Finnigan Neptune MC-ICP-MS. Instrumental mass fractionation was corrected by normalising to a $^{193}\text{Ir}/^{191}\text{Ir}$ ratio of 1.68299 (Berglund and Wieser, 2011). All quoted $^{187}\text{Os}/^{188}\text{Os}$ ratios and Os and Re abundances were blank corrected. Average Os blanks were ~ 1 ppt, with an average $^{187}\text{Os}/^{188}\text{Os}$ of 0.30 ($n = 9$). The average Re blank was ~ 5 ppt ($n = 10$). Initial $^{187}\text{Os}/^{188}\text{Os}$ ratios ($^{187}\text{Os}/^{188}\text{Os}_{(i)}$) were calculated assuming a depositional age of 55.9 Ma and a Re decay constant of 1.666×10^{-11} (Smoliar et al., 1996). The uncertainty of $^{187}\text{Os}/^{188}\text{Os}_{(i)}$ has been estimated from separate digestions of an in-house mudrock standard (Monterey mudrock 00N118) as ± 0.015 (2 S.D., $n = 8$).

3. Results

The stratigraphy of the Peri-Tethys Ocean records have been discussed in detail by Gavrilov et al. (2003) and Dickson et al. (2014a). All sites contain mudrocks variably enriched in organic carbon by up to ~ 18 wt.%. These mudrocks were deposited during a negative $\delta^{13}\text{C}_{\text{org}}$ excursion of $\sim 4\text{‰}$ (Dickson et al., 2014a), which can be attributed to isotopically light carbon release during the PETM. These features, together with primary biostratigraphic constraints at each site from nannofossil and dinocyst taxonomy, allow the sections to be correlated (Fig. 2).

^{192}Os concentrations in all samples are greatly elevated above the average crustal concentration (Peucker-Ehrenbrink and Jahn, 2001). At Kheu River and Guru-Fatima, $^{187}\text{Os}/^{188}\text{Os}_{(i)}$ increases from ~ 0.32 below



the CIE to a maximum of 0.38–0.39 during the CIE. $^{187}\text{Os}/^{188}\text{Os}_{(i)}$ values at Dzhengutay also increase to 0.39 within the CIE with a similar overall range to the other Tethys sites. The $^{187}\text{Os}/^{188}\text{Os}_{(i)}$ records from Kheu River and Guru Fatima also display shifts to relatively unradiogenic values near the base of the CIE. The lowest $^{187}\text{Os}/^{188}\text{Os}_{(i)}$ at both Guru-Fatima and Kheu River occur immediately after the first $\delta^{13}\text{C}_{\text{org}}$ data point indicating the PETM CIE. However, fully deciphering the phasing of these lead-lag relationships is limited by the temporal resolution of each record, which is relatively low over the CIE onset due to the limited availability of sample material.

There is an increase in $^{187}\text{Os}/^{188}\text{Os}_{(i)}$ of Arctic Ocean seawater from 0.39 to 0.55 during the PETM, which occurs at 390.66 mcd, 4.5 m below the first negative shift in $\delta^{13}\text{C}_{\text{org}}$ that is taken to denote the onset of the CIE (Sluijs et al., 2006; Stein et al., 2006; Dickson et al., 2012). As with the Tethys Ocean sites, the relatively radiogenic Arctic Ocean $^{187}\text{Os}/^{188}\text{Os}_{(i)}$ recorded at Site M0004A returns to less radiogenic values above the PETM.

4. Discussion

4.1. Data integrity

The high ^{192}Os concentrations in most of the samples confirm a substantial enrichment of hydrogenous Os over the average continental crust (detrital Os) contribution. Furthermore, the Re–Os data for each of the four sites are generally tightly clustered around an isochron age of 55.9 Ma (Fig. 3). Large differences in the contribution of lithogenic Os to the measured $^{187}\text{Os}/^{188}\text{Os}$ ratios, or a significant amount of post-depositional remobilisation of Re or Os, would impart a greater degree of scatter to the plots (e.g. Peucker-Ehrenbrink and Hannigan, 2000; Jaffe et al., 2002; Georgiev et al., 2012) than is observed. In the case of the three Tethys sites, the Re–Os data from the PETM intervals define identical $^{187}\text{Os}/^{188}\text{Os}_{(i)}$ of 0.36, further demonstrating the robustness of the datasets and showing that each location sampled the same, well-mixed late Paleocene–early Eocene seawater Os reservoir. It is noteworthy that the steady-state $^{187}\text{Os}/^{188}\text{Os}_{(i)}$ of Peri-Tethys seawater of 0.36 inferred from Fig. 3 is extremely close to the pre- and post-PETM $^{187}\text{Os}/^{188}\text{Os}$ values measured for open ocean seawater at DSDP Site 213 and 549 (Ravizza et al., 2001). This observation implies that there was little or no hydrographic restriction in the northern Peri-Tethys and that the study locations were able to freely exchange seawater with the wider Tethys Ocean. These lines of evidence demonstrate that the new data are robust and that variations in $^{187}\text{Os}/^{188}\text{Os}_{(i)}$ at each site can be used to track variations in the Os-isotope compositions of early Eocene seawater.

4.2. Weathering of radiogenic Os during the PETM

All four studied sections exhibit a shift towards more radiogenic $^{187}\text{Os}/^{188}\text{Os}$ values during the PETM CIE, with the Tethys sites having similar magnitude shifts of ~0.06. The range of the $^{187}\text{Os}/^{188}\text{Os}_{(i)}$ excursions recorded at the three Tethys Ocean sites are similar to the magnitude of the shift towards more radiogenic $^{187}\text{Os}/^{188}\text{Os}$ values during the PETM at DSDP Sites 213 and 549 in the Indian Ocean and North Atlantic Ocean respectively (Ravizza et al., 2001), at Zumaya in Spain (Schmitz et al., 2004), and also in Pacific Ocean Fe–Mn crusts (Klemm et al., 2005) (supplementary online material). The Site 549 data (Ravizza et al., 2001; Peucker-Ehrenbrink and Ravizza, 2012) are systematically slightly higher than the Tethys Ocean datasets, which may be due to the leaching of small quantities of lithogenic Os from the clay-rich deposits at that site. Likewise, Arctic Ocean $^{187}\text{Os}/^{188}\text{Os}_{(i)}$ values recorded at Site M0004A are also systematically higher than at the Tethys Ocean sites, which is consistent with a range of observations suggesting that seawater exchange between the Arctic Basin and global ocean occurred at a rate that was too slow to allow the $^{187}\text{Os}/^{188}\text{Os}$ of Arctic Ocean seawater to equilibrate fully with the global ocean during the portion of the

late Paleocene and early Eocene studied. Nonetheless, the consistent observation of relatively more radiogenic $^{187}\text{Os}/^{188}\text{Os}$ during the CIE at the different locations leads us to conclude that the Os-isotope records (Fig. 2) reflect a shift in the $^{187}\text{Os}/^{188}\text{Os}$ of global seawater towards relatively radiogenic values during the PETM. This observation requires a change in the global balance and/or composition of Os fluxes to the ocean across this event (Ravizza et al., 2001; Cohen et al., 2007).

The overall increase in seawater $^{187}\text{Os}/^{188}\text{Os}$ during the PETM could have been caused by an increase in the flux to the oceans of radiogenic Os weathered from continental rocks, by an increase in the average $^{187}\text{Os}/^{188}\text{Os}$ of weathered continental rocks, or by a decrease in the flux of unradiogenic Os to seawater. An increase in the flux of continentally-derived Os at a global scale is the most parsimonious interpretation of the data in the light of evidence for a perturbed hydrological cycle during the PETM (Bowen et al., 2004; Pagani et al., 2006; Handley et al., 2012) and for exceptionally high fluxes of terrestrial sediments to continental margins (Schmitz and Pujalte, 2007; John et al., 2008; Sluijs et al., 2008a; Dickson et al., 2014a). In principle, the shift could also have been caused by the preferential weathering of radiogenic Os from exposed organic-rich mudrocks, thereby raising the average $^{187}\text{Os}/^{188}\text{Os}$ of weathering fluxes. However, there is no evidence for a change in the terrestrial exposure of such deposits during the PETM. Additionally, Svensen et al. (2004, 2010) have suggested that hydrothermal fluids could have been expelled rapidly into the Vøring and Møre basins (northeast Atlantic Ocean) at the onset of the PETM after the heating by igneous intrusions of Cretaceous mudrocks, which are likely to have had more radiogenic $^{187}\text{Os}/^{188}\text{Os}$ than early Eocene seawater (Ravizza, 2007; Turgeon and Creaser, 2008; Bottini et al., 2012). However, assuming a seawater residence time for Os of ~ 10^4 years, and a duration for the PETM of 10^5 years (Röhl et al., 2007; Charles et al., 2011) the PETM $^{187}\text{Os}/^{188}\text{Os}$ records obtained here and in previous studies (Ravizza et al., 2001; Peucker-Ehrenbrink and Ravizza, 2012) require the flux of radiogenic Os to be sustained over multiple residence times to explain the prolonged excursion to more radiogenic seawater $^{187}\text{Os}/^{188}\text{Os}$ values (Röhl et al., 2007; Charles et al., 2011). The prolonged duration for the radiogenic $^{187}\text{Os}/^{188}\text{Os}$ excursion is therefore incompatible with the very short timescale for the postulated hydrothermal fluid release of only a few thousand years (Svensen et al., 2004).

At steady state, the Os-isotope composition of seawater can be described by mixing between unradiogenic and radiogenic Os input fluxes. The endmember $^{187}\text{Os}/^{188}\text{Os}$ compositions of these fluxes are assumed to be 0.12 and 1.4 respectively (Luck and Allègre, 1983; Peucker-Ehrenbrink and Jahn, 2001). The relative contribution (mole fraction, F) of the radiogenic endmember can be described by:

$$F_r = (R_s - R_u) / (R_r - R_u). \quad (1)$$

Where subscripts *r*, *s* and *u* denote the radiogenic, seawater and unradiogenic $^{187}\text{Os}/^{188}\text{Os}$ compositions respectively (Ravizza et al., 2001). The contribution of the unradiogenic end member can then be calculated using:

$$F_u = (1 - F_r). \quad (2)$$

The fractional increase in radiogenic Os fluxes during the PETM has been calculated with the assumption that flux of unradiogenic Os to the oceans remained constant. Then, the fractional increase in the radiogenic contribution (ΔF_r) can be calculated:

$$\Delta F_r = ((F_{u \text{ [pre-event]}} / F_{u \text{ [event]}}) - F_{u \text{ [pre-event]}}) / F_{r \text{ [pre-event]}}. \quad (3)$$

Applying this approach to data from the best resolved Peri-Tethys site (Kheu River), yields a result suggesting a 38% increase in the flux of radiogenic Os for the PETM compared with pre-PETM fluxes. The magnitude of the increase in $^{187}\text{Os}/^{188}\text{Os}_{(i)}$ during the PETM at Guru-Fatima is higher than at Kheu River, but is based on a single

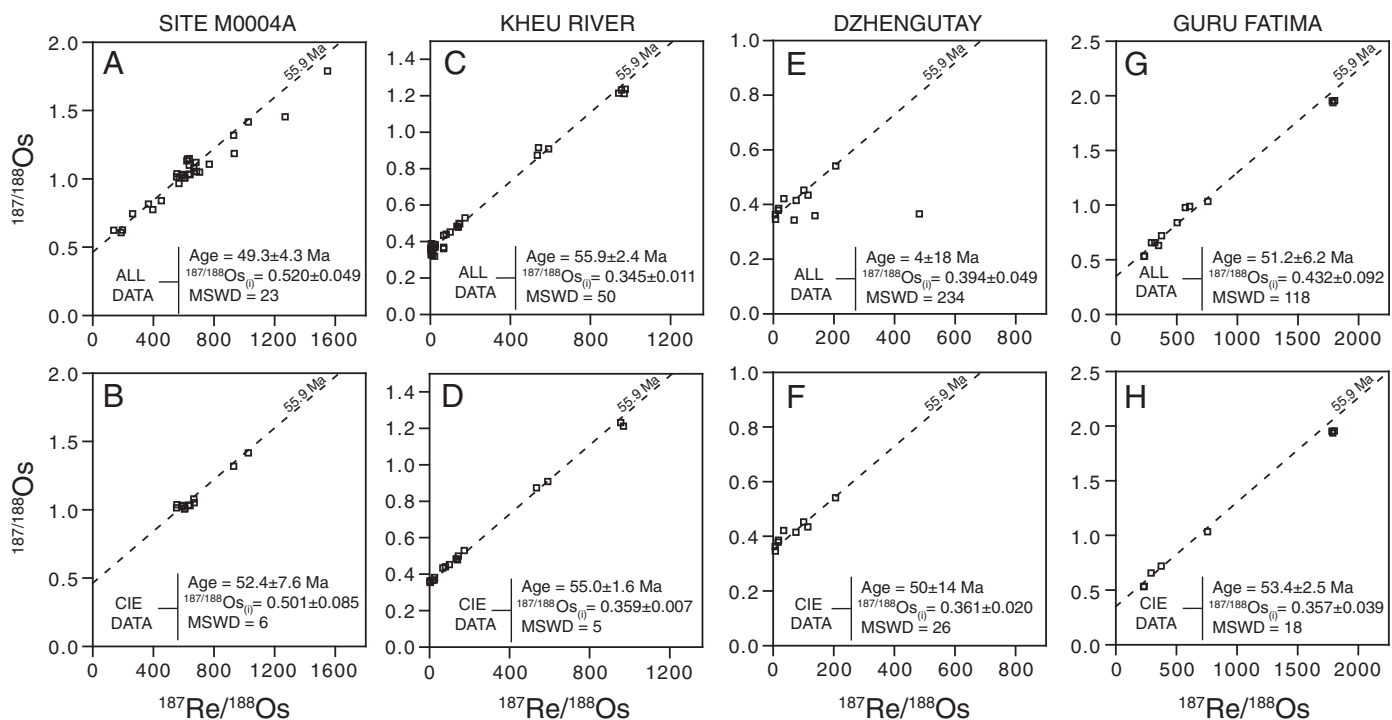


Fig. 3. $^{187}\text{Re}/^{188}\text{Os}$ – $^{187}\text{Os}/^{188}\text{Os}$ evolution plots for A, B: Site M0004A; C, D: Kheu River; E, F: Dzhengutay and G, H: Guru-Fatima. The upper row of graphs shows all data for each site, while the lower row of graphs shows only the Re–Os data from within the PETM as defined by carbon isotope stratigraphy. Regression statistics were calculated using the long-term reproducibility (2 S.D.) of an in-house mudrock standard, which was 1.7% for $^{187}\text{Os}/^{188}\text{Os}$ and 2.5% for $^{187}\text{Re}/^{188}\text{Os}$.

$^{187}\text{Os}/^{188}\text{Os}_{(i)}$ measurement of 0.43 during the CIE. A similar calculation cannot be made for Dzhengutay because pre-PETM samples are not available. For comparison, the calculated change in radiogenic Os flux during the PETM based on the DSDP Site 549 dataset (Ravizza et al., 2001) suggests an increase in radiogenic Os flux of 44%, which is very close to our estimate using data from the Tethyan Kheu River site. The fact that $^{187}\text{Os}/^{188}\text{Os}_{(i)}$ closely tracks the evolution of the CIE during the PETM is consistent with a mechanistic link between elevated global temperatures, moisture availability and weathering fluxes (Gaillardet et al., 1999), as also inferred for other global warming events in Earth history (e.g. Ravizza et al., 2001; Cohen and Coe, 2002; Cohen et al., 2004; Pagani et al., 2006; Bottini et al., 2012; Pogge van Strandmann et al., 2013).

4.3. Unradiogenic Os fluxes near the beginning of the PETM

Our records contain two key lines of evidence for a phase of volcanism at the onset of the PETM. The first is the short-term transient decrease in $^{187}\text{Os}/^{188}\text{Os}_{(i)}$ of ~0.05 near the base of the CIE at Kheu River and Guru-Fatima (Fig. 4) (the behaviour of $^{187}\text{Os}/^{188}\text{Os}_{(i)}$ at the onset of the PETM is unknown at Dzhengutay, because samples from the lower part of that section were not sampled). The similarity between the observed $^{187}\text{Os}/^{188}\text{Os}_{(i)}$ decrease in the two Peri-Tethys sites with a previously observed decrease in $^{187}\text{Os}/^{188}\text{Os}$ at the base of the PETM at Zumaya, Spain (Schmitz et al., 2004), suggests that the decrease in $^{187}\text{Os}/^{188}\text{Os}$ was likely to have been at least a regional phenomenon. The timings of the $^{187}\text{Os}/^{188}\text{Os}$ decrease at each site are consistent, beginning near the base of the negative $\delta^{13}\text{C}_{\text{org}}$ excursion, and ending within nannofossil zone NP 9 (Fig. 3). These features constrain the duration of the transient stratigraphic shift in $^{187}\text{Os}/^{188}\text{Os}$ to a few tens of thousands of years at most (Charles et al., 2011). The $^{187}\text{Os}/^{188}\text{Os}$ decrease at the start of the PETM is consistent with a proportionally larger flux of unradiogenic Os to the oceans near the start of the PETM. Eq. (3) was used to calculate the magnitude of the unradiogenic flux increases recorded in the initial stages of the PETM

(Fig. 3), but substituting F_u for F_r and vice-versa. This calculation resulted in fluxes of unradiogenic Os for Kheu River, Guru Fatima and Zumaya that were 33%, 39% and 12% higher, respectively, compared to pre-excursion fluxes.

There is no convincing evidence for an extraterrestrial impact in PETM deposits that could explain the shift towards relatively unradiogenic $^{187}\text{Os}/^{188}\text{Os}$ at the start of the PETM (Schmitz et al., 2004). However, a recent $^{187}\text{Os}/^{188}\text{Os}$ record from the Svalbard Central Basin (core BH9/04) suggests that a large amount of volcanic ash was deposited in the Central basin over an interval of approximately 8000 years shortly before the onset of the PETM (Fig. 4, Wiczeorek et al., 2013). The magnitude of the unradiogenic Os-isotope excursion in the Central Basin is about six times larger than in the Tethys sections, probably because the proximity of that site made it sensitive to the direct input of unradiogenic Os from mafic material (ash) from the NAIP. It is noteworthy that the $^{187}\text{Re}/^{188}\text{Os}$ and $^{187}\text{Os}/^{188}\text{Os}$ data from Svalbard (Wiczeorek et al., 2013) exhibit a high degree of scatter when examined around a 55.9 Ma reference isochron. In contrast, the new Tethys records reported here have $^{187}\text{Re}/^{188}\text{Os}$ and $^{187}\text{Os}/^{188}\text{Os}$ data that are more tightly defined around 55.9 Ma isochrons (Fig. 3). These observations confirm that the addition of unradiogenic Os to Svalbard sediments, as identified by Wiczeorek et al. (2013), was more than a regional-scale phenomenon, and that volcanism caused a significant (although locally disproportionate) impact on the Os-isotope composition of global seawater during the early stages of the PETM.

The second line of evidence for volcanism near the onset of the PETM comes from the sharp increase in the $^{187}\text{Os}/^{188}\text{Os}_{(i)}$ of Arctic Ocean seawater below the onset of the PETM at Site M0004A that is not observed in a similar stratigraphic position at any site outside the Arctic Basin (Fig. 2). This shift is interpreted to record a short interval (between 390.66–388.63 mcd) when hydrological restriction became sufficiently pronounced so as to cause the $^{187}\text{Os}/^{188}\text{Os}$ of Arctic Ocean seawater to evolve independently from the global seawater trend. Taking the age of the PETM onset and the age of the C25n/C24r magnetic reversal from Westerhold et al. (2008), the approximate timing of hydrographic

restriction in the Arctic Ocean can be estimated to have occurred ~50–500 kyr prior to the onset of the CIE. The broad range of estimates is partly the result of a paucity of age-control between the C25n/C24r reversal and the PETM (Backman et al., 2008), along with incomplete recovery of the PETM interval itself, which makes identification of the CIE onset highly imprecise (± 0.9 m). The relative ages noted here should therefore be treated with a degree of caution.

The temporary period of pronounced hydrographic restriction at Site M0004A is consistent with low sedimentary Mo/U ratios and very low $\delta^{98/95}\text{Mo}$ (Dickson et al., 2012). The abrupt increase in $^{187}\text{Os}/^{188}\text{Os}_{(i)}$ is unlikely to have been caused by an increase in the delivery of radiogenic Os to the Arctic Ocean from surrounding landmasses, because proxy data for moisture availability and continental temperatures do not show significant changes in pan-Arctic temperatures or hydrology before the onset of the CIE (Fig. 2, supplementary information) (Pagani et al., 2006; Weijers et al., 2007). The most likely explanation for the increase in the $^{187}\text{Os}/^{188}\text{Os}$ of Arctic Ocean seawater is therefore a reduction in the flux of less radiogenic Os into the Arctic Basin from the global ocean, as hydrological restriction in the basin became more pronounced (Fig. 1).

The temporary period of marked hydrological restriction in the Arctic Ocean preceding the onset of the PETM could have been caused by the tectonic uplift of the North Atlantic seaway. Evidence suggesting a regional relative sea-level (RSL) fall of >200 lm is associated with the Lamba/Flett sequence boundary in the Faroe-Shetland Basin and the Lista IIIb/Forties sequence boundary in the North Sea (Mudge and Bujak, 2001; Smallwood and Gill, 2002), the ages of which are constrained by the highest occurrence of the dinocyst *Alisocysta margarita* and the lowest occurrence of *Apectodinium augustum* (Mudge and Bujak, 2001). This RSL fall has been attributed to regional mantle-plume related uplift, lithospheric thinning and the commencement of an active period of NAIP volcanism (Smallwood and Gill, 2002; MacLennan and Jones, 2006). A fall in eustatic sea-level of several tens of metres, deduced from the sequence boundary on the New Jersey shelf, in New Zealand, and in the Tethys Ocean (Gavrilov et al., 2003; Sluijs et al., 2008b; Harding et al., 2011), is likely to have further contributed to the change in RSL, but cannot account for its full magnitude.

The timing of RSL fall in the North Atlantic seaway (Sluijs et al., 2008b) is consistent with available age constraints at Site M0004A (Expedition 302 Scientists, 2006; Backman et al., 2008) for the onset of enhanced hydrological restriction in the Arctic Ocean inferred from our Os-isotope record (Fig. 2). It is likely that seawater exchange across the North Atlantic seaway was limited throughout the PETM, since re-flooding took place after the last occurrence of the dinocyst *Cerodinium wardense* (Mudge and Bujak, 2001), which occurs stratigraphically above the PETM in Site M0004A (Expedition 302 Scientists, 2006). A slight alleviation of hydrographic restriction in the Arctic basin at the minimum of the CIE (Dickson et al., 2012) was probably facilitated by

a eustatic sea-level rise of 20–30 m at the onset of the PETM (Gavrilov et al., 2003; Sluijs et al., 2008b; Harding et al., 2011) that deepened the Arctic-Tethys connection through the central Asian Turgay Straits (Fig. 1). Seawater exchange through this seaway would have been slow enough to maintain a small difference between seawater $^{187}\text{Os}/^{188}\text{Os}$ within the Arctic Basin and the $^{187}\text{Os}/^{188}\text{Os}$ of the global ocean (Fig. 2), but was sufficiently voluminous for Arctic Ocean seawater $\delta^{98/95}\text{Mo}$ to record the global seawater $\delta^{98/95}\text{Mo}$ (Dickson et al., 2012). This difference in isotopic responses arises because the residence time of Mo in seawater is approximately an order of magnitude longer than for Os, and thus would require an almost complete cessation of seawater exchange before the $\delta^{98/95}\text{Mo}$ of Arctic Ocean seawater could begin to evolve independently from that of the global ocean.

It has been suggested that multiple sources of carbon could be necessary to reconcile observations of carbonate dissolution and the shape and magnitude of the PETM CIE (Zeebe et al., 2009; Dunkley-Jones et al., 2010; Carozza et al., 2011). Tectonic uplift of the North Atlantic seaway by NAIP volcanic activity could have altered North Atlantic Ocean circulation, generating warming at intermediate depths sufficient to destabilise gas hydrates buried in marine sediments (Bice and Marotzke, 2002; Sluijs et al., 2007; Roberts et al., 2009; Lunt et al., 2011). This scenario requires a time lag of at least several thousand years between the emergence of the North Atlantic seaway and the release of additional fossil carbon, and is consistent with the commencement of Arctic Basin restriction prior to the onset of the PETM observed at Site M0004A. A key test of this hypothesis will be the recovery of a complete PETM section from the Arctic Ocean by future drilling.

5. Conclusions

The new Os-isotope data presented here from the Peri-Tethys and Arctic Ocean sites all exhibit a small increase towards more radiogenic Os-isotope values during the PETM, reflecting a proportional increase in the flux of radiogenic Os to the oceans in response to elevated continental weathering rates. The data also indicate that seawater $^{187}\text{Os}/^{188}\text{Os}$ became relatively unradiogenic for a short interval of time either at, or slightly before the onset of the PETM. Together with evidence for enhanced hydrological restriction in the Arctic Basin in response to the emplacement of the NAIP, these data strongly support the hypothesis that volcanism triggered the carbon-cycle feedbacks that caused rapid global warming and environmental change during the PETM (Eldholm and Thomas, 1993; Svensen et al., 2004; MacLennan and Jones, 2006; Cohen et al., 2007; Storey et al., 2007a; Wiczeorek et al., 2013). Lastly, the new results show that there were clear differences between the Os-isotope compositions of seawater in the Arctic basin and in the global ocean during the early Eocene. Since restricted basins, such as the Arctic, are inherently prone to forming

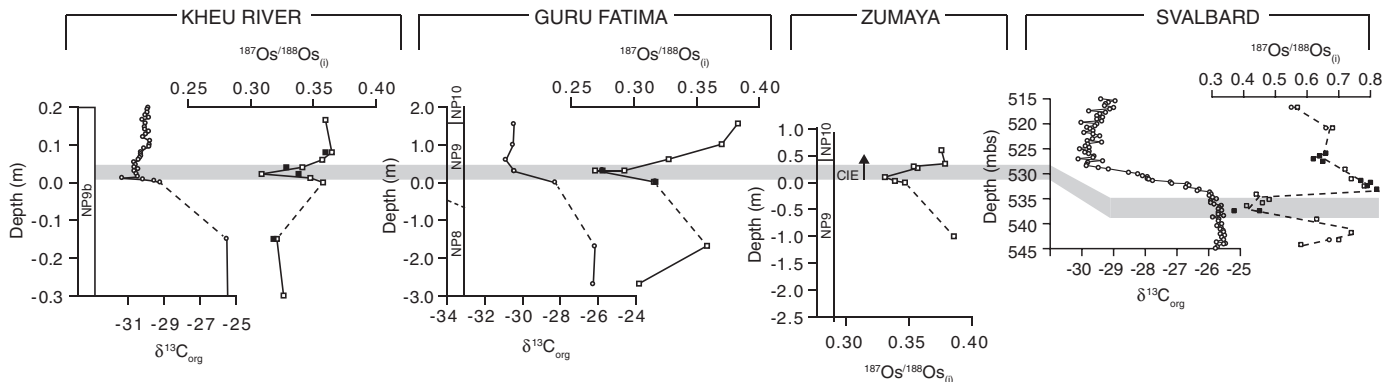


Fig. 4. Expanded view of C- and Os-isotope data across the onset of the PETM at Kheu River and Guru-Fatima (this study), Zumaya (Schmitz et al., 2004), and Svalbard core BH9/05 (Wiczeorek et al., 2013). The four sites all record excursions of local seawater $^{187}\text{Os}/^{188}\text{Os}$ to more unradiogenic values near the onset of the PETM.

organic-rich mudrock deposits, these observations reinforce the importance (e.g. Dickson et al., 2012, 2014b) of understanding the original depositional and hydrographic setting of the deposits before inferences about global seawater chemistry can be made (e.g. Paquay and Ravizza, 2012; Du Vivier et al., 2014).

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <http://dx.doi.org/10.1016/j.palaeo.2015.08.019>.

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