

# An osmium isotope excursion associated with the late Paleocene thermal maximum: Evidence of intensified chemical weathering

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**Abstract.** In the latest Paleocene an abrupt shift to more negative  $\delta^{13}\text{C}$  values has been documented at numerous marine and terrestrial sites [Bralower *et al.*, 1997; Cramer *et al.*, 1999; Kaiho *et al.*, 1996; Kennett and Stott, 1991; Koch *et al.*, 1992; Stott *et al.*, 1996; Thomas and Shackleton, 1996; Zachos *et al.*, 1993]. This carbon isotope event (CIE) is coincident with oxygen isotope data that indicate warming of surface waters at high latitudes of nearly 4°–6°C [Kennett and Stott, 1991] and more moderate warming in the subtropics [Thomas *et al.*, 1999]. Here we report  $^{187}\text{Os}/^{188}\text{Os}$  isotope records from the North Atlantic and Indian Oceans which demonstrate a >10% increase in the  $^{187}\text{Os}/^{188}\text{Os}$  ratio of seawater coincident with the late Paleocene CIE. This excursion to higher  $^{187}\text{Os}/^{188}\text{Os}$  ratios is consistent with a global increase in weathering rates. The inference of increased chemical weathering during this interval of unusual warmth is significant because it provides empirical evidence supporting the operation of a feedback between chemical weathering rates and warm global climate, which acts to stabilize Earth's climate [Walker *et al.*, 1981]. Estimates of the duration of late Paleocene CIE [Bains *et al.*, 1999; Bralower *et al.*, 1997; Norris and Röhl, 1999; Röhl *et al.*, 2000] in conjunction with the Os isotope data imply that intensified chemical weathering in response to warm, humid climates can occur on timescales of  $10^4$ – $10^5$  years. This interpretation requires that the late Paleocene thermal maximum Os isotope excursion be produced mainly by increased Os flux to the ocean rather than a transient excursion to higher  $^{187}\text{Os}/^{188}\text{Os}$  ratios in river runoff. Although we argue that the former is more likely than the latter, we cannot rule out significant changes in the  $^{187}\text{Os}/^{188}\text{Os}$  ratio of rivers.

## 1. Introduction

The interplay between global temperature and chemical weathering rates is a critical part of the ongoing debate over the underlying mechanisms that both perturb and stabilize Earth's climate system. The hypothesis that a negative feedback between global temperature and silicate weathering rates acts to stabilize the long-term climate of the Earth [Walker *et al.*, 1981] is appealing because of its simplicity but is extremely difficult to test. The feedback operates such that rising temperature accelerates silicate-weathering rates (schematically represented by the Urey reaction,  $\text{CaSiO}_3 + \text{CO}_2 \rightarrow \text{SiO}_2 + \text{CaCO}_3$ ), causing a drawdown of atmospheric  $\text{CO}_2$ . This in turn leads to cooler temperatures via diminished greenhouse warming. The idea that chemical weathering plays an important role in regulating Earth's climate history led to the development of a series of models which hindcast long-term (i.e., Phanerozoic) changes in atmospheric  $\text{CO}_2$  content based on geochemical mass balance calculations [Berner, 1994, and references therein]. Interest in the history of silicate weathering was further heightened by the hypothesis that orogenesis could accelerate the above reaction and overwhelm the supposed negative temperature feedback, giving rise to glaciation [Raymo and Ruddiman, 1992]. Recent studies of modern rivers show that  $\text{CO}_2$  consumption during chemical weathering is strongly dependent upon lithology and tectonic settings with little or no dependence on temperature, leading to the conclusion that

the temperature feedback on silicate weathering rate is largely unimportant in regulating global climate [Edmond and Huh, 1997]. In response, others have noted that in the absence of a Walker-style weathering feedback, there is no mechanism to prevent extreme variations in the  $\text{CO}_2$  content of the ocean-atmosphere system [Bickle *et al.*, 1998; Broecker and Sanyal, 1998].

The late Paleocene thermal maximum [Zachos *et al.*, 1993] represents a unique opportunity to examine the response of the Earth system to unusual warmth. This event occurred ~55 million years ago [Norris and Röhl, 1999]. It is identified in the marine record by an abrupt negative carbon isotope excursion coincident with the extinction of 35–50% of deep-sea foraminifera [Aubry *et al.*, 1998; Thomas and Shackleton, 1996]. Associated oxygen isotope data indicate sea surface temperatures at high latitudes increased by as much as 4°–6°C [Kennett and Stott, 1991] during the carbon isotope event (CIE) with more modest warming at lower latitudes [Thomas *et al.*, 1999]. Terrestrial records indicate unusually warm and humid conditions as well [Schroeder, 1992]. The duration of the LPTM is difficult to constrain. Interpolation between stratigraphic datums [Bralower *et al.*, 1997], models of the carbon cycle which attribute the CIE to methane hydrate decomposition [Bains *et al.*, 1999; Dickens *et al.*, 1997], and astronomically tuned estimates based on cyclostratigraphy [Norris and Röhl, 1999; Röhl *et al.*, 2000] suggests the duration of the CIE is roughly  $2 \times 10^5$  years. The high-resolution carbon isotope data and cyclostratigraphy results also indicate that the initial excursion to light carbon isotope ratios occurred in  $<10^4$  years. If the weathering feedback proposed by Walker *et al.* [1981] plays an important role in regulating Earth's climate on this timescale, then the unusual warmth of the late Paleocene should be accompanied by a net increase in global silicate weathering.

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Paper number 2000PA000541.

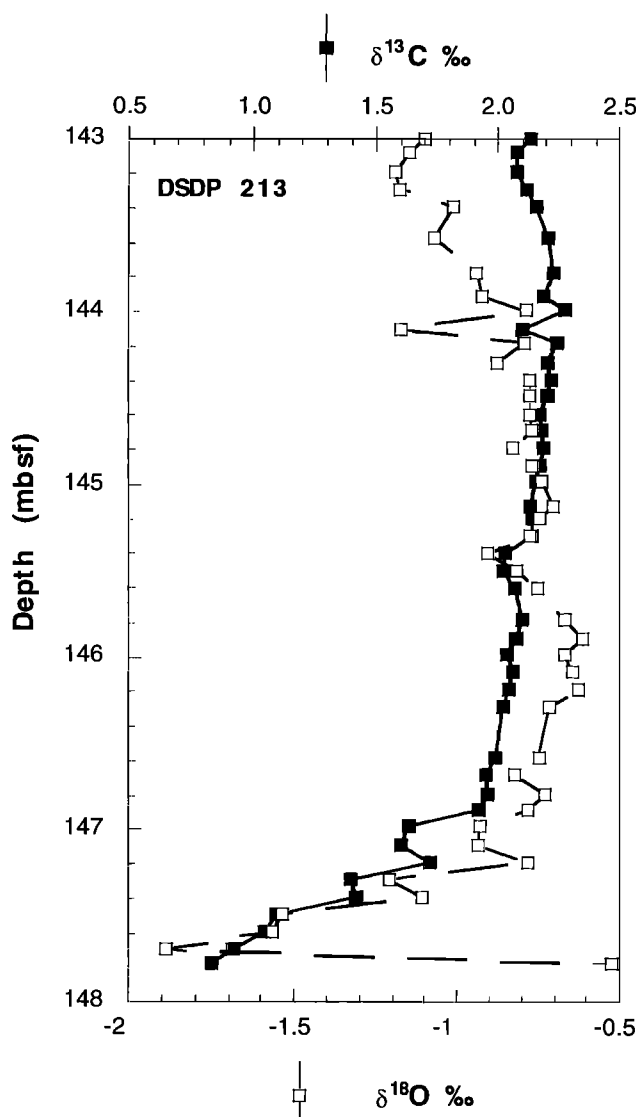
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The marine osmium (Os) isotope record is the only paleoceanographic tool currently available that has the potential to constrain changes in chemical weathering associated with brief climatic excursions such as the LPTM. Both pelagic clays and metalliferous carbonates preserve a record of past variations in the Os isotopic composition of seawater [Oxburgh, 1998; Pegrarn *et al.*, 1992; Pegrarn and Turekian, 1999; Peucker-Ehrenbrink *et al.*, 1995; Ravizza, 1993; Reusch *et al.*, 1998]. At any point in time, the  $^{187}\text{Os}/^{188}\text{Os}$  ratio of seawater reflects the balance between sources of Os with low ratios, such as hydrothermal and extraterrestrial sources, and continental sources with much higher  $^{187}\text{Os}/^{188}\text{Os}$  ratios. In this respect, the marine Os isotope record is analogous to the marine Sr isotope record, a widely exploited record of the geologic history of chemical weathering, with both systems providing globally integrated records of dissolved input to the ocean through time. The marine residence time of Sr is approximately  $\sim 2 \times 10^6$  years [Palmer and Edmond, 1992], too long to record short-duration perturbations in ocean chemistry related to intensified silicate weathering. The marine residence time of Os is 2–3 orders of magnitude shorter than that of Sr [Levasseur *et al.*, 1999; Oxburgh, 1998; Peucker-Ehrenbrink and Ravizza, 1996; Sharma *et al.*, 1999]. Consequently, it is possible that the marine Os isotope record could preserve evidence of transient perturbations in global chemical weathering rates. Given our current understanding of the marine Os cycle, a pulse of intensified chemical weathering is expected to produce an excursion to higher  $^{187}\text{Os}/^{188}\text{Os}$  ratios followed by a recovery to lower ratios. This study was designed to seek evidence of such an Os isotope excursion in the late Paleocene.

## 2. Samples

In order to construct a record of  $^{187}\text{Os}/^{188}\text{Os}$  variations across the LPTM event we have analyzed sediments recovered from two Deep Sea Drilling Project (DSDP) sites. One is located in the Indian Ocean (Site 213), and the other is located in the North Atlantic (Site 549). Site 213 was selected for initial analysis because it is lithologically similar to basal metalliferous carbonates which accumulate on recently formed oceanic crust and have been demonstrated to record detailed  $^{187}\text{Os}/^{188}\text{Os}$  variations of Neogene seawater [Oxburgh, 1998; Peucker-Ehrenbrink *et al.*, 1995; Ravizza, 1993; Reusch *et al.*, 1998]. Nannofossil [Aubry and Sanfilippo, 1999] and foraminifera [Berggren and Norris, 1997] biostratigraphy at DSDP 213 are consistent with a late Paleocene age. Bulk carbonate  $\delta^{13}\text{C}$  data from Site 213 show that these sediments capture the latter part of the CIE but not the onset of the event (Figure 1).<sup>1</sup> Sediments from DSDP Site 549 were selected for further investigation because previous work demonstrates this sequence records the CIE associated with the LPTM [Aubry, 1998; Stott *et al.*, 1996]. Lithologically, the sediments from DSDP Site 549 are red to buff colored clay bearing nannofossil oozes, suggesting a significant component of hydrogenous Fe oxides. These sediments are not, however, analogous to basal metalliferous sediments which have been used in previous Os isotope studies because they are located far above basement and presumably accumulated far removed from mid-ocean ridge hydrothermal activity.

<sup>1</sup>Supporting data for Figure 1 is available electronically at World Data Center-A for Paleoclimatology, NOAA/NGDC, 325 Broadway, Boulder, CO 80303 (e-mail: paleo@mail.ngdc.noaa.gov; URL: <http://www.ngdc.noaa.gov/paleo>).



**Figure 1.** Carbon and oxygen isotope data from analyses of bulk carbonate from Deep Sea Drilling Project (DSDP) Site 213. The low  $\delta^{13}\text{C}$  ratios at the bottom of this record correspond to the latter half of the carbon isotope event (CIE), which defines the late Paleocene thermal maximum (LPTM). Depth is reported in meters below seafloor (mbsf).

## 3. Methodology

Os isotope analyses of bulk sediments were performed by magnetic sector inductively coupled plasma source-mass spectrometry (ICP-MS). In this study, cellulose filter papers containing the Os preconcentrated by NiS fire assay were digested in closed Teflon vessels with 1 mL of nitric acid and then diluted fivefold with water. Os was separated from this solution and introduced directly into the plasma as  $\text{OsO}_4$  by bubbling the Ar sample gas through the solution [Hassler *et al.*, 2000]. The main advantage of this method relative to more common thermal ionization methods is the speed of analysis. An individual Os isotope analysis on the ICPMS requires  $\sim 15$  min of instrument time. The potential of this method to enhance sample throughput is important for high-resolution paleoceanographic studies. Analyses were performed over a period of 6 months on four separate days. On these days a total of 11 analyses

**Table 1a.** Re-Os and Bulk Carbonate C and O Isotope Data for Site 213<sup>a</sup>

Sample	Depth, mbsf	Re, ppt	Os, ppt	<sup>187</sup> Re/ <sup>188</sup> Os	<sup>187</sup> Os/ <sup>188</sup> Os	δ <sup>13</sup> C, ‰	δ <sup>18</sup> O, ‰
16R-1, 102-106	143.02		42		0.4089 ± 0.0063	2.13	-1.101
16R-1, 141-144	143.41		33		0.3494 ± 0.0023	2.156	-1.014
16R-2, 36-40	143.86		47		0.3416 ± 0.0028	2.23	-0.94
16R-2, 100-104	144.50	126	46	13.6	0.3530 ± 0.0057	2.201	-0.776
16R-2, 140-143	144.90		34		0.3465 ± 0.0039	2.17	-0.769
16R-2, 140-143	144.90		25		0.3443 ± 0.012		
16R-3, 41-44	145.41		31		0.3578 ± 0.004	2.032	-0.905
16R-3, 100-101	146.00		136		0.3628 ± 0.0044	2.038	-0.666
16R-3, 140-143	146.40		52		0.3417 ± 0.0026		
16R-4, 36-39	146.86		38		0.3494 ± 0.0022	1.917	-0.781
16R-4, 73-75	147.23	42	83	2.5	0.3748 ± 0.0036	1.724	-0.784
16R-4, 93-95	147.43	132	192	3.4	0.4017 ± 0.0025	1.419	-1.109
16R-4, 101-103	147.51	295	233	6.3	0.4124 ± 0.0119	1.096	-1.539
16R-4, 122-125	147.72	167	354	2.4	0.4015 ± 0.0033	0.92	-1.887

<sup>a</sup>Reported uncertainties in <sup>187</sup>Os/<sup>188</sup>Os ratios are based on 2σ in-run counting statistics. Note that the complete bulk carbonate C and O isotope data set is not tabulated but is plotted in Figure 1. Here mbsf is meters below seafloor and ppt is parts per thousand.

of between 400 and 1250 pg of Os standard were analyzed. After discarding one outlier, the mean <sup>187</sup>Os/<sup>188</sup>Os ratio after correction for instrumental mass bias was  $0.1740 \pm 0.0006$  (1 standard deviation). This value compares well with the accepted value established by repeated thermal ionization analysis of the same solution ( $0.1741 \pm 0.0003$ ; 1 standard deviation) [Hassler et al., 2000]. Measured <sup>190</sup>Os/<sup>188</sup>Os ratios for the standard analyses ( $1.9864 \pm 0.0035$ ; 1 standard deviation) were also indistinguishable from the accepted value (1.9840), indicating that there is no detectable carryover of Os between sample and standard analyses. If carryover did occur, elevated <sup>190</sup>Os/<sup>188</sup>Os ratios should be measured in standards because all samples are spiked with <sup>190</sup>Os in order to determine Os concentrations by isotope dilution.

Between 2 and 5 g of sediment were fused for each analysis. The reagents used in the NiS fire assay determine procedural blanks. The magnitude of the fusion blank correction is variable because the mass ratio of sediment to reagents varied among the sample suite. In all samples from Site 549 and in those samples from Site 213 representative of the LPTM, procedural blank corrections were 2.2% of the total Os concentration or less. In the low Os concentration samples from Site 213, blank correction were as large as 12%. Uncertainties associated with fusion blank corrections are the single most important factor limiting the precision and accuracy of these low-concentration samples.

## 4. Results

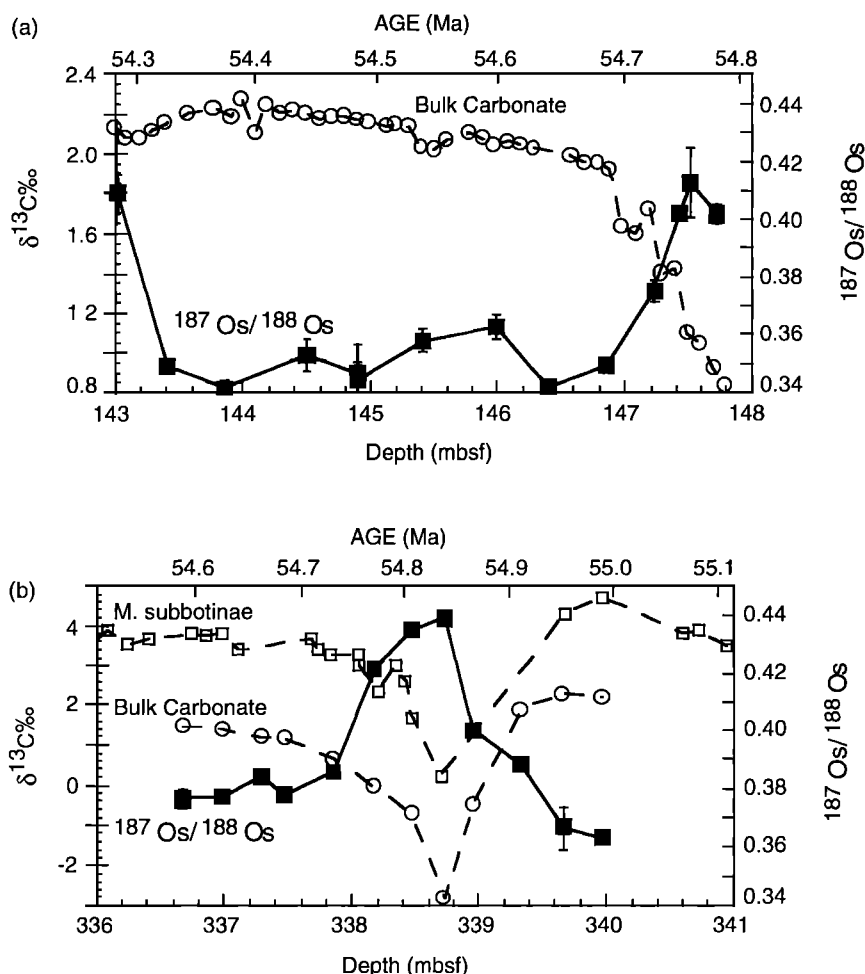
Measured <sup>187</sup>Os/<sup>188</sup>Os ratios at the two sites (Tables 1a and 1b) range from 0.34 to 0.44. These values are similar to those previously reported for Pacific metalliferous sediments [Peucker-Ehrenbrink et al., 1995] and Pacific pelagic clays [Pegram and Turekian, 1999] of Paleocene to Eocene age. Os concentrations of bulk sediment from Sites 213 and 549 are similar to those previously measured in metalliferous carbonates which have been shown to record past changes in the Os isotopic composition of seawater [Oxburgh, 1998; Pegram and Turekian, 1999; Peucker-Ehrenbrink et al., 1995; Ravizza, 1993; Reusch et al., 1998]. Measured Re/Os ratios are low enough that corrections for in situ decay of <sup>187</sup>Re are unimportant.

The <sup>187</sup>Os/<sup>188</sup>Os variations are well correlated with variations in stable carbon isotopes. At both the North Atlantic and Indian Ocean sites the highest <sup>187</sup>Os/<sup>188</sup>Os ratios are closely associated with the lowest δ<sup>13</sup>C values (Figure 2). As δ<sup>13</sup>C shifts toward higher values near the top of the carbon isotope excursion, <sup>187</sup>Os/<sup>188</sup>Os ratios decline to lower values. The amplitude of the excursion captured at both sites is ~0.06 <sup>187</sup>Os/<sup>188</sup>Os units, an increase of >10% relative to post-LPTM ratios. The North Atlantic record (Site 549), which spans the carbon isotope anomaly, shows that <sup>187</sup>Os/<sup>188</sup>Os isotope ratios recover to values similar to pre-LPTM (Figure 2b) values, indicating a transient perturbation of the marine Os cycle. There is a

**Table 1b.** Re-Os and Bulk Carbonate C and O Isotope Data for Site 549<sup>a</sup>

Sample	Depth, mbsf	Re, ppt	Os, ppt	<sup>187</sup> Re/ <sup>188</sup> Os	<sup>187</sup> Os/ <sup>188</sup> Os	δ <sup>13</sup> C, ‰	δ <sup>18</sup> O, ‰
16R-4, 68-72	336.68	35	145	1.2	0.3764 ± 0.0031	1.457	-0.53
16R-4, 98-102	336.98	41	129	1.6	0.3773 ± 0.0016	1.388	-0.527
16R-5, 11-15	337.29	34	138	1.2	0.3839 ± 0.0013	1.192	-0.846
16R-5, 29-32	337.47		119		0.3779 ± 0.0013	1.147	-0.881
16R-5, 67-71	337.85	69	132	2.6	0.3856 ± 0.0017	0.637	-1.025
16R-5, 99-103	338.17	44	141	1.6	0.4212 ± 0.0021	-0.056	-1.764
16R-5, 129-133	338.47	77	159	2.4	0.4350 ± 0.0012	-0.721	-2.022
16R-6, 5-8	338.73	50	199	1.3	0.4387 ± 0.0018	-2.816	0.627
16R-6, 28-33	338.96	49	288	0.8	0.4000 ± 0.0023	-0.473	-1.169
16R-6, 65-69	339.33	72	243	1.5	0.3883 ± 0.0021	1.879	-1.003
16R-6, 98-102	339.66	65	172	1.9	0.3666 ± 0.0073	2.293	-0.651
16R-6, 129-131	339.97		259		0.3633 ± 0.0014	2.191	-0.425

<sup>a</sup>Reported uncertainties in <sup>187</sup>Os/<sup>188</sup>Os ratios are based on 2σ in-run counting statistics.



**Figure 2.** Comparison of bulk sediment  $^{187}\text{Os}/^{188}\text{Os}$  variations to carbon isotope variations in (a) Site 213 and (b) Site 549. Carbon isotope data for the planktonic foraminifer *M. subbotinae* at Site 549 are from Stott *et al.* [1996]. Note that the largest  $^{187}\text{Os}/^{188}\text{Os}$  ratios are associated with the lightest carbon isotope ratios at both sites and that the amplitude of Os isotope excursion is similar at both sites. Depth is reported in meters below seafloor (mbsf). The light carbon isotope ratios that correspond to the CIE provide the basis for correlating the two Os isotope records. Age assignments are based upon the carbon isotope stratigraphy and an age of 55 Ma for the initiation of the CIE [Norris and Röhl, 1999] and an estimated duration for the CIE of 220 kyr [Röhl *et al.*, 2000]. These age assignments are intended to facilitate correlation of the two records based on our interpretation of the carbon isotope data. Note that the 55 Ma age for the LPTM conflicts with currently assigned ages for nearby biostratigraphic and magnetostratigraphic datums [Berggren *et al.*, 1995]. This inconsistency reflects the need for an improved and internally consistent geochronology for the upper Paleocene to the lowermost Eocene [Aubry *et al.*, 1998].

systematic offset in  $^{187}\text{Os}/^{188}\text{Os}$  ratio between the two sites of  $\sim 0.03$   $^{187}\text{Os}/^{188}\text{Os}$  units, with the North Atlantic being more radiogenic than the Indian Ocean. The highest Os concentrations at both sites occur close to but not exactly coincident with the highest  $^{187}\text{Os}/^{188}\text{Os}$  ratios. Bulk sediment Os concentrations and  $^{187}\text{Os}/^{188}\text{Os}$  ratios do not show the hyperbolic relation required by two-component physical mixing models. This indicates two-component physical mixing of isotopically distinct end-members is not controlling the observed Os isotope variations.

## 5. Discussion

### 5.1. A Seawater Os Isotope Record of the LPTM from DSDP Sites 213 and 549

We interpret the  $^{187}\text{Os}/^{188}\text{Os}$  variations at Sites 213 and 549 as a record of the Os isotopic composition of seawater across the LPTM.

Several lines of argument support this interpretation. First, by analogy to other marine sediments used to reconstruct the seawater Os isotope record [Ravizza, 1993], the Os concentrations at both sites are sufficiently high that hydrogenous (i.e., seawater derived) Os should dominate the sediment Os budget. Second, the absolute  $^{187}\text{Os}/^{188}\text{Os}$  ratios are similar to one another and to existing data from Pacific sediments of similar age (see Table 2 and discussion of LL44-GPC3 in section). It is unlikely that such a similarity would result as a consequence of physical mixing of isotopically distinct components. Third, the Os isotope excursion at both sites must be nearly synchronous because it coincides so with the CIE. Fourth, the amplitude of the  $^{187}\text{Os}/^{188}\text{Os}$  excursion, as defined by the maximum  $^{187}\text{Os}/^{188}\text{Os}$  and the post-CIE plateau, at these widely separated sites is essentially the same.

As noted above, there is a systematic offset between the North Atlantic and Indian Ocean sites of  $\sim 0.03$   $^{187}\text{Os}/^{188}\text{Os}$  units. It is pos-

**Table 2.** Summary of  $^{187}\text{Os}/^{188}\text{Os}$  Variations in Cores From the Pacific, Indian, and Atlantic Oceans

Location/Site	Approximate Duration <sup>a</sup>	$^{187}\text{Os}/^{188}\text{Os}$
North Pacific/ LL44-GPC3	≈ 3 million years	0.32–0.41
Indian Ocean/DSDP 213	≈ 220,00 years	0.34–0.41
North Atlantic/DSDP 549	≈ 220,00 years	0.36–0.44

<sup>a</sup>Duration estimates are based on sedimentation rate estimates for GPC3 [Janecek and Rea, 1983] and the estimated duration of LPTM carbon isotope event [Röhl et al., 2000]

sible that this difference is the result of a subtle offset between the  $^{187}\text{Os}/^{188}\text{Os}$  of the bulk sediment and that of contemporaneous seawater. It is equally likely that this difference reflects a true contrast in the  $^{187}\text{Os}/^{188}\text{Os}$  ratio between the North Atlantic and Indian Oceans. Analyses of the surfaces of manganese crusts indicate a similar contrast may exist in the modern ocean [Burton et al., 1999]. In spite of the uncertainty as to the cause of this systematic offset between Sites 213 and 549, synchronous Os isotope excursions of similar amplitude at these two widely separated sites provide strong evidence for a transient whole-ocean shift to more continent-like  $^{187}\text{Os}/^{188}\text{Os}$  ratios during the LPTM.

The youngest sample from the Site 213 record has a  $^{187}\text{Os}/^{188}\text{Os}$  ratio nearly as high as samples from the LPTM interval of this core. It is difficult to judge the significance of this sample because it is an isolated occurrence. If abrupt excursions of this sort are common in the marine Os record, the likelihood that the correlated Os and carbon isotope variations described above is fortuitous increases. It is also possible that this sample records part of a minor warming event following the LPTM because it coincides with a local minimum in bulk carbonate  $\delta^{18}\text{O}$  (Figure 1) and is not discordant in the  $^{187}\text{Os}/^{188}\text{Os}$ - $\delta^{18}\text{O}$  correlation (Figure 3a). This study of the LPTM and a study of recent glacial episodes [Oxburgh, 1998] are the only high-resolution studies of seawater Os isotope variations made to date. Consequently, there is little basis for evaluating how commonly abrupt excursions in the marine Os isotope record occur. The relatively good agreement between Neogene records based on different sediment cores sampled at low temporal resolution [Pegram et al., 1992; Pegram and Turekian, 1999; Peucker-Ehrenbrink et al., 1995; Ravizza, 1993; Reusch et al., 1998] suggest that such large-amplitude, abrupt excursions are not ubiquitous. Nevertheless, additional high temporal resolution Os isotope data sets are needed to better address this concern.

## 5.2. Cause and Significance of the LPTM $^{187}\text{Os}/^{188}\text{Os}$ Excursion

Our preferred interpretation of the seawater Os isotope record is that the excursion to higher seawater  $^{187}\text{Os}/^{188}\text{Os}$  ratios results from an increase in the total flux of Os supplied to the ocean by continental weathering. The LPTM Os isotope excursion could also result from an increase in the average  $^{187}\text{Os}/^{188}\text{Os}$  ratio of soluble Os from the continents. Although we consider these two scenarios separately below, these two possibilities are not mutually exclusive. Throughout this discussion we make the implicit assumption that fluxes of unradiogenic Os to the ocean, related to seafloor hydrothermal activity and/or cosmic dust deposition, remained constant during the LPTM because at present, there is no evidence to suggest a transient reduction of these inputs.

**5.2.1. Changes in total Os flux to the ocean associated with enhanced continental input during the LPTM.** The simplest interpretation of the LPTM Os isotope shift is that it reflects an episode of increased chemical weathering on the continents, which results in an increase in the total flux of radiogenic Os to the oceans. A crude estimate of the relative increase in Os flux can be obtained by considering the  $^{187}\text{Os}/^{188}\text{Os}$  ratio of seawater to be the result of mixing between unradiogenic hydrothermal Os and radiogenic continental Os with fixed  $^{187}\text{Os}/^{188}\text{Os}$  for both end-members. At steady state the mole fraction  $F$  of  $^{188}\text{Os}$  in seawater derived from continental weathering is

$$F = (R_s - R_h)/(R_s - R_h), \quad (1)$$

where  $R$  denotes the  $^{187}\text{Os}/^{188}\text{Os}$  ratio and the subscripts  $s$ ,  $h$ , and  $r$  denote seawater, hydrothermal, and rivers, respectively. To compare the relative increase in continental Os during the LPTM peak with the post-LPTM plateau, we assume each can be approximated as a separate steady state mixture and calculate the ratio of the mixing fractions as

$$F_{\text{LPTM}}/F_{\text{post-LPTM}} = [R_s(\text{LPTM}) - R_h]/[R_s(\text{post-LPTM}) - R_h]. \quad (2)$$

Using  $^{187}\text{Os}/^{188}\text{Os}$  ratio of the hydrothermal end-member (0.12) and the  $^{187}\text{Os}/^{188}\text{Os}$  ratios for the LPTM and post-LPTM from Site 549 yields a fraction ratio of 1.23. This ratio indicates a 23% larger contribution of continental Os to seawater at the height of the LPTM compared to the period immediately thereafter. Using data from Site 213 to make the same calculation yields a 26% larger continental Os contribution during the LPTM.

**5.2.2. Changes in the  $^{187}\text{Os}/^{188}\text{Os}$  of riverine input during the LPTM.** The magnitude of the change in riverine  $^{187}\text{Os}/^{188}\text{Os}$  ratio that would have been required to produce the observed seawater Os record can be estimated by assuming other relevant parameters ( $F$  and  $R_h$ ) remained constant. As above, we assume that the LPTM and the period of time immediately thereafter can be represented as separate steady state mixtures of Os derived from continental and hydrothermal sources. In this case, the mixing equation is recast in the form

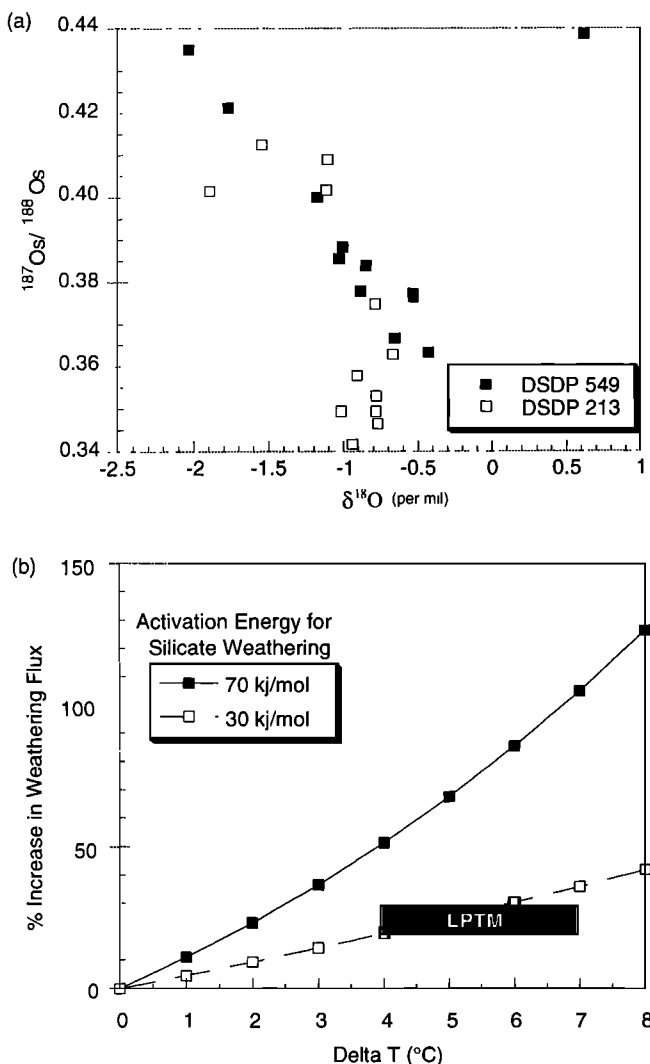
$$R_w = R_s F + R_h (1-F), \quad (3)$$

where the notation used is identical to (1). Writing separate equations for LPTM and post-LPTM conditions and subtracting them yields

$$R_w(\text{LPTM}) - R_w(\text{post-LPTM}) = F [R_s(\text{LPTM}) - R_s(\text{post-LPTM})]. \quad (4)$$

For a wide range of assumed  $^{187}\text{Os}/^{188}\text{Os}$  for post-LPTM input, ranging from 0.5 to 1.5, the increase in  $^{187}\text{Os}/^{188}\text{Os}$  in LPTM riverine input required to produce the Os isotope excursion observed in seawater corresponds to a  $^{187}\text{Os}/^{188}\text{Os}$  ratio roughly 20% larger than post-LPTM values. Given the large range of  $^{187}\text{Os}/^{188}\text{Os}$  ratio measured in modern rivers (0.4 – 2.5) [Levasseur et al., 1999; Sharma et al., 1999], we cannot rule out the possibility that changes in the  $^{187}\text{Os}/^{188}\text{Os}$  of riverine input to the oceans is an important contributor to the LPTM Os isotope excursion.

**5.2.3. Discerning between changes in the flux and isotopic composition of riverine Os during the LPTM.** Although it is not possible to state with any degree of certainty that increased continental Os flux to the ocean during the LPTM to the ocean caused the excursion to higher  $^{187}\text{Os}/^{188}\text{Os}$  ratios, there are several lines of argument that are supportive of this interpretation. These include (1) independent evidence of an accelerated hydrologic cycle during the



**Figure 3.** (a) The plot of  $^{187}\text{Os}/^{188}\text{Os}$  versus  $\delta^{18}\text{O}$  of bulk carbonate, which suggests that seawater  $^{187}\text{Os}/^{188}\text{Os}$  ratios increase with increasing temperatures. Note that bulk carbonate oxygen isotope data are only a proxy for local temperature variations. The sample from Site 549 that plots away from the correlation is from the  $\delta^{13}\text{C}$  minimum and has experienced the most extensive carbonate dissolution; percent carbonate in this sample is only 3% versus 40–50% above and below the CIE. Thus we suspect the larger  $\delta^{18}\text{O}$  of this sample reflects the influence of dissolution-resistant benthic foraminifer. (b) The percent increase in weathering flux, inferred from Os isotope data, and the estimated average surface temperature increase associated with the LPTM, which are used to define the dark field labeled “LPTM.” The curves represent the calculated temperature dependence of silicate weathering rates based on activation energies measured in the laboratory. The overlap of the LPTM field with the 30 kJ/mol activation energy curve indicates that Os isotope-based weathering flux estimates are consistent with available data constraining both the LPTM temperature increase and the temperature dependence of silicate weathering rates.

LPTM, (2) the magnitude of the increase in temperature and weathering flux estimated for the LPTM, and (3) the abrupt onset of the LPTM. Each of these is discussed in turn below.

Several independent lines of evidence suggest an accelerated hydrologic cycle operated during the LPTM. Many workers have argued that increased abundance of kaolinite and/or increased kaolinite/illite ratios associated with some LPTM sections provide direct evidence of warm, humid climates [Cramer *et al.*, 1999;

Gibson *et al.*, 1993; Kaiho *et al.*, 1996; Robert and Kennett, 1994]. However, the timescale of kaolinite formation is long compared to the duration of the LPTM [Thiry, 2000]; therefore clay mineralogy cannot provide time-resolved information about continental weathering intensity. Climate simulations [Sloan and Thomas, 1998] indicate that increased precipitation over land surfaces was likely during the LPTM. Changes in nannofossil morphology associated with LPTM suggest an adaptation toward more buoyant forms, consistent with the inference of decreased surface water density [Aubry *et al.*, 2000]. In the context of these independent lines of evidence, it is reasonable to interpret the shift in the  $^{187}\text{Os}/^{188}\text{Os}$  ratio of seawater at the LPTM as the result of increased Os flux from the continents. The Os isotope data make a significant contribution to this line of investigation because they provide the only compelling evidence that enhanced weathering and runoff was globally rather than locally significant.

Laboratory measurements of the activation energy of silicate weathering [Kump *et al.*, 2000; White *et al.*, 1999] predict a specific relationship between silicate weathering rates and temperature. At both Sites 213 and 549 the  $\delta^{18}\text{O}$  of bulk carbonate and  $^{187}\text{Os}/^{188}\text{Os}$  are correlated with one another (Figure 3a). Considering oxygen isotopes as a proxy for local temperature and Os isotopes as a proxy for weathering flux, this plot qualitatively indicates weathering flux increases with increasing temperature. To examine this relationship in a more rigorous way would require knowledge of an average temperature increase representative of weathering continental environments. We contend that a reasonable guess at such a temperature increase is in the range of 4°–7°C. This is based on sea surface temperature estimates [Kennett and Stott, 1991; Thomas and Shackleton, 1996; Thomas *et al.*, 1999] showing increases of 4°–6° and 1°–4° at high and low latitudes, respectively. This temperature range and the 20–30% increase in weathering flux estimated above are consistent with an effective activation energy for weathering of ~30 kJ/mol (Figure 3b), a value at the low end of the ranges measured in silicate weathering rate experiments [White *et al.*, 1999]. Although this comparison is a gross extrapolation, it shows that interpreting the Os isotope excursion as a proxy for weathering flux yields an estimated weathering rate increase that is consistent with available data constraining both the LPTM temperature increase and the temperature dependence of silicate weathering rates.

The abruptness of the onset of the LPTM also suggests that the associated Os isotope excursion is more likely related to changing total Os flux from the continents rather than changing  $^{187}\text{Os}/^{188}\text{Os}$  of river input. The short and transient nature of the Os isotope excursion associated with the LPTM makes it unlikely that tectonic processes could produce the observed Os isotopic excursion by varying the nature of the exposed lithologies during the course of the LPTM. This is a fundamentally important contrast between interpreting short-term variations in the Os isotopic composition of seawater, as we do here, and interpreting long-term Cenozoic trends. There is one particular scenario of variable riverine  $^{187}\text{Os}/^{188}\text{Os}$  through the LPTM that warrants specific consideration: the possibility that the Os isotope excursion might reflect a brief episode of erosion of sedimentary organic matter with large  $^{187}\text{Os}/^{188}\text{Os}$  ratios. The clear correlation of high  $^{187}\text{Os}/^{188}\text{Os}$  with light  $\delta^{13}\text{C}$  values (Figure 2) motivates us to address this scenario explicitly because a similar correlation is apparent in the Neogene Os isotope record [Ravizza, 1993], albeit on a much longer timescale. In addition, exactly this mechanism is invoked to explain the long-term shift in bulk carbon isotopes to lighter values as a result of the initial stages of the collision of India and Asia from the Paleocene

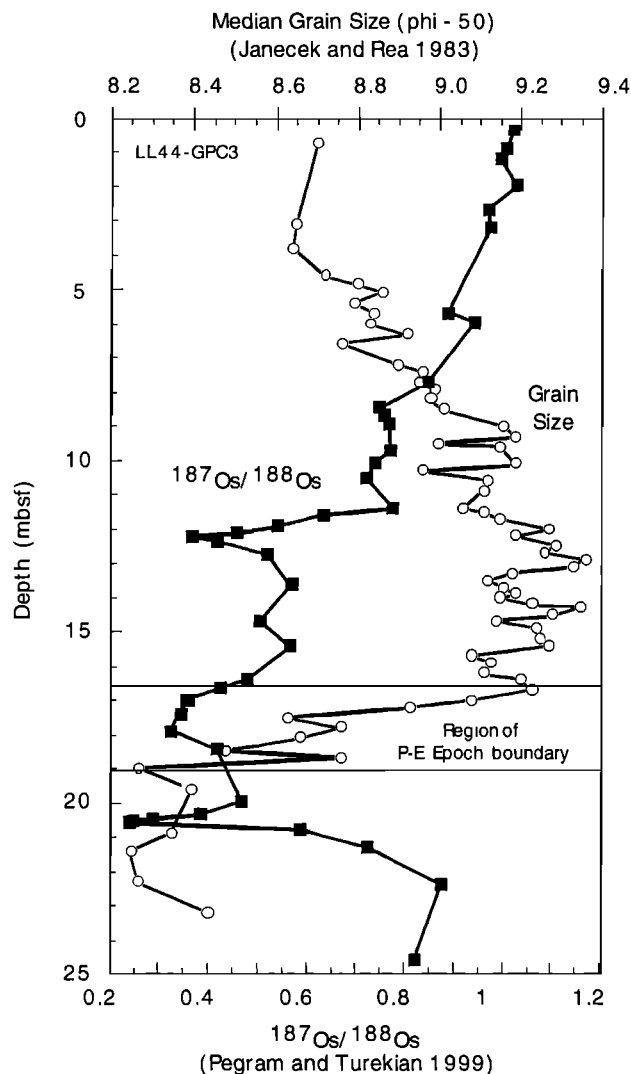
to the Eocene and to suggest that the unusual warmth associated with this period may have resulted from a related increase in atmospheric  $\text{CO}_2$  levels [Beck *et al.*, 1995, 1998]. If the CIE is attributed to a net decrease in the size of the sedimentary organic carbon reservoir rather than gas hydrate release, then the excursion to higher  $^{187}\text{Os}/^{188}\text{Os}$  can easily be attributed to erosion of radiogenic ancient sedimentary organic matter. Other workers have argued that the CIE is too large and abrupt to be explained by burial and erosion of sedimentary organic matter, and favor attributing the CIE to gas hydrate decomposition [Dickens *et al.*, 1997; Thomas and Shackleton, 1996]. Recent work demonstrating a very abrupt ( $<10^4$  years) onset for the CIE [Bains *et al.*, 1999; Norris and Rohl, 1999; Rohl *et al.*, 2000] strongly supports this latter view and argue against interpreting the Os isotope excursion as the result of the erosion of ancient sedimentary organic matter.

There are other scenarios that might give rise to large and rapid changes in the  $^{187}\text{Os}/^{188}\text{Os}$  of riverine input that cannot be discounted. For example, shifts in continental climate, such as changes in precipitation patterns or/and mean annual temperatures, could be called upon to produce this effect either by increasing weathering in one region at the expense of another or by changing the extent to which an isotopically heterogeneous terrain is weathered. Therefore our interpretation of the LPTM Os isotope excursion as evidence for increased continental weathering rates during the LPTM must be regarded as tentative. Better constraining the processes responsible for this Os isotope excursion is important because the implied increase in chemical weathering during this episode of unusual warmth supports the operation of a feedback in which atmospheric  $\text{CO}_2$  levels are regulated by the temperature dependence of silicate weathering rates.

### 5.3. Comparison of the LPTM to Recent Glacial-Interglacial Variations in the Seawater Os Isotope Record

During the last two major glacial periods (isotope stages 2 and 6), brief excursions to lower  $^{187}\text{Os}/^{188}\text{Os}$  ratios have been found in Pacific metalliferous sediments and interpreted as an indication of diminished chemical weathering on the continents during cold, arid glacial periods [Oxburgh, 1998]. Both climatically and in terms of the direction of the Os isotope excursion, the LPTM is the opposite of the much more recent glacial episodes. Just as global aridity and colder temperatures were invoked by Oxburgh to explain shifts to lower  $^{187}\text{Os}/^{188}\text{Os}$  during recent glacial periods, we attribute the higher  $^{187}\text{Os}/^{188}\text{Os}$  at the LPTM to generally warmer, more humid conditions as described above. The coherent response of the marine Os isotope record to these contrasting climate regimes supports the notion that high-resolution Os isotope studies may be broadly applicable to studying the possible feedback between global weathering rates and climate change.

Two additional aspects of the comparison between recent glacial episodes and the LPTM deserve mention. First is the significant difference of the duration of the excursion. While the  $^{187}\text{Os}/^{188}\text{Os}$  minima associated with recent glacial episodes span at most a few thousand years, the LPTM event spanned roughly 200,000 years [Bains *et al.*, 1999]. Thus the slope of the seawater Os curve during the LPTM recovery is modest compared to that associated with glacial transitions. Second, interpretation of the LPTM Os excursion is less complicated than those associated with recent glacials. The late Paleocene and early Eocene are considered to be ice-free periods [Sloan and Thomas, 1998; Zachos *et al.*, 1993]. Therefore other potential explanations of glacial Os isotope excursions, re-



**Figure 4.** A reinterpretation of the timing of Os isotope variations in LL44-GPC3 [Pegram and Turekian, 1999] based on grain size data [Janecek and Rea, 1983]. The abrupt shift to smaller median grain size of eolian material (larger phi values) marks the Paleocene-Eocene (P-E) epoch boundary in several Pacific cores [Rea, 1998]. This correlation indicates that the long-term  $^{187}\text{Os}/^{188}\text{Os}$  of seawater is characterized by a broad minimum in the vicinity of the P-E boundary.

lated to weathering of glaciated terrains [Peucker-Ehrenbrink and Blum, 1998], are not directly relevant.

### 5.4. Paleocene-Eocene Transition as Recorded in LL44-GPC3 and Its Relationship to the LPTM

The most complete single Os isotope record is from LL44-GPC3, a North Pacific pelagic clay sequence [Pegram and Turekian, 1999]. A dramatic decrease in eolian grain size occurs in several Pacific cores close to the Paleocene-Eocene (P-E) epoch boundary [Rea, 1998] including GPC3. This change in grain size in GPC3 [Janecek and Rea, 1983] provides a stratigraphic marker which allows identification of the portion of the GPC3 Os isotope record that includes the LPTM and P-E boundary intervals (Figure 4). Detailed correlation of Os isotope data between Pacific GPC3 and the North Atlantic and Indian Ocean is not possible because of the

relatively low temporal resolution of the GPC3 record. We discuss the GPC3 Os isotope record here for two reasons. First, the lower-resolution GPC3 record provides a broader temporal context in which long-term warming from the Paleocene into the Eocene can be examined. Second, and more importantly, the similarity in absolute  $^{187}\text{Os}/^{188}\text{Os}$  ratios between GPC3 and the North Atlantic and Indian Ocean sites (Table 2) provides strong empirical evidence that Os isotopic variations at all three sites are controlled mainly by changes in the  $^{187}\text{Os}/^{188}\text{Os}$  ratio of seawater through time.

The GPC3 record is characterized by a minimum ( $^{187}\text{Os}/^{188}\text{Os} \approx 0.32$ ) during the period of most rapid grain size decrease and higher  $^{187}\text{Os}/^{188}\text{Os}$  ratios ( $\approx 0.41$ ) before and after the grain size transition (Figure 3). This feature probably spans several million years on the basis of sedimentation rate estimates [Janecek and Rea, 1983; Kyte et al., 1993]. The higher  $^{187}\text{Os}/^{188}\text{Os}$  ratios after the P-E epoch boundary are substantiated by a spot analysis of Pacific metalliferous sediments of early Eocene age ( $^{187}\text{Os}/^{188}\text{Os} \approx 0.48$ ) [Peucker-Ehrenbrink et al., 1995]. A single analysis of leachable Os in a pelagic clay of late Paleocene age ( $^{187}\text{Os}/^{188}\text{Os} \approx 0.45$ ) [Peucker-Ehrenbrink et al., 1995] is distinctly higher than the GPC3 data but similar to the highest values measured at Site 549. The range of  $^{187}\text{Os}/^{188}\text{Os}$  ratios measured in Sites 213 and 549 are very similar to those reported from GPC3 (Table 2). However, the shape of the high- and low-resolution records is different. The higher-resolution data sets spanning the LPTM are characterized by a local maximum coincident with the CIE (Figure 2), while the GPC3 record is characterized by a broad minimum as described above. In total, the data suggest that the long-term transition from the late Paleocene into the early Eocene is characterized by generally low  $^{187}\text{Os}/^{188}\text{Os}$  ratios with at least one brief excursion to higher  $^{187}\text{Os}/^{188}\text{Os}$  within the broad minimum defined by the GPC3 record.

It is noteworthy that the age model for GPC3 [Kyte et al., 1993] used by Pegram and Turekian [1999] yields a mid-Paleocene age for the local minimum in the seawater  $^{187}\text{Os}/^{188}\text{Os}$  record rather than the Paleocene-Eocene boundary age we suggest here. In using the eolian grain size data to reinterpret the timing of this minimum, we open the possibility that the generally low  $^{187}\text{Os}/^{188}\text{Os}$  ratio of seawater during the Paleocene-Eocene transition resulted from increased supply of unradiogenic Os from recent magmatic activity. Several potential sources have been identified: (1) increased seafloor hydrothermal activity related to plate reorganization [Owen and Rea, 1985], (2) extensive North Atlantic volcanism [Thomas and Shackleton, 1996], and (3) Caribbean volcanism [Bralower et al., 1997]. The prospect of drawing a causative link between the low  $^{187}\text{Os}/^{188}\text{Os}$  ratio of seawater and any of these magmatic episodes is important because each of these has been suggested as a potential trigger for methane hydrate decomposition. At present, this link is only speculative and other possibilities for explaining

this minimum, such as ophiolite weathering and recycling of extra-terrestrial Os derived from the K-T boundary impact [Pegram and Turekian, 1999], remain reasonable hypotheses.

## 6. Conclusions

We have documented a large (10%) increase in the  $^{187}\text{Os}/^{188}\text{Os}$  ratio at two widely separated sites that is coincident with the late Paleocene thermal maximum. On the basis of the coherence of these two new records with one another and with existing data from Pacific sediments we have concluded that there was a transient whole-ocean shift to higher seawater  $^{187}\text{Os}/^{188}\text{Os}$  ratios during the LPTM. The transient nature of the excursion and independent supporting data indicative of an accelerated hydrologic cycle suggest that this Os isotope excursion is evidence of a globally significant increase in chemical weathering. This interpretation supports the operation of a feedback between climate and chemical weathering rates and suggests that  $\text{CO}_2$  drawdown associated with such a feedback may have played an important role in arresting LPTM warming. The validity of this interpretation depends critically upon our assumption that the  $^{187}\text{Os}/^{188}\text{Os}$  of riverine flux did not change significantly during the LPTM. Comparison of the LPTM Os excursion reported here to those associated with recent glaciation reveal a coherent picture in which brief periods of extreme warmth and humidity are characterized by excursions to high  $^{187}\text{Os}/^{188}\text{Os}$  ratios, while the opposite is true of brief episodes of extreme cold and aridity. Thus available Os isotope data suggest that a weathering-based mechanism does indeed act to ameliorate Earth's climate [Walker et al., 1981] during climatic extremes on timescales of  $10^4$ – $10^5$  years. We stress that these high temporal resolution studies reveal little about the factors controlling the long-term evolution of the Os isotopic composition of seawater. In the context of establishing the coherence of these new LPTM Os data with existing data from LL44 GPC3, we have reinterpreted age-depth relations in this core and infer that the Paleocene-Eocene epoch boundary falls within a broad minimum in the seawater  $^{187}\text{Os}/^{188}\text{Os}$  record, indicative of a relative increase in the amount of seawater Os derived from young mantle-derived rocks. This is consistent with evidence of widespread volcanism at this time.

**Acknowledgments.** We thank Lary Ball and the W.H.O.I ICP Facility for operation and support of the Finnigan MAT sector field inductively coupled plasma mass spectrometer (SF-ICPMS) in making these measurements. GR thanks B. Peucker-Ehrenbrink and J. Howard for helpful comments on early drafts of this manuscript. T. Bralower, R. Oxburgh, and an anonymous reviewer offered many constructive comments. Curators of the Ocean Drilling Program provided sample material essential for this study. This work was supported by NSF Awards OCE-99190500 (RDN), OCE-9819296 (GR) and EAR-9804864 (GR).

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(Received May 19, 2000; revised December 14, 2000; accepted December 27, 2000.)