Diagenetic behavior of barite in a coastal upwelling setting

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Received 13 November 2009; revised 28 July 2010; accepted 19 August 2010; published 14 December 2010.

[1] Multiproxy data from ODP Hole 1017E (Point Conception, California) provide an excellent opportunity to examine the behavior of barium, within a well-characterized sedimentary system. $Barium_{excess}$ is generally considered to be a productivity proxy; however, in nearshore environments, Ba_{excess} records can be compromised by both sediment provenance and barite remobilization. For the last 60 kyr, ODP Hole 1017E exhibits significant changes both in primary productivity driven by coastal upwelling and in the sediment redox chemistry of underlying sediments. Significant barite enrichment occurs at an active diagenetic front that marks the boundary between sulfate-rich and sulfate-poor pore waters. This boundary also intersects a sediment facies change from deposition of relatively coarse-grained sediment before 35 ka to an interval of fine-grained, organic-rich sediment after (i.e., Interstadial Event 8). Changes in diffusion rates associated with the sediment facies change cause a strong but misleading correlation between a mobile zone of barite enrichment and rapid climate change. Thus, within the Ba_{excess} record at ODP Hole 1017E is a history of redox chemistry that has corrupted the paleoproductivity record of $Ba_{biogenic}$.

Citation: Hendy, I. L. (2010), Diagenetic behavior of barite in a coastal upwelling setting, *Paleoceanography*, *25*, PA4103, doi:10.1029/2009PA001890.

1. Introduction

[2] A common assumption in sedimentology is that stratigraphic position determines age relationships such that material within the same stratum is of equivalent age [*Steno and Winter*, 1916]. This principle often extends to the correlation between potentially mobile elements and sedimentary particles. Associated with decaying organic matter (Corg) in ocean water, marine barite ($BaSO_4$) is a major carrier of particulate barium to the seafloor and thus Ba has been directly related to marine Corg sedimentation [*Bishop*, 1988; *Ganeshram et al.*, 2003; *Goldberg and Arrhenius*, 1958; *Paytan and Griffith*, 2007]. Ba concentration corrected for the presence of detrital Ba (Ba_{excess}) has been shown to be a reasonable proxy of past changes in oceanic productivity in well-oxygenated deep sea sediments dominated by biogenic sediments and with minimal terrigenous sediment input [*Eagle et al.*, 2003]. Paleoproductivity reconstructions where Ba has been used as a proxy include the Last Glacial Maximum in equatorial upwelling systems] *Paytan and Kastner*, 1996], sapropel formation in the Mediterranean [*Weldeab et al.*, 2003], and at the Paleocene-Eocene Thermal Maximum [*Bains et al.*, 2000; *Paytan et al.*, 2007].

[3] However, it is not reasonable to assume $Ba_{biogenic}$ is equivalent to Ba_{excess} in every marine environment. $Ba_{biogenic}$ is an interpretation that assumes that all Ba concentrations higher than estimated detrital input are the product of marine Corg sedimentation (marine barite). Implicit in this assumption is that sources and delivery of detrital sediment remain constant through time. Furthermore, there are still unconstrained issues associated with Ba_{excess}, including the precise carrying phase of the element and the significance of diagenetic remobilization. Ba in aluminosilicate phases (i.e., lithogenic Ba) is typically immobile, while barite ($BaSO_4$) is extremely susceptible to dissolution under suboxic to anoxic conditions [*Brumsack*, 1986; *van Os et al.*, 1991]. The solubility of barite in sediments remains low until sulfate depletion begins. As depletion of sulfate continues, the solubility of barite increases significantly, resulting in barite dissolution and higher dissolved Ba concentrations within the sediment pore waters [*McManus et al.*, 1998; *Torres et al.*, 1996]. In continental margin settings where there is significant detrital input and high oxidant demand for Corg respiration, the use of Ba_{excess} as a proxy for paleoproductivity reconstruction is problematic. Thus understanding the history of sediment redox conditions and detrital sediment delivery is crucial for an accurate interpretation of Ba as a paleoproductivty proxy.

[4] ODP Hole 1017E, (34′32″°N, 121′6″°W; 956 m water depth), ~60 km to the west of Point Conception, on the Southern California Margin provides an ideal location to examine complications associated with the sedimentary Ba record. This site lies beneath a persistent modern upwelling cell and has yielded high-resolution paleoclimate records due to significant terrestrial sediment input [*Cannariato and Kennett*, 1999; *Irino and Pedersen*, 2000; *Kennett et al.*, 2000; *Tada et al.*, 2000]. Bottom water oxygen concentrations at ODP Hole 1017E have fluctuated through time due to its position in the lower oxygen minimum zone (OMZ) and high Corg rain rates from overlying productive surface waters. Presently the OMZ is a significant feature along the

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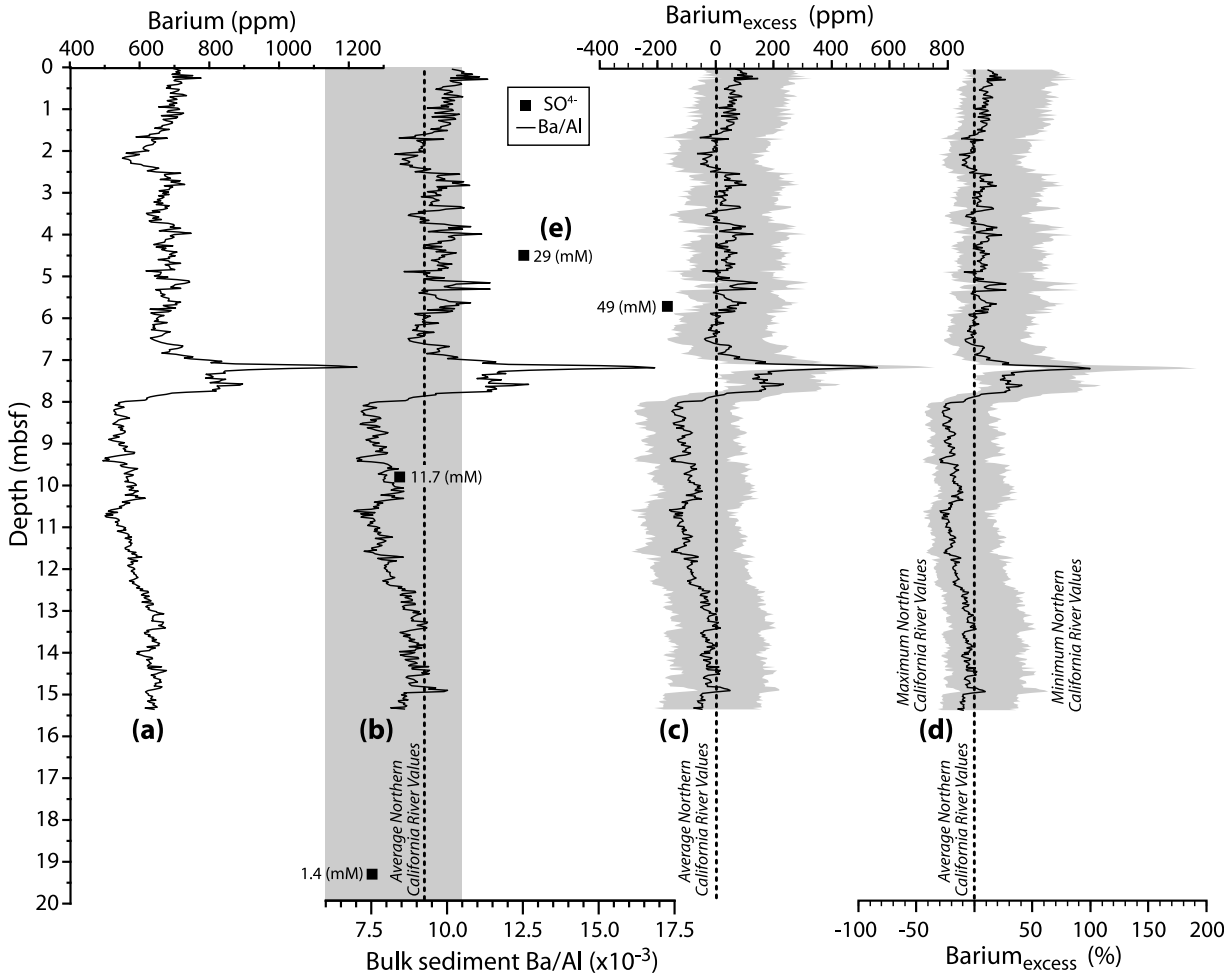

Figure 1. Comparison of the concentration of (a) total barium (ppm) relative to (b) aluminum and (c) barium$_{excess}$ (ppm), and (d) barium$_{excess}$ as a percent value of detrital Ba with (e) pore water sulfate concentrations (square symbols with concentrations indicated) at ODP Hole 1017E. Gray shading indicates the maximum and minimum values of northern California rivers, while the dashed line represents the average value.

California Margin; however, during the last glacial, waxing and waning of the OMZ has been recorded both at this site and others [*Cannariato and Kennett*, 1999; *Zheng et al.*, 2000].

[5] Multiproxy results from ODP Hole 1017E have allowed researchers both to determine the history of past productivity changes as well as understanding the redox chemistry of the sediments [*Cannariato and Kennett*, 1999; *Hendy et al.*, 2004; *Hendy and Pedersen*, 2005; *Irino and Pedersen*, 2000; *Seki et al.*, 2002; *Tada et al.*, 2000]. Here the record of Ba$_{excess}$ is presented, demonstrating how the history of marine barite preservation was compromised at the site. However, unexpectedly the position of an active diagenetic front appears to be predetermined by the paleoproductivity and paleohydrodynamic history of the site. Thus, a significant quantity of mobile Ba has precipitated within sediments associated with a known climatic event (Interstadial Event 7), producing a pronounced Ba$_{excess}$ peak that could simply be misinterpreted as Ba$_{biogenic}$ associated with climatically driven high ocean productivity.

2. Methods

[6] Concentrations of Ba (Figure 1a) were determined for 337 samples from 5.9 to 15.4 mbsf using a Phillips PW 24000 X-ray spectrometer equipped with a 3 Kw Rh tube following standard methods [*Calvert*, 1983; *van Geen et al.*, 1996]. All other major and minor elements, trace metals and productivity proxies are discussed in detail by *Hendy et al.* [2004] and *Hendy and Pedersen* [2005]. Ba levels above the detrital background recorded in Northern California rivers of ~500 ppm or Ba/Al ratios of 0.0092 (Figure 1b) [*Dean et al.*, 1997] were calculated using the following formula [*Paytan and Griffith*, 2007]:

$$\mathrm{Ba_{excess}} = \mathrm{Ba_{sample}} - \left((\mathrm{Ba/Al})_{\mathrm{background}} \times \mathrm{Al_{sample}}\right)$$

[7] Ba_{excess} is displayed in Figure 1 as both Ba_{excess} (ppm) (Figure 1c) and Ba_{excess} (%) (Figure 1d) with shading to display maximum and minimum values spanning the range of Ba concentrations found in California rivers. This highlights the potential influence of changes in the terrigenous provenance of detrital input.

[8] Major and minor element distributions has been related to grain size at ODP Hole 1017E [*Irino and Pedersen*, 2000; *Tada et al.*, 2000]. Major and minor element data were simplified by a Q-mode factor analysis with varimax rotation using the computer program CABFAC to provide factors that describe the distribution of elements known to be associated with different grain sizes [*Imbrie and Kipp*, 1971; *Leinen and Pisias*, 1984]. Two factors explaining 97.3% of the total variance were extracted from the data set with communalities mostly >0.95. Loading in factor 1 (54.4% of total variance) is dominated by Ni, Cu, Zn, Fe, Mg and Ca. These elements are often associated with the clay fraction. Factor 2 (42.9% of the total variance) loading is influenced by Zr, Si, Na, and K. These elements are frequently found in larger (silt-sand) grains [*Hendy et al.*, 2004]. These interpretations are supported by grain size analysis at the site [*Irino and Pedersen*, 2000; *Tada et al.*, 2000].

[9] Chronology presented in this contribution is discussed in greater detail by *Hendy et al.* [2004]. The climatic event dates are based on the correlation of *N. pachyderma* coiling ratios between ODP Hole 893A and 1017E as described by *Hendy* [2010]. The chronology of ODP Hole 893A is described by *Hendy et al.* [2002] and interstadials (IS) 5 to 17 are assumed to be synchronous with interstadial events in the GISP2.

3. Sedimentary Barium Record at Point Conception

[10] Ba_{excess} is used to describe Ba concentrations in sediments that exceed detrital input, which is assumed to be constant through time, and as such this term does not constrain the origin of Ba. The Ba_{excess} record from the sediment water interface to 7.2 mbsf varies between −50 and 75 ppm (600 and 720 ppm total Ba), increasing at 2.6, 4, 5.1 and 5.6 mbsf and decreasing at 2.1 mbsf (Figure 1). A dramatic increase in Ba (200 ppm Ba_{excess} or 830 ppm total Ba) occurs at 7.7 mbsf, with Ba_{excess} values peaking at 600ppm (1200 ppm total Ba) at 7.2 mbsf. This is the only region in the upper 15 m of the core where Ba_{excess} values exceed the entire regional detrital Ba range. Below this horizon to 15.5 mbsf Ba_{excess} falls to background levels, varying between −100 and 0 ppm (530 and 650 ppm total Ba or 75 to 88 Ba/Al), which is similar to the average regional detrital input [*Dean et al.*, 1997]. Below the sediment depth (8 to 11 mbsf) of extreme Ba enrichment, Ba_{excess} values drop zero indicating only detrital Ba remains and elemental variations are likely related to changes in sediment provenance.

4. Barium as a Productivity Indicator

[11] Barium concentrations are enriched in sediments characterized by high concentrations of biogenic opal and Corg [*Bishop*, 1988; *Dehairs et al.*, 1987; *Dymond and Collier*, 1996; *Goldberg and Arrhenius*, 1958] and high barite concentrations are attributed to overlying productive surface waters [*Gingele and Dahmke*, 1994]. Profiles of dissolved Ba in the water column are characterized by a minimum in the nutrient-depleted euphotic zone and a steady increase with water depth [*Jeandel et al.*, 1996; *Monnin et al.*, 1999; *Sternberg et al.*, 2008], whereas concentrations of particulate Ba are observed to increase just below the euphotic zone, decreasing slightly with water depth [*Dehairs et al.*, 1980; *Dymond and Collier*, 1996; *Sternberg et al.*, 2008]. It would appear that precipitation of marine barite occurs within or just below the euphotic zone and it undergoes gradual dissolution with depth. Laboratory and field experiments demonstrate that barite is rapidly produced in suspensions of decaying phytoplankton as a result of Ba release during the early stages of organic decay [*Bishop*, 1988; *Ganeshram et al.*, 2003]. These mechanisms strongly support both the use of sedimentary Ba as a proxy for determining relative productivity changes through time, and thus the assumption that Ba_{excess} is equivalent to $Ba_{biogenic}$.

[12] If all Ba_{excess} is assumed to be $Ba_{biogenic}$ at ODP Hole 1017E, then Ba_{excess} should be consistent with paleoproductivity reconstructions. A number of independent, coherent paleoproductivity proxies (e.g., % upwelling species, % carbonate carbon, % opal, Corg/Al [*Hendy et al.*, 2004]; Figure 2), exist for comparison. Productivity increased during warm climatic intervals including the Holocene and interstadial events, with the most pronounced interval of high productivity occurring during the Bølling. In sediments <35 ka intervals of increased productivity appear to correspond to low Ba_{excess} concentrations, while periods of decreased productivity appear to correspond to high Ba_{excess} in sediments. The interval of extreme Ba enrichment between 34 and 39 ka corresponds to minor productivity increases at Interstadial Events (IS) 7 and 8. From 40 to 60 ka, Ba_{excess} variations are insignificant and appear inconsistent with other productivity proxies. It is apparent from comparison between the records (Figure 2) that variability in the Ba_{excess} record at ODP Hole 1017E is *not* driven by changes in the productivity of the persistent upwelling cell off Point Conception. This result should be anticipated as the site is located nearshore within the OMZ.

5. Detrital Sediment Provenance and Barium

[13] Due to the nearshore location of ODP Hole 1017E, a significant detrital proportion of Ba in the sediments should be derived from terrigenous silicates, and Fe-Mn oxides and hydroxides. Delivery of detrital Ba to ODP Hole 1017E is predominantly from riverine input [*Dean et al.*, 1997; *Klump et al.*, 2000]; however, site is located offshore of a semiarid environment and therefore eolian deposition [*Schroeder et al.*, 1997] cannot be excluded. Fe oxides efficiently scavenge dissolved species from seawater and as common components of eolian dust provide another Ba delivery mechanism to sediment [*Schroeder et al.*, 1997], 20 to 40% of total Ba in some sediment is associated with aluminosilicate fractions [*Gonneea and Paytan*,

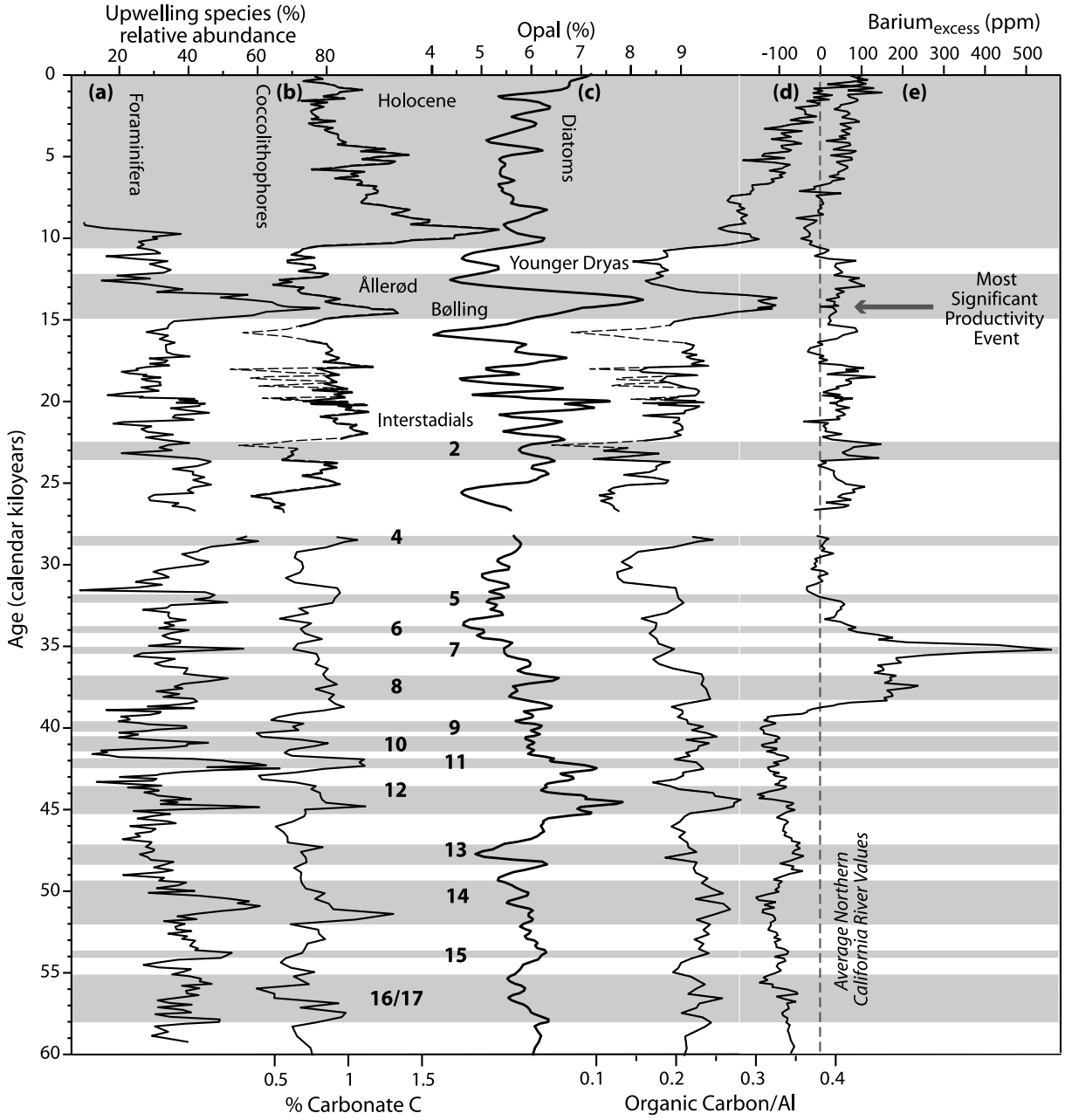

Figure 2. Comparison of proxy records associated with phytoplankton and zooplankton [*Hendy et al.*, 2004] with barium. (a) The relative abundance (%) of upwelling associated species *G. quinqueloba* and *G. bulloides*, (b) percent (%) carbonate composition of the sediments, (c) percent (%) opal$_{(diatom)}$ composition of the sediments, (d) Corg to Al weight ratio of the sediments, and (e) barium$_{excess}$ (ppm). Gray bands represent warm intervals (interstadials and the Holocene). Interstadials (D-O events) are numbered according to the GISP2 scheme with major climatic events labeled.

2006; *Klump et al.*, 2000]. In this nearshore environment, variation in sediment provenance at the site may be as much as 60% of total Ba or 300ppm (see gray shading in Figures 1c and 1d). Thus much of the Ba variation downcore could be the result of changing detrital sediment provenance. The interval between 7 and 8 mbsf (34 to 40 ka), however, remains enriched in Ba beyond the highest regional detrital value.

6. Barium and Barite Dissolution

[14] It may be reasonable to assume that most Ba$_{excess}$ is similar to Ba$_{biogenic}$ in oxic depositional environments;

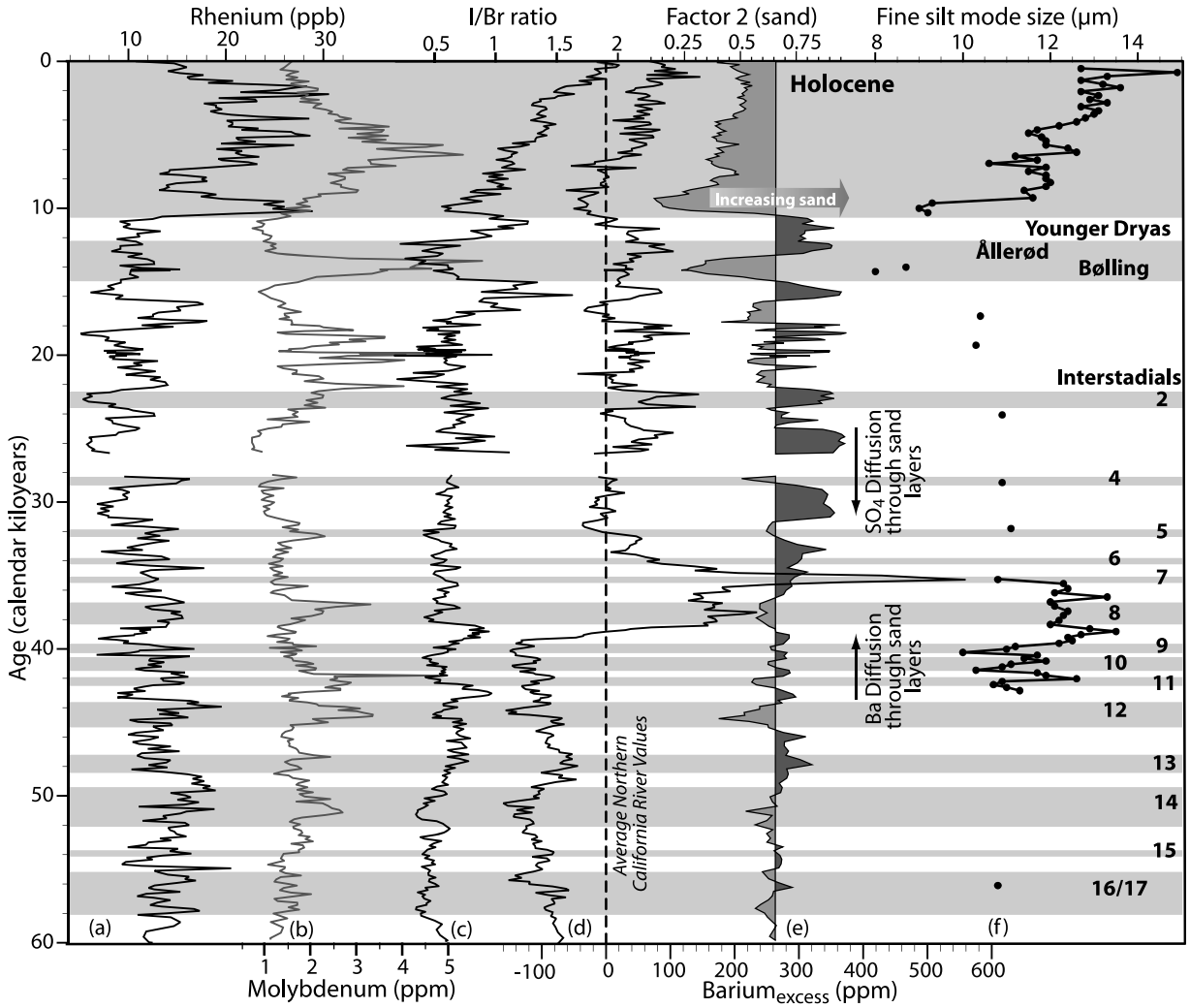

Figure 3. Comparison of redox indicators [*Hendy and Pedersen*, 2005] with barium. Suboxic indicators (a) rhenium (ppb), (b) molybdenum (ppm), (c) iodine/bromine ratio, and (d) barium$_{excess}$ (ppm) with sedimentary factors associated with (e) factor 2 (grain size [*Hendy et al.*, 2004]), and (f) fine silt mode grain size [*Tada et al.*, 2000]. Gray bands represent warm intervals (interstadials and the Holocene). Interstadials (D-O events) are numbered according to the GISP2 scheme with major climatic events labeled.

however, pore waters at ODP Hole 1017E are presently suboxic. Authigenic Ba in marine deposits occurs almost entirely as barite ($BaSO_4$), which although stable in oxygenated seawater, readily dissolves under sulfate-depleted conditions [*Von Breymann et al.*, 1992]. High dissolved Ba concentrations in the upper few centimeters of marine sediment suggest that regeneration of Ba occurs within the upper few millimeters where maximum remineralization of Corg and other biogenic components occurs [*Paytan and Kastner*, 1996]. High benthic fluxes of dissolved Ba have been found in sediments underlying regions of high productivity in the pelagic realm [*Paytan and Kastner*, 1996] and in suboxic sediments [*McManus et al.*, 1994].

[15] At ODP Hole 1017E, 95% of the dissolved pore water oxygen is removed in the upper few centimeters of the sediments where trace metal diffusion and subsequent precipitation in the sediments occurs. Similar redox conditions in the upper few centimeters of ODP Hole 1017E, appear to have prevailed throughout the Holocene and much of the Last Glacial as Re and Mo are consistently enriched (Figures 3a and 3b) [*Hendy and Pedersen*, 2005]. Notable exceptions occurred during stadial events prior to major interstadials (e.g., the Younger Dryas and prior to IS 11, IS 8, and the Bølling; Figure 3c) when I/Br ratios increase [*Hendy and Pedersen*, 2005]. Iodine enrichments relative to bromine indicate organic matter deposition under oxic bottom water conditions [*Calvert and Pedersen*, 1993]. Thus, during the aforementioned stadial intervals oxic conditions must have prevailed. Ba$_{excess}$ increased during two of these intervals (just prior to the Bølling and during the Younger Dryas) coincident with increased I/Br ratios [*Hendy and Pedersen*, 2005].

[16] The antiphase behavior of the Ba_{excess} record relative to the records of redox-sensitive trace metals such as Mo and Re indicates that the redox history of the site has compromised Ba_{excess}. Under these conditions Ba dissolves close to the sediment-water interface and is lost to the overlying water column. Examples of intervals where anoxic sediment conditions existed include; the early Holocene (8 ka), the Bølling (14.7 ka), 18 to 16 ka, and 22.5 to 20.5 ka. The reverse is true (i.e., increases in Ba_{excess} simultaneous with decreases in trace metals) during IS 2, the LGM, just prior to the Bølling and during the Allerød and Younger Dryas (Figure 3). Yet, the period of extreme Ba enrichment between 36 and 34 ka (IS 5 to 8) is different from these examples in that there is a concurrent increase, not a decrease, in the concentrations of redox-sensitive trace metals. Prior to 34 ka, the antiphase relationship between Ba_{excess} and redox-sensitive trace metals does not exist. It appears that the waxing and waning of the OMZ that controlled the shallow redox history at ODP Hole 1017E was not the *only* influence on Ba_{excess} at the site.

7. Barium Remobilization and Diagenetic Fronts

[17] Barite may also be formed by direct precipitation. When Ba-enriched hydrothermal fluids react with seawater sulfate massive barite deposits form, however, this mechanism is restricted to active hydrothermal regions (e.g., the East Pacific Rise [*Feely et al.*, 1987]). Nonhydrothermal barite deposits also occur in layers or concretions in marine sediments. Massive sediment-hosted barite with no associated massive sulfide occurs in a variety of geologic settings and several diagenetic models have been proposed for the origin of these nonvolcanogenic barites. One favored mechanism for diagenetic barite formation is the remobilization of $Ba_{biogenic}$ (in the presence of sulfate reduction) and subsequent precipitation at an authigenic front [*Goldberg and Arrhenius*, 1958; *Torres et al.*, 1996].

[18] Below 8 mbsf (38 ka) at ODP Hole 1017E, Ba_{excess} variations are muted and the values approach or fall below the detrital values suggesting little to no Ba_{excess} remains in the sediment. The apparent absence of barite in sediments older than 37 ka suggests that at some point complete barite dissolution occurred. The extreme Ba_{excess} enrichment immediately above this zone of Ba_{excess} absence (i.e., 7–8 mbsf, 38–34 ka) is suggestive of barite precipitation at a diagenetic front. But what other evidence do we have for this authigenic front? Limited pore water studies at ODP Hole 1017E [*Lyle et al.*, 1997] suggest that pore water SO_4^{2-} is almost completely depleted (<10 μM) somewhere between 5.5 and 9.5 mbsf (Figure 1e). By 19 mbsf, SO_4^{2-} is fully depleted and methanogenesis occurs [*Lyle et al.*, 1997]. The major Ba_{excess} peak occurs within the interval of sulfate depletion (i.e., 6.5 to 8 mbsf) suggesting a linkage between the two.

[19] We hypothesize that $BaSO_4$ dissolution in the sulfate-depleted interval below ~8 to 9 mbsf resulted in upward diffusion of Ba^{2+} from the site of dissolution producing a pore water Ba gradient. Simultaneously, SO_4^{2-} migrates down from regions of high concentration in the upper core. Where dissolved Ba and SO_4^{2-} converge in the sediments, barite precipitates. Under conditions of ongoing sedimentation and geochemical steady state, continuous repetition of dissolution, diffusion, and precipitation will transport Ba progressively upward in the sediment profile and ultimately concentrate it into a thin layer at the top of the sulfate reduction zone [*Gobeil et al.*, 1997]. A steeper SO_4^{2-} concentration gradient will yield a sharper diagenetic front [*de Lange et al.*, 1994], and there is no downward migration of Ba by this mechanism [*Gobeil et al.*, 1997].

[20] The depth of the Ba enrichment peak (Figure 3d) therefore demonstrates the vertical range of an *active* diagenetic front at ODP Hole 1017E. The modern sulfate depletion front is not, however, associated with redox sensitive metal enrichment because the significant burial depth of the front prevents trace metal diffusion from bottom waters. Most examples of barite fronts have been observed in deeply buried sediments [*Riedinger et al.*, 2006; *Torres et al.*, 1996]. However, one recent study found barite fronts at relatively shallow depth (~4 mbsf) in association with burial of large amounts of organic matter under the Benguela upwelling system [*Riedinger et al.*, 2006].

8. Modern Authigenic Front and Submillennial Climate Change

[21] The coincidence of the Ba_{excess} peak at 7.2 mbsf with IS 7 (Figure 3d) may be highly suggestive of a climatic cause for the enrichment, but Ba_{excess} was not directly manipulated by submillennial climate change. A sediment facies change between stadial and interstadial (Figure 3) [*Hendy et al.*, 2004; *Tada et al.*, 2000] may have led to an indirect influence on Ba_{excess}. Increased Corg deposition occurred during interstadials when the local upwelling cell was active [*Hendy et al.*, 2004]. Past productivity shifts and resulting changes in sedimentary Corg concentration are currently controlling the oxidant demand at depth at ODP Hole 1017E. High oxidant demand would result in a more rapid SO_4^{2-} reduction and upward migration of the active SO_4^{2-} depletion front within the diagenetic zone. Grain size also has a major affect on porosity and hence diffusion rates within the sediment. Fine grain sediment is less porous reducing diffusion rates, restricting Ba movement up-core and SO_4^{2-} down-core, and hence promoting precipitation of authigenic barite.

[22] Interstadials (IS) 5, 7 and 8 have major element sediment compositions indicative of low sand and high clay content, and the fine silt mode grain size decreases (Figures 3e and 3f) [*Hendy et al.*, 2004]. There is a sharp increase in Ba_{excess} at IS 8 where dissolution of authigenic barite slows due to low diffusion rates of SO_4^{2-} out of the fine-grained sediments of the interstadial and low oxidant demand in the Corg-poor sediments of the preceding stadial event. At the termination of IS 5, 6 and 7 there are sharp decreases in Ba_{excess}. Here authigenic barite formation is delayed by slow upward diffusion of Ba through the fine-grained sediment of IS 5 and 6, despite the SO_4^{2-}-rich pore waters in the Corg-poor, coarse sediments of the following stadials. A potential future scenario could be that the sulfate depletion front will quickly diffuse upward through the Corg-poor, coarse sediment of younger stadial events before slowing again at a younger interstadial event (IS 4). Thus, it would appear that

the paleoceanographic history of sediment deposition at the ODP Hole 1017E has preconditioned the position of an active diagenetic Ba front.

[23] Significant Ba_{excess} enrichments have been identified in sediments associated with past climatic change, and have been employed as indicators of increased export production [*Bains et al.*, 2000; *Brumsack*, 2006; *Paytan et al.*, 1996; *Paytan et al.*, 2007; *Weldeab et al.*, 2003]. As Ba is one of an elemental suite provided by commonly employed bulk sediment geochemistry techniques, interpretation of this element is easily incorporated into paleoceanographic studies. However, caution should be used when the Corg content of sediments increases dramatically or the oxygen concentration of overlying bottom waters decreases [*Brumsack*, 2006; *McManus et al.*, 1998].

9. Implications of the Ba_{excess} Record at Point Conception

[24] The sedimentary record from ODP Hole 1017E serves as a warning for interpretation of Ba_{excess} as $Ba_{biogenic}$ in the geologic record. Knowledge of the depositional environment (nearshore and within the lower OMZ) would exclude this site as an appropriate location for Ba_{excess} use as a paleoproductivity proxy. Furthermore, although benthic foraminiferal assemblages [*Cannariato and Kennett*, 1999] and redox sensitive metals [*Hendy and Pedersen*, 2005] demonstrate that sulfide production occurred at the bottom water-sediment interface, indicators capable of identifying the deep diagenetic front within the core are less readily obtainable.

[25] Changes in OMZ strength, productivity and their associated proxies are decoupled from the Ba diagenetic front in both space (~7 mbsf) and time (~35 kyr). Trace metal enrichment and benthic foraminiferal assemblages temporally concurrent with the active diagenetic front are displaced ~7 m up core. Trace metal enrichment and benthic foraminiferal assemblages that occur at the same stratigraphic depth and therefore are spatially congruent with the front were generated 35 kyr before Ba precipitation at the front occurred. Thus, the benthic foraminiferal assemblage and trace metal concentration at ODP Hole 1017E are ineffective in identifying the origin of the most significant Ba enrichment (the modern mobile Ba diagenetic front) in the sediments at the site.

[26] The deep sulfate reduction front was identified by pore water analyses. Pore water analyses are destructive, requiring large amounts of sediment, and consequently are restrictive. Sulfur isotopes within the Ba_{excess} peak could identify the origin of Ba_{excess} within ODP Hole 1017E. Barite produced within the water column should have $\delta^{34}S$ values similar to seawater; however as microbial reduction of dissolved sulfate occurs, ^{32}S enrichment in the newly formed H_2S should deplete the remaining pore water sulfate. Thus the $\delta^{34}S$ values of barite forming at the mobile Ba diagenetic front should be predictably high relative to $Ba_{biogenic}$ [*Paytan et al.*, 2002]. Finally as Ba_{excess} is suggested to overestimate $Ba_{biogenic}$ due to the incorporation of terrigenous silicates [*Eagle et al.*, 2003], it has been suggested that in environments where a significant detrital input occurs, a sequential extraction technique is required [*Reitz et al.*, 2004]. This precludes new and increasingly employed analytical methods such as scanning XRF where bulk sediment Ba values are produced.

10. Conclusions

[27] ODP Hole 1017E, located beneath highly productive surface waters, provides an excellent opportunity to examine the burial, dissolution and precipitation of barite in marine sediment. In this location, high productivity as a result of persistent upwelling produces biogenic barite deposition. In the upper few cm of the sediment column, Corg degradation and low bottom water oxygen concentrations result in sulfate reduction, dissolving much of the $Ba_{biogenic}$ and precipitating Re out of seawater. Consequently, throughout the upper 7m of the core Ba_{excess} and Re are antiphase. This relationship changes within a zone of extreme Ba_{excess} between 38 and 34 ka (IS 5 to 8) that directly overlies sediments where pore water sulfate is completely reduced and suggests that extreme Ba_{excess} enrichment is in fact a modern authigenic front. Changes in sediment grain size and Corg content, related to rapid climate and associated hydrographic change, appear to have preconditioned the position of the authigenic front. Thus, despite the significant temporal disconnect between rapid climate change events and the modern authigenic front, the two processes have become coupled. The results of this test case demonstrate that Ba_{excess} as a paleoproductivity proxy should be carefully assessed, particularly in nearshore highly productive ocean settings. Additional information on sedimentary redox conditions from pore water analysis, and/or sulfur isotopes should be provided in support of Ba_{excess} based paleoproductivity reconstructions.

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