Clay assemblage and oxygen isotopic constraints on the weathering response to the Paleocene-Eocene thermal maximum, east coast of North America

Cédric M. John1*, Neil R. Banerjee2, Fred J. Longstaffe2, Cheyenne Sica2, Kimberly R. Law2, and James C. Zachos3
1Department of Earth Science and Engineering, Imperial College London, Prince Consort Road, London SW7 2BP, UK
2Department of Earth Sciences, The University of Western Ontario, London, Ontario N6A 5B7, Canada
3Earth & Planetary Sciences Department, University of California–Santa Cruz, Santa Cruz, California 95064, USA

ABSTRACT
The Paleocene-Eocene thermal maximum, a transient global warming event, is characterized by extensive evidence of a more active hydrological cycle. This includes a widespread pulse of kaolinite accumulation on continental margins, viewed as the by-product of either enhanced chemical weathering consistent with much more humid conditions and/or increased erosion of previously deposited laterites. The former would be more consistent with year-round humid conditions, whereas the latter might be indicative of extreme seasonal precipitation patterns. To assess these hypotheses, we present a new high-resolution clay mineral assemblage and oxygen isotope record from Bass River, a site on the New Jersey margin (east coast of North America), which shows a sharp rise in the abundance of kaolinite beginning a few thousand years before the onset of the carbon isotope excursion (CIE). The δ18O of the <2-µm-size fraction exhibits a shift toward lower values during the event. On the basis of a coeval shift in clay assemblages, the shift in δ18Oclays can be explained by a shift in the relative percent of the primary clay phases rather than a change in the isotopic composition of kaolinite, as would be expected if the kaolinite had been produced primarily during the Paleocene-Eocene thermal maximum. This finding points to accelerated exhumation and erosion of kaolinitic soils, most likely Cretaceous laterites.

INTRODUCTION
The Paleocene-Eocene thermal maximum is the most pronounced greenhouse warming event of the past 100 m.y., with proxy records indicating a rise in global sea-surface temperature (SST) of 5–8°C (Kennett and Stott, 1991; Zachos et al., 2006). This short-lived (<200 k.y.) warming is marked by a large negative carbon isotope excursion (CIE) of 3.5‰, indicative of a rapid release of 4500–6800 Gt of isotopically depleted carbon (Dickens et al., 1995; Zachos et al., 2005).

The extreme rise in mean global temperature appears to have had a major impact on the hydrological cycle. Soil isotopic records (Bowen et al., 2004) and fossil plants indicate a generally more humid climatic state during the Paleocene-Eocene thermal maximum, though initially preceded in some regions by a brief spell (<20 k.y.) of aridity (Wing et al., 2005; Kraus and Riggins, 2007; Jaramillo et al., 2010). Marine evidence for increased precipitation and/or continental erosion includes increased sedimentation rates on mid- and high-latitude margins (John et al., 2008; Nicolo et al., 2010), δD composition of terrestrial plants and aquatic-derived n-alkanes from Arctic records indicating increased precipitation and decreased seawater salinity (Pagani et al., 2006), and surface-water freshening and higher river discharge in the North Sea (Zacke et al., 2009).

A fundamental question is whether these “hydrologically related” changes in the character of sedimentation reflect higher humidity and increased annual precipitation and/or a shift toward a more extreme seasonal cycle of precipitation during the Paleocene-Eocene thermal maximum. The latter, if coupled with a long dry season, would enhance erosion and siliciclastic sediment transport, but not necessarily result in enhanced chemical weathering. A widespread increase in kaolinite content, a clay mineral typical of tropical soils (Gaucher, 1981), has been interpreted as evidence for more intense chemical weathering under the greenhouse climate of the Paleocene-Eocene thermal maximum (Bolle and Adatte, 2001; Gibson et al., 2000; Robert and Kennett, 1994). By analogy, if intensive pedogenesis occurred during the event, then this would have important implications for the future of soils in the current global warming trend, and by extension for agriculture and sustainability in the next centuries. Some limited direct evidence exists for intensive pedogenesis in continental Paleocene-Eocene thermal maximum sections (Clechenko et al., 2007), but not all marginal marine sections show a distinct increase in kaolinite at the Paleocene-Eocene thermal maximum (Bolle and Adatte, 2001). In some sections, massive fan-deposits have been found at the base of the section, implying high-energy floods, and thus regional short-duration, high-flux precipitation events (Schmitz and Pujalte, 2007). Considering the widespread occurrence of Paleogene and Mesozoic lateritic soils (Bolle and Adatte, 2001) and their tendency to persist in the geologic record (Thiry, 2000), it has generally been assumed that the kaolinite peak recorded in many continental sections could be a signal of enhanced exhumation and reworking of ancient kaolinite-rich soils rather than increased chemical weathering.

In this paper, we focus on the character of the clay minerals deposited during the Paleocene-Eocene thermal maximum, including changes in their assemblages, accumulation rates and bulk isotopic composition. We selected a well-dated continental margin section: Ocean Drilling Program (ODP) Site 174A (Miller et al., 1998; John et al., 2008), located on the New Jersey margin (Fig. DR1 in the GSA Data Repository), a region where an increase in kaolinite at the Paleocene-Eocene boundary had previously been documented (Gibson et al., 2000). We first quantified the temporal evolution of the kaolinite peak by reconstructing new high-resolution records of clay mineralogy across the CIE. We then measured the oxygen isotope composition of the bulk clay mineralogy (δ18Oclays) across the Paleocene-Eocene thermal maximum. Establishing the relative timing and scale of the clay assemblage and isotopic changes provides a rudimentary, but effective approach for assessing whether or not an increase in kaolinite at the Paleocene-Eocene thermal maximum implies an increase in the local rate of authigenesis, or the supply from preexisting laterites.

RESULTS
Details of the methodology are provided in the Data Repository. The mineralogy of the <2-µm-size fraction includes quartz, illite, smectite, and kaolinite (Fig. DR2). Quartz and illite content is relatively constant in the section (7% for quartz, 38% for illite; Fig. DR1), while kaolinite and smectite dominate the mineral assemblages and are anticorrelated (ranging between 10%–60% for kaolinite and 5–40% for smectite).
for smectite; Fig. DR2). Based on comparisons of air-dried, glycolated, and heated samples (550 °C), both smectite and mixed smectite-illite clays were identified in samples with bulk clay oxygen isotopic compositions ≤19‰. The possibility that chlorite layers, or even vermiculite layers, form part of the mixed-layer phase cannot be ruled out based on the existing X-ray diffraction (XRD) data. For samples with bulk isotopic composition ≥20‰ and high smectite content, no mixed-layer clays are observed. The (006) diffraction data for the swelling clays suggest that the smectite is dioctahedral. The ratio of kaolinite to smectite content (hereafter “K/S ratio”; Fig. 1A) is a measure of the relative proportion of each mineral. Close examination of the K/S ratio reveals an increase of ~0.4 m below the onset of the CIE (Fig. 1A, step 1). A plateau (maxima) in K/S ratio is reached between 1.9 m and 3.2 m above the onset of the CIE (Fig. 1A, step 2), and the ratio decreases from 3.2 m to 9.3 m above the onset of the CIE (Fig. 1A, steps 3 and 4). At 9.3 m above the onset of the CIE, the K/S ratio returns to pre-CIE values. Hence, the K/S ratio across the Paleocene-Eocene boundary at Bass River is characterized by an increase in kaolinite over smectite starting 40 cm below the CIE, peaking 2–3 m above the CIE, and returning to pre-CIE values less than 10 m above the CIE.

Broadly speaking, the δ18Oclay curve follows an antithetical pattern to that of the K/S ratio curve (Fig. 1, compare A and B): δ18Oclay values decrease gradually from 7.9 m (23.1‰) to 0.2 m (20.8‰) below the onset of the CIE, and then decrease rapidly from 0.2 m below the onset of the CIE to 2.1 m above the onset of the CIE (step 1 in Fig. 1B, minimum value of 18.1‰). The 2.1 m mark above the position of the CIE marks the lowest δ18Oclay value recorded in this study. From 2.1 m to 9.3 m above the position of the CIE, the δ18Oclay values increase from 18.1‰ to 22.5‰ (steps 2–4, Fig. 1B). The last data point 12.0 m above the CIE has a δ18Oclay value of 19.5‰.

**DISCUSSION**

**Timing of Clay Mineral Input at Bass River**

The rate of change in clay accumulation can provide some insight as to whether or not kaolinite was reworked. Kaolinite in the Bass River core comes from terrigenous weathering (Gibson et al., 2000), and the K/S ratio is a proxy for terrigenous kaolinite clay input. The chronology of the Bass River core, which is tightly constrained by correlation of the CIE to the orbitally tuned record of ODP Site 690 by John et al. (2008), indicates that the increase in K/S ratio across the Paleocene-Eocene boundary at Bass River occurred in less than 40 k.y. (step 1 in Fig. 1A) and that the entire excursion in kaolinite lasted <150 k.y. This is in marked contrast with the time scale required for the development of thick kaolinitic soils, which is estimated to be 1–2 m.y., even during peak warmth and the high atmospheric CO2 conditions of the Cretaceous (Schmitt, 1999; Thiry, 2000).

The relative timing of the kaolinite pulse at Bass River to the changes in local temperature might have some significance. Sluijs et al. (2007) documented an increased in TEX86, a proxy for SST, just prior to the CIE at Bass River, which is coeval with the rise in K/S (Fig. 2). If the kaolinite increase at the Paleocene-Eocene thermal maximum were to be interpreted as a phase of more intense chemical weathering, then the implication is the increase in weathering and subsequent transport of clays to the New Jersey margin must have taken place in a geologic instant (<2 k.y.). This is two to three orders of magnitude faster than the rates of pedogenesis of large volumes of kaolinite and its transport to continental margins (Schmitt, 1999; Thiry, 2000), which suggests that the majority of kaolinite transported to the ocean during the Paleocene-Eocene thermal maximum was largely reworked from Cretaceous laterites.

**Implications of the Oxygen Isotope Signature of the Clay Fraction**

Several factors could contribute to the ~3‰ lowering of δ18Oclay recorded across the Paleocene-Eocene thermal maximum interval (Fig. 1B). First, the δ18O values of kaolinite (and smectite) formed at equilibrium during a Paleocene-Eocene thermal maximum temperature increase of 5–8 °C would decrease by ~1.0‰–1.5‰ during weathering, assuming no change in the oxygen isotopic composition of meteoric water; smectites formed under these conditions would behave similarly (Savin and Lee, 1988; Sheppard and Gilg, 1996).

Second, neoformed terrigenous clay minerals developed during weathering typically reflect the isotopic composition of regional precipitation and associated soil water (Mizota and Longstaffe, 1996; Stern et al., 1997; Gilg, 2000). Such weathering is accelerated under warmer and more humid conditions (either year-round or seasonal). On the one hand, the δ18O values of precipitation at any one location typically increase with higher local surface temperatures, likely in the range of ~1‰–2‰ for the change associated with the Paleocene-Eocene thermal maximum (Rozanski et al., 1993). In this scenario, the putative lowering of δ18Oclay values arising from temperature-dependent fractionation during kaolinite formation described here would be more or less offset by the anticipated increase in the δ18O value of local precipitation. On the other hand, anomalously low precipitation δ18O values are known for tropical regions dominated by monsoonal weather patterns or those significantly affected by the Intertropical Convergence Zone (Yurtsever and Gat, 1981; Lawrence and White, 1991; Bird et al., 1993). Meteoric water of such an origin has been implicated in formation of weathering clays and hydroxides having δ18O values as much as 4‰–5‰ lower than expected (Bird et al., 1993).

Third, the strong covariance between bulk δ18Oclay values and the K/S ratio could arise...
from mixing between end members of quite different oxygen isotopic composition. Kaolinite and smectite formed during weathering at the same temperature from water of the same oxygen isotopic composition would have very similar δ¹⁸O values (Sheppard and Gilg, 1996). Accordingly, a mixing scenario implies quite different sources for the two main clay end members, with kaolinite having a more δ¹⁸O-poor composition.

Assessing whether the observed trend in δ¹⁸OClays values could result from a shift in the assemblage of clay minerals presents challenges in the absence of pure end-member compositions. We have approached this problem by assuming that each clay species had constant (but distinct) isotopic compositions, and that the relative abundance of kaolinite and smectite controlled δ¹⁸OClays. A full derivation is presented in Appendix DR1 in the Data Repository. Results suggest that the shape of the measured δ¹⁸OClays curve (Fig. 1C) could be obtained by varying the relative proportion of smectite and kaolinite as long as the offset in δ¹⁸O values between the two minerals is ~9.8‰ (see Appendix DR1). This isotopic separation is much larger than expected (≤0.5‰) for kaolinite and smectite formed during weathering at similar temperatures from water of similar oxygen isotopic compositions. Based on the calculated difference in oxygen isotopic compositions and XRD data, we derive a theoretical δ¹⁸OClays curve (Fig. 1C; see Appendix DR1) that accounts for all but one of the measured data points, suggesting that the assumptions inherent in our estimates are sound. That is to say, the isotopic composition of each constituent of the <2-µm-size fraction did not change across the Paleocene-Eocene thermal maximum, and that the observed shift toward lower δ¹⁸OClays values across the CIE can be explained as a simple function of the relative mixing between kaolinite and smectite from sources with different but fixed isotopic compositions. Lower Cretaceous kaolinite of weathering origin from New Jersey has an average δ¹⁸OClays value of ~19‰ (18.4‰–20.6‰; Lawrence and Rashkes-Meaux, 1993). If such a composition is representative, it would therefore suggest an average smectite δ¹⁸O value of ~29‰. We also note that for samples with high kaolinite content, some of the swelling clay is a typical of pedogenesis. By contrast, samples with high smectite content lack mixed-layer clays. In sum, the change in clay mineralogy and associated variation in δ¹⁸OClays values recorded on the New Jersey margin could have been produced by an increase in the exhumation, erosion, and transport of kaolinite-rich sediments during the Paleocene-Eocene thermal maximum.

CONCLUSIONS

Our data for the New Jersey margin sections can be explained by increased physical erosion of existing kaolinite-rich sediment during the increased precipitation and runoff associated with the Paleocene-Eocene thermal maximum. Viewing the increase in kaolinite as a signal for enhanced physical rather than chemical weathering would represent a paradigm shift for some Paleocene-Eocene thermal maximum clay studies. We argue, however, that this change in thinking is realistic: Our data and model reconcile the observations of increased physical weathering (Schmitz and Pujalate, 2007), a long time-lag for the establishment of lateritic soils (Thiry, 2000), and the abundance of kaolinite in the pre–Paleocene-Eocene thermal maximum record (Bolle and Adatte, 2001). The clay mineral signal is likely to reflect the amount of fluvial discharge during the Paleocene-Eocene thermal maximum and, by extension, has implications for sediment transport to continental margins. The present conclusion and the reported increase in mass accumulation rates of carbon during the Paleocene-Eocene thermal maximum (John et al., 2008) suggest that continental margins could have been an effective sink for atmospheric carbon, which ultimately is more likely to have influenced the earliest Eocene climate at the time scale of the Paleocene-Eocene thermal maximum than chemical weathering of crystalline rocks.

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