Using sulfur isotopes to elucidate the origin of barite associated with high organic matter accumulation events in marine sediments

A. Paytan

Department of Geological and Environmental Science, Stanford University, Stanford, California 94305-2115, USA

F. Martinez-Ruiz

Instituto Andaluz de Ciencias de la Tierra (CSIC-UGR), Campus Fuentenueva, 18002 Granada, Spain

M. Eagle
A. Ivy
S.D. Wankel

Department of Geological and Environmental Science, Stanford University, Stanford, California 94305-2115, USA

ABSTRACT

Events of widespread deposition of organic-carbon–rich marine sediments, identified as ocean anoxic events, occurred in the middle of the Cretaceous. Similar deposits termed *sapropels* occurred during the Pliocene and Pleistocene in the Mediterranean Basin. High biological productivity and/or anoxia have been invoked as possible causes for these widespread high organic carbon deposition events. We use the S isotopic composition of barite associated with these events to confirm that high barite accumulation rates are a result of elevated marine biological productivity and not a diagenetic artifact. The accumulation and good preservation of biogenic barite, which dissolves when pore-water sulfate concentrations are low, in association with high organic matter and authigenic pyrite, indicates that the rate of bacterial sulfate reduction was low enough for downward diffusion of seawater sulfate to replenish the pore water and prevent depletion of sulfate. The organic C to S burial ratios in samples with high barite accumulation is typically high (>5 wt ratio), supporting burial in high-productivity open-ocean regions, where pyrite formation is restricted.

Keywords: ocean anoxic events, sapropels, sulfur isotopes, marine productivity, barite.

INTRODUCTION

Time intervals in the geological record during which ocean conditions promoted accumulation of organic rich sediments, such as black shales, have usually been referred to as ocean anoxic events (OAEs) (Arthur et al., 1990). The enhanced organic matter burial rates could have led to a significant drop in atmospheric CO_2 concentrations (Freeman and Hayes, 1992; Arthur et al., 1988; Kuypers et al., 1999), thereby providing negative feedback to "greenhouse" climates. Widespread occurrences of such black shale deposits are found in the mid-Cretaceous. Although restricted to the Mediterranean, and spanning shorter time intervals, Mediterranean sapropels—defined as discrete layers >1 cm thick and containing >2% total organic carbon (Kidd et

*apaytan@pangea.stanford.edu

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al., 1978)—have been considered as possible younger analogues of black shales (Calvert, 1983; Nijenhuis et al., 1999). The increased burial rates of organic matter during both Cretaceous OAEs and Mediterranean sapropel deposition periods have usually been attributed to two different mechanisms (Arthur et al., 1990; Calvert and Pedersen, 1993): (1) decreased organic matter mineralization promoted by decreased oxygen content in seawater as a result of ocean stagnation (Stanley, 1978; Bralower and Thierstein, 1987; Sarmiento et al., 1988; Nolet and Corliss, 1990; Aksu et al., 1995; Barron et al., 1995; Erbacher et al., 2001), and/or (2) increased export production and rapid supply of organic matter to the sediment, which overwhelmed mineralization (Schlanger and Jenkyns, 1976; Calvert, 1983; Weissert et al., 1985; Weissert, 1989; Calvert and Pedersen, 1992). These two models imply different causes for the high organic matter accumulation and ocean anoxia. In the "ocean stagnation" model, external physical processes (temperature, evaporation, runoff, continent configuration) caused intense vertical gradients of temperature and salinity, which resulted in stable stratification, reduced ventilation of deep water, and finally, oceanic anoxia. In contrast, the "high productivity" model invokes biogeochemical processes internal to the ocean; extensive use of oxygen for (partial) organic matter mineralization results in lower oceanic dissolved oxygen content and even anoxia. In the latter model, changes in the carbon cycle caused the lower oxygen levels and are not merely a result of anoxic conditions induced by reduced deepwater circulation. The causes for increased productivity, however, are ultimately driven by nutrient availability in the euphotic zone. These nutrients are supplied via intensified upwelling or continental runoff, which, in turn, are controlled by tectonic and climatic changes such as uplift, precipitation, and wind stress (Parrish, and Curtis, 1982; Rossignol-Strick, 1985; Weissert, 1989; Schmidt and Mysak, 1996). Changes in hydrothermal activity (Larson and Erba, 1999) and water column redox state (VanCappellen and Ingall, 1996; Slomp et al., 2002; Filippelli et al., 2003) may also have contributed to nutrient availability.

High organic carbon accumulation in marine sediments is considered an indicator of increased biological production (Berger et al., 1988, 1989); however, a number of parameters, including seawater oxygen content, influence organic carbon preservation in marine sediments (Berger et al., 1988, 1989; Anderson et al., 2001; Sarmiento et al., 1988; Pedersen and Calvert, 1990; Canfield, 1994). At very low dissolved oxygen concentrations, organic carbon preservation increases (Sarmiento et al., 1988; Canfield, 1994); accordingly, the high organic carbon accumulation in marine sediments during mid-Cretaceous OAEs and Mediterranean sapropel deposition cannot be interpreted unequivocally as an indication of increased export production or of low oxygen conditions induced by water stagnation. Here we provide evidence from S isotope analyses of barite, which is associated with these events (i.e., separated from the black shale or sapropel layers), that support increased export production as the dominant cause of organic matter accumulation in the open ocean during these time intervals.

Marine barite forms in microenvironments in association with decaying organic matter (Bishop, 1988; Dehairs et al., 1980; Ganeshram et al., 2003); therefore, barite fluxes measured in sediment traps and in suspended particles correlate well with biological productivity in the overlying water column, and barite accumulation rates (BaAR) in marine sediments are related to export production (Dehairs et al., 1980; Bishop, 1988; Dymond et al., 1992; Paytan et al., 1996; Eagle et al., 2003). Barite is relatively resistant to diagenetic alteration after burial in sediments where pore waters are sulfate rich and has been used to reconstruct paleoproductivity at various oceanic locations and time intervals (Schmitz, 1987; Gingele and Dahmke, 1994; Rutsch et al., 1995; Paytan et al., 1996; Dean et al., 1997; Nürnberg et al., 1997; Bonn and Gingele, 1998; Schroeder et al., 1997; Thompson and Schmitz, 1997; Murray et al., 2000; Bains et al., 2000; Klump et al., 2000). In particular, high excess Ba content (total barium minus the fraction associated with terrigenous material) has long been recognized in many eastern Mediterranean sapropel layers and is considered the most reliable proxy for the identification of sapropel layers and for determining the original sapropel thickness (e.g., Van Santvoort et al., 1996; Nijenhuis et al., 1998; Wehausen and Brumsack, 1998; Thomson et al., 1999; Martinez-Ruiz et al., 2000; Weldeab et al., 2003). Similarly, high barite accumulation rates have recently been reported for mid-Cretaceous OAEs in several deep-sea cores (Paytan, 2002). These high excess Ba or barite accumulations that coincide with the organic carbon–rich layers have been interpreted as evidence for high oceanic productivity during these events (based on the relation between excess Ba, barite, and productivity in the present day ocean). This interpretation assumes that the excess Ba (which is presumed to be associated with barite) and/or the barite observed in these sediments originated in the water column and precipitated in association with decaying organic matter and therefore could be directly related to export production.

In sulfate- reducing sediments, where pore waters have low sulfate concentrations, however, barite is remobilized and is not preserved (Dean, and Schreiber, 1977; Torres et al., 1996a, 1996b; McManus et al., 1998, Bréhéret and Brumsack, 2000; Schenau et al., 2001). In such sediments, the remobilized Ba may diffuse within the sediment column, and upon contact with sulfate-containing pore waters, barite may precipitate diagenetically as "barite fronts" within sediments (Bolze et al., 1973; Dean and Schreiber, 1977; Brumsack and Gieskes, 1983; Cecile et al., 1983; Brumsack, 1986; Pruysers et al., 1991; van Os et al., 1991; von Breymann et al., 1992; Falkner et al., 1992; Torres et al., 1996b; Bréhéret and Brumsack, 2000) (see also the schematic diagram in Fig. 1). As demonstrated in Figure 1, when sulfate is depleted in pore waters as a result of sulfate reduction, pore waters become significantly undersaturated with respect to barite, and barite is remobilized, releasing Ba to pore waters. This process also enriches the residual pore-water sulfate in ^{34}S. As pore-water Ba diffuses upward in the sediments and encounters solutions with sulfate, barite will precipitate diagenetically within the sediment in distinct fronts. This barite will be enriched
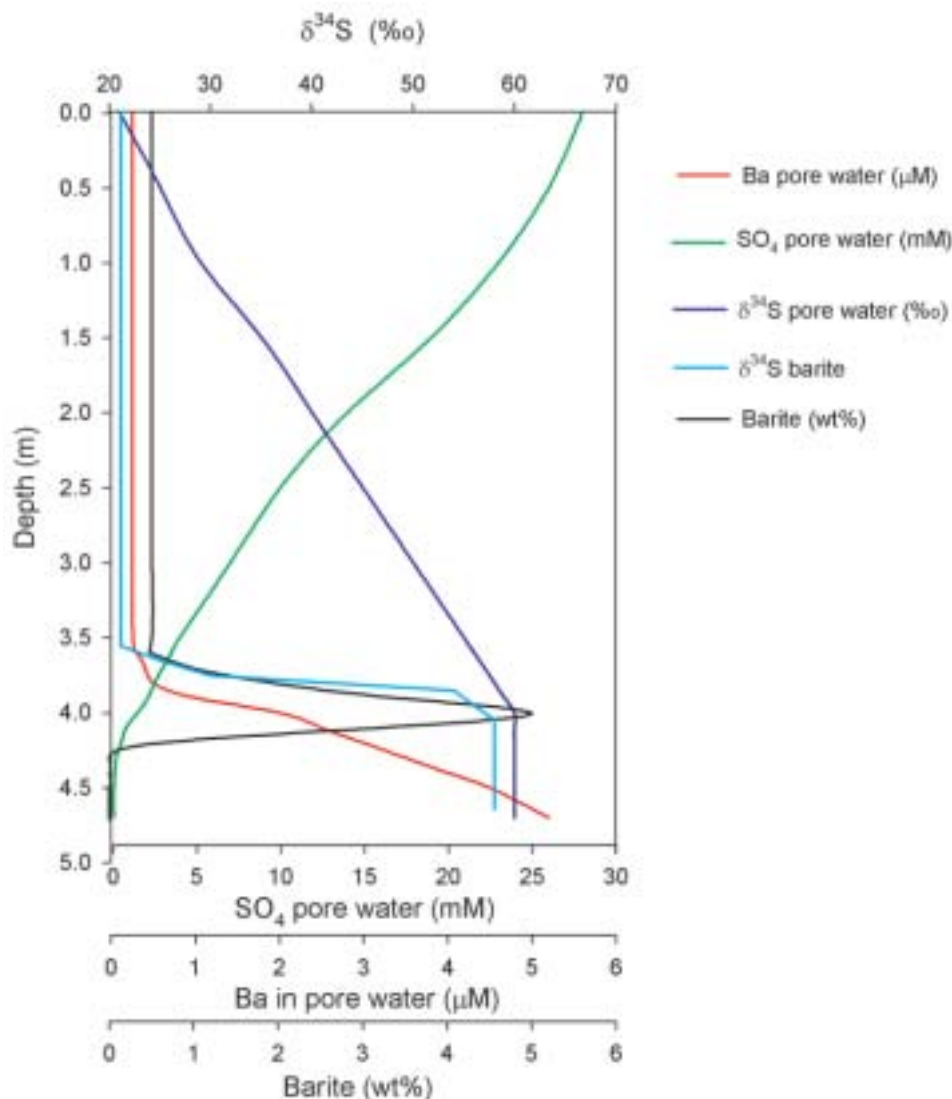
Figure 1. Schematic diagram of: A. Concentration-depth profiles for pore-water sulfate, sulfide, dissolved Ba and the isotopic composition of pore-water sulfate. B. Barite concentrations in the solid phase. Modified from Brumsack, 1986 and Torres et al., 1996b.

in ^{34}S as well. Accordingly, the interpretation that increased barite accumulation suggests high biological productivity is contingent upon proof that indeed the barite in these organic rich layers has formed in the water column and is not a postdepositional diagenetic artifact. We use the S isotopic composition of barite separated from OAE and sapropel deposits to distinguish between the two potential barite sources. If the barite associated with the high organic matter accumulation event has precipitated in the water column and has been preserved in the sediments since the time of deposition, the S isotope ratio recorded in this barite should reflect contemporaneous seawater sulfate S isotope ratios (Paytan et al., 1998; Paytan et al., 2002). If, on the other hand, the barite has precipitated diagenetically within the sediment due to extensive sulfate reduction and Ba remobilization, the S isotopic composition of this diagenetic barite is expected to be significantly heavier than that of contemporaneous seawater sulfate, due to the preferential removal of light S in the process of sulfate reduction,

increasing the isotopic composition of the residual sulfate in pore waters (Torres et al., 1996b; Aquilina et al., 1997; Naehr et al., 2000; Paytan et al., 2002)

METHODS

Barite was separated from the sediment using a sequential leaching procedure that includes reaction with 6N hydrochloric, sodium hypochlorite, hydroxylamine, and an HF-HNO$_3$ mixture (Table 1; Collier and Edmond, 1984; Paytan et al., 1998; Eagle et al., 2003). During barite extraction, each of the leaching steps targets a major (operationally defined) sedimentary fraction, leaving a final residue composed of barite and a few other refractory minerals. The extraction yield was determined to be better than 90% (Eagle et al., 2003). This method was modified from the procedure described in Eagle et al. (2003) by using 6N HCl in a glove bag under a N$_2$ atmosphere to remove the carbonate and

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sulfides and prevent oxidation of S and potential reprecipitation of barite during preparation. The insoluble residue of the sequential leaching procedure is examined under a scanning electron microscope (SEM) to determine barite content. Rutile and anatase (TiO_2) were the most common minerals other than barite in the residue. Only samples with no S bearing phases other than barite present in the residue were analyzed.

We used samples from several Deep Sea Drilling Project (DSDP) and Ocean Drilling Program (ODP) cores. The Cretaceous deep oceanic sediments spanning OAE time intervals are from ODP Sites 305, 417, 418, 551, 766, and 1049. Barite accumulation rates for these cores have been published previously (Paytan et al., 2002) and indicate increased accumulation rates in all OAEs present in these cores. Barite was also extracted from sapropel samples of Pliocene to Pleistocene age recovered from eastern Mediterranean cores (ODP Sites 964, 966 and 967). Ba enrichments associated with sapropel layers in some of these cores have been previously reported (Thomson et al., 1995, 1999; Nijenhuis et al., 1998; Wehausen and Brumsack, 1998; Warning and Brumsack, 2000; Calvert and Fontugne, 2001; Weldeab et al., 2003), and it has also been shown and generally accepted that the Ba excess in sapropel layers is derived from marine barite (Thomson et al., 1995; Martinez-Ruiz et al., 2000).

Sulfur isotope analyses were done by continuous-flow mass spectrometry using a Carlo Erba NA 1500 elemental analyzer connected to a Micromass Isoprime mass spectrometer. Samples of 4–8 mg were introduced in tin boats with ~5 mg vanadium pentoxide mixed with each sample. A commercial tank of SO_2 was used as a reference gas for $\delta^{34}S$ measurements, and results are reported relative to the Canyon Diablo Troilite standard, with a standard deviation (2σ) of ±0.3‰.

RESULTS AND DISCUSSION

In all the cores used, the time interval identified as the time frame of sapropel or OAE deposition is characterized by higher barite or excess Ba deposition compared to sections below or above (Wehausen and Brumsack, 1998; Thomson et al., 1995, 1999; Martinez-Ruiz et al., 2000; Warning and Brumsack, 2000; Calvert and Fontugne, 2001; Paytan, 2002). This enrichment, at least in sapropels, has been recognized for quite some time (Calvert, 1983; Calvert and Pedersen, 1992; Thomson et al., 1995, 1999; Van Santvoort et al., 1996; Weldeab et al., 2003) and has been interpreted as indicating high biological productivity. However, post depositional barite precipitation has not been ruled out (Dean, and Schreiber, 1977; Brumsack, 1986; Bréhéret and Brumsack, 2000), although based on the peak shape of the Ba enrichment it has been suggested that in most cases, at least for the sapropels, these are not diagenetic features (Weldeab et al., 2003). In some sapropel layers, however, it has been specifically suggested that the cause for the Ba enrichment is post burial redistribution of Ba (van Os et al., 1991, 1994; Weldeab et al., 2003). Using the S isotope signature of the barite is an independent and conclusive indicator for the origin of the barite associ-

TABLE 1. BARITE SEPARATION SEQUENTIAL LEACHING

1. Weigh ~10 g dry sediment.

2. Remove carbonates and sulfides with 6 N hydrochloric acid under a N_2 atmosphere (room temperature, ~12 h).

3. Wash three times with DI water (repeat after each step).

4. Remove organic matter in 5% sodium hypochlorite (50 °C, ~12 h).

5. Remove Fe-Mn oxyhydroxides with 0.2 N hydroxylamine in 25% acetic acid (by volume) (80 °C, ~12 h).

6. Digest in 1:2 40% hydrofluoric acid:1 N nitric acid (room temperature, ~12 h).

7. Digest in 1:1 40% hydrofluoric acid:1 N nitric acid (room temperature, ~12 h).

8. Digest in 2:1 40% hydrofluoric acid:1 N nitric acid (room temperature, ~12 h).

9. Rinse residue in saturated $AlCl_3$ in 0.1 N HNO_3 to remove fluorides (90 °C, 1 h).

10. Ash sample at 700 °C for 2 h.

11. Weigh residue and check purity with SEM or XRD.

Note: After Paytan et al. (1998) and Eagle et al. (2003). DI—distilled water; SEM—scanning electron microscope; XRD—X-ray diffraction.

ated with the sapropel and black shale deposits studied here (in addition to the model based peak shape characteristics).

The S isotopic composition of barite separated from some sapropel and black shale sections is presented in Table 2. As can be seen, barite samples analyzed here record the S isotopic composition of contemporaneous seawater sulfate (e.g., ~21–22‰ for the Pliocene and Pleistocene and ~16–19‰, depending on the exact age, for the mid Cretaceous [Paytan et al., 1998; Nielsen 1978; Claypool et al., 1980]). It should be emphasized that although the S isotopic compositions of sapropel and OAE barite samples are compared with a seawater isotope curve derived from barite, the seawater S isotope curve was constructed from multiple cores from a wide range of sites, is consistent with evaporite based records (Claypool, et al., 1980), and has been shown to record contemporaneous seawater sulfate S isotopic composition (Paytan et al., 2004).

It is expected that barite of diagenetic origin that has precipitated from pore fluids that have encountered some degree of sulfate loss due to bacterial sulfate reduction will not record the open seawater isotopic composition. Sulfate reduction leads to enrichment of the heavy S isotope (^{34}S) in the residual sulfate of pore fluids (Harrison and Thode, 1958; Hartmann and Nielsen, 1969; Jørgensen, 1979; Habicht and Canfield, 1997). Barite precipitation within the sedimentary column occurs when Ba-rich fluids (from barite dissolution by the sulfate-reduction process) migrate by diffusion or advection toward sections in the sediment where sulfate is available (Dean and Schreiber, 1977; Brumsack, 1986; Torres et al., 1996a, 1996b; Bréhéret and Brumsack, 2000). The S isotopic composition of such fluids is expected to be significantly enriched compared to seawater (see Fig. 1). Indeed, at one Cretaceous site

TABLE 2. SULFUR ISOTOPES IN BARITE AND C/S WEIGHT RATIOS
IN BULK SEDIMENT OF SAPROPEL AND OCEAN ANOXIC EVENT DEPOSITS

Leg	Site	Core	Section	Interval	Depth below surface (m)	Longitude	Latitude	Water depth (m)	Age	δ^{34}S (‰)	C/S wt. ratio
Mediterranean Sapropels											
160	964A	9H	3	42–44	76.72	36°15′N	17°44′E	3657	Pliocene	21.12	11.2
160	964B	4H	3	31–37	30.43	36°15′N	17°45′E	3658	mid. Pleistocene	21.55	na
160	964B	4H	3	117–122	31.28	36°15′N	17°45′E	3658	mid. Pleistocene	21.32	na
160	964B	6H	2	90–98	48.53	36°15′N	17°45′E	3658	early Pleistocene	20.12	7.5
160	964C	9H	3	86–92	75.46	36°15′N	17°45′E	3660	Pliocene	21.46	na
160	967B	6H	7	14–20	52.44	34°04′N	32°43′E	2555	Pliocene	20.97	na
					74.48	34°04′N	32°43′E	2552	late Pliocene	21.03	10.6
160	967C	8H	6	48–50	28.54	33°50′N	24°53′E	2200	early Pleistocene	20.22	6.5
160	969A	4H	2	34–37	28.61	33°50′N	24°53′E	2200	early Pleistocene	19.92	na
160	969A	4H	2	41–48	3.80	33°50′N	24°52′E	2201	late Pleistocene	19.82	12
160	969E	1H	3	80–82	0.265	36°04′N	21°58′E	2687	Holocene	21.32	4
GL94											
Cretaceous ocean anoxic events											
32	305	42	1	108–112	383.58	32°00′N	157°51′E	2921	OAE 2	18.90	23.4
32	305	59	1	88–91	551.38	32°00′N	157°51′E	2921	OAE 1b	16.81	na
51	417D	21	2	110–113	337.10	25°06′N	68°02′W	5482	OAE 1a	16.40	12.7
51	418B	30	2	112–115	275.00	25°02′N	68°03′W	5514	OAE 1b	15.35	na
80	551	5	1	145–148	134.91	48°54′N	13°30′W	3887	OAE 2	19.10	31.1
80	551	5	2	91–94	133.95	48°54′N	13°30′W	3887	OAE 2	18.84	21.9
80	551	5	CC	1–4	135.21	48°54′N	13°30′W	3887	OAE 2	19.02	4.2
123	766A	14	CC	7–10	130.9	19°55′S	110°27′E	3997	OAE 2	19.04	10.5
123	766A	16	4	55–59	147.95	19°55′S	110°27′E	3997	OAE 1d	16.32	na
123	766A	21	1	2226	191.22	19°55′S	110°27′E	3997	OAE 1b	16.14	na
123	766A	27	1	40–44	249.30	19°55′S	110°27′E	3997	OAE 1a	17.23	8.5
170	1049C	12	1	42–44	139.72	30°08′N	76°06′W	2670	OAE 1b	16.33	na
170	1049C	12	2	127–129	142.07	30°08′N	76°06′W	2670	OAE 1b	16.29	5.1
170	1049C	12	3	100–102	143.30	30°08′N	76°06′W	2670	OAE 1b	16.26	na

Note: C/S—organic carbon to sulfur ratio; OAE—ocean anoxic event.

(Table 2, DSDP Site 765) barite with S isotopic composition significantly higher than expected for the appropriate age was found; this sample (765C-30-CC at 635.3 m depth, age ca. 108 Ma) was not high in organic matter and is not from an OAE interval. It is possible that similar diagenetic barite is present in association with some sapropel and black shale sections. Although such barite deposits cannot be used to infer past levels of productivity, it must be kept in mind that the ultimate source of the Ba in these deposits is marine barite (Torres et al., 1996a).

In addition to the S isotope signature, diagenetic barite crystals are typically large (20–700 µm), flat, tabular-shaped crystals and tend to appear as barite beds in the sedimentary column (Torres et al., 1996a, 1996b; Paytan et al., 2002). Figure 2A and B are scanning electron micrographs of the barite crystals separated from Cretaceous black shales and from sapropel deposits, respectively, and Figure 2C is barite from Site 765C 30-CC (diagenetic). The barite crystals observed in the OAE and sapropel sections are all elliptical crystals or aggregates, ranging in size from 0.5 to 5 µm, and differ from the diagenetic barite shown in Figure 2C. These crystals are similar in shape and size to barite observed in the water column and extracted from sediment trap samples (Dehairs et al., 1980; Bishop, 1988; Paytan et al., 2002) and support a water column origin. Similar barite morphology has been observed in all of the core samples presented here. The identification of barite that forms in the water column in association with organic matter export in these sections reaffirms the "increased productivity" model as the main cause for the high organic matter accumulation in these time intervals at the studied sites.

The occurrence and preservation of marine barite in these sediments suggest that the water column and pore waters were not significantly depleted of sulfate (e.g., sulfate reduction rates were not high relative to sulfate diffusion into the sediment from the overlying seawater). Solubility calculations (Rushdi et al., 2000) indicate that for typical pore water in the open ocean with Ba concentrations of ~200 nM (Paytan and Kastner, 1996) at 2 °C and 3500 m depth, when sulfate concentrations are lower than 22 mM, undersaturation conditions exist, and barite will dissolve. On the other hand, when Ba-rich pore fluids with concentrations of over 2000 nM, as seen in some sediments where barite is remobilized (Brumsack, 1986; Torres et al., 1996a), diffuse and reach pore waters with sulfate concentrations as low as 3mM, super saturation is achieved and barite may precipitate (Rushdi et al., 2000). Such low sulfate concentrations at the site of diagenetic barite precipitation (the "barite front") are likely to have high δ^{34}S values (Brumsack, 1986) (see Fig. 1). The abundance of marine and not diagenetic barite in association with the

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sapropel and OAE deposits investigated here suggests that sufficient sulfate was present in the pore fluids of these sediments. These results are in agreement with Passier et al. (1996, 1999), who used different lines of evidence (pyrite distribution and morphology, $\delta^{34}S$ of pyrite) to show that sapropel sulfate reduction rates were not very high and took place in an open system, where sulfate supply via diffusion or advection was large relative to sulfate reduction rates, implying that pore water was not significantly depleted of sulfate during and after pyrite deposition.

It is evident, however, that at least some sulfate reduction has taken place in some of these sediments, as indicated by the presence of pyrite (e.g., Passier et al., 1999, and references therein). Even sediments lacking high pyrite concentrations most likely have experienced sulfate reduction, but pyrite precipitation may have been suppressed due to iron limitation, in particular in the carbonate rich sediments of sites 305 and 766 (Canfield, 1989, 1994; Canfield et al., 1992, 1996). Sedimentary settings conducive to sulfate reduction coupled with barite preservation are those where high rates of downward diffusion of sulfate from deep water into pore water prevents barite dissolution, while high organic content consumes other oxidants, promoting sulfate reduction. Such sedimentary conditions, where high accumulation and preservation of both barite and pyrite are found, are not prevalent in the present day ocean. At present in settings where pyrite is abundant (e.g., continental margins, anoxic and suboxic basins, etc.), marine barite microcrystals are not preserved beyond the upper few centimeters of the sediments (Paytan, personal observation). This is due to the dependence of pyrite formation on high organic matter burial, which, at present, is more widespread in continental margins, and to the low barite preservation at these settings (McManus et al., 1998). The co-occurrence of these two phases simultaneously indicates that continental margins (at least as represented today) are not good analogues for the deposition environment of sapropels and black shales investigated here and implies that a significant fraction of organic carbon burial during these events occurred in open ocean settings.

As an additional test to determine the oceanic/sedimentary setting where high organic matter, barite, and pyrite burial will persist (as during sapropels and OAEs), we have determined the organic C to total S ratio in some of our samples (Table 2). In the modern ocean, carbon and sulfur burial rates are coupled through burial of organic C and pyrite in marine environments (Holland, 1973; Berner, 1987; Kump and Garrels, 1986; Canfield et al., 2000). Pyrite forms in sediments by the reduction of seawater sulfate at the expense of sedimentary organic carbon, and this is a strictly anaerobic process. Sedimentary sulfide formation is more abundant in shelf, deltaic, estuarine, and hemipelagic muds than in the deep ocean (Berner, 1982). Berner (1982) noted that sediments accumulating in shelf and deltaic environments tend to have a remarkably constant organic C to pyrite ratios (Corg/Spy) (~7.5 molar ratio; 2.8 wt ratio). Analyses of shales indicate that the ratio of 2.8 was maintained throughout the Phanerozoic (Raiswell and Berner, 1986). The relationship between organic carbon and sulfide burial can change when the locus of carbon
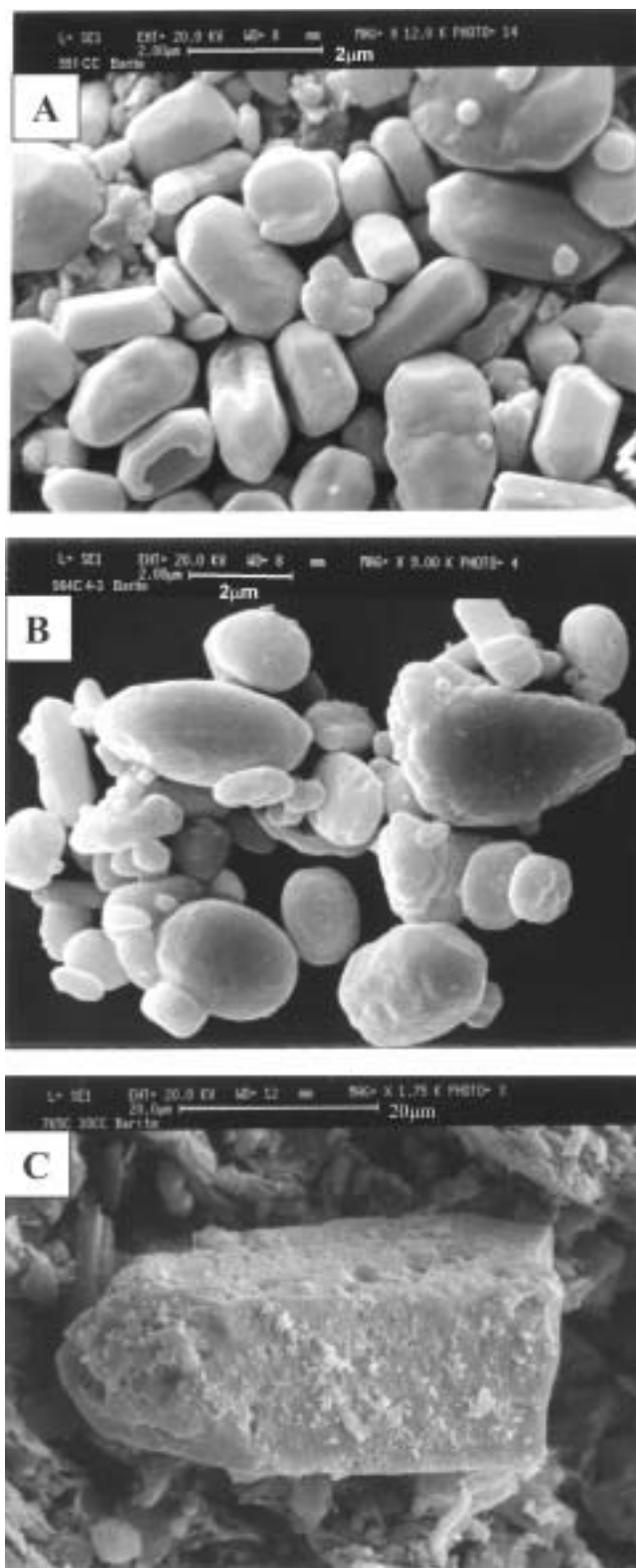

Figure 2. Scanning electron microscope micrographs. A. Primary, unaltered barite microcrystals from Leg 80 site 551 section CC, 0–7 cm. B. Primary, unaltered barite microcrystals from Leg 160 site 964B section 4–3 31–37 cm. C. Diagenetically altered barite crystals from section 765C-30-CC at 635.3 m, 108 Ma.

burial shifts away from normal shelf-deltaic environments (Berner and Raiswell, 1983). Several environments inhibit the burial of pyrite (Berner, 1984; Lyons and Berner, 1992; Calvert et al., 1996; Canfield et al., 1996; Wilkin et al., 1997; Raiswell and Canfield, 1998). Among these are high-productivity open-ocean regions and shallow water calcareous sediments, where pyrite formation may be limited by the availability of dissolved iron, and terrestrial environments (soils, swamps, coal basins), where sulfate is in limited supply. In contrast, pyrite burial rates are high in euxinic environments, where sulfides may form in the water column (Raiswell and Berner, 1985). The Corg/Spy burial, therefore, could be used to establish the burial conditions (e.g., normal marine, euxinic, and freshwater burial environments). As seen in Table 2, the organic C to total S ratio varies significantly among our core samples but is always higher than a 2.8 weight ratio (this is despite the use of total, not pyrite, S). The high Corg/S burial ratio in most of our samples suggests a net shift of organic carbon sedimentation to settings where the rates of bacterial sulfate reduction and pyrite burial were low enough for downward diffusion of sulfate to prevent significant pore-water sulfate depletion. This could be accomplished in highly productive pelagic settings where the overall sedimentation rates are relatively low (compared to continental margin settings), while organic C and barite formation and burial are high. Similar C/S ratios have previously been recorded in some organic rich sapropels (Passier and de Lange, 1998) and have been interpreted as reflecting the limitation of pyrite formation by the availability of reactive iron oxides.

Results obtained here, therefore, suggest that the barite associated with sapropel and Cretaceous OAEs deposits (at least at the sites investigated here) did not formed diagenetically within sulfate-poor sediments but rather is of seawater origin. These results confirm the marine origin of the barite deposits and thus the association of sapropel and OAEs with periods of high biological productivity. The above conclusion that high organic carbon deposition events resulted from increased productivity and were not necessarily associated with changes in oceanic circulation (e.g., stagnation) has important implications to the understanding and modeling of the global sulfur, carbon, and oxygen cycles. In particular, during the mid-Cretaceous when such events were relatively frequent, widespread, and persisted for a long time (in the order of a million years), changes in organic matter burial may have exerted feedbacks in the global carbon cycle (e.g., lower atmospheric CO_2 and reduced greenhouse effect). Increased C burial without ocean stagnation has two implications: (1) the supply of nutrients to the surface ocean through upwelling is maintained, supporting high productivity, and (2) re-supply of deep water oxygen at a fast enough rate that it would be available for effective oxidation of sulfides. This would result in an overall relatively lower burial of pyrite and other reduced S minerals and thus may have acted as negative feedback in the coupled C-S-O cycle (e.g., maintaining a general negative correlation between the burial of reduced C and S acts to sustain atmospheric oxygen at a relatively constant level). Indeed, the mid-Cretaceous $\delta^{34}S$

values are considerably lower than Cenozoic values (~16‰ and 22‰, respectively; see Paytan et al., 2004) and a decrease in $\delta^{34}S$ in the last million years of Earth's history is also observed (Paytan et al., 1998), suggesting lower pyrite burial.

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