

# Barite accumulation, ocean productivity, and Sr/Ba in barite across the Paleocene–Eocene Thermal Maximum

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## ABSTRACT

**The Paleocene–Eocene Thermal Maximum (PETM), ca. 55 Ma, was a period of extreme global warming caused by rapid emission of greenhouse gases. It is unknown what ended this episode of greenhouse warming, but high oceanic export productivity over thousands of years (as indicated by high accumulation rates of barium, Ba) may have been a factor in ending this warm period by carbon sequestration. However, Ba has a short oceanic residence time (~10 k.y.), so a prolonged global increase in Ba accumulation rates requires an increase in input of Ba to the ocean, increasing barite saturation. We use a novel proxy for barite saturation (Sr/Ba in marine barite) to demonstrate that the seawater saturation state with respect to barite did not change across the PETM. The observations of increased barite burial, no change in saturation, and the short residence time can be reconciled if Ba burial decreased at continental margin and shelf sites due to widespread occurrence of suboxic conditions, leading to Ba release into the water column, combined with increased biological export production at some pelagic sites, resulting in Ba sink reorganization.**

**Keywords:** Paleocene–Eocene Thermal Maximum, barite, paleoproductivity, carbon sequestration.

## INTRODUCTION

The Paleocene–Eocene Thermal Maximum (PETM) was a period of extreme global warming ca. 55 Ma characterized by widespread negative oxygen and carbon isotope values in carbonate and organic matter. These isotope anomalies indicate that isotopically light carbon was rapidly (within a few millennia) emitted into the ocean–atmosphere system, causing global warming of 5–9 °C (e.g., review in Bowen et al., 2006), and widespread carbonate dissolution in the oceans (e.g., Zachos et al., 2005). Recovery took ~170 k.y. (Röhl et al., 2006).

There is no agreement on the source of the isotopically light carbon: one explanation for the carbon isotope excursion (CIE) is the release of ~2000–2500 Gt of isotopically light (~–60‰) carbon from oceanic methane clathrates (Dickens et al., 1995). Arguments against this hypothesis include discrepancies between the size of the Paleocene gas hydrate reservoir, the amount of oceanic carbonate dissolution, and discordance between the temperature increase recorded and amount of greenhouse gas needed (Pagani et al., 2006a). Various alternate sources of isotopically light carbon have been proposed (e.g., Pagani et al., 2006b; review in Thomas, 2007).

We lack not only understanding of the cause of this global warming event, but also its ending. Increased biological productivity on land (Beerling, 2000) or in the oceans (Bains et al., 2000) could have caused CO<sub>2</sub> drawdown. There is strong evidence for increased productivity on shelves, in epicontinental basins, and along some continental margins (e.g., Gibbs et al., 2006; Thomas, 2007). However, in the open ocean the productivity record remains problematic, with conflicting interpreta-

tion based on different proxies for productivity, even for the same sites (Stoll et al., 2007; Bains et al., 2000).

Barite formation in the water column and its accumulation in sediments are closely related to export production (e.g., Paytan and Griffith, 2007). Barite precipitates continuously in seawater, and is a closed system after burial. Barite is not affected by diagenesis in oxic sediments (Paytan et al., 1998), but its preservation in the sediment depends on seawater saturation levels with respect to barite (Dymond et al., 1992; Paytan and Griffith, 2007). Thus, knowledge of barite saturation in the water column is required for quantitative interpretation of barite accumulation rate records.

The Sr/Ba ratio in barite has been suggested as a proxy for the degree of barite saturation (Van Beek et al., 2003). Marine barite crystals forming in the water column have a wide range of Sr concentrations (Bertram and Cowen, 1997), and high-Sr barite is significantly more soluble than low-Sr barite (Moninn and Cividini, 2006; Rushdi et al., 2000). Barite crystals with high Sr/Ba values thus dissolve preferentially in the water column and at the sediment–water interface, and the degree of preferential dissolution strongly depends on the saturation state of the ocean with respect to barite (Moninn and Cividini, 2006; Averyt and Paytan, 2003).

The present average Sr/Ba of barite in core top sediments is 36.6 mmol/mol (Van Beek et al., 2003; Averyt and Paytan, 2003, 2007), ranging from ~25 to 45 mmol/mol. This range reflects variability in seawater and microenvironment Sr concentration, the effect of temperature on partition coefficients, spatial variability within a crystal, the presence of accessory minerals in the barite sample separates, and the saturation

variability within the present-day ocean (see Averyt and Paytan, 2003, 2007, for detailed discussion). We thus propose that Sr/Ba variability in barite greater than the natural variability envelope can be used to evaluate changes in seawater saturation state, and its effect on observed barite accumulation rates. We use this new proxy for paleoseawater barite saturation to evaluate whether the high Ba concentrations at a continental margin site (Schmitz et al., 1997) and high barite accumulation rates at several pelagic sites (Bains et al., 2000; Gray 2007) across the PETM reflect increased export production, or are a result of enhanced preservation due to changes in the oceanic Ba content.

## METHODS

We used a sequential leaching extraction (Paytan et al., 1993; Eagle et al., 2003), to separate barite across the PETM (54.5–55.5 Ma) from sediments from Ocean Drilling Program (ODP) Hole 1221C, a site with high PETM barite accumulation rates (Faul and Paytan 2005; Gray, 2007), and Pacific Deep Sea Drilling Project Sites 577 and 305, as well as ODP Site 1263 in the southeast Atlantic Ocean. The sites are in different ocean basins, at different depths (paleodepths range from lower bathyal to upper abyssal) and different latitudes (Fig. 1). The Sr and Ba contents of the barite samples were determined using inductively coupled plasma-optical emission spectroscopy (Averyt et al., 2003). Barite was dissolved using EDTA and Sr/Ba was determined along with a matrix-matched standard solution. Samples were drift-corrected to a known quality-control standard which was interspersed in the run every fourth sample. We converted all published ages for samples from the four sites to the long-term time scale of Berggren et al. (1995) as used by Zachos et al. (2001), with the time scale for the PETM interval using correlation to Site 690 (Röhl et al., 2000), as described by Zachos et al. (2005). Information on the age models is given in GSA Data Repository.<sup>1</sup>

## RESULTS AND DISCUSSION

Samples deposited before, after, and during the PETM at all sites have the same Sr/Ba ratio (Fig. 2), within the natural variability as observed in present-day core tops ( $\pm 10$  mmol/mol; Averyt and Paytan, 2003, 2007). The average Sr/Ba during the PETM (36.5 mmol/mol) is almost identical to that recorded in present-day core tops (36.6 mmol/mol) showing no transient increase at the CIE. The Ba/Ca values in planktonic foraminifera across the boundary also do not vary across the PETM (Hall et al., 2004).

<sup>1</sup>GSA Data Repository item 2007279, information about the numerical ages used in Figure 2, and the sources these ages were derived from, as well as the Sr/Ba data for each of the samples presented in the figure, is available online at [www.geosociety.org/pubs/ft2007.htm](http://www.geosociety.org/pubs/ft2007.htm), or on request from [editing@geosociety.org](mailto:editing@geosociety.org) or Documents Secretary, GSA, P.O. Box 9140, Boulder, CO 80301, USA.

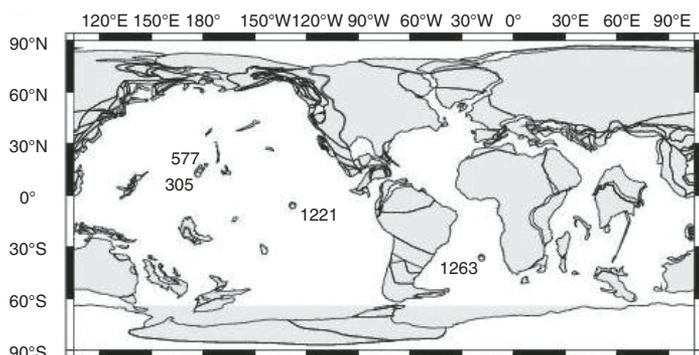


Figure 1. Map of the world ocean during the Paleocene–Eocene Thermal Maximum (PETM) with the location of samples used in this work for Sr/Ba analysis (modified from Hay et al., 1999).

The consistent Sr/Ba values across the event at geographically distinct areas suggest that this ratio represents a global signal.

The short residence time of Ba (~10 k.y.) in the ocean precludes a widespread increase in Ba burial over a period of time much longer than this residence time, such as the duration of the peak PETM (~60–80 k.y.), without an increase in the supply of Ba to the ocean. Dickens et al. (2003) argued that such a supply could have been provided by gas hydrate dissociation, which could also have caused the CIE. In gas hydrate systems microbial sulfate reduction may be prevalent, leading to depletion in sulfate, so that the solubility of barite increases, barite dissolves, and the dissolved Ba concentration of pore waters increases (Torres et al., 1996a, 1996b). When methane-charged fluids escape from gas hydrate reservoirs into the oceans, they thus may carry dissolved Ba, so that a large, rapid

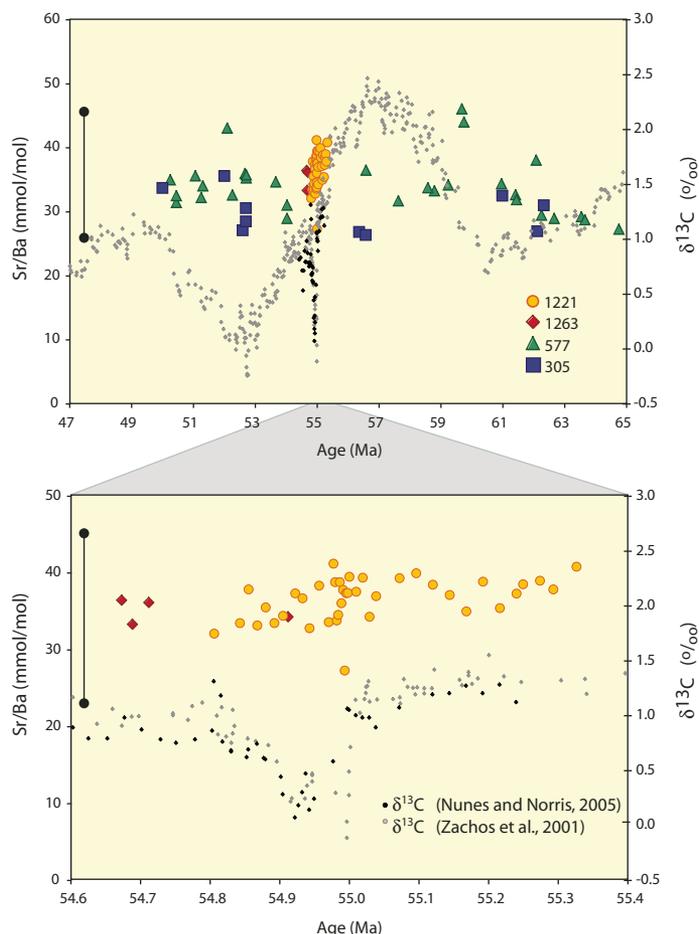


Figure 2. Sr/Ba ratios of marine barite across the Paleocene–Eocene Thermal Maximum (PETM). A: Time interval between 47 and 65 Ma. B: High-resolution record between 55.6 and 54.7 Ma. Analytical error on the Sr/Ba ratio is smaller than the symbol; bar on left side of the figure represents range of present-day Sr/Ba ratios in barite. Expected Sr/Ba ratio of a barite sample that has not undergone any dissolution (average Sr/Ba of particulate barite in seawater; Bertram and Cowen, 1997) is 80 mmol/mol and outside the range in this figure. Small gray symbols are the  $\delta^{13}\text{C}$  data in the compilation of benthic foraminiferal  $\delta^{13}\text{C}$  in Zachos et al. (2001) (5-point moving averages); black symbols are benthic foraminiferal values at Site 1221 (Nunes and Norris, 2005, 2006); circles are barite samples from Ocean Drilling Program (ODP) Hole 1221C (Pacific Ocean;  $12^{\circ}02'N$ ,  $143^{\circ}41'W$ ; paleowater depth ~3000 m); triangles are from ODP Site 1263C ( $28^{\circ}31'S$ ,  $02^{\circ}46'E$ ; paleowater depth ~1500 m), squares are from Deep Sea Drilling Project (DSDP) Site 305 ( $32^{\circ}00'N$ ,  $157^{\circ}51'E$ ; paleowater depth ~1800–2100 m); and diamonds are from DSDP Site 577 ( $32^{\circ}27'N$ ,  $157^{\circ}43'E$ ; paleowater depth ~2500 m).

global increase in the seawater Ba concentrations may occur, altering the saturation state of the ocean with respect to barite and resulting in globally enhanced preservation of marine barite (Dickens et al., 2003).

One problem with this theory is the method of dispersal of large amounts of Ba in concentrations that result in supersaturation with respect to barite throughout the world oceans without local precipitation. In present-day settings discharge of Ba-rich pore fluids results in local precipitation of barite mounds and chimneys upon contact with seawater (Torres et al., 1996a; Naehr et al., 2000) and the barite crystals are morphologically distinct from those forming in seawater (Paytan et al., 2002).

Our data indicate an additional problem with this hypothesis: if seawater had been supersaturated with respect to barite, one would expect the Sr/Ba value of this barite to be at least ~80 mmol/mol, the average Sr/Ba of ovoid barite crystals in the water column today (Sr/Ba of individual crystals ranges from 0 to 260 mmol/mol; Bertram and Cowen, 1997). We thus conclude that the high barite accumulation rate during the PETM is not an artifact of increased preservation due to increased barite saturation, but represents an increase in export production at the sites where it has been observed. Our data indicate that there was no large, rapid emission of Ba into the oceans at the time of influx of isotopically light carbon, i.e., the base of the CIE.

We agree with Dickens et al. (2003), however, that a significant increase in global barite accumulation rates over more than a few thousand years is inconsistent with the short oceanic residence time of Ba. We argue that these problems can be resolved if the Ba (and barite) records are not representative of a global increase of Ba burial. In the present oceans, most Ba burial occurs in continental margin settings (McManus et al., 1998). During the PETM, dissolved oxygen concentrations at mid-water depth may have been relatively low, possibly driven by methane oxidation in addition to the lower oxygen solubility at higher temperatures (e.g., Thomas, 2007). Such conditions promote Ba regeneration in continental margin settings, lowering the burial rates at these sites. Schmitz et al. (1997) did not observe high Ba concentrations at the shallowest Tethys site (where hypoxia occurred), and saw higher values at the deeper site. During the PETM, increased organic carbon fluxes and high productivity in continental margin, epicontinental, and shelf regions (e.g., Crouch et al., 2001) led to dysoxic and in some places anoxic conditions (e.g., Gavrilov et al., 2003; Speijer and Wagner, 2002; Gibbs et al., 2006), so that sulfate-reducing bacteria thrived, lowering Ba burial. Such changes in the loci of sedimentary barite deposition could explain increased barite accumulation in open ocean locations without the need to invoke changes in input to the ocean, an option suggested by Dickens et al. (2003). We then must argue that we cannot use the barite accumulation rate data at a few sites to infer a global increase in export production and barite burial; they can only be used to infer increased export productivity at the sites where the increase in barite accumulation was recorded. Other proxies that are less sensitive to redox cycling in the sediment should be used to infer productivity fluctuations in settings where sulfate reduction in the sediment was prevalent.

## CONCLUSIONS

Our new proxy data show that the barite saturation of the oceans did not change during the PETM, suggesting that there is no evidence for massive Ba release from gas hydrate dissociation. One could contend that this is an argument against gas hydrate dissociation. Our data and our understanding of the marine Ba cycle indicate that increased barite accumulation rates at some open ocean sites during the PETM are the result of increased export production at these sites, and not of increased preservation. At shelf and margin sites, anoxia and severe hypoxia occurred during the PETM (e.g., Speijer and Wagner 2002), so that sedimentary Ba may have been regenerated. Globally averaged Ba burial rates may thus not have changed during the PETM, but the loci of burial have changed. This explanation

does not exclude the possibility that export production increased globally, supported by intensification of the hydrological cycle and enhanced terrestrial weathering fluxes that supply nutrients to the oceans. However, we cannot use barite accumulation records to decide whether export production was high or low in coastal margin settings because at these sites sulfate reduction–related barite regeneration compromised the utility of this proxy. Other microfossil, sedimentological, and geochemical productivity proxies should be used in conjunction with barite data to corroborate global export production reconstructions, and to evaluate whether biotic CO<sub>2</sub> drawdown was important in ending the PETM.

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