Excess barite accumulation during the Paleocene-Eocene Thermal Maximum: Massive input of dissolved barium from seafloor gas hydrate reservoirs

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ABSTRACT

A $-2‰$ to $-3‰$ excursion characterizes carbon isotope records across the Paleocene-Eocene Thermal Maximum (PETM), probably signifying transfer of ~2000 gigatons of CH_4 carbon from seafloor gas hydrate reservoirs to the ocean and atmosphere. During at least 30 k.y. of this carbon cycle perturbation, euhedral barite apparently accumulated in deep-sea sediment faster than before or after. This excess burial of "biogenic barite" has been argued to reflect elevated global primary productivity in surface waters, an interpretation in disagreement with microfossil assemblages. In this paper, we develop a numerical model for the marine Ba cycle to explore possible mechanisms for widespread barite accumulation. This model immediately highlights a fundamental problem with the productivity explanation: Ba has a short residence time in the ocean (~8000 yr) so that excess Ba output on a global scale over periods >1000 yr signifies excess Ba input. However, a greater Ba input from conventional sources, hydrothermal waters and rivers, seems untenable. Assuming that available Ba records represent increased global output, we suggest an unconventional explanation for widespread barite accumulation. Prior to the PETM, gas hydrate reservoirs stored enormous masses of CH_4 and dissolved Ba^{2+}. During the PETM, substantial quantities of gas hydrate converted to free CH_4 gas, increasing pore pressures, and releasing significant amounts of CH_4 and dissolved Ba^{2+} to intermediate waters of the ocean. Consequently, dissolved Ba^{2+} concentrations in the deep ocean rose, a smaller fraction of sinking barite particles dissolved, and "biogenic barite" accumulation increased. The model satisfactorily explains available records but forces us to link components of the marine CH_4 and Ba cycles, an endeavor with few constraints.

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INTRODUCTION

Prodigious amounts of ^{12}C-rich carbon suddenly entered the ocean and atmosphere during the Paleocene-Eocene Thermal Maximum (PETM) as evidenced by an abrupt –2‰ to –3‰ δ^{13}C excursion in global carbon isotope records (Fig. 1A) and intense carbonate dissolution in deep-sea sediments (e.g., Kennett and Stott, 1991; Bralower et al., 1995, 1997; Thomas and Shackleton, 1996; Katz et al., 1999). Thermal dissociation of oceanic gas hydrates followed by release and oxidation of ~2000 gigatons (Gt = 10^{15} g) of CH$_4$ carbon provides the most satisfactory explanation for this carbon cycle perturbation (Dickens et al., 1995; Kaiho et al., 1996; Katz et al., 1999; Dickens, 2001a). An especially important issue is how the excess carbon exited the ocean and atmosphere after initial injection, however it was released (Dickens, 1999). High-resolution carbon isotope records display a relatively fast logarithmic increase in δ^{13}C following the prominent negative excursion (Fig. 1A), suggesting a period of greater net carbon output to the lithosphere (Dickens, 1999, 2001b; Norris and Röhl, 1999). This carbon removal phase lasted between 150 and 220 k.y. (Katz et al., 1999; Norris and Röhl, 1999; Röhl et al., 2000) but its cause remains uncertain. Several plausible processes exist, including expansion of the terrestrial biosphere, enhanced burial of marine organic carbon in open ocean or marginal basins, and recharge of seafloor gas reservoirs (cf. Kaiho et al., 1996; Bains et al., 2000; Beerling, 2000; Zachos and Dickens, 2000; Dickens, 2000, 2001a, b; Speijer and Wagner, 2002).

One potential mechanism to enhance carbon output after onset of the PETM is through greater marine biological productivity, with an associated increase in export production. A large carbon input to the ocean or atmosphere, through CH$_4$ or otherwise, should elevate atmospheric pCO$_2$ (Walker and Kasting, 1992; Dickens, 2000) and continental weathering (Walker et al., 1981; Berner et al., 1983). Greater nutrient delivery to the oceans, a boon of weathering, might then increase primary production and organic carbon fluxes from surface waters to the seafloor (Zachos and Dickens, 2000).

As a test for a weathering induced "PETM marine productivity feedback," Bains et al. (2000) have presented an intriguing set of geochemical records. These authors have shown a strong antithetical relationship between the δ^{13}C of marine carbonate and the accumulation of euhedral barite across the first 30–40 k.y. of the PETM at two widely separated, open-ocean locations, Ocean Drilling Program (ODP) Site 690 in the Southern Ocean (Fig. 1A) and ODP Site 1051 in the North Atlantic. Bains et al. (2000) state that additional deep-water sections have this unusual geochemical relationship across the PETM, and Schmitz et al. (1997) demonstrated such a link at the Ben Gurion deep-water section in Egypt. Euhedral barite in pelagic sediment relates to sinking marine organic matter (e.g., Paytan et al., 1996). Thus, one interpretation for the observed relationship is that enhanced weathering increased primary productivity and the burial flux of organic carbon for ~30–40 k.y. after massive carbon input (Bains et al., 2000). Some records appear to support this overall explanation. Specifically, across the PETM, kaolinite accumulation increased around many continents (Robert and Kennett, 1994; Kaiho et al., 1996; Gawenda et al., 1999; Harrington and Kemp, 2001; Schmitz et al., 2001), osmium isotope ratios (^{187}Os/^{188}Os) rose in seawater (Ravizza et al., 2001), and heterotrophic dinoflagellate cysts abounded in shallow marine waters (Crouch et al., 2001). However, pelagic
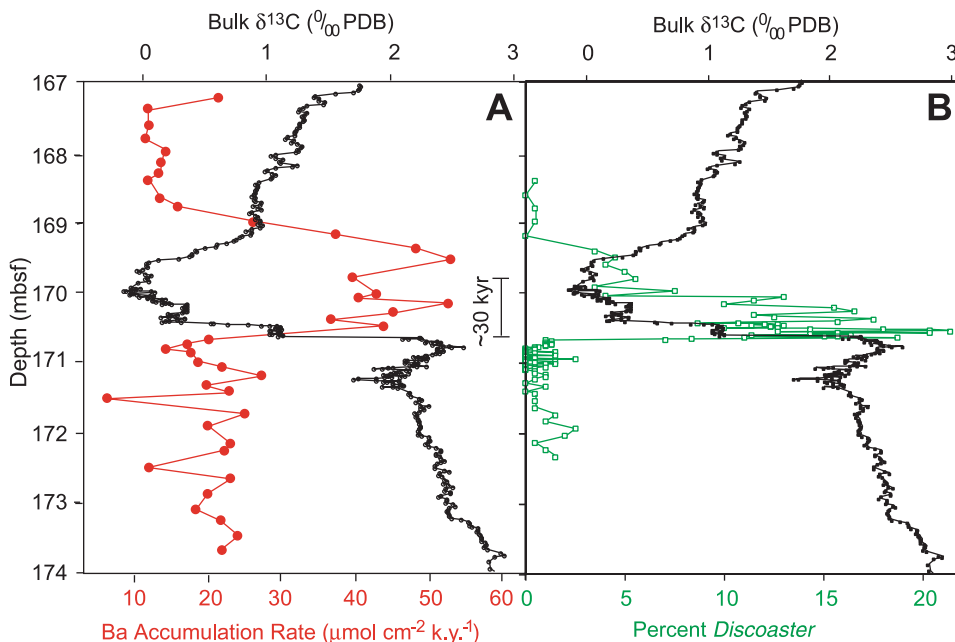

Figure 1. Three environmental records across the Paleocene-Eocene Thermal Maximum at Ocean Drilling Program (ODP) Site 690, Maud Rise, South Atlantic Ocean. A: Carbon isotopes of bulk carbonate (black) and estimated sedimentary Ba accumulation rate (Bains et al., 2000). B: Carbon isotopes of bulk carbonate (black) and discoaster abundance (Bralower et al., 2002).

microfossil assemblages, including those at sites with elevated barite accumulation, often indicate decreased surface water productivity during the PETM (e.g., Kelly et al., 1996; Thomas, 1998, this volume; Thomas et al., 1999; Bolle et al., 2000; Bralower, 2002). For example, at ODP Site 690, the abundance of discoasters, acknowledged oligotrophic taxa (e.g., Haq and Lohmann, 1976; Aubry, 1998; Boersma et al., 1998), increases markedly over the interval of elevated barite accumulation at the start of the PETM (Fig. 1B).

In this paper, we develop a numerical model for the marine barium cycle to elucidate potential causes for widespread increases in euhedral barite accumulation. Our primary goal is to present at least one plausible simulation for the PETM whereby biogenic barite accumulation increases globally without a rise in marine productivity. We quickly conclude that the short residence time of Ba in the ocean precludes elevated productivity as a primary explanation for prolonged increases in barite accumulation. However, a sudden increase in the barite saturation state of the deep ocean, caused by massive release of dissolved Ba^{2+} from marine gas hydrate deposits, provides a satisfactory explanation.

THE BASIC MARINE BARIUM CYCLE

Any explanation for a significant widespread increase in Ba accumulation during the PETM necessitates an understanding of the marine barium cycle. At a basic level, this cycle (Fig. 2)
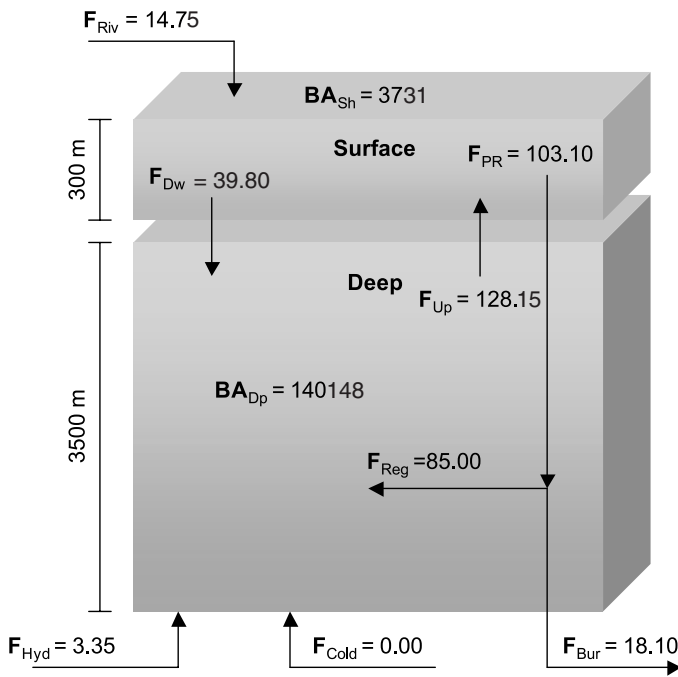

Figure 2. Basic steady-state box model for the present-day marine barium cycle (adapted from Wolgemuth and Broecker, 1970; Paytan and Kastner, 1996). A flux of Ba from cold seeps (F_{Cold}) has been included in the model but set at zero for consistency with previous literature. Masses are in Gmol; fluxes are in Gmol/yr.

contains two ocean reservoirs—surface water and deep water—and a series of external and internal mass fluxes (Wolgemuth and Broecker, 1970; Paytan and Kastner, 1996). Rivers add relatively large quantities of dissolved Ba^{2+} to surface water. Barite then precipitates in microenvironments within sinking and decomposing organic matter, leading to a particulate rain of euhedral barite crystals from surface water to deep water (Chow and Goldberg, 1960; Dehairs et al., 1980, 1992; Bishop, 1988; Stroobants et al., 1991). Although some of this "biogenic barite" accumulates into the sediment (e.g., Schmitz, 1987; Dymond et al., 1992; Gingele and Dahmke, 1994; Paytan et al., 1996), a large fraction dissolves on the seafloor or within shallow sediment (e.g., Chow and Goldberg, 1960; Francois et al., 1995; McManus et al., 1998, 1999; Klump et al., 2001). Deep water thus receives substantial amounts of Ba^{2+} through regeneration of barite (Wolgemuth and Broecker, 1970; Payton and Kastner, 1996). Submarine hydrothermal systems (e.g., Elderfield and Schultz, 1996; Monnin et al., 2001) and cold seeps (Torres et al., 1996a) introduce additional dissolved Ba^{2+} to deep water. As a consequence of this overall cycling, Ba^{2+} concentrations in deep water greatly exceed those in surface water (e.g., Paytan and Kastner, 1996; Monnin et al., 1999). Advection of water by thermohaline circulation returns Ba^{2+} from deep water to surface water, closing the mass balance loop (Wolgemuth and Broecker, 1970; Paytan and Kastner, 1996). This basic view of the marine Ba cycle excludes metal oxyhydroxide accumulation, an additional and potentially important Ba sink in deep-sea sediments (Schroeder et al., 1997).

Temporal variations in one or more of the Ba fluxes, external or internal, can change Ba concentrations in surface and deep reservoirs, as well as other Ba fluxes, including sedimentary barite accumulation. These changes can be described through a series of flux equations and assessed by numerical methods as for other geochemical cycles (e.g., Berner et al., 1983; Kump and Arthur, 1999; Dickens, 2001a, 2000b). Paytan and Kastner (1996) presented the most recent steady-state box model for the modern marine Ba cycle. After adding a Ba^{2+} flux from cold seeps, their model (Fig. 2) provides a framework for developing an appropriate set of equations to evaluate Ba fluxes in the time domain.

A NUMERICAL MODEL FOR THE MARINE BARIUM CYCLE

Given the basic barium cycle (Fig. 2), the equation to describe changes in surface water Ba abundance (BA_{sh}) is:

$$dBA_{Sh}/dt = F_{Riv} + F_{Up} - F_{Dw} - F_{PR} \qquad (1)$$

where F_{Riv}, F_{Up}, F_{Dw}, and F_{PR}, are Ba fluxes associated with rivers, upwelling, downwelling and particulate rain, respectively, and t is time. Likewise, the equation to describe changes in deep water Ba abundance (BA_{Dp}) is:

$$dBA_{Dp}/dt = F_{Reg} + F_{Hyd} + F_{Cold} + F_{Dw} - F_{Up} \qquad (2)$$

where F_{Reg}, F_{Hyd} and F_{Cold} are Ba fluxes associated with benthic regeneration, seafloor hydrothermal vents and cold seeps, respectively, and other terms are the same as above. As in many box models for global biogeochemical cycles, all of the flux terms have been normalized for area, in this case the ocean or 2.40×10^{14} m² (Appendix 1).

Processes outside the surface and deep waters dictate the magnitude of the three external inputs, F_{Riv}, F_{Hyd}, and F_{Cold}. By contrast, processes within the ocean control the magnitude of the internal fluxes, F_{Dw}, F_{Up}, F_{PR}, F_{Reg}, and the single external output, F_{Bur}.

Downwelling and upwelling fluxes depend on dissolved Ba^{2+} concentrations in surface ($[Ba]_{Sh}$) and deep water ($[Ba]_{Dp}$), and the advective flow between these water masses (Fig. 2). The appropriate expressions for these fluxes are (Paytan and Kastner, 1996):

$$F_{Dw} = [Ba]_{Sh} C \qquad (3)$$

and

$$F_{Up} = [Ba]_{Dp} C \qquad (4)$$

where C is the mass of water that exchanges between surface and deep reservoirs over time.

The sinking of organic matter incorporates Ba from the surface water column (Dehairs et al., 1980, 1992; Bishop, 1988; Stroobants et al., 1991; McManus et al., 1999). Consequently, the particulate rain should be related to the downward supply of solid organic carbon (P_{Org}) and dissolved Ba^{2+} concentrations in shallow to intermediate water (Dymond et al., 1992). A straightforward expression for this process is:

$$F_{PR} = [Ba]_{Sh} D P_{Org} \qquad (5)$$

where D is a coefficient linking Ba concentrations in surface water to Ba contents in organic matter before it sinks into deep water and decomposes. For simplicity, we have set D as a constant (Appendix 1). Clearly, this assumption masks the true complexity of Ba uptake because the amount of Ba in sinking organic carbon varies (e.g., Francois et al., 1995; Dehairs et al., 2000). Although we could incorporate more complicated expressions for D into our model (e.g., Dymond et al., 1992), as we shall see, the actual relationship between dissolved Ba^{2+} in shallow water and solid Ba in organic matter is somewhat irrelevant when considering global Ba accumulation over significant time.

The key parameter of interest to this paper—the burial flux of Ba (F_{Bur})—is the fraction of the particulate rain that escapes dissolution at or near the seafloor. This flux can be coupled to aforementioned fluxes as follows:

$$F_{Bur} = F_{PR} - F_{Reg} \qquad (6)$$

or

$$F_{Bur} = f F_{PR} \qquad (7)$$

where f represents the fraction (0–1) of the particulate barite rain incorporated into the sediment. A critical observation is that this fraction depends on the barite saturation state of bottom water (Monnin et al., 1999; Klump et al., 2001) so that "bottom water Ba concentration has a significant influence on barite preservation" (Francois et al., 1995, p. 301). A simple expression to describe this effect is:

$$f = k [Ba]_{Dp}/[Ba]_{Sat} \qquad (8)$$

where $[Ba]_{Sat}$ is the dissolved Ba^{2+} concentration at barite saturation, and k is a "time factor" to increase dissolution because barite dissolves on and in the upper few centimeters beneath the seafloor (e.g., Paytan and Kastner, 1996; McManus et al., 1998). As such, at low $[Ba]_{Dp}$, a greater fraction of barite dissolves, decreasing F_{Bur}, and increasing $F_{Re.g.}$, This expression, especially with constant k, oversimplifies barite preservation and dissolution because it omits other processes that can affect seafloor barite accumulation, such as changes in sedimentation rate (Dymond et al., 1992; Francois et al., 1995; McManus et al., 1999). However, the expression satisfactorily explains observations in modern deep waters, such as the greater barite accumulation beneath Ba-rich deep waters (Francois et al., 1995; Monnin et al., 1999).

All the internal Ba fluxes depend on dissolved Ba^{2+} concentrations. These, of course, are dictated by the total abundances of Ba in surface and deep waters:

$$[Ba]_{Sh} = BA_{Sh}/M_{Sh} \qquad (9)$$

and

$$[Ba]_{Dp} = BA_{Dp}/M_{Dp} \qquad (10)$$

where M_{Sh} and M_{Dp} are the masses of water in the surface and deep ocean reservoirs, respectively. For simplicity, we assume that the surface and deep water masses are rectangular prisms with similar horizontal areas (Wolgemuth and Broecker, 1970). Thus:

$$[Ba]_{Sh} = M_{Sh}/Az_{Sh}\rho_{sw} \qquad (11)$$

and

$$[Ba]_{Dp} = M_{Dp}/Az_{Dp}\rho_{sw} \qquad (12)$$

where z_{Sh} and z_{Dp} are the depths of the surface and deep water reservoirs, respectively, ρ_{sw} is the density of seawater.

MODEL SIMULATIONS AND THE PRODUCTIVITY PROBLEM

Initial conditions

In their steady-state box model of the modern marine Ba cycle, Paytan and Kastner (1996) have quantified all Ba masses

and fluxes except discharge from cold seeps (F_{Cold}). Their fluxes (Appendix 1) are similar to those in previous models of the marine Ba cycle (Wolgemuth and Broecker, 1970; Dehairs et al., 1980), and we assume they are reasonably accurate. Implicit in this assumption is that modern Ba fluxes from cold seeps are trivial, a potentially incorrect view (McManus et al., 1999). Three of the parameters introduced above (D, f, $[Ba]_{Sat}$) are not expressly included in the box model by Paytan and Kastner (1996) but are necessary for coupling the Ba fluxes in numerical simulations. Assuming steady-state conditions, these parameters can be derived easily from given masses and fluxes (Appendix 1). The downward supply of solid organic carbon (P_{Org}) is initially set at 7500 Gmol/yr. This is an average value taken from the range of P_{Org} in current models of the Holocene carbon cycle (see discussion by Dickens, 2001b).

Two time "constants" can be calculated with the given steady-state fluxes and concentrations (Appendix 1). The total mass of water ($M_{Sh} + M_{Dp} = 1.31 \times 10^{21}$ kg) exchanges between the shallow and deep ocean in ~1200 yr. The residence time of Ba in the ocean is ~8000 yr.

Increased productivity

The raising of global primary productivity and the downward flux of organic matter by 15%, 50% and 100% results in predictable, although perhaps nonintuitive, changes in the global accumulation of biogenic Ba (Fig. 3). At first, in all simulations, F_{Bur} increases. However, F_{Bur} begins to decrease immediately afterwards. This result stems from the rapid cycling of water and the limited amount of Ba in the ocean. Removal of Ba via an enhanced particulate rain of barite quickly depletes the supply of Ba in the small, surface water reservoir (BA_{Sh}) and reduces the downward transport of dissolved Ba^{2+} (F_{Dw}). Although upwelling (F_{Up}) replenishes the surface water Ba reservoir, this comes at the expense of Ba in deep water (BA_{Dp}), which then decreases barite preservation.

Our model of the Ba cycle (Fig. 2), and any ensuing numerical simulations, contains numerous potential errors, particularly regarding variations in the internal cycling of Ba or adjustments for the PETM. For example, if the particulate rain of barite (F_{PR}) is made largely independent of surface Ba concentrations ($[Ba]_{Sh}$), as suggested by Francois et al. (1995), the duration and shape of significantly elevated Ba accumulation will change. Interestingly, however, appropriate changes in key parameters generally decrease F_{Bur}. For example, the 4–6 °C increase in deep ocean temperature and the pronounced dissolution of deep-sea carbonate during the PETM (e.g., Thomas and Shackleton, 1996; Katz et al., 1999) would raise barite solubility, either directly or by lowering sedimentation rates (Francois et al., 1995; Monnin, 1999). Likewise, weakened ocean-atmosphere circulation (i.e., a lower C, equations 3, 4), which may have occurred during the PETM (e.g., Kennett and Stott, 1991; Hovan and Rea, 1992; Thomas and Shackleton, 1996), would reduce F_{Up}, the critical short-term supply of Ba to sur-
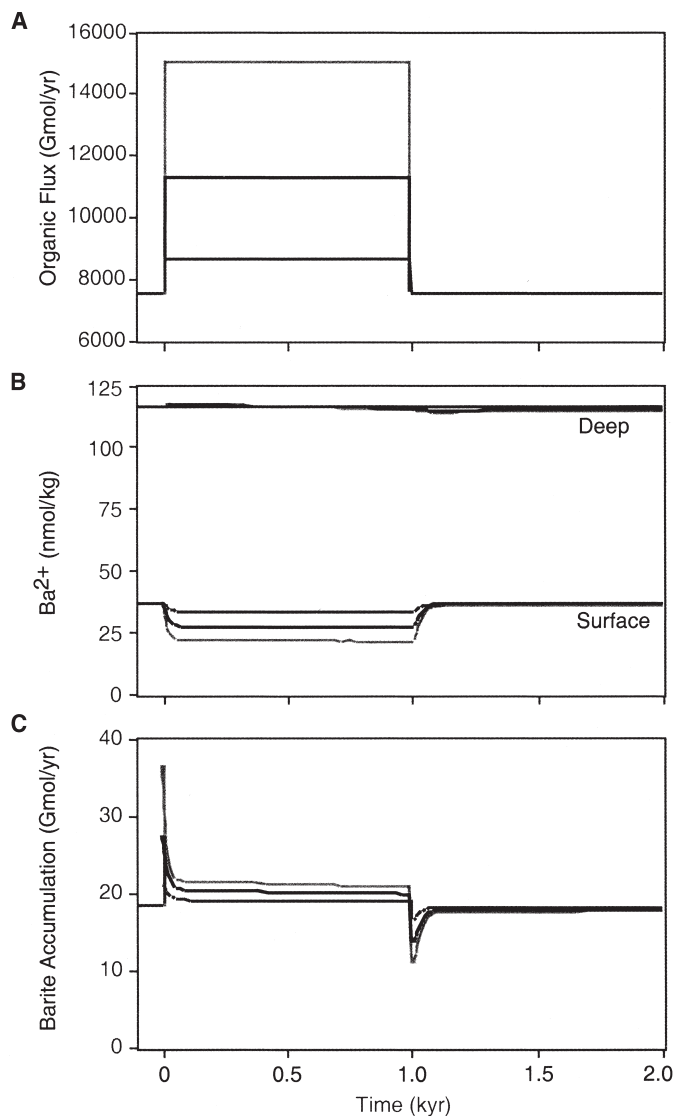

Figure 3. Numerical simulations of global deep-sea barium accumulation given 15%, 50% and 100% increases in primary productivity. A: Productivity input. B: Dissolved Ba^{2+} concentrations in surface and deep ocean reservoirs. C: Ba accumulation.

face water. This, in turn, would decrease the amount of dissolved Ba^{2+} available to organic matter.

Importantly, and as alluded to by McManus et al. (1999, p. 60), irrespective of how internal Ba fluxes are expressed in detail (equations 3–8), a significant global increase in Ba outputs (>10%) over appreciable time (>1000 yr) necessitates elevated Ba inputs because Ba has a relatively short residence time. Consider an extreme simulation where all parameters internal to the marine Ba cycle are adjusted to maximize Ba outputs. In this case, a doubling of global Ba outputs will deplete all Ba in the ocean within 8000 yr unless Ba inputs increase ($[BA_{Sh} + BA_{Dp}]/F_{Bur} = 7950$ yr). A similarly short residence time likely existed in the Paleocene, because barite is close to saturation in

the modern ocean (Monnin et al., 1999); that is, the ocean cannot store significantly more Ba than at present without invoking wholesale changes in SO_4^{2-} caused by other, unidentified processes. If truly global, a significant increase in biogenic barite accumulation on time scales greater than several thousand years should not be viewed as representing elevated primary productivity but rather as an increase in Ba inputs. This crucial concept has been stressed previously for other "biolimited" species with short marine residence times (e.g., phosphorous and silica; Delaney and Filippelli, 1994; Dickens and Owen, 1999).

Conventional external fluxes

Given conventional models of the marine Ba cycle (Fig. 2), a significant increase in global biogenic barite accumulation implies an increase in Ba from hydrothermal effluents or riverine discharge. But neither of these inputs is a satisfactory source of Ba for 30–40 k.y. of the Paleocene.

Seafloor volcanism peaked in the late Paleocene and early Eocene with emplacement of flood basalts in the North Atlantic Igneous Province (e.g., Eldholm and Thomas, 1993; Heister et al., 2001). This intensified volcanism, although partly subaerial, potentially raised global hydrothermal fluxes to the ocean (Olivarez and Owen, 1989). However, the volcanism, and by inference any excess hydrothermal activity, lasted for several millions of years, preceding and postdating the PETM (Heister et al., 2001). There is no evidence for a special, short-term burst of seafloor hydrothermal activity precisely coinciding with the onset of the PETM.

Some shallow marine environments received a greater discharge of siliciclastic material, especially kaolinite, across the PETM (Robert and Kennett, 1994; Kaiho et al., 1996; Gawenda et al., 1999; Harrington and Kemp, 2001; Schmitz et al., 2001). Several authors (e.g., Robert and Kennett, 1994; Gawenda et al., 1999) have suggested this high kaolinite flux reflects higher humidity and intensified chemical weathering, which might signify globally increased riverine dissolved loads during the PETM. However, as emphasized by Thiry (2000), the formation of sufficient kaolinite by chemical weathering would take several million years. Consequently, the short-term kaolinite spike is much better explained by mechanical erosion (Thiry, 2000; Schmitz et al., 2001). A similar argument may apply to rapid changes in riverine Ba fluxes. Barite and common minerals hosting significant Ba (e.g., feldspar) have very slow dissolution rates (e.g., Dove and Czank, 1995; White et al., 2001), which may preclude a rapid (30–40 k.y.) weathering-induced discharge of dissolved Ba^{2+} from continents. However, we cannot rigorously exclude the possibility of a short-term fluvial input of Ba-rich clays that released dissolved Ba^{2+} upon contact with seawater.

A significant global increase in deep-sea barite accumulation >30–40 k.y. probably implies a sudden increase in a Ba flux outside of current models for the marine Ba cycle. Interestingly, such a flux would have existed precisely at the onset of the PETM if release of seafloor CH_4 caused the dramatic perturbations in the global carbon cycle.

METHANE AND BARIUM CYCLING IN MARINE GAS HYDRATE DEPOSITS

Methane cycling

Gas hydrate reservoirs are dynamic systems (Fig. 4) where carbon cycles between dissolved gas, gas hydrate and free gas over time (e.g., Xu and Ruppel, 1999; Davie and Buffett, 2001; Dickens, 2001a; Kastner, 2001). Within SO_4^{2-} depleted pore waters, several microbially mediated reactions generate new CH_4 from sedimentary organic matter. This dissolved gas migrates laterally and vertically. Eventually, at appropriate pressure and temperature conditions, and sufficient gas concentrations, gas hydrate precipitates in pore space. Sedimentation over time slowly buries these solid clathrates of CH_4 and water to higher temperatures because of the geothermal gradient. At some pressure and temperature, gas hydrate is no longer stable and dissociates to gas-saturated water and free CH_4 gas bubbles. Although much of the CH_4 released at depth recycles through the above processes, some CH_4 escapes to shallow sediments. In a few places, such as where faults intersect the seafloor, high advection rates lead to CH_4 venting and aerobic oxidation of methane by microbes in the water column (Paull et al., 1995; Suess et al., 1999; Valentine et al., 2001). In many places, however, the upward flux of CH_4 encounters SO_4^{2-} diffusing down from the seafloor. This drives anaerobic oxidation of methane by Archaea-Bacteria consortia (Hinrichs et al., 1999; Boetius et al., 2000) at a sulfate/methane interface (SMI) in the sediment column (Borowski et al., 1996, 1999; Fossing et al., 2000). As exemplified by studies on the Blake Ridge (Fig. 4), the SMI often occurs between 10 and 40 mbsf above gas hydrate reservoirs (e.g., Borowski et al., 1999).

Barium cycling

Most Ba in pelagic sediment occurs in aluminosilicate phases, Fe-Mn oxyhydroxides, or discrete microscopic euhedral crystals of barite (e.g., Dehairs et al., 1980; Dymond et al., 1992; Gingele and Dahmke, 1994; McManus et al., 1998). Although the Ba in aluminosilicates is essentially immobile during early diagenesis, the Ba in metal oxyhydroxides and barite is susceptible to fluctuations in pore water chemistry. In particular, barite will be affected by the SO_4^{2-} content of surrounding pore water (Von Breymann et al., 1990, 1992; Torres et al., 1996b). The solubility of barite is very low in deep marine waters (K_{sp} ~1.0 and 2.5 × 10 [10]; Church and Wolgemuth, 1972; Monnin, 1999). Thus, in sediment/pore water systems with even minor concentrations of dissolved SO_4^{2-}, most labile Ba exists in barite with only small amounts as dissolved Ba^{2+} (Blount, 1977; McManus et al., 1998). However, when pore waters become depleted in SO_4^{2-}, the solubility of barite in-
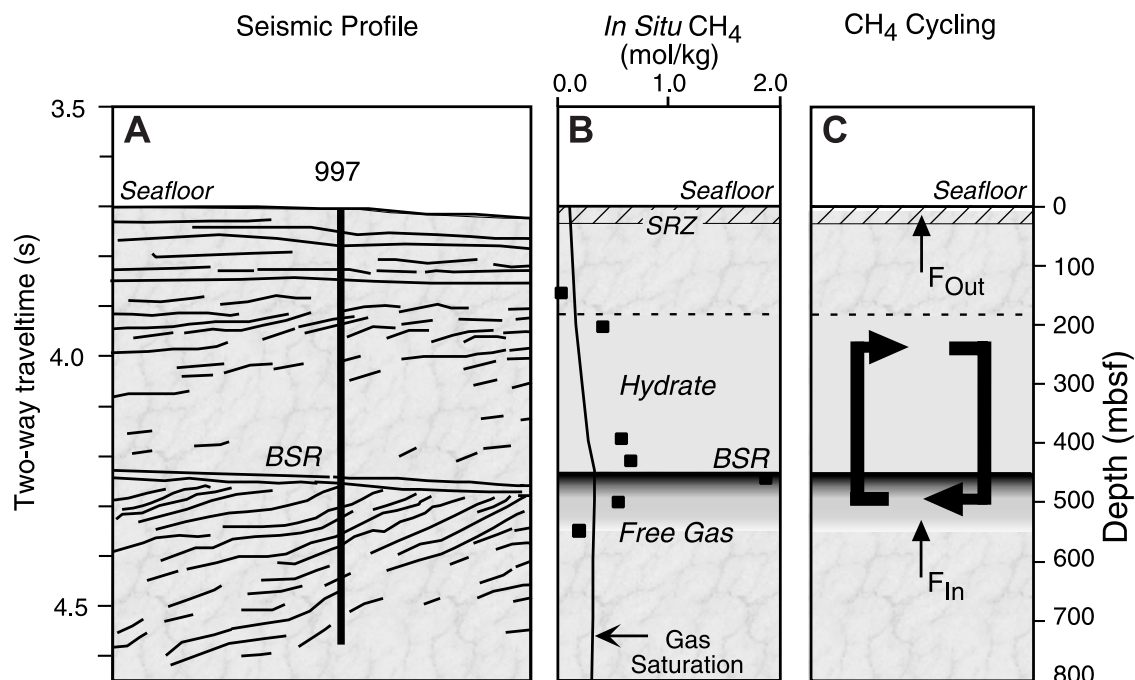
Figure 4. Methane cycling in a modern gas hydrate reservoir, Ocean Drilling Program (ODP) Site 997, Blake Ridge, southeast United States margin (adapted from Paull et al., 1996; Dickens et al., 1997; Dickens, 2001a). A: Schematic of seismic reflection profile showing site location and the bottom-simulating reflector (BSR), an acoustic interface between overlying gas hydrate and underlying free gas bubbles. B: Methane solubility curves and in situ gas concentrations at Site 997. C: Inferred CH_4 cycling at Site 997.

creases greatly and dissolved Ba^{2+} concentrations can increase by four orders of magnitude (Brumsack and Gieskes, 1983; Von Breymann et al., 1990, 1992).

The coupled cycling of carbon and sulfur in and above marine gas hydrate deposits profoundly affects Ba cycling in surrounding sediment and water (Figs. 5, 6). During sediment burial, particulate barite moves downward from SO_4^{2-} rich pore water into SO_4^{2-} depleted pore water where it slowly dissolves. In turn, dissolved Ba^{2+} slowly diffuses upward from SO_4^{2-} depleted pore water into SO_4^{2-} rich pore water where it precipitates as barite. In most gas hydrate systems (e.g., the Blake Ridge, Figures 4, 5; Peruvian Margin, Figure 6), microbial processes consume SO_4^{2-} and CH_4 beneath the seafloor, and upward Ba^{2+} diffusion exceeds downward barite burial. The continual cycling of Ba therefore traps enormous amounts of dissolved Ba^{2+} beneath shallow sedimentary "barite fronts" (Von Breymann et al., 1990, 1992; Gingele and Dahmke, 1994; Torres et al., 1996b; Dickens, 2001c). When CH_4 charged fluids of gas hydrate reservoirs escape to the ocean, however, they carry significant amounts of dissolved Ba^{2+}, sometimes leading to precipitation of barite mounds and chimneys on the seafloor (e.g., Torres et al., 1996a; Fu and Aharon, 1998; Naehr et al., 2000).

A LOW-PRODUCTIVITY MODEL FOR EXCESS BARITE ACCUMULATION

A straightforward model for excess Ba accumulation across the PETM can be constructed by considering gas hydrate reservoirs as repositories of CH_4 *and* dissolved Ba^{2+} (Fig. 7). Prior to the PETM and similar to the present-day situation, the upper few hundred meters of sediments on continental slopes at appropriate pressures and temperatures contained enormous quantities of CH_4 as solid gas hydrate (e.g., Kvenvolden, 1988, 1999; Dickens, 2001d). These hydrates were greatly enriched in ^{12}C (e.g., Kvenvolden, 1995) and surrounded by pore waters with extremely high dissolved Ba^{2+} concentrations (e.g., Figure 6). For reasons that remain unclear, but which may have involved the passage of a critical ocean-atmosphere threshold condition and sinking of waters at a warmer source region, temperatures at intermediate water depths rose by 4–6 °C (Kennett and Stott, 1991; Bralower et al., 1995; Thomas and Shackleton, 1996; Katz et al., 1999). This warming propagated into the sediments, converting once solid gas hydrates into free gas bubbles (Dickens et al., 1995). Free gas formation increased pore pressures at depth, leading to sediment failure and the release of massive quantities of CH_4 (e.g., Kayen and Lee, 1991; Paull et al., 1996;
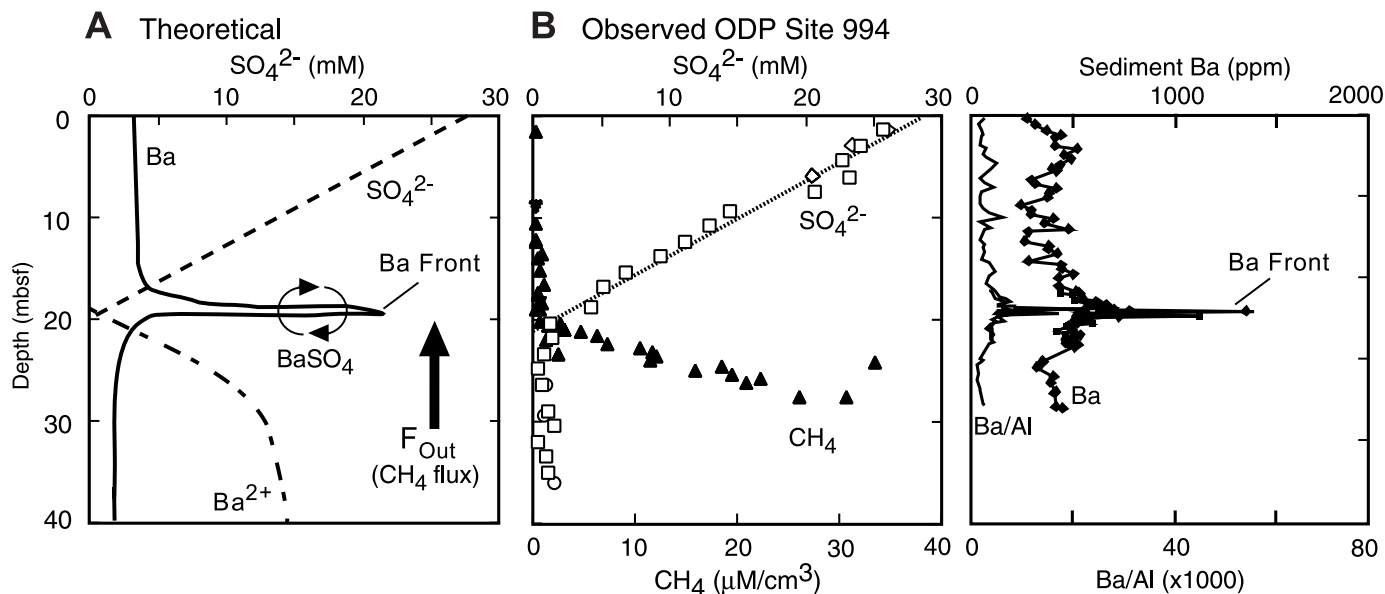
Figure 5. Theoretical and observed cycling of Ba above a gas hydrate reservoir. A: Schematic of expected Ba cycling (adapted from Torres et al., 1996b). B: Measured concentrations of headspace CH_4, dissolved SO_4^{2-} and sedimentary Ba at ODP Site 994, Blake Ridge (Dickens, 2001c).

Katz et al., 1999) *and* dissolved Ba^{2+} into the ocean. In the Paleocene, CH_4 and Ba release would have occurred on slopes between 900 and 2000 m water depth (Fig. 7) because all gas hydrate in sediment at these depths would dissociate with a 4–6 °C rise in bottom water temperature (Dickens et al., 1995; Dickens, 2001d). The gaseous CH_4 reacted to produce ^{12}C-enriched CO_2, either via OH radicals in the atmosphere or via aerobic oxidation in the water, and the Ba^{2+} would increase deep ocean Ba^{2+} concentrations provided that it did not precipitate locally upon contact with SO_4^{2-} rich waters. Consequently, discrete barite particles raining from shallow water would experience lower dissolution, and "biogenic" barite would accumulate faster, independent of productivity changes.

Barium release from gas hydrate reservoirs is an appealing mechanism to explain excess biogenic barite accumulation during the PETM because it is a direct and necessary expectation given release of CH_4 as an explanation for the prominent negative carbon isotope excursion. At issue is whether this mechanism is plausible; that is, can massive discharge of methane-laden pore waters supply the requisite flux of Ba to significantly change global dissolved Ba^{2+} concentrations?

Limited information exists to quantitatively couple the seafloor cycles of CH_4 and Ba. Sites 995 and 997 on the Blake Ridge (Fig. 4) remain the only scientific drill holes where CH_4 abundances have been determined in a gas hydrate reservoir at in situ conditions by multiple and direct methods (Dickens et al., 1997, 2000). At these sites, pore space CH_4 concentrations average ~0.55 mol/kg in sediment horizons with gas hydrate and free gas (Dickens et al., 1997, 2000). Sites 685 and 688 on the Peruvian Margin (Fig. 7) remain the only locations

with gas hydrate where dissolved Ba^{2+} concentrations have been determined (cf. Kvenvolden and Kastner, 1990; Von Breymann et al., 1990). Here, dissolved Ba^{2+} concentrations average ~0.45 mmol/kg in intervals with gas hydrate and free gas (Von Breymann et al., 1990). Thus, with available data, we estimate a ~1200:1 molar ratio of CH_4 to Ba in marine gas hydrate deposits.

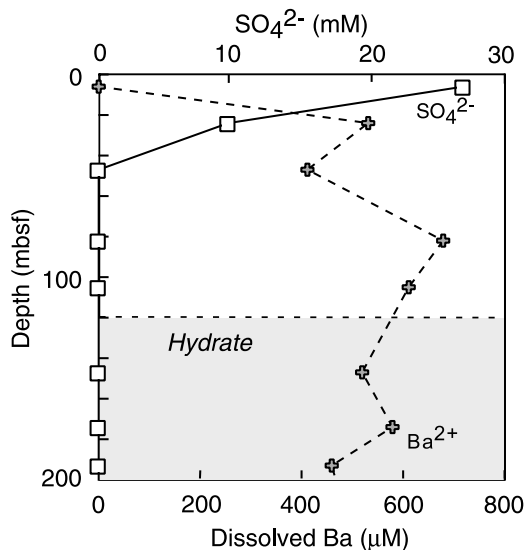
Figure 6. Solid and dissolved Ba concentrations at ODP Site 688, Peruvian Margin (Von Breymann et al., 1990). Gas hydrate, predominantly composed of CH_4, occurs beneath ~100 m (Kvenvolden and Kastner, 1990).
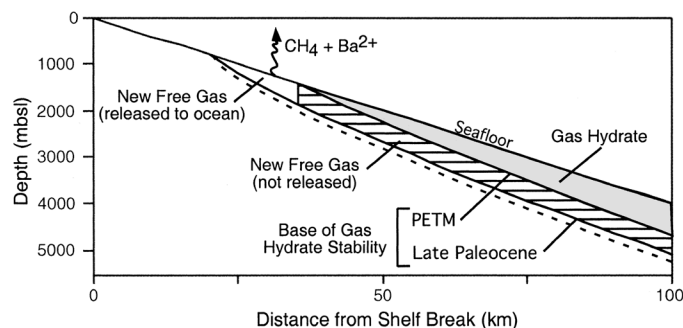
Figure 7. Schematic showing hypothesized release of CH_4 and Ba from the seafloor during the PETM.

Given release of ~2000 Gt (1.62×10^5 Tmol) of CH_4 carbon from the seafloor during the PETM (Dickens, 2001a, 2001b), ~19 Gt (135 Tmol) of Ba could have entered the deep ocean. Over 10–30 k.y., the apparent duration of massive carbon injection (Kennett and Stott, 1991; Katz et al., 1999; Norris and Röhl, 1999; Röhl et al., 2000), the new "cold seep" flux would raise global Ba fluxes from 14 Gmol/yr by an additional 4–14 Gmol/yr if all of the Ba stayed dissolved in seawater and did not precipitate locally as barite. Numerical simulations of global biogenic Ba accumulation (F_{Bur}) after injecting 135 Tmol of Ba into the deep ocean >10–30 k.y. (Fig. 8) differ significantly from those driven by elevated productivity (Fig. 3). As with enhanced productivity, F_{Bur} increases rapidly in all simulations. However, this elevated output of Ba continues over considerable time, mimicking the duration of CH_4 and Ba inputs. Importantly, because expulsion of ^{12}C-rich fluid drives the Ba input, the records of seawater $\delta^{13}C$ and sedimentary Ba accumulation (1) vary antithetically at the onset of the PETM (nominally 30–40 k.y.) even if productivity dropped significantly, and (2) become decoupled afterwards when $\delta^{13}C$ slowly increases and barite accumulation plummets. The second result occurs because the residence time of carbon in the ocean (~100 k.y.) is much longer than that of barium.

Anomalous barite accumulation across the PETM can be linked to massive CH_4 input through less direct scenarios (e.g., Bains et al., 2000) if the existing Ba records are not globally representative. However, changes in the loci of sedimentary barite deposition do not necessarily imply variations in surface water productivity. In particular, benthic foraminifera assemblages and other information strongly suggest that deep ocean dissolved O_2 contents dropped across the PETM (Kaiho et al., 1996; Bralower et al., 1997; Thomas, 1998; Katz et al., 1999). This O_2 deficiency, perhaps driven by CH_4 oxidation (Dickens, 2000), could have dissolved metal oxyhydroxides in the water column and on the seafloor (e.g., Johnson et al., 1992; Dickens and Owen, 1994). Thus, a potentially important Ba output could have diminished, a change that should have raised deep ocean dissolved Ba^{2+} concentrations and enhanced the preservation of biogenic barite in certain locations.
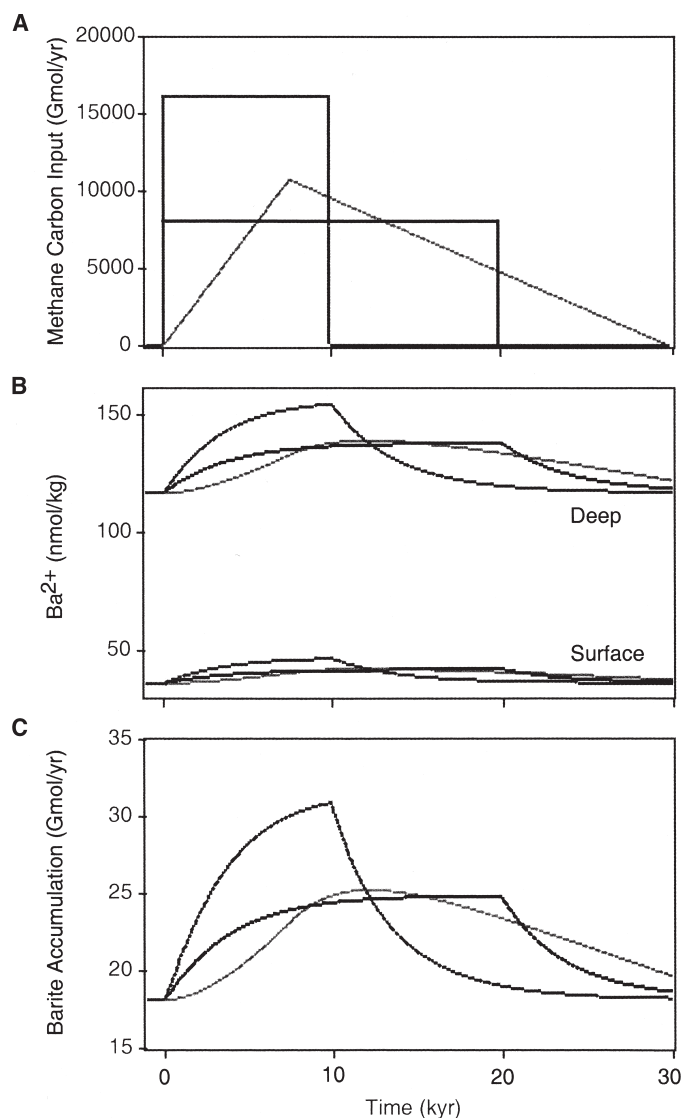

Figure 8. Numerical simulations of global deep-sea barium accumulation assuming three different injections of ~2000 Gt of CH_4 carbon and a 1200:1 molar CH_4:Ba ratio in pore space of gas hydrate reservoirs. A: Methane input. B: Dissolved Ba^{2+} concentrations in surface and deep ocean reservoirs. C: Ba accumulation.

CONCLUSIONS AND FUTURE RESEARCH

Schmitz et al. (1997) and Bains et al. (2000) have documented coeval, antithetical changes in carbonate $\delta^{13}C$ and Ba accumulation across the first 30–40 k.y. of the PETM in several sections deposited in deep water (Fig. 1). The prominent negative $\delta^{13}C$ excursion probably signifies massive release of ^{12}C-rich CH_4 from seafloor gas hydrate deposits to the ocean and its subsequent removal to the lithosphere (e.g., Dickens et al., 1995; Dickens, 2001a, 2001b). The excess accumulation of Ba, caused by an increase in the flux of discrete euhedral barite crystals, suggests a greater burial of biogenic Ba at these sites (Schmitz

et al., 1997; Bains et al., 2000). Following previous work (e.g., Schmitz, 1987), Bains et al. (2000) have argued that this observation reflects a time of globally elevated marine primary productivity, presumably driven by higher atmospheric pCO_2 (via CH_4 oxidation), enhanced terrestrial weathering, and additional nutrient delivery to the ocean. However, this interpretation immediately raises two problems. First, it is inconsistent with other proxies for productivity, such as microfossil assemblages, which suggest oligotrophic conditions in the open ocean during the PETM. Second, and as emphasized in this paper, there is a serious mass balance problem. The ocean contains a relatively small amount of Ba with a short residence time. Consequently, a widespread increase in biogenic Ba burial over an extended time interval (>1000 yrs) requires an increase in the external supply of Ba to the ocean, even if primary productivity rose.

We assume that current models for the marine Ba cycle, although primarily developed for the Holocene and somewhat unconstrained, apply to Paleogene conditions. Thus, there appear to be two general explanations for the available barite records across the PETM: (1) decreased Ba accumulation at unidentified locations counterbalanced the excess Ba accumulation observed in pelagic records, or (2) some external flux of Ba to the ocean increased significantly. Additional records of Ba accumulation are needed to address the first possibility. In particular, Ba accumulation records are needed from locations where suboxic conditions could have remobilized metal oxyhydroxides and associated Ba. The second possibility may require a basic reconstruction of the marine Ba cycle whereby massive release of CH_4 from gas hydrates somehow contributes considerable dissolved Ba^{2+} to the ocean. Trace element analyses of sediment and waters in and above gas hydrate reservoirs, albeit limited (Von Breymann et al., 1990; Torres et al., 1996a, b; Fu and Aharon, 1998; Naehr et al., 2000; Dickens, 2001c), suggest that they store abundant dissolved Ba^{2+} (Figs. 5, 6). We thus speculate that massive quantities of dissolved Ba^{2+} (nominally 135 Tmol) vented into the ocean during the start of the PETM (Fig. 8), and this increased biogenic barite accumulation in deep-sea sediment through enhanced preservation. This scenario explains the unusual coupling between $\delta^{13}C$ and Ba records and the presence of oligotrophic microfossil assemblages across intervals with excess biogenic barite (Fig. 1).

Although our explanation for excess biogenic barite is plausible in the general sense, we note at least one significant problem in the details. Given a marine Ba cycle with Holocene masses and fluxes (Fig. 3), an inferred 10–30 k.y. injection of ~2000 Gt of CH_4 carbon (cf. Katz et al., 1999; Röhl et al., 2000; Dickens, 2001a), and the postulated ~1200:1 molar ratio of CH_4 to Ba in marine gas hydrate deposits, global Ba fluxes and accumulation can at most double. However, Bains et al. (2000) indicate a three-fold increase of biogenic barite burial at ODP Site 690 and a six-fold increase at Site 1051. Although faster CH_4 injection would increase Ba fluxes and accumulation, excessively rapid Ba release would surpass local barite saturation, leading to direct precipitation of authigenic barite on the seafloor (e.g.,

Torres et al., 1996a; Fu and Aharon, 1998; Naehr et al., 2000) instead of enhanced preservation of biogenic barite. One solution to this problem is to consider barite dissolution analogous to that of carbonate whereby a "barite lysocline" moves vertically in response to changes in saturation (Monnin et al., 1999). In this case, barite accumulation during massive CH_4 injection at the PETM might increase significantly more at sites farthest from saturation (young, deep waters) than at sites closest to saturation (old, intermediate waters). This possibility cannot be rigorously assessed with available data, but could be evaluated with future Ba accumulation records across the PETM and along depth transects.

Isotopic signatures consistent with thermal dissociation of gas hydrate and release of CH_4 have been documented across other brief intervals of the geological record, notably events in the Aptian and Toarcian (Hesselbo et al., 2000; Jahren et al., 2001; Padden et al., 2001). If the mechanism proposed here is correct, seafloor Ba fluxes also may have increased significantly during these times. We note, however, that barite preservation would be complicated in O_2 deficient deep ocean waters with SO_4^{2-} reduction, conditions that did not occur in the open ocean during the PETM but may have during earlier CH_4 release events (Hesselbo et al., 2000).

ACKNOWLEDGMENTS

APPENDIX 1. NOMENCLATURE AND PARAMETERS FOR THE BASIC MODEL OF THE MARINE BARIUM CYCLE.

Primary parameters		Units	Standard conditions[†]
BA_{Sh}	Abundance of Ba in surface water	Gmol (= 10^9 mol)	3731
BA_{Dp}	Abundance of Ba in deep water	Gmol	140148
F_{Riv}	River Ba flux	Gmol/yr *	14.75
F_{Up}	Upwelling Ba flux	Gmol/yr *	128.15
F_{Dw}	Downwelling Ba flux	Gmol/yr *	39.80
F_{PR}	Particulate rain Ba flux	Gmol/yr *	103.10
F_{Hyd}	Hydrothermal Ba flux	Gmol/yr *	3.35
F_{Cold}	Cold Seep Ba flux	Gmol/yr *	0.00 [¶]

Primary parameters		Units	Standard conditions[†]
F_{Reg}	Benthic regeneration Ba flux	Gmol/yr *	85.00
F_{Bur}	Burial Ba flux	Gmol/yr *	18.10
$[Ba]_{Sh}$	Dissolved Ba^{2+} in surface water	$nmol/kg_{sw}$	36
$[Ba]_{Dp}$	Dissolved Ba^{2+} in deep water	$nmol/kg_{sw}$	116
$[Ba]_{Sat}$	Dissolved Ba^{2+} at saturation	mol/kg_{sw}	330
C	Exchange of surface and deep water	kg_{sw}/yr	1.105×10^{18} [§]
D	Coefficient between Ba^{2+} in shallow water and solid Ba in organic matter	kg_{sw}/mol (carbon)	3.8157×10^{-4}
P_{Org}	Sinking organic carbon flux	Gmol/yr *	7500 [F]
f	Fraction of F_{PR} buried	(0–1)	0.17556
k	"Time factor" for barite preservation	(0–1)	0.4994
M_{Sh}	Mass of surface water	kg	1.04×10^{20}
M_{Dp}	Mass of deep water	kg	1.21×10^{21}
A	Area of surface and deep water	m^2	2.40×10^{14}
z_{Sh}	Depth of surface water	m	300
z_{Dp}	Depth of deep water	m	3500
ρ_{sw}	Density of seawater	kg/m^3	1030

Notes:

*Fluxes have been normalized by area (A).

[†]Except where noted below, standard conditions refer to the Holocene steady-state marine barium cycle as presented by Paytan and Kastner (1996).

[¶]Cold seep flux has been set at zero for consistency with previous models.

[§]Exchange flux has been modified from Paytan and Kastner (1996) to normalize for area (A) and include density of seawater.

[F]Organic carbon burial flux taken from average for Holocene carbon cycle (see Dickens, 2001b). Digits in values have been retained for purposes of numerical calculations and do not imply significance.

REFERENCES CITED

Aubry, M.-P., 1998, Early Paleogene calcareous nannoplankton evolution: A tale of climatic amelioration, *in* Aubry, M.-P., et al., eds., Late Paleocene and early Eocene climatic and biotic evolution: New York, Columbia University Press, p. 158–203.

Bains, S., Norris, R.D., Corfield, R.M., and Faul, K.L., 2000, Termination of global warmth at the Paleocene–Eocene boundary through productivity feedback: Nature, v. 407, p. 171–174.

Beerling, D.J., 2000, Increased terrestrial carbon storage across the Paleocene–Eocene boundary: Palaeogeography, Palaeoclimatology, Palaeoecology, v. 161, p. 395–405.

Berner, R.A., Lasaga, A.C., and Garrels, R.M., 1983, The carbonate-silicate geochemical cycle and its effect on atmospheric carbon dioxide over the past 100 million years: American Journal of Science, v. 283, p. 641–683.

Bishop, J.K.B., 1988, The barite–opal–organic carbon association in oceanic particulate matter: Nature, v. 332, p. 341–343.

Blount, C.W., 1977, Barite solubilities and thermodynamic quantities up to 300°C and 1400 bars: American Mineralogist, v. 62, p. 942–957.

Boersma, A., Premoli Silva, I., and Hallock, P., 1998, Trophic models for the well-mixed and poorly mixed warm oceans across the Paleocene–Eocene epoch boundary, *in* Aubry, M.-P., et al., eds., Late Paleocene–early Eocene biotic and climatic events in the marine and terrestrial records: New York, Columbia University Press, p. 204–213.

Boetius, A., Ravenschlag, K., Schubert, C.J., Rickert, D., Widdel, F., Gieseke, A., Amann, R., Jørgensen, B.B., Witte, U., and Pfannkuche, O., 2000, A marine microbial consortium apparently mediating anaerobic oxidation of methane: Nature, v. 407, p. 623–626.

Bolle, M.P., Pardo, A., Adatte, T., Von Salis, K., and Burns, S., 2000, Climatic evolution on the southeastern margin of the Tethys (Negev, Israel) from the Paleocene to the early Eocene: Focus on the late Paleocene thermal maximum: Journal of the Geological Society of London, v. 157, p. 929–941.

Borowski, W.S., Paull, C.K., and Ussler, W., III, 1996, Marine pore water sulfate profiles indicate in situ methane flux from underlying gas hydrate: Geology, v. 24, p. 655–658.

Borowski, W.S., Paull, C.K., and Ussler, W., III, 1999, Global and local variations of interstitial sulfate gradients in deep-water, continental margin sediments: Sensitivity to underlying methane and gas hydrates: Marine Geology, v. 159, p. 131–154.

Bralower, T.J., 2002, Evidence for surface water oligotrophy during the late Paleocene Thermal Maximum: Nannofossil assemblage data from Ocean Drilling Program Site 690, Maud Rise, Weddell Sea: Paleoceanography, v. 17, paper no. 10.1029/2001PA000662.

Bralower, T.J., Zachos, J.C., Thomas, E., Parrow, M., Paull, C.K., Kelly, D.C., Premoli Silva, I., Sliter, W.V., and Lohmann, K.C., 1995, Late Paleocene to Eocene paleoceanography of the equatorial Pacific Ocean: Stable isotopes recorded at Ocean Drilling Program Site 865, Allison Guyot: Paleoceanography, v. 10, p. 841–865.

Bralower, T.J., Thomas, D.J., Zachos, J.C., Hirschmann, M.M., Röhl, U., Sigurdsson, H., Thomas, E., and Whitney, D.L., 1997, High-resolution records of the late Paleocene thermal maximum and circum-Caribbean volcanism: Is there a causal link?: Geology, v. 25, p. 963–966.

Brumsack, H.J., and Gieskes, J.M., 1983, Interstitial water trace metal chemistry of laminated sediments from the Gulf of California, Mexico: Marine Chemistry, v. 14, p. 89–106.

Chow, T.J., and Goldberg, E.D., 1960, On the marine geochemistry of barium: Geochimica et Cosmochimica Acta, v. 20, p. 192–198.

Church, T.M., and Wolgemuth, K., 1972, Marine barite saturation: Earth and Planetary Science Letters, v. 15, p. 35–44.

Crouch, E.M., Heilmann-Clausen, C., Brinkhuis, H., Morgans, H.E.G., Rogers, K.M., Egger, H., and Schmitz, B., 2001, Global dinoflagellate event associated with the late Paleocene thermal maximum: Geology, v. 29, p. 315–318.

Davie, M.K., and Buffett, B.A., 2001, A numerical model for the formation of gas hydrate below the seafloor: Journal of Geophysical Research, v. 106, p. 497–514.

Dehairs, F., Chesselet, R., and Jedwab, J., 1980, Discrete suspended particles of barite and the barium cycle in the ocean: Earth and Planetary Science Letters, v. 49, p. 528–550.

Dehairs, F., Baeyens, W., and Goeyens, L., 1992, Accumulation of suspended barite at mesopelagic depths and export production in the Southern Ocean: Science, v. 258, p. 1332–1335.

Dehairs, F., Fagel, N., Antia, A.N., Peinert, R., Elskens, M., and Goeyens, L., 2000, Export production in the Bay of Biscay as estimated from barium-barite in settling material: A comparison with new production: Deep-Sea Research I, v. 47, p. 583–601.

Delaney, M.L., and Filippelli, G.M., 1994, An apparent contradiction in the role of phosphorus in Cenozoic chemical mass balances for the world ocean: Paleoceanography, v. 9, p. 513–527.

Dickens, G.R., 1999, The blast in the past: Nature, v. 401, p. 752–755.

Dickens, G.R., 2000, Methane oxidation during the late Paleocene thermal maximum: Bulletin de la Société Géologique de France, v. 171, p. 37–49.

Dickens, G.R., 2001a, Modeling the global carbon cycle with a gas hydrate capacitor: Significance for the latest Paleocene thermal maximum, *in* Paull C.K., and Dillon, W.P., eds., Natural gas hydrates, occurrence, distribution and detection: Washington, D.C., American Geophysical Union Geophysical Monograph Series, v. 124, p. 19–38.

Dickens, G.R., 2001b, Carbon addition and removal during the late Paleocene thermal maximum: Basic theory with a preliminary treatment of the isotope record at ODP Site 1051, Blake Nose, *in* Kroon, D., et al., eds., Western North Atlantic Palaeogene and Cretaceous palaeoceanography: Geological Society [London] Special Publication 183, p. 293–305.

Dickens, G.R., 2001c, Sulfate profiles and barium fronts in sediment on the Blake Ridge: Present and past methane fluxes through a large gas hydrate reservoir: Geochimica et Cosmochimica Acta, v. 65, p. 529–543.

Dickens, G.R., 2001d, The potential volume of oceanic methane hydrates with variable external conditions: Organic Geochemistry, v. 32, p. 1132–1193.

Dickens, G.R., and Owen, R.M., 1994, Late Miocene–early Pliocene manganese redirection in the central Indian Ocean: Expansion of the intermediate water oxygen minimum zone: Paleoceanography, v. 9, p. 169–181.

Dickens, G.R., and Owen, R.M., 1999, The latest Miocene–early Pliocene biogenic bloom: A revised Indian Ocean perspective: Marine Geology, v. 161, p. 75–91.

Dickens, G.R., O'Neil, J.R., Rea, D.K., and Owen, R.M., 1995, Dissociation of oceanic methane hydrate as a cause of the carbon isotope excursion at the end of the Paleocene: Paleoceanography, v. 10, p. 965–971.

Dickens, G.R., Paull, C.K., Wallace, P., and the ODP Leg 164 Scientific Party, 1997, Direct measurement of in situ methane quantities in a large gas hydrate reservoir: Nature, v. 385, p. 426–428.

Dickens, G.R., Wallace, P., Paull, C.K., and Borowski, W.S., 2000, Detection of methane gas hydrate in the pressure core sampler (PCS): Volume-pressure-time relations during controlled degassing experiments, *in* Paull, C.K., et al., eds., Proceedings of the Ocean Drilling Program, Scientific Results: Texas A & M University, College Station, Texas, USA, v. 164, p. 113–128.

Dove, P.M., and Czank, C.A., 1995, Crystal chemical controls on the dissolution kinetics of the isostructural sulfates celestite, anglesite, and barite: Geochimica et Cosmochimica Acta, v. 59, p. 1907–1915.

Dymond, J., Suess, E., and Lyle, M., 1992, Barium in deep-sea sediments: A geochemcial proxy for paleoproductivity: Paleoceanography, v. 7, p. 163–181.

Elderfield, H., and Schultz, A., 1996, Midocean ridge hydrothermal fluxes and the chemical composition of the ocean: Annual Review of Earth and Planetary Sciences, v. 24, p. 191–224.

Eldholm, O., and Thomas, E., 1993, Environmental impact of volcanic margin formation: Earth and Planetary Science Letters, v. 117, p. 319–329.

Fossing, H., Ferdelman, T.G., and Berg, P., 2000, Sulfate reduction and methane oxidation in continental margin sediments influenced by irrigation (southeast Atlantic off Namibia): Geochimica Cosmochimica Acta, v. 64, p. 897–910.

Francois, R., Honjo, S., Manganini, S.J., and Ravizza, G.E., 1995, Biogenic barium fluxes to the deep sea: Implications for paleoproductivity reconstruction: Global Biogeochemical Cycles, v. 9, p. 289–303.

Fu, B., and Aharon, P., 1998, Sources of hydrocarbon-rich fluids advecting on the seafloor in the northern Gulf of Mexico: Transactions Gulf Coast Association of Geological Societies, v. 48, p. 73–81.

Gawenda, P., Winkler, W., Schmitz, B., and Adatte, T., 1999, Climate and bioproductivity control on carbonate turbidite sedimentation (Paleocene to earliest Eocene Gulf of Biscay, Zumaia): Journal of Sedimentary Research, v. 69, p. 1253–1261.

Gingele, F., and Dahmke, A., 1994, Discrete barite particles and barium as tracers of paleoproductivity in South Atlantic sediments: Paleoceanography, v. 9, p. 151–168.

Haq, B.U., and Lohmann, G.P., 1976, Early Cenozoic calcareous nannoplankton biogeography of the Atlantic Ocean: Marine Micropaleontology, v. 1, p. 119–194.

Harrington, G.J., and Kemp, S.J., 2001, U.S. Gulf Coast vegetation dynamics during the latest Paleocene: Palaeogeography, Palaeoclimatology, Palaeoecology, v. 167, p. 1–21.

Heister, L.E., O'Day, P.A., Brooks, C.K., Neuhoff, P.S., and Bird, D.K., 2001, Pyroclastic deposits within the East Greenland Tertiary flood basalts: Journal of the Geological Society of London, v. 158, p. 269–284.

Hesselbo, S.P., Gröcke, D.R., Jenkyns, H.C., Bjerrum, C.J., Farrimond, P., Bell, H.S.M., and Green, O.R., 2000, Massive dissociation of gas hydrate during a Jurassic oceanic anoxic event: Nature, v. 406, p. 392–395.

Hinrichs, K.-U., Hayes, J.M., Sylva, S.P., Brewer, P.G., and DeLong, E.F., 1999, Methane-consuming archaebacteria in marine sediments: Nature, v. 398, p. 802–805.

Hovan, S.A., and Rea, D.K., 1992, Paleocene Eocene boundary changes in atmospheric and oceanic circulation: A Southern Hemisphere record: Geology, v. 20, p. 15–18.

Jahren, A.H., Arens, N.C., Sarmiento, G., Guerrero, J., and Amundson, R., 2001, Terrestrial record of methane hydrate dissociation in the Early Cretaceous: Geology, v. 29, p. 159–162.

Johnson, K.S., Berelson, W.M., Coale, K.H., Coley, T.L., Elrod, V.A., Fairey, W.R., Iams, H.D., Kilgore, T.E., and Nowicki, J.L., 1992, Manganese flux from continental margin sediments in a transect through the oxygen minimum: Science, v. 257, p. 1242–1245.

Kaiho, K., Arinobu, T., Ishiwatari, R., Morgans, H.E.G., Okada, H., Takeda, N., Tazaki, K., Zhou, G., Kajiwara, Y., Matsumoto, R., Hirai, A., Niitsuma, N., and Wada, H., 1996, Latest Paleocene benthic foraminiferal extinction and environmental changes at Tawanui, New Zealand: Paleoceanography, v. 11, p. 447–465.

Kastner, M., 2001, Gas hydrates in convergent margins: Formation, occurrence, geochemistry, and global significance, *in* Paull, C.K., et al., eds., Natural gas hydrates, occurrence, distribution, and detection: Washington, D.C., American Geophysical Union Geophysical Monograph Series, v. 124, p. 67–86.

Katz, M.E., Pak, D.K., Dickens, G.R., and Miller, K.G., 1999, The source and fate of massive carbon input during the latest Paleocene Thermal Maximum: Science, v. 286, p. 1531–1533.

Kayen, R.E., and Lee, H., 1991, Pleistocene slope instability of gas hydrate-laden sediment on the Beaufort Sea Margin: Marine Geotechnology, v. 10, p. 125–141.

Kelly, D.C., Bralower, T.J., Zachos, J.C., Premoli Silva, I., and Thomas, E., 1996, Rapid diversification of planktonic foraminifera in the tropical Pacific (ODP Site 865) during the late Paleocene thermal maximum: Geology, v. 24, p. 423–426.

Kennett, J.P., and Stott, L.D., 1991, Abrupt deep sea warming, paleoceanographic changes, and benthic extinctions at the end of the Paleocene: Nature, v. 353, p. 319–322.

Klump, J., Hebbeln, D., and Wefer, G., 2001, High concentrations of biogenic barium in Pacific sediments after Termination, I: A signal of changes in productivity and deep water chemistry: Marine Geology, v. 177, p. 1–11.

Kump, L.R., and Arthur, M.A., 1999, Interpreting carbon isotope excursions: Carbonates and organic matter: Chemical Geology, v. 161, p. 181–198.

Kvenvolden, K.A., 1988, Methane hydrate: A major reservoir of carbon in the shallow geosphere: Chemical Geology, v. 71, p. 41–51.

Kvenvolden, K.A., 1995, A review of the organic geochemistry of methane in natural gas hydrate: Organic Geochemistry, v. 23, p. 997–1008.

Kvenvolden, K.A., 1999, Potential effects of gas hydrate on human welfare: Proceedings of the National Academy of Sciences, v. 96, p. 3420–3426.

Kvenvolden, K.A., and Kastner, M., 1990, Gas hydrates of the Peruvian outer continental margin: *in* Seuss, E., et al., eds., Proceedings of the Ocean Drilling Program, Scientific Results: Texas A & M University, College Station, Texas, USA, v. 112, p. 517–526.

McManus, J., Berelson, W.M., Klinkhammer, G.P., Johnson, K.S., Coale, K.H., Anderson, R.F., Kumar, N., Burdige, D.J., Hammond, D.E., Brumsack, H.J., McCorkle, D.C., and Rushdi, A., 1998, Geochemistry of barium in marine sediments: Implications for its use as a paleoproxy: Geochimica et Cosmochimica Acta, v. 62, p. 3453–3473.

McManus, J., Berelson, W.M., Hammond, D.E., and Klinkhammer, G.P., 1999, Barium cycling in the North Pacific: Implications for the utility of Ba as a paleoproductivity and paleoalkalinity proxy: Paleoceanography, v. 14, p. 53–61.

Monnin, C., 1999, A thermodynamic model for the solubility of barite and ce-lestite in electrolyte solutions and seawater to 200 °C and to 1 kbar: Chemical Geology, v. 153, p. 187–209.

Monnin, C., Jeandel, C., Cattaldo, T., and Dehairs, F., 1999, The marine barite saturation state of the world's oceans: Marine Chemistry, v. 65, p. 253–261.

Monnin, C., Wheat, C.G., Dupre, B., Elderfield, H., and Mottl, M.M., 2001, Barium geochemistry in sediment pore water and formation waters of the oceanic crust on the eastern flank of the Juan de Fuca Ridge (ODP Leg 168): Geochemistry, Geophysics, Geosystems, v. 2, paper no. 2000 GC000073.

Naehr, T.H., Stakes, D.S., and Moore, W.S., 2000, Mass wasting, ephemeral fluid flow, and barite deposition on the California continental margin: Geology, v. 28, p. 315–318.

Norris, R.D., and Röhl, U., 1999, Carbon cycling and chronology of climate warming during the Paleocene–Eocene transition: Nature, v. 401, p. 775–778.

Olivarez, A.M., and Owen, R.M., 1989, Plate tectonic reorganizations: Implications regarding the formation of hydrothermal ore deposits: Marine Mining, v. 14, p. 123–138.

Padden, M., Weissert, H., and de Rafelis, M., 2001, Evidence for Late Jurassic release of methane from gas hydrate: Geology, v. 29, p. 223–226.

Paull, C.K., Ussler, W., III, Borowski, W.S., and Spiess, F.N., 1995, Methane-rich plumes on the Carolina continental rise: Associations with gas hydrates: Geology, v. 23, p. 89–92.

Paull, C.K., Buelow, W.J., Ussler, W., III, and Borowski, W.S., 1996, Increased continental-margin slumping frequency during lowstands above gas hydrate-bearing sediments: Geology, v. 24, p. 143–146.

Paytan, A., and Kastner, M., 1996, Benthic barium fluxes in the central equatorial Pacific: Implications for the oceanic Ba cycle: Earth and Planetary Science Letters, v. 142, p. 439–450.

Paytan, A., Kastner, M., and Chavez, F.P., 1996, Glacial to interglacial fluctuations in productivity in the equatorial Pacific as indicated by marine barite: Science, v. 274, p. 1355–1357.

Ravizza, G., Norris, R.N., Blusztajn, J., and Aubry, M.-P., 2001, An osmium isotope excursion associated with the late Paleocene thermal maximum: Evidence of intensified chemical weathering: Paleoceanography, v. 16, p. 155–163.

Robert, C., and Kennett, J.P., 1994, Antarctic subtropical humid episode at the Paleocene–Eocene boundary: Clay mineral evidence: Geology, v. 22, p. 211–214.

Röhl, U., Bralower, T.J., Norris, R.D., and Wefer, G., 2000, New chronology for the late Paleocene thermal maximum and its environmental implications: Geology, v. 28, p. 927–930.

Schmitz, B., 1987, Barium, equatorial high productivity, and the wandering of the Indian continent: Paleoceanography, v. 2, p. 63–77.

Schmitz, B., Charisi, S.D., Thompson, E.I., and Speijer, R.P., 1997, Barium, SiO_2 (excess), and P_2O_5 as proxies of biological productivity in the Middle East during the Paleocene and the latest Paleocene benthic extinction event: Terra Nova, v. 9, p. 95–99.

Schmitz, B., Pujalte, V., and Núñez-Betelu, K., 2001, Climate and sea-level perturbations during the incipient Eocene Thermal Maximum: Evidence from siliciclastic units in the Basque Basin (Ermua, Zumaia and Trabakua Pass), northern Spain: Palaeogeography, Palaeoclimatology, Palaeoecology, v. 167, p. 299–320.

Schroeder, J.O., Murray, R.W., Leinen, M., Pflaum, R.C., and Janecek, T.R., 1997, Barium in equatorial Pacific carbonate sediment: Terrigenous, oxide, and biogenic associations: Paleoceanography, v. 12, p. 125–146.

Speijer, R.P., and Wagner, T., 2002, Transgressive black shales associated with the late Paleocene Thermal Maximum (LPTM): Organic geochemical and micropaleontologic evidence from the southern Tethyan Margin, *in* Koeberl, C., and MacLeod, K., eds., Catastrophic events and mass extinctions: Impacts and beyond: Boulder, Colorado, Geological Society of America Special Paper, v. 356, p. 533–550.

Stroobants, N., Dehairs, F., Goeyens, L., Vanderheijden, N., and Van Grieken, R., 1991, Barite formation in the Southern Ocean water column: Marine Chemistry, v. 35, p. 411–421.

Suess, E., Torres, M.E., Bohrmann, G., Collier, R.W., Greinerft, J., Linke, P., Rehder, G., Tréhu, A., Wallman, K., Winckler, G., and Zuleger, E., 1999, Gas hydrate destabilization: Enhanced dewatering, benthic material turnover, and large methane plumes at the Cascadia Margin: Earth and Planetary Science Letters, v. 170, p. 1–15.

Thiry, M., 2000, Palaeoclimatic interpretation of clay minerals in marine deposits: An outlook from the continental origin: Earth Science Reviews, v. 49, p. 201–221.

Thomas, D.J., Bralower, T.J., and Zachos, J.C., 1999, New evidence for subtropical warming during the late Paleocene thermal maximum: Stable isotopes from Deep Sea Drilling Project Site 527, Walvis Ridge: Paleoceanography, v. 14, p. 561–570.

Thomas, E., 1998, The Paleocene–Eocene benthic foraminiferal extinction and stable isotope anomalies, *in* Aubry, M.-P., et al., eds., Late Paleocene–early Eocene biotic and climatic events in the marine and terrestrial records: New York, Columbia University Press, p. 214–243.

Thomas, E., and Shackleton, N.J., 1996, The Paleocene–Eocene benthic foraminiferal extinction and stable isotope anomalies, *in* Knox, R.W.O'B., et al., eds., Correlations of the early Palaeogene in northwest Europe: Geological Society [London] Special Publication 101, p. 401–411.

Torres, M.E., Bohrmann, G., and Suess, E., 1996a, Authigenic barites and fluxes of barium associated with fluid seeps in the Peru subduction zone: Earth and Planetary Science Letters, v. 144, p. 469–481.

Torres, M.E., Brumsack, H.J., Bohrmann, G., and Emeis, K.-C., 1996b, Barite fronts in continental margin sediments: A new look at barium remobilization in the zone of sulfate reduction and formation of heavy barites in diagenetic fronts: Chemical Geology, v. 127, p. 125–139.

Valentine, D.L., Blanton, D.C., Reeburgh, W.S., and Kastner, M., 2001, Water column methane oxidation adjacent to an area of active hydrate dissociation, Eel River Basin: Geochimica et Cosmochimica Acta, v. 65, p. 2633–2640.

Von Breymann, M.T., Emeis, K.-C., and Camerlenghi, A., 1990, Geochemistry of sediments from the Peru upwelling area: Results from Sites 680, 682, 685, and 688, *in* Suess, E., et al., eds., Proceedings of the Ocean Drilling Program, Scientific Results: Texas A & M University, College Station, Texas, USA, v. 112, p. 491–503.

Von Breymann, M.T., Brumsack, H., and Emeis, K.-C., 1992, Deposition and diagenetic behavior of barium in the Japan Sea, *in* Sciotto, K.A., et al., eds., Proceedings of the Ocean Drilling Program, Scientific Results: Texas A & M University, College Station, Texas, USA, v. 127/128, p. 651–665.

Walker, J.C.G., and Kasting, J.F., 1992, Effects of fuel and forest conservation on future levels of atmospheric carbon dioxide: Palaeogeography, Palaeoclimatology, Palaeoecology, v. 97, p. 151–189.

Walker, J.C.G., Hays, P.B., and Kasting, J.F., 1981, A negative feedback mechanism for the long-term stabilization of Earth's surface temperature: Journal of Geophysical Research, v. 86, p. 9776–9782.

White, A.F., Bullen, T.D., Schulz, M.S., Blum, A.E., Huntington, T.G., and Peters, N.E., 2001, Differential rates of feldspar weathering in granitic regoliths: Geochimica et Cosmochimica Acta, v. 65, p. 847–869.

Wolgemuth, K., and Broecker, W.S., 1970, Barium in seawater: Earth and Planetary Science Letters, v. 8, p. 372–378.

Xu, W., and Ruppel, C., 1999, Predicting the occurrence, distribution, and evolution of methane gas hydrate in porous marine sediments: Journal of Geophysical Research, v. 104, p. 5081–5095.

Zachos, J.C., and Dickens, G.R., 2000, An assessment of the biogeochemical feedback response to the climatic and chemical perturbations of the LPTM: GFF, v. 122, p. 188–189.