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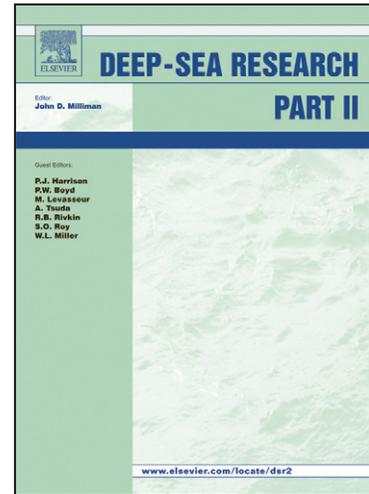
PII: S0967-0645(07)00042-2
DOI: doi:10.1016/j.dsr2.2007.01.007
Reference: DSR II 2035

To appear in: *Deep-Sea Research II*

Accepted date: 10 January 2007

Cite this article as: Adina Paytan and Elizabeth M. Griffith, Marine barite: Recorder of variations in ocean export productivity, *Deep-Sea Research II* (2007), doi:10.1016/j.dsr2.2007.01.007

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Marine barite: recorder of variations in ocean export productivity

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Keywords: (Palaeoceanography; Barite; Carbon cycle; Primary production; Biological production; Marine Sediments)

Abstract

Marine barite (BaSO_4) is produced in the water column in association with decaying organic matter and its distribution in the water column and in core top sediments closely corresponds to the organic carbon flux from the surface ocean to the deep ocean (export production). Barite preservation in non-sulfate-reducing sediments is high, compared to other proxies used to reconstruct both export carbon fluxes (export production) and carbon burial rates. Thus the accumulation rate of marine barite is one of the most promising methods (or proxy variables for export production) and has been used to understand and reconstruct past biogeochemical processes in the ocean, including export productivity. Like any other paleoceanographic proxy, there are assumptions and complications associated with the application of barite accumulation rates to reconstruct export production. Specifically, because barite constitutes only a small fraction of the total sediment (<1%) computing precise barite accumulation rates depends on accurate estimates of bulk sediment mass accumulation rates, which are hard to determine, particularly at high temporal resolution. Moreover, the significance of variable barite preservation dependent on seawater saturation levels with respect to barite and

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sedimentation rates has not yet been fully investigated. Several studies have demonstrated the utility of this proxy, and if used wisely marine barite accumulation rates in marine sediments can provide valuable information about changes in carbon export to depth and the response of the carbon cycle to climate perturbations in the geological record. Ideally, to achieve higher confidence in paleo-reconstructions of export production, several independent proxies should be applied simultaneously at any given site or time interval.

1. Introduction

Carbon flux to the deep ocean, also referred to as export production, is one of the most important parameters in the global carbon cycle related to carbon sequestration and climate change as it is an important mechanism by which carbon dioxide is removed from the atmosphere via the surface ocean to depth and thus impacts climate on time scales of thousands of years (Broecker, 1982; Berger et al., 1989; Hansell et al., 1997). Export production is much larger than carbon burial since only a small fraction of export production eventually gets buried in sediments. This parameter, however, is not easy to measure directly or even estimate in the present day ocean, let alone for the past. Many methods have been applied to reconstruct both export carbon fluxes (export production) and carbon burial rates, including mass accumulation rates of organic carbon, “reactive” phosphorus, calcium carbonate and biogenic opal in marine sediments, microfossil assemblages, carbon isotopes of carbonates, organic biomarkers and several geochemical indicators such as Al/Ti, Ba/Ti, $^{231}\text{Pa}/^{230}\text{Th}$, $^{10}\text{Be}/^{230}\text{Th}$, U and Sr/Ca. Geochemical indicators for nutrient content and utilization (N, P, Fe, Si, nitrogen isotopic composition of organic matter, silicon isotopic composition of diatom frustules, Cd/Ca ratio of

planktonic foraminifera) have also been applied to address this topic (see Paytan et al., 2004a and references therein). One of the most promising methods (or proxy variables for export production) is the accumulation rate of barite in marine sediments. Marine barite (BaSO_4) and excess barium (the fraction of Ba in marine sediments that is not of terrigenous origin; also referred to as biogenic Ba, bio-Ba or Ba_{xs}) have been used extensively in the past decade to understand and reconstruct past biogeochemical processes in the ocean, including export productivity.

Barium (Ba) and in particular, the mineral barite (BaSO_4), were first suggested as tracers that track productivity when Goldberg and Arrhenius (1958) looked at the composition and distribution of marine sediments and found high Ba accumulation in sediments underlying productive areas in the Pacific Ocean. Turekian and Tausch (1964) confirmed this same relationship for the Atlantic Ocean. However, due to analytical limitations related to the relatively low barite abundance in the sediments (typically 0.2 weight percent; e.g. Eagle et al., 2003) and a lack of understanding of the formation mechanisms of this mineral (Turekian and Tausch, 1964), not much attention was given to this sedimentary component as a potential recorder of oceanic processes.

In the following decades, the apparent relationship between barite and productivity was further investigated. In the 1970s, as part of the GEOSECS expeditions, the general distribution of Ba in the water column was established (see figure 1a) (Turekian and Johnson, 1966; Ku et al., 1970; Wolgemuth and Broecker, 1970; Bacon and Edmond, 1972; Li et al., 1973; Chan et al., 1976, 1977) and is now being further refined to capture both temporal and spatial variability (e.g. Jeandel et al., 1996; Monnin et al., 1999; Jacquet et al., 2004, 2005; Guieu et al., 2005). These studies revealed the nutrient-like

distribution of dissolved Ba, indicating direct or indirect involvement of Ba in the marine biological cycle. Later, sediment trap and high-volume filtration studies showed a striking relationship between organic carbon flux, biogenic debris in the water column, and Ba abundance (Dehairs et al., 1980, 1991, 1992; Bishop, 1988; Dymond et al., 1992; Dymond and Collier, 1996).

The first attempt to utilize barium for reconstruction of paleoceanographic processes was by Schmitz (1987). The Ba content in Indian Ocean sediment cores was used to determine when each core was situated under the equatorial high productivity zone in order to reconstruct the rate of movement of the Indian Plate towards Asia (Schmitz, 1987). It is only in the last decade or so that the use of barite and excess Ba for quantitative paleoproductivity and marine chemistry reconstruction has gained popularity. This is in part because of evolving instrumental capabilities (e.g. ICP-MS), but also because of the increasing awareness of previously unrecognized problems associated with the use of the more traditional productivity proxies such as organic carbon, opal or carbonate accumulation rates, $\delta^{13}\text{C}$ of marine sediments and faunal assemblages. This stimulated the desire to development new and independent proxies for past primary productivity and export production in particular.

1.1. Marine Barite Formation

Today, the water column in vast areas of the ocean is under-saturated with respect to barite, although it is at or slightly above saturation at some depths in the Southern Ocean and the Pacific Ocean (figure 1b) (Church and Wolgemuth, 1972; Monnin et al., 1999; Rushdi et al., 2000). However, sediment traps (Dehairs et al., 1980; Dymond et al., 1992; Dymond and Collier, 1996) and large volume filtration techniques (Bishop, 1988) have

shown that barite crystals are abundant in sinking and suspended particulate matter in the water column (figure 2). The particulate barite in seawater is mostly observed in the form of aggregates of sub-micron spherical barite crystals as well as euhedral and ellipsoidal crystals ranging in size from 0.5 to 5 microns (see figure 2). The prevailing occurrence of barite crystals in under-saturated seawater led to the suggestion that barite precipitates either through direct biologic mediation (e.g. within living organisms) or inorganically from seawater in microenvironments which become saturated with respect to barite (Goldberg and Arrhenius, 1958; Arrhenius, 1959; Church, 1970; Ganeshram et al., 2003).

Arrhenius (1959) first suggested that barite precipitates in fecal pellets as a result of increased sulfate ion concentrations during the decay of proteinaceous matter in microenvironments. It was also thought that barite was precipitated by particular protozoa or algae to serve as statoliths to maintain orientation and depth by adjusting their density (e.g. Arrhenius and Bonatti, 1965; Tendal, 1972; Gooday and Nott, 1982; Swinbanks and Shirayama, 1986). So far, however, no abundant living marine planktonic organism with intra-cellular barite crystals has been identified.

Barite crystals are common inside of the cells of the benthic protozoan *Xenophyophores* (benthic deposit feeders), but it is not clear if these organisms actively precipitate barite or selectively retain it in their cells during filter-feeding (Fresnel et al., 1979; Gooday and Nott, 1982). Bertram and Cowen (1997) described organisms that contained barite crystals within their tests or covering their tests, however these organisms are not abundant in the ocean. Although there is no quantitative estimate of the contribution of these organisms to the total barite budget, it is most likely insignificant. Moreover, the

shape of the barite crystals within these organisms is different from the crystals most common in the water column and sediments (Bertram and Cowen, 1997).

Based on the above observations, an abiotic mechanism of barite formation is more likely than direct biological precipitation. It has been suggested that decaying organic matter, acantharian shells and other biogenic remains provide the additional Ba and/or sulfate (SO_4) needed to reach barite saturation within microenvironments and thus promote barite precipitation (Goldberg and Arrhenius, 1958; Bishop, 1988; Bernstein et al., 1992, 1998). The barium content of different marine organisms is considerably higher than seawater concentrations, providing a potential source of Ba to the microenvironments (Fisher et al., 1991) (table 1). Although this process is thought to occur mainly in the upper water column where most of the organic matter is regenerated (Dehairs et al., 1980), it could potentially operate at any water depth where organic aggregates exist and decompose, including at the sediment-water interface.

Acantharia (protozoan zooplankton) have also been proposed as mediators of barite formation (Bernstein et al., 1992), since their celestite (SrSO_4) shells readily dissolve in seawater and could provide both Ba (present in celestite at concentrations of thousands of ppm) and sulfate to promote barite supersaturation in microenvironments. However, the lack of a clear correlation between barite concentration and acantharian abundance and the formation of barite in laboratory decay experiments in the absence of acantharia indicate that they are not required for the formation of barite in the water column (Ganeshram et al., 2003).

Indirect evidence for the potential of phytoplankton to locally concentrate Ba and promote the formation of supersaturated microenvironments for barite precipitation

comes from observations of a spring bloom in the Delaware estuary. A dramatic decrease in dissolved Ba within the bay and estuary occurred at the end of a spring bloom followed by rapid regeneration of Ba during the subsequent month (Stecher and Kogut, 1999). More direct evidence (figure 3) was put forth by Ganeshram et al. (2003) who performed time-series decay experiments with laboratory-cultured diatoms and coccolithophorids as well as natural coastal plankton to test this mechanism of formation. The plankton decomposed in dark oxic conditions, and Ganeshram et al. (2003) found that barite crystals did indeed form and increase in abundance with time in their pure culture experiments. Their study also showed that living plankton contains a relatively large pool of labile Ba, which is readily released during decomposition.

Additional support for an abiotic mechanism involving the decay of organic matter comes from the observation that the highest particulate barite concentration in the water column in most regions of the ocean is associated with the oxygen minimum zone, where most organic carbon degradation occurs. This points to a relationship between barite formation in the water column and organic matter degradation (Dehairs et al., 1980, 1991, 1992). The increasing flux of excess Ba (Ba in excess of the contribution from crustal material) with depth in sediment traps indicates that Ba is continuously removed from solution during vertical transport and degradation of biogenic aggregates (see figure 4; Dymond et al., 1992). If this is indeed the case, the source of the measured excess Ba should be attributed to barite precipitation.

A seasonal transect in the Australian sector of the Southern Ocean showed that mesopelagic excess Ba accumulation records the changes in plankton biomass from the mixed layer over a time scale of a few weeks (Cardinal et al., 2005). This study also

confirmed that mixed layer excess Ba is strongly associated with sinking phytoplankton and its increase with depth is associated with the decomposition of organic aggregates (Cardinal et al., 2005). More detailed studies suggest that the processes controlling barite formation may relate to changes in the ecosystem (Dymond and Collier, 1996) and to the kinetics of organic matter aggregation during settling and decomposition (Dymond and Collier, 1996; Dehairs et al., 2000; Jeandel et al., 2000; Sanchez-Vidal et al., 2005).

What these general observations imply in regard to the use of barite for paleoproductivity reconstruction will be discussed further in section 3.

2. Methods and Proxy Calibrations

The dissolved Ba profiles in seawater are characterized by depletion in the surface water and enrichment at depth, with the deep Pacific Ocean having higher concentrations than the deep Atlantic Ocean (Ku et al., 1970; Wolgemuth and Broecker, 1970; Bacon and Edmond, 1972; Li et al., 1973; Chan et al., 1976, 1977; Dehairs et al., 1980; Dymond et al., 1992), see figure 1a. Such profiles usually indicate direct or indirect involvement in the biological cycle. The oceanic distribution of Ba most likely results from the uptake of Ba in association with biological activity in the upper water column and its regeneration at depth (Chow and Goldberg, 1960; Collier and Edmond, 1984). Indeed, studies in specific regions of the ocean have shown that dissolved Ba correlates well with silica and alkalinity (Bacon and Edmond, 1972; Lea and Boyle, 1989; Lea, 1993).

It has been shown in many areas of the oceans that the major carrier of particulate Ba in the water column and in many pelagic sediments is the mineral barite (e.g. Church, 1970; Collier and Edmund, 1984; Bishop, 1988; Dymond et al., 1992; McManus et al., 1998). Particulate Ba appears to be associated with particulate organic carbon content and the

biological productivity of the overlying water column (Dehairs et al., 1991, 1992; Dymond et al., 1992; Dymond and Collier, 1996). Barite extracted from core top sediments indeed confirm that barite accumulation rates correlate well with export production in the overlying water column, as seen in figure 5 (Goldberg et al., 1969; Church, 1970; Gingele and Dahmke, 1994; Francois et al., 1995; Paytan et al., 1993; Paytan, 1996; Eagle et al., 2003). Based on these relationships, quantitative algorithms have been suggested for the use of excess Ba, Ba/Ti and Ba/Al elemental ratios, or barite accumulation rates for the reconstruction of paleoproductivity and export production. These proxies are discussed below.

2.1. Excess Ba

Excess Ba (defined as the fraction of total Ba not associated with terrigenous material as determined from the total Al or Ti content) in particulate material correlates with the organic C flux to depth, thus export productivity (Bishop, 1988; Dehairs et al., 1980, 1991, 2000; Dymond et al., 1992; Francois et al., 1995). As mentioned earlier, the major carrier of particulate Ba in the water column is the mineral barite (e.g. Collier and Edmund, 1984; Bishop, 1988; Dymond et al., 1992; McManus et al., 1998).

Dymond et al. (1992) looked at the distinct depth dependence of organic C and excess Ba abundance in sediment traps in three oceanic regions and parameterized it by fitting an algorithm to determine new production (grams C per m² per year) from the excess Ba flux to the sediments (equations 1 and 2).

$$[\text{Ba}_{\text{excess}}] = [\text{Ba}_{\text{total}}] - (\text{Ba}/\text{Al}_{\text{terrigenous}}) \times [\text{Al}_{\text{total}}] \quad (1)$$

$$P_{\text{new}} = [(F_{\text{Ba}} 0.171 \text{Ba}^{2.218} Z^{0.476-0.00478\text{Ba}}) / (2056)]^{1.504} \quad (2)$$

Where F_{Ba} is the accumulation rate of Ba_{excess} corrected for Ba_{excess} preservation in sediments (see Dymond et al. [1992] for a predictive formulation), Ba is the concentration of barium at 1700m water depth, and z is the water depth. The new productivity (P_{new}) units are $gC/m^2/yr$.

This study was the first attempt to use excess Ba for quantitative productivity reconstruction. Estimates for the sediment mass accumulation rate (MAR) and excess Ba content in the sediment were used to calculate the flux of excess Ba to the sediments. The excess Ba flux can then be converted to export production at any given time using the relationship observed in sediment traps (Dymond et al., 1992). This algorithm takes into account the effects of water depth and dissolved Ba concentration in seawater at the depth and location of barite formation since these parameters seem to impact the observed relationship between excess Ba flux and export production, most likely by influencing barite preservation and/ or formation rates. Dymond et al. (1992) clearly stated that this relation, which is based mostly on sediment trap data, might be problematic when working with sediments. This is because the Ba/Al ratio of terrigenous material could be variable and Ba might be associated with phases that are measured as part of the excess Ba but may not be directly related to export production (e.g. Fe-Mn oxides and hydroxides which Dymond et al. [1992] estimated could account for up to 30% of sedimentary excess Ba). It is important to emphasize that the above relationship is based on a considerable number of sediment trap samples but only a handful of core top sediments. This might influence the relationship by not accurately taking into account processes that occur on the seafloor during sedimentation.

Francois et al. (1995) simplified the algorithm (equation 3) arguing that the Ba concentration in seawater is not an important factor in controlling barite flux to the seafloor (i.e. Ba and z in equation 2 are unnecessary).

$$P_{\text{new}} = 1.95 \times F_{\text{Ba}}^{1.41} \quad (3)$$

Both the Dymond et al. (1992) and Francois et al. (1995) equations have been used widely by many groups in a variety of ocean settings in the last decade to quantitatively determine or infer changes in export productivity using sedimentary excess Ba accumulation rates (e.g. Rutsch et al., 1995; Dean et al., 1997; Nürnberg et al., 1997; Bonn et al., 1998; Bains et al., 2000).

It is important to emphasize that the above relationships for the use of excess Ba to reconstruct past export production rates (equations 1-3) hold true only if (1) there is no significant contribution of Ba from sources other than barite (assuming barite is the mineral directly related to export production) or that all components of excess Ba are related to export productivity in a predictable (and temporally consistent) way, (2) terrigenous material has a precisely known Ba/Al ratio and this ratio is constant in time and space, (3) all the Al measured is associated only with terrigenous material, and (4) the observed modern relationship between barite and export C is consistent and prevalent in the past. The latter requires that the calibration relationships (from sediment traps or core top sediments) have been sufficiently characterized and represent conditions throughout the present day ocean and that these relations are constant in time and capture past variability. The requirements listed above however, have not always been tested or met (see Eagle et al., 2003; Averyt and Paytan, 2004; Anderson and Winckler, 2005 for more detailed discussion). Uncertainties in the quantitative calculations of export

production may also stem from inherited problems with the sediment trap data used for establishing the relation between excess barium flux and export production, as these were not corrected for trap efficiency (Guieu et al., 2005).

2.2. Ba/Ti and Ba/Al Elemental Ratios

Bulk Ba/Ti or Ba/Al elemental ratios have also been suggested as a productivity proxy (Goldberg and Arrhenius, 1958; Murray and Leinen, 1996; Reitz et al., 2004). In the use of these proxies similar assumptions to those mentioned for excess Ba are made (see section 2.1.). The variations in Ba of non-lithogenic material through time are implicit in the bulk ratio measurement (e.g. normalization to a predominantly terrigenous element like Al or Ti) and are interpreted as changes in excess Ba and likewise, can be related to export productivity (Murray and Leinen, 1996; Murray et al., 2000). A normalizing ratio (e.g. Ba/Ti) has the advantage of not requiring conversion of concentrations to accumulation rates and therefore not gaining errors associated with this conversion (Murray et al., 2000). However, all the limitations associated with the assumptions mentioned previously apply to this proxy as well. Specifically, it requires that all of the Al or Ti be from terrestrial sources. Without additional information, a decrease in the Ba/Ti ratio could be attributed to either an increase in Ti flux which is not strongly associated with Ba (e.g. dust flux) or a decrease in Ba related to a decrease in productivity, assuming all of the Ba is indeed related to productivity (e.g. Winckler et al., 2005). Modern fluxes of Ti from dust are known to decrease from north to south across the equatorial Pacific (Murray and Leinen, 1996; Rea, 1994). All other factors being equal, this observation could bias productivity reconstructions that use core top data from this site in establishing a calibration without accounting for the modern meridional

gradient in Ti flux (Anderson and Winckler, 2005). Moreover, data suggests that in areas where volcanic input is significant and variable over time, normalizing to Ti may compromise the results (Schroeder et al., 1997; Murray et al., 2000; Averyt and Paytan, 2004).

Ti normalization (in pelagic settings away from volcanic input) can be useful in eliminating errors associated with bulk Al measurements used for normalization, because the latter could include a nonterrigenous Al component from diatom tests, Al associated with other sedimentary phases (Van Bennekom et al., 1989; Dixit et al., 2001) or Al adsorbed onto sinking particles (Murray et al., 1993; Murray and Leinen, 1996). Specifically, it has been hypothesized that excess Al could be a proxy for particle flux or opal flux, thus complicating its earlier use as an independent normalization element for calculating Ba excess (Murray et al., 1993; Murray and Leinen, 1996; Dymond et al., 1997).

Concentrations and ratios of Ba, Al, and Ti in sediments may also be affected by differences in the solubility of Al and Ba carried in dust, changes in the sediment provenance from which the dust originated (e.g. Klump et al., 2000), and/or scouring and delivery of material from sediments from other locations with different elemental ratios (e.g. Wells et al., 1999; Mackey et al., 2002). Any of these processes could systematically and/or randomly influence downcore Ba/Al and Ba/Ti records in sediments.

Implicit in the previous discussion is that these proxies are applied to the open ocean environment. In the central equatorial Pacific, for example, lithogenic Ba is a small part of total Ba in sediments (e.g. <2% in core top TT013-72PC, Eagle et al., 2003; Anderson

and Winckler, 2005). In highly dynamic environments, such as margin systems, the application of excess Ba or Ba/Ti (Al) ratios as a proxy for export productivity must be used cautiously (e.g. McManus et al., 2002). In margin systems, the relationship between particulate excess Ba and organic carbon is clearly different from the open ocean (e.g. Dymond et al., 1992; Francois et al., 1995; Dehairs et al., 2000; McManus et al., 2002; Eagle et al., 2003; Sanchez-Vidal et al., 2005) and the terrigenous fraction is large. These studies have shown that margin systems have proportionally lower biogenic barium flux than the open ocean and that the Ba/Ti (Al) in the terrigenous material in margin sediment varies greatly in space and time. Thus precise knowledge of the Ba/Ti (Al) of this material is crucial for accurate determination of excess Ba (Eagle et al., 2003; Reitz et al., 2004).

2.3. Marine Barite

To avoid some of the problems (discussed above) associated with excess Ba and Ba/Ti (Al) elemental ratios, Paytan (1996) measured the weight percent of barite directly by applying a sequential leaching procedure modified from Church (1970). The resulting residue consists of barite and a few other refractory minerals (e.g. rutile and anatase). This extraction yields are close to 95% of the barite in most sediments (Eagle et al., 2003). The residue is then examined using scanning electron microscopy to determine barite content and thus concentration (see Eagle et al., 2003 and Robin et al., 2003 for detailed methods). A slightly different method for barite extraction, which works best in sediments with high barite content, was described in Turchyn and Schrag (2004). Using the extraction methods the weight percent barite in each sample is determined directly, however to convert barite concentrations to accumulation rates the bulk

sediment mass accumulation rates (MAR) at each site/time interval are needed. Mass accumulation rates can be obtained from measurements of excess ^{230}Th , or ^3He , or from dry bulk density and sedimentation rate data derived from ^{14}C or ^{210}Pb dating or from ^{18}O stratigraphy (e.g. Eagle et al., 2003; Francois et al., 2004). Errors associated with age-models and their effect on determining barite accumulation rates and thus export production will be discussed in section 3.5.

To establish a quantitative empirical relation between barite accumulation and export production, barite accumulation rates in core top sediments were compared to modern day primary production estimates (based on in situ ^{14}C incorporation or measured Chl *a*) for several oceanic areas. The correlation observed is quite strong within ocean regions, each exhibiting different regression slopes (Paytan et al., 1996; Eagle et al., 2003). It is not surprising that this relationship is regional, since barite forms in association with aggregates of decaying matter, which is more directly related to the exported fraction of primary production (i.e. carbon export) and not total primary production. The exported fraction of primary production does vary considerably throughout the ocean although it is more constant within regions.

Eagle et al. (2003) converted primary production to carbon export (new production) using the appropriate *f* ratio (the portion of new production from total production) for each region to produce a global regression curve relating barite accumulation rate and carbon export (see figure 5). This strong empirical correlation suggests that barite accumulation rate measurements can be used in the major open ocean basins as a quantitative proxy for estimating rates of carbon export through time (Eagle et al., 2003).

Looking more closely at the empirical relationship plotted in figure 5, it is apparent that the Atlantic samples generally tend to fall below the global regression curve. This could be a result of (1) lower preservation rates of barite caused by the lower Ba concentrations in Atlantic bottom water (Monnin et al., 1999), (2) an inappropriate f ratio that is too low and not representative of the measured sites (Eagle et al., 2003), or (3) a systematic error in the relation associated with accumulation rate calculations (Anderson and Winckler, 2005). This illustrates that quantitative interpretation of changes in export carbon based on barite accumulation rates may include sources of error associated with mass accumulation rate estimates, f ratio estimates (in the calibration), and effects of differential preservation of barite. Despite these issues, if the same mechanisms governing barite precipitation and preservation are assumed for the past (including any relationship between preservation, dissolved Ba concentrations and sedimentation rate) then barite accumulation rate is an excellent proxy for estimating oceanic carbon export. These assumptions and limitations will be further discussed in the following section.

3. Critical Analysis of the Proxies

As summarized above and discussed in detail by Eagle et al. (2003), Averyt and Paytan (2004), and Anderson and Winckler (2005), the use of both excess Ba and Ba/Ti (Al) ratios for quantitative reconstruction of export production is limited by several embedded and compounded assumptions that do not always hold true and that can often be difficult to determine precisely and be accounted for when reconstructing changes in past export productivity. A similar assessment of assumptions, limitations and needs for the application of marine barite as quantitative export productivity proxy is given below.

3.1. Assumptions Associated with Barite Formation and Relationship to Carbon

Export

Although the relationship between export carbon and marine barite holds, it is more complicated than originally thought. In a study by Dymond and Collier (1996), very high carbon export fluxes resulted in relatively less excess Ba than expected from the relationship of excess Ba to lower carbon fluxes. They attributed this to different community structure or composition of organisms (Dymond and Collier, 1996).

However, this feature could also be explained by some kinetic process which might lower the decomposition rate of sinking organic matter at very high rates of productivity since the organic matter settles faster to the seafloor and has less time to decompose and form barite in the water column.

Another factor that may be important in understanding the mechanism for creating barite super-saturated microenvironments includes the catalytic effect of opal surfaces (Bishop, 1988; Sternberg et al., 2005). Bishop (1988) proposed that diatoms could accumulate enough Ba to induce barite formation during their decay, whether intracellularly or on opal surfaces. Sternberg et al. (2005) attempted to test this original hypothesis by culturing the diatom, *Thalassiosira weissflogii*, under chemically well-defined conditions and paying particular attention to the formation of Fe hydroxide precipitates in the culture medium. This study found that the diatom *T. weissflogii* takes up very little Ba intracellularly (see also table 1), but a relatively large amount of Ba becomes adsorbed on the hydrous ferric oxide (FeO_x) associated with the cell surface of the diatom. The adsorption of Ba on Fe hydroxides, as seen in these experiments, occurs in the ocean, however its significance is not known nor is the chemical behavior of hydrous ferric

oxide in microenvironments within settling particulate matter well understood. This adsorption mechanism does not, however, appear to control the transport of Ba out of the surface ocean because this would require the Ba/Fe ratio in average suspended matter to be much lower than has been measured (Sternberg et al., 2005). Manganese oxyhydroxides have also been suggested to be an important scavenging phase for particulate Ba in regions where there is high Mn in the settling particles, however the global significance of this process is not known (Balakrishnan Nair et al., 2005). The above observations indicate that it is important to understand the processes that control barite formation (e.g. settling dynamics of organic matter aggregates and Ba association with various forms in the water column) to allow some appreciation of the effect of these processes and their potential variability in space and time on any empirical relation between barite accumulation and export flux.

3.2. Barite Preservation

Dissolved Ba profiles in seawater indicate that most of the ocean is under-saturated with respect to barite in much of the water column (Church and Wolgemuth, 1972), although some depths in the Southern Ocean and the Pacific Ocean are at or slightly above saturation (Jeandel et al., 1996; Monnin et al., 1999; Rushdi et al., 2000). Therefore, it can be assumed that some of the barite formed in the water column dissolves at depth. However, because of the low solubility of barite and since much of it reaches the sea floor within fast settling fecal pellets, it is thought that a relatively large fraction of barite formed does reach the sediments (Paytan and Kastner, 1996).

Barite is a highly refractory mineral in oxic sediments, but several processes can regulate its preservation in marine sediments (McManus et al., 1998). The fraction of barite that

is preserved in the sedimentary column is expected to be directly related to the degree of undersaturation at the sediment water interface and the exposure time of barite in the uppermost sediments to these conditions (e.g. sedimentation rate and amount of barite delivered to the sediment). Although little research has been done so far to quantitatively determine the various parameters influencing barite preservation, existing data suggest that at least in some pelagic settings of the present day ocean the fraction of barite preserved is relatively large.

In fact, barite shows promise as a paleoproductivity proxy because it is a highly refractory mineral with preservation as high as 30% in oxic sediments, compared with less than 1% for organic carbon and ~5% for biogenic silica (Dymond et al., 1992; Paytan and Kastner, 1996). Pore-water Ba concentrations examined by Paytan and Kastner (1996) to determine the Ba recycling efficiency within the top surface sediments in Equatorial Pacific oxic pelagic environments, are higher than in the overlying bottom water, with a pronounced subsurface maximum exceeding barite solubility. These results suggest that Ba regenerated in the upper few millimeters of sediment is not controlled only by barite solubility (Paytan and Kastner, 1996). A few centimeters down-core, Ba concentrations reach a relatively constant value that approximates barite saturation (Paytan and Kastner, 1996). Under these conditions, it is expected that the fraction of barite that has not dissolved will be preserved in the record as long as pore fluids remain sulfate rich (i.e. saturation with respect to barite is maintained). Indeed, geochemical investigations of both S and Sr isotopes suggest that downcore, barite is not affected by burial diagenesis in oxic sediments (Paytan et al., 1993, 2002, 2004b).

Despite the relatively large fraction preserved, existing data indicate that the preservation of barite is indeed variable in the present day ocean and thus is not expected to be constant over time (e.g. McManus et al., 1998; Eagle et al., 2003; Paytan, unpublished). Specifically, barite accumulation rates in core top sediments in the Pacific and Southern Oceans are somewhat higher than those seen in Atlantic sites where overlying export production rates at present are similar (Eagle et al., 2003) (figure 5). Similarly, depth dependent variability in barite accumulation rates is seen in core tops from the Ontong Java Plateau that are in close proximity to each other (Paytan, unpublished). This occurs despite the fact that they underlie the same water mass with the same export production characteristics. The barite accumulation seems to be directly related to the degree of barite saturation at the seafloor depth, which is dictated primarily by the depth profile of dissolved Ba in seawater (figure 1).

These observations, however, are based on a very limited data set. A more quantitative approach that is based on a much larger number of core top samples is needed to quantify the preservation efficiency of barite and relate it to variables that could influence its preservation (e.g. deep water saturation state, sedimentation rates, sediment properties, and barite rain rate to the sediment). Accordingly, some independent measure of these variables that could potentially impact barite preservation at the time and site of barite deposition are needed to quantitatively convert barite accumulation rates to export production in the paleo-record. Specifically, Ba/Ca in benthic carbonate secreting organisms (Lea and Boyle, 1989; Hall and Chan, 2004) and Sr/Ba ratios in barite (van Beek et al., 2003) have been suggested as potential proxies for bottom water Ba concentrations and the degree of barite saturation, respectively.

The above considerations hold only for oxic sediments; as soon as pore waters become anoxic, sulfate reduction will occur and barite will not be preserved as sulfate concentrations decrease and drop below barite saturation. This dissolution will typically result in sharp Ba peaks in pore waters and sometimes the precipitation of diagenetic barite at the oxic-anoxic boundary. McManus et al. (1998) suggested that the preservation of barite might even be compromised in some sub-oxic sediments where some sulfate reduction takes place (e.g. the California continental margins and some glacial age Southern Ocean sediments, McManus et al., 1994, 1998). According to McManus et al. (1998), barite preservation can be compromised under conditions of high carbon export and low bottom water temperature even when pore water sulfate is not heavily depleted. However, data from sapropel sections in the Mediterranean and from Cretaceous sediments indicate that barite can be well preserved at least in some sub-oxic conditions (Paytan, 2002; Martinez-Ruiz et al., 2003). This could imply that sub-oxic sediments where barite is not preserved at present might have been anoxic or sulfate-reducing in the past. Likewise, it could indicate that there is a kinetic control on barite preservation that depends on the rate of sulfate reduction in the sediments compared to their irrigation and sulfate supply from the water above.

Thus, when using barite for paleoproductivity studies, attention must be given to the site selection. Analyses of pore water chemistry (e.g. sulfate concentration) and redox-sensitive trace metals in the sediments (e.g. authigenic U, Fe, Mn, Mo, or I) should be done to verify that the sediments are not sulfate-reducing at the site in the present or were in the past. Marine barite is not a reliable proxy in sulfate-reducing sediments. Any use of Ba or barite for productivity work should make certain that the sediments are and have

always been under conditions that did not compromise barite preservation. The analysis of S isotopes in the barite along with crystal morphology can be used to effectively determine if the barite underwent dissolution and reprecipitation (Paytan et al., 2002; see discussion of non-marine barite in the following section).

3.3. Non-marine Barite

Goldberg et al. (1969) first characterized different types of barite from the California coast based on their origin (marine or continental) and isotopic and elemental composition. Barite can be further differentiated by the precise mode of precipitation. For example, barite can precipitate in the marine environment in the water column in association with decaying organic matter (“marine barite” as described in section 1.1), in association with submarine hydrothermal activity (“hydrothermal barite”), or diagenetically in sulfate-reducing conditions (“diagenetic barite”), see figure 2 (Paytan et al., 2002).

Submarine hydrothermal activity can induce barite precipitation when Ba-rich hydrothermal fluids encounter sulfate rich seawater, forming massive barite mounds and chimneys near active hydrothermal vents or along faults where these fluids are expelled (e.g. Feely et al., 1987, 1990; Kusakabe et al., 1990; Moore and Stakes, 1990). However, because of undersaturated corrosive seawater, particulate hydrothermal barite is not likely to survive transport more than a few tens to a maximum of a few hundreds of kilometers away from its source (Feely et al., 1987).

Another mode of barite formation in the marine environment is diagenetic precipitation in sulfate-reducing conditions at the oxic-anoxic boundary within sediment or when such fluids are expelled into seawater (e.g. Bolze et al., 1974; Breheret and Brumsack, 2000;

Torres et al., 1996). “Non-marine” barite formation is not related to marine organic matter degradation and may record fluid chemistry that is significantly different than contemporaneous seawater (Paytan et al., 2002). Therefore, these types of barite are not acceptable for paleoceanographic studies in general and for export production reconstruction in particular. However, because the habits and sizes of these barite crystals are considerably different from authigenic marine barite that precipitates in the water column, they can easily be identified and avoided, see figure 2. Further testing of the isotopic (S and Sr isotopes) and elemental (Sr/Ca/Ba ratios) composition of the questionable barite samples can also indicate the process of its formation and elucidate its suitability for paleoceanographic studies (Paytan et al., 2002). Through careful site selection and examination of each sample, these potential problems should easily be avoided.

3.4. Calibration conditions

Implicit in any proxy is the assumption that the present range of environmental variables encompasses the full range throughout Earth’s history, and that this range is sufficiently represented in a modern calibration. Likewise, it is also necessary to assume that the relationships that are determined for the modern ocean can be applied to the past. It is important to explore these assumptions when evaluating the current calibration relating barite to carbon export. Specifically, in the case of marine barite, additional core-top data are needed to establish the quantitative dependence of barite preservation on bottom water Ba concentration or other variables, as mentioned in the Section 3.2. It will also be important to be able to correct for these variables down-core (e.g. using Ba/Ca in benthic

forams or Sr/Ba in barite to determine water column saturation) so that quantitative estimates can be determined and compared between sites and for different time intervals.

3.5. Age models and mass accumulation rates

Potentially large and uncertain sources of error in quantitative estimates of export productivity using accumulation rate of sedimentary components can result from inaccuracies in age models and the calculation of the sediment bulk MAR. Specifically, using linear sedimentation rates extrapolated between age tie-points separated by periods greater than the time scale of possible changes in sedimentation rates is problematic (e.g. Anderson and Winckler, 2005). In addition, post-depositional sediment focusing or redistribution may influence the measured sedimentation rates such that they do not relate solely to water column processes (e.g. “rain rate”).

As previously mentioned in Section 2.2, normalization to a relatively constant or known flux can eliminate errors associated with the use of linear accumulation rate estimates. Alternatively, the flux of ^{230}Th (corrected for radioactive decay and for lithogenic ^{230}Th) could be used to calculate instantaneous sedimentation rates. Similarly, because extraterrestrial ^3He (from interplanetary dust particles) influx to Earth is thought to be nearly constant through time (Marcantonio et al., 1996, 2001; Francois et al., 2004), ^3He could also be used to determine instantaneous sedimentation rates. Therefore, ^{230}Th -normalized or ^3He -normalized barite or barium concentrations or their accumulation rates based on the instantaneous rates can be used instead of using age model based bulk sediment MAR.

However, because the flux of ^3He to the Earth has not been extensively calibrated for samples older than 250 kyr, it currently cannot be systematically used for old samples.

Similarly, the 75 kyr half-life of ^{230}Th limits its use for samples younger than 250 to 300 kyr. Currently there is not a consensus on the best approach to correct for sediment redistribution at high resolution for old samples (Winckler et al., 2005). However, efforts are underway to constrain ^3He through 1 Myr (Winckler et al., 2005).

It has recently been suggested that systematic errors in determining (and using) sediment mass accumulation rates can result from proxy calibrations that are based on core tops that have undergone some CaCO_3 dissolution (Anderson and Winckler, 2005). This may indeed influence quantitative export productivity estimates determined using proxies that require conversion to accumulation rates. Such carbonate dissolution effects, if important, will affect any algorithm based on the correlation of proxy accumulation rate to export carbon.

4. Barite Accumulation Rate Application to Paleoproductivity Studies

4.1. Glacial-Interglacial Fluctuations in Productivity

Large glacial to interglacial fluctuations in atmospheric CO_2 concentrations have been observed in ice cores and could be related to variations in ocean productivity (Neftel et al., 1982; Barnola et al., 1987). Paytan et al. (1996) measured the barite accumulation rate fluctuations in two cores from the equatorial Pacific Ocean for the past 450,000 years (see figure 6). Pronounced variations in the barite accumulation rates indicate that export production likely increased during glacials in this region. Using an empirical correlation obtained from core-top sediments in the equatorial Pacific, it appears that the export production during glacials, in this region, was typically about twice as high as during interglacials (Paytan et al., 1996). This is consistent with other biologically related proxies, such as organic C, opal, benthic assemblages, and CaCO_3 .

The weight percent barite on a CaCO_3 -free basis was also determined and provides an estimate of changes that are independent of accumulation rate. The data is consistent with higher barite accumulation rates during the glacial periods, however details in the features are slightly different (Paytan et al., 1996). This is likely because concentration of barite is also influenced by the amount of opal and other components in the sediments in addition to the CaCO_3 .

However, when using ^{230}Th - and/or ^3He -normalized accumulation rates, the glacial-interglacial paleoproductivity changes disappear or even reverse (Paytan et al., 1996). This implies that it is possible that sediment focusing and redistribution could hamper any interpretation of accumulation rate based records with this region (Paytan et al., 2004a). Alternatively, it could mean that the processes that controlled ^{230}Th and ^3He fluxes and accumulation in marine sediments over time are not fully characterized at present and could have been different in the past (Paytan et al., 2004a; Lyle et al., 2005). This study illustrates that while the percent barite in marine sediments can be easily obtained, calculating barite accumulation rates, which is the parameter related to export production, is limited by the knowledge of bulk sediment mass accumulation. More work should be done to resolve the discrepancy between the various approaches used to determine sediment mass accumulation rates in order to improve our ability to quantitatively and accurately determine these rates.

4.2. Paleocene – Eocene Thermal Maximum

The Paleocene – Eocene thermal maximum (PETM, ~55 Ma) was one of the most significant and abrupt periods of global change during the Cenozoic. This abrupt global warming saw Earth's surface temperature rise by between five and eight degrees C (e.g.

Kennett and Stott, 1991; Thomas and Shackleton, 1996; Katz et al., 1999; Zachos et al., 2003). This event led to the extinction of numerous deep-sea benthic foraminifera (e.g. Miller et al., 1987; Thomas, 1990; Thomas and Shackleton, 1996; Thomas, 1998) and a major turnover in land mammals (e.g. Gingerich, 1989). During a period of ~30,000 yr, the carbon isotopic composition of marine carbonates decreased up to 3‰ (e.g. Kennett and Stott, 1991; Bralower et al., 1995; Thomas and Schackleton, 1996) and gradually returned to near-initial values within ~150,000 yr (Norris and Röhl, 1999). These changes have been linked to intense volcanic activity that expelled gigatonnes of carbon dioxide and/or the massive release of biogenic methane from gas hydrate dissociation (e.g. Dickens et al., 1995, 1997). Regardless of the trigger, these observations imply that there were major perturbations in the global carbon cycle (e.g. pronounced carbonate dissolution on the seafloor) and extreme warmth (e.g. migration of low-latitude biota to high latitudes).

The response of marine export productivity to this event is controversial; some evidence indicates an increase in oceanic productivity (e.g. peaks in biogenic Ba [Schmitz et al., 1997; Bains et al., 2000], Sr/Ca in coccolith carbonate [Stoll and Bains, 2003], dinoflagellate assemblages [Crouch et al., 2001]) and others a decrease over this interval (e.g. nannofossil assemblages [Kelly et al., 1996; Bralower, 2002]). Faul and Paytan (2005) presented initial results from the equatorial Pacific across the Paleocene – Eocene boundary of barite mass accumulation rates from ODP Leg 199 Hole 1221C. This high-resolution record shows large fluctuations in barite accumulation over this time interval, which are interpreted as fluctuations in export productivity. As seen in figure 7, low barite accumulation rates occur before and immediately after the Benthic Extinction

Event (BEE) with two distinct peaks around 55.20 and 55.22 Ma. Observed organic C burial is not high where barite burial is high, which may indicate that C sequestration was restricted to the deep ocean and not the sediments, or that postdepositional oxidation of organic matter affected the sediments.

Another explanation for the increase in barite accumulation during the PETM has also been suggested. Dickens et al. (2003) proposed that this increase in accumulation was instead due to an increase in the preservation of barite over this interval because of excess dissolved barium in the deep waters from the release of seafloor gas hydrates (which contain high levels of dissolved barium). However, Ba/Ca data in foraminifers during this interval indicate no change in deep sea Ba concentration and a decrease in Ba concentration in the surface ocean (Hall et al., 2004). While better knowledge of the effect of seawater saturation level on barite preservation is needed in order to quantitatively compute export production fluxes from barite accumulation rates at each individual site, the distribution of locations (Schmitz et al., 1997; Bains et al., 2000; Faul and Paytan, 2005) that show an increase in barite accumulation rates at the PETM points to feedbacks and close correspondence between the global carbon cycle, ocean circulation, and the biological pump during this period of abrupt global change and recovery.

4.3. Cretaceous Ocean Anoxic Events

During the mid-Cretaceous, between 125 and 80 million years, large deposits of organic rich sediments, such as black shales, occurred in the ocean during several intervals. The cause of these events of increased burial rates of organic matter, referred to as ocean anoxic events (OAEs) (Arthur et al., 1988), is still under debate. Two opposing models

have been suggested, invoking either high biologic productivity in the ocean or ocean stagnation. Paytan (2002) measured the barite accumulation rates in several deep sea open ocean cores and found peaks during these mid-Cretaceous events (see figure 8). This implies that the high accumulation of organic matter is a result of increased productivity that overwhelmed respiration in the open ocean environment, causing anoxic conditions in the water column. Isotope analyses of the barite confirm the water column (not diagenetic) origin of this barite (Paytan et al., 2004b). The high export production throughout the ocean and the widespread organic carbon burial most likely affected climate through sequestration of carbon dioxide, and provided a negative feedback to the greenhouse climate that was prevalent at the time (Paytan, 2002).

5. Summary and Perspectives

Barite that forms in the water column is typically referred to as biogenic or marine barite because of its apparent association with particulate organic carbon content and the biological productivity of the overlying water (Dehairs et al., 1991, 1992; Dymond et al., 1992; Dymond and Collier, 1996). Marine barite shows promise as a paleoproductivity proxy because it is a highly refractory mineral with preservation as high as 30% in oxic sediments (Dymond et al., 1992; Paytan and Kastner, 1996). The barite accumulation rate in oxic sediments can therefore serve, at this stage, as a qualitative proxy for estimating paleo-carbon export to the deep sea, and when the processes controlling barite preservation are better quantified, it could be used for quantitative reconstruction of export production. Care must be given to site selection and sample testing to avoid using diagenetic or hydrothermal barite. Sediment accumulation rates greatly influence

calculations of barite accumulation rates and thus should be determined as precisely as possible.

Acknowledgements

We would like to thank Joseph Street, Kristen Averyt, and Meagan Gonneea for reviewing an earlier version of this manuscript. Reviews by G. Filippelli and an anonymous reviewer greatly improved this manuscript. This work was funded by several NSF (OCE and EAR) grants to A.P. E.M.G. is supported by the U. S. Department of Defense National Defense Science and Engineering Graduate (NDSEG) Fellowship.

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Accepted manuscript

Figure/Table Captions

Figure 1. A. Typical profile of temperature and barium concentration versus depth from the Pacific, GEOSECS station 217 (44°36'N 176°50'W), adapted from Monnin et al. (1999) B. Maximum degree of saturation of ocean water with respect to strontian barite at their respective depths for stations from the Atlantic, Pacific, Indian and Southern Oceans, adapted from Rushdi et al. (2000).

Figure 2. Scanning electron micrographs of barite crystals, adapted from Paytan et al. (2002). A. Marine barite, core-top sediments, Pleiades expedition, core 77, 1.03°N, 119.55°W. B. Marine barite, Deep Sea Drilling Project Site 574C, 29.1 Ma. C. Marine barite, sediment trap, <8 µm fraction from Juan de Fuca Ridge black smoker. D. Hydrothermal barite, Mariana backarc chimney 1831-R1-C. E. Hydrothermal barite, Mid-Atlantic Ridge, chimney at Lucky Strike, ALV 2602-3. F. Diagenetic barite, ODP Leg 132, Site 765C 34-1, 47–60 cm, ca. 112 Ma.

Figure 3. Increase in number of barite crystals with time in suspension of decaying phytoplankton, batch cultured *Emiliania huxleyi*, adapted from Ganeshram et al. (2003).

Figure 4. The flux of barium versus the flux of organic carbon from seasonal sampling cups from ten sediment traps, adapted from Dymond et al. (1992).

Figure 5. Accumulation rate of marine barite versus carbon export calculated from the application of an appropriate f ratio to primary productivity estimates for the overlying water column, adapted from Eagle et al. (2003).

Figure 6. Accumulation rate of marine barite in the equatorial Pacific during the past 450,000 years from cores VNTR01-08PC at 110°W (open circles) and TT013-PC72 at 140°W (full circles), adapted from Paytan et al. (1996). Glacial periods (isotope stages 2, 4, 6, 9, and 10) are represented by gray areas on the age scale.

Figure 7. Accumulation rate of marine barite in the equatorial Pacific during the Paleocene/Eocene boundary (~55 Ma) from Ocean Drilling Program (ODP) Leg 199 Site 1221, from Faul and Paytan (2005; unpublished).

Figure 8. Accumulation rate of marine barite in the Pacific and Indian Oceans during the mid-Cretaceous from Deep Sea Drilling Program (DSDP) Sites 305 (32°00.13'N, 157°51.00'E) and 766 (19°55.925'S, 110°27.243'E), adapted from Paytan (2002).

Table 1. Range of Ba concentrations in marine phytoplankton and algae.

Table 1.

	Species	Ba in cells ($\mu\text{g/g}$ dry wt.)	Reference
Coccolithaceae	<i>Emiliana huxleyi</i>	2	Fisher et al. (1991)
Rhodophyceae	<i>Porphyridium cruentum</i>	5	Fisher et al. (1991)
Diatoms	<i>Phaeodactylum tricornutum</i>	7.2	Fisher et al. (1991)
	<i>Thalassiosira rotula</i>	7.0	Fisher et al. (1991)
	<i>Thalassiosira weissflogii</i>	0.1 to 0.4	Sternberg et al. (2005)
Chrysophyceae	<i>Olisthodiscus luteus</i>	467	Fisher et al. (1991)
	<i>Pseudopedinella pyriformis</i>	1158	Fisher et al. (1991)
Prymnesiophyceae	<i>Monochrysis lutheri</i>	1320	Fisher et al. (1991)
Prasinophyceae	<i>Heteromastix longifilis</i>	392	Fisher et al. (1991)
	<i>Micromonas squamata</i>	2840	Fisher et al. (1991)
	<i>Micromonas squamata</i>	2840	Fisher et al. (1991)
Chlorophyceae	<i>Tetraselmis levis</i>	589	Fisher et al. (1991)
	<i>Dunaliella primolecta</i>	2290	Fisher et al. (1991)
	<i>Chlamidomonas</i> sp.	2620	Fisher et al. (1991)
Bacillariophyceae	<i>Chaetoceros curvisetum</i>	4000	Fisher et al. (1991)

Figure 1.

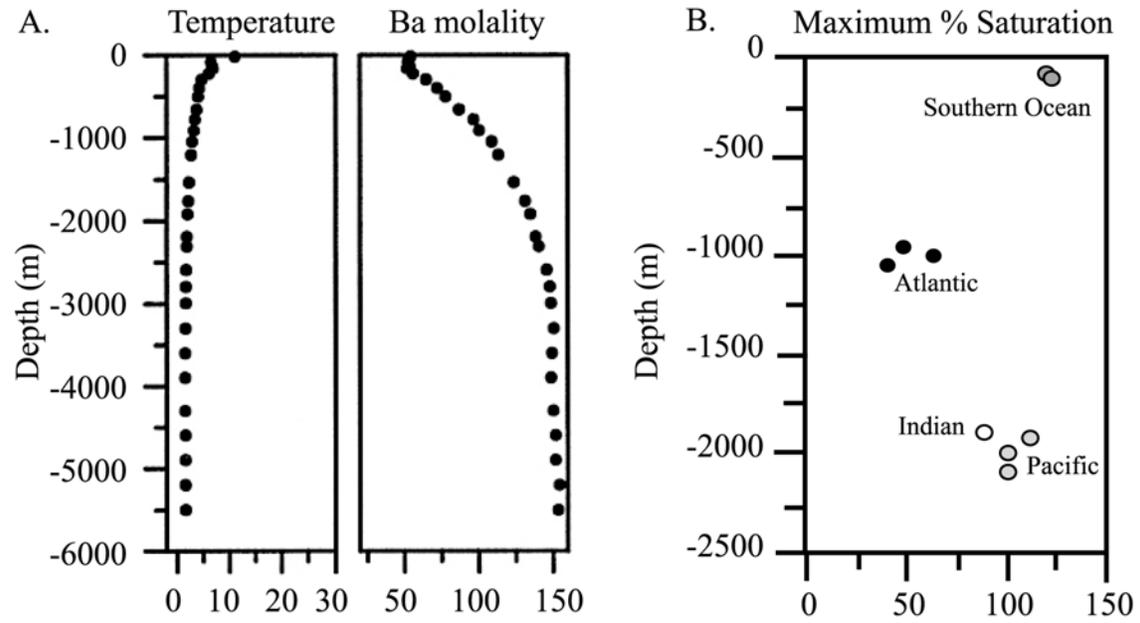


Figure 2.

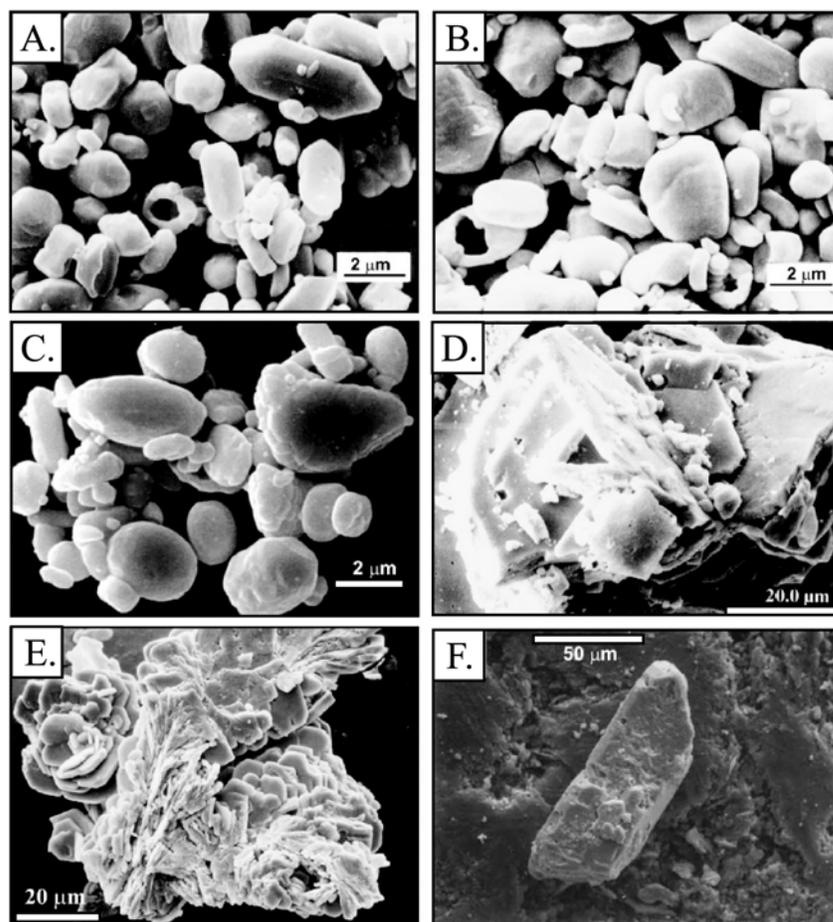


Figure 3.

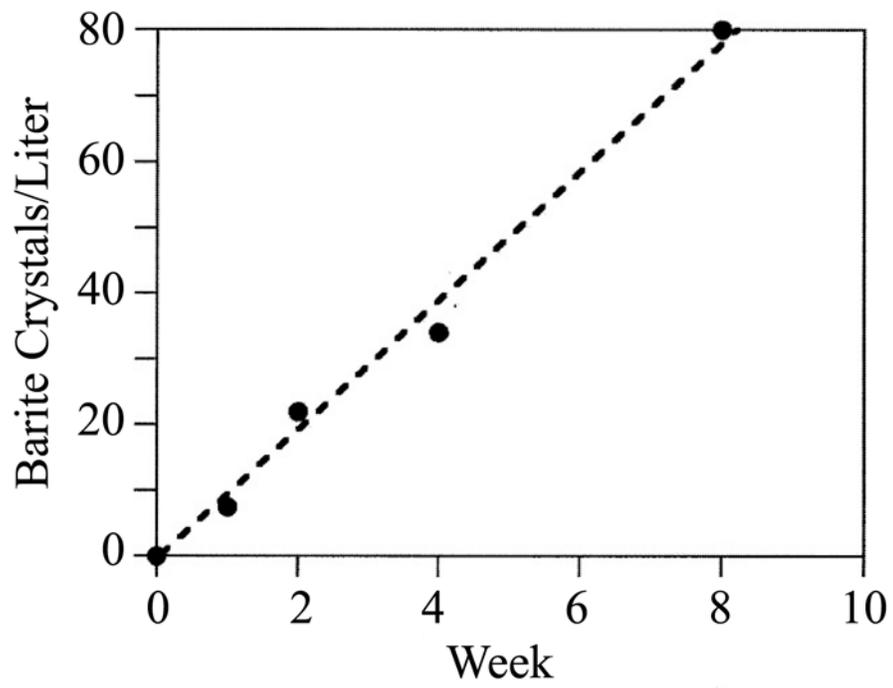


Figure 4.

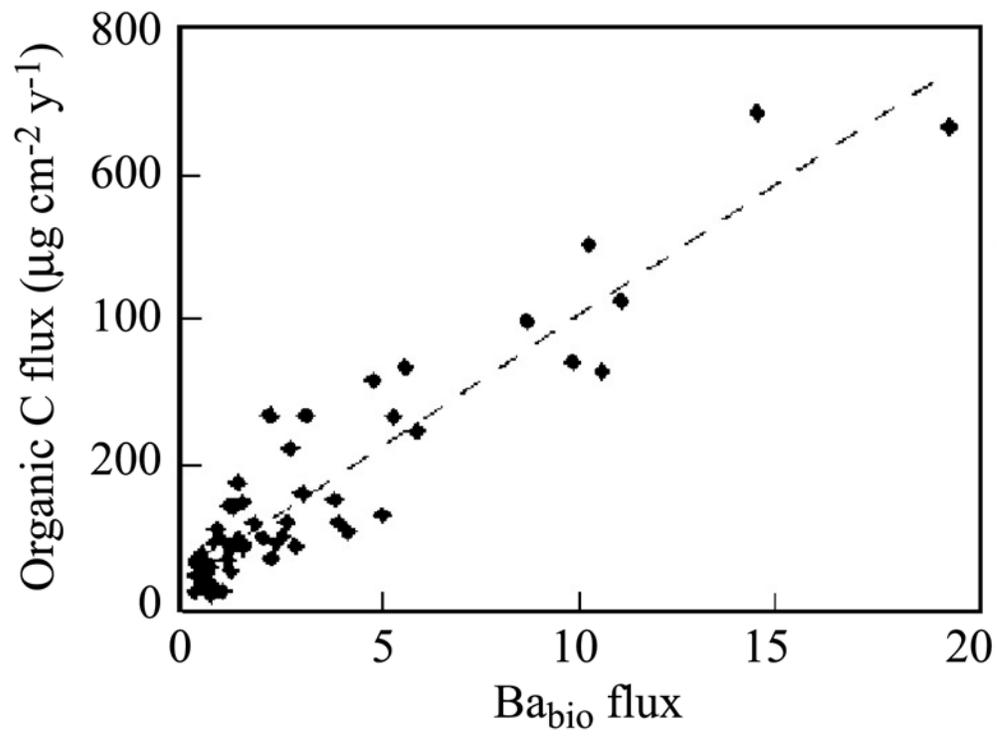


Figure 5.

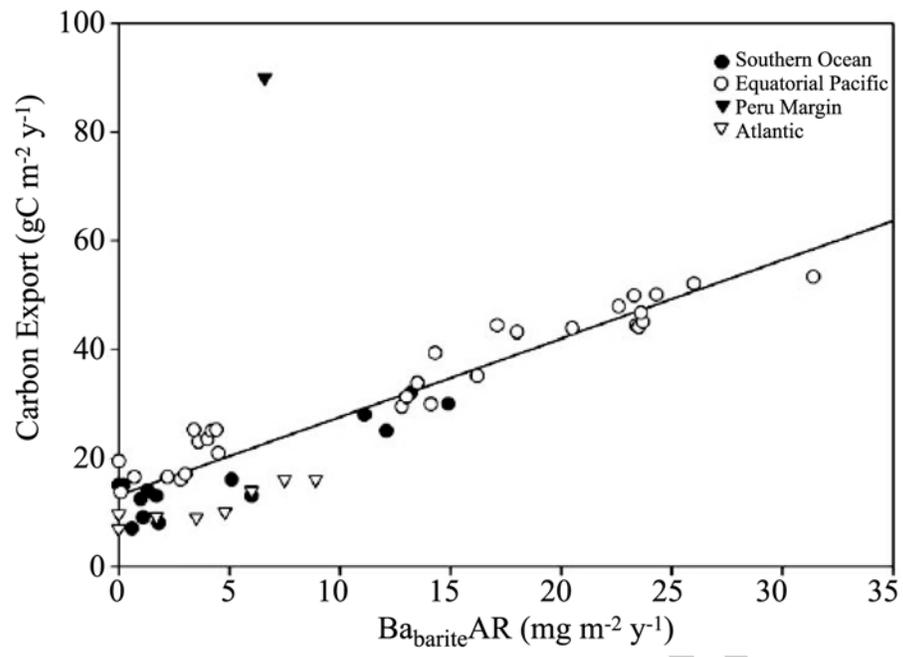


Figure 6.

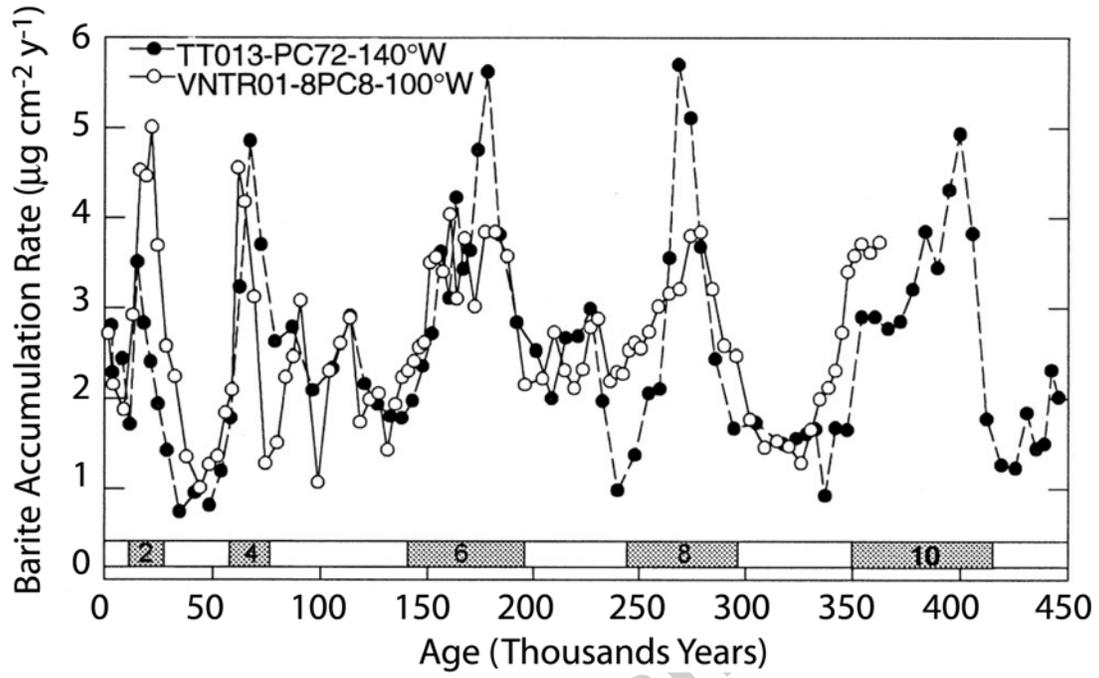


Figure 7.

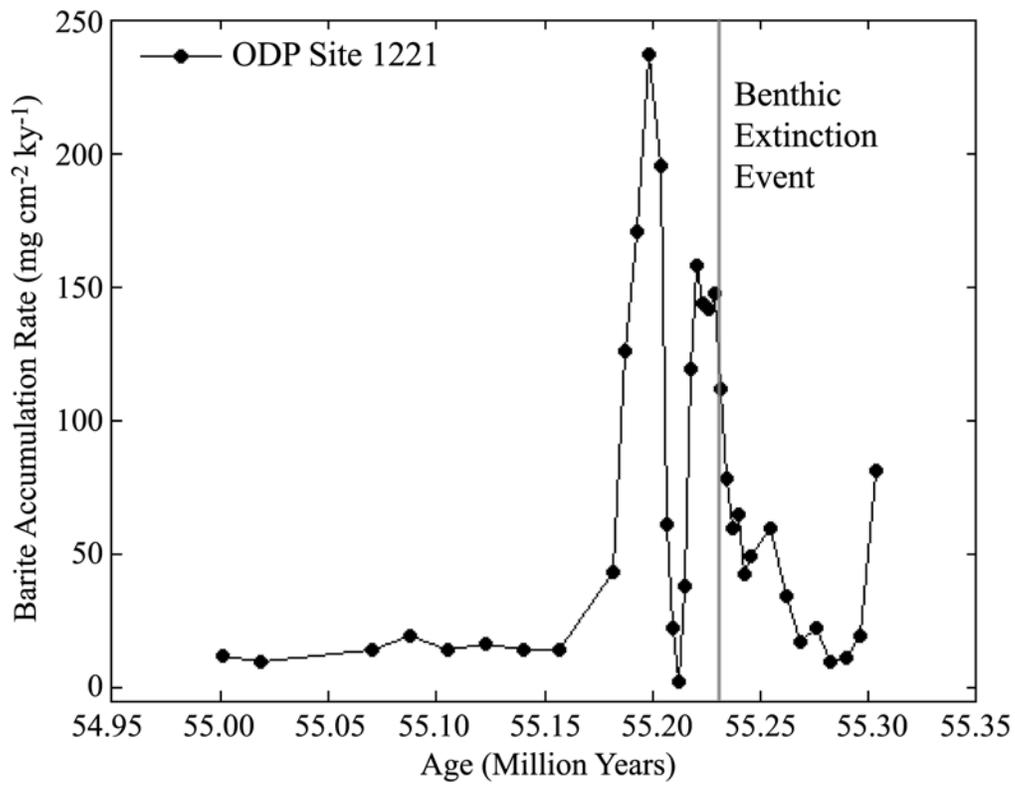


Figure 8.

