

# Barite in the ocean – occurrence, geochemistry and palaeoceanographic applications

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## ABSTRACT

The mineral barite ( $\text{BaSO}_4$ ) can precipitate in a variety of oceanic settings: in the water column, on the sea floor and within marine sediments. The geological setting where barite forms ultimately determines the geochemistry of the precipitated mineral and its usefulness for various applications. Specifically, the isotopic and elemental composition of major and trace elements in barite carry information about the solution(s) from which it precipitated. Barite precipitated in the water column (marine or pelagic barite) can be used as a recorder of changes in sea water chemistry through time. Barite formed within sediments or at the sea floor from pore water fluids (diagenetic or cold seeps barite) can aid in understanding fluid flow and sedimentary redox processes, and barite formed in association with hydrothermal activity (hydrothermal barite) provides information about conditions of crust alteration around hydrothermal vents. The accumulation rate of marine barite in oxic-pelagic sediments can also be used to reconstruct past changes in ocean productivity. Some key areas for future work on the occurrence and origin of barite include: fully characterizing the mechanisms of precipitation of marine barite in the water column; understanding the role and potential significance of bacteria in barite precipitation; quantifying parameters controlling barite preservation in sediments; determining the influence of diagenesis on barite geochemistry; and investigating the utility of additional trace components in barite.

**Keywords** Authigenic minerals, barite, formation fluids, marine sediments, palaeoceanography.

## INTRODUCTION

Sea water is largely undersaturated with respect to barite ( $\text{BaSO}_4$ ). Thus, most of the barite found in the ocean is formed by the mixing of fluids; one containing barium ( $\text{Ba}^{2+}$ ) and another containing sulphate ( $\text{SO}_4^{2-}$ ), such that supersaturation is achieved upon mixing. Barite is one of the few marine authigenic minerals reported to form in the water column, as well as within marine sediments and around hydrothermal vents and

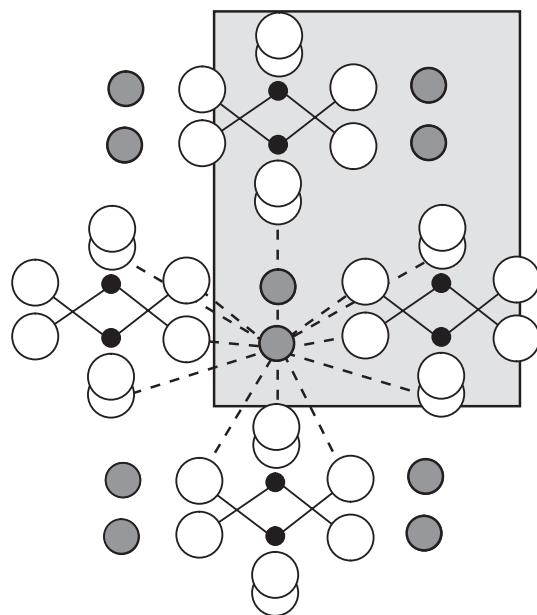
cold seeps. Because of its diverse modes of formation, the geochemistry of barite can be utilized for palaeoenvironmental as well as hydrogeological and hydrothermal studies. Several elements (for example, S, O, Ba, Sr, Ca, Ra, Pb and Nd) in sea water are incorporated into barite and used for reconstructing the chemistry of the forming solution(s). The accumulation rate of marine barite in oxic pelagic sediments has also been used to reconstruct changes in ocean biological productivity [Paytan & Griffith (2007) and

references therein]. This review provides a summary of current understanding of the occurrence of barite in the ocean, the mechanisms of its formation, its geochemistry and applications for palaeoceanographic studies and identifies areas for further investigation.

## BARITE CRYSTALLOGRAPHY AND CRYSTAL CHEMISTRY

The crystallographic structure of the mineral barite ( $\text{BaSO}_4$ ) is orthorhombic, dipyramidal, and has the space group  $\text{Pnma}$ . The sulphur (S) and two oxygen (O) atoms of each sulphate ( $\text{SO}_4^{2-}$ ) tetrahedron in the barite structure lie on a mirror plane (Gaines *et al.*, 1997). The other two oxygen atoms are equidistant above and below the plane. The barium ( $\text{Ba}^{2+}$ ) ions lie on the same mirror plane and are in 12-fold coordination with oxygen atoms which belong to seven different  $\text{SO}_4$  groups (Fig. 1). Solid solution appears to be regular and continuous between barite and celestine ( $\text{SrSO}_4$ ) (Zhu, 2004; Monnin & Cividini, 2006), but incomplete with anhydrite ( $\text{CaSO}_4$ ). Anhydrite is also orthorhombic, but of the space group  $\text{Cmcm}$  with calcium ( $\text{Ca}^{2+}$ ) in eight-fold coordination with O belonging to only six different  $\text{SO}_4$  groups (Gaines *et al.*, 1997).

Substitution of cations other than  $\text{Ba}^{2+}$  into barite is controlled by the degree of similarity in charge, ionic radius and electronegativity of the trace cation to  $\text{Ba}^{2+}$  (Table 1). In addition to strontium ( $\text{Sr}^{2+}$ ) and  $\text{Ca}^{2+}$ , substitution of potassium ( $\text{K}^+$ ), radium ( $\text{Ra}^{2+}$ ), lead ( $\text{Pb}^{2+}$ ) and rare-earth elements (REE) also occur (Church, 1979; Guichard *et al.*, 1979; Morgan & Wandless, 1980). Minor substitution of Ba by Fe, Cu, Zn, Ag, Ni, Hg and V was also reported (Chang *et al.*, 1996; and references therein). The compounds  $\text{BaSeO}_4$ ,  $\text{PbSeO}_4$ ,  $\text{SrSeO}_4$ ,  $\text{BaCrO}_4$ ,  $\text{KMnO}_4$ ,  $\text{KClO}_4$  and the mineral avogadrite ( $(\text{K}, \text{Cs})\text{BF}_4$ ) are isostructural with barite, and the anionic groups  $[\text{MnO}_4]$ ,  $[\text{SeO}_4]$  and  $[\text{CrO}_4]$  have been shown to substitute for  $\text{SO}_4^{2-}$  in synthetic material (Chang *et al.*, 1996). The temperature dependence of the degree of substitution for cations or anions in barite has not been well-established, except for  $\text{Sr}^{2+}$  (Zhu, 2004; Monnin & Cividini, 2006). Barite is stable over the entire range of pressures and temperatures of the Earth's crust in the absence of other reactive components (Hanor, 2000). However, the problem of determining the stability of barite in natural systems is complicated because barite rarely exists in nature as a pure end-member



**Fig. 1.** Barite ( $\text{BaSO}_4$ ) structure projected on the  $[001]$  surface shows the 12 coordinated divalent atoms of Ba (modified from Dove & Czank, 1995; Chang *et al.*, 1996). White, black and grey circles are O, S and Ba atoms, respectively.

**Table 1.** Ionic radii (six-fold coordination) of selected cations and their electronegativity (modified from Huheey *et al.*, 1993; Hanor, 2000). Barium ion is in bold text.

Cation	Ionic radius (Angstroms)	Electronegativity (Pauling Scale)
$\text{K}^+$	1.33	0.82
$\text{Mg}^{2+}$	0.72	1.31
$\text{Ca}^{2+}$	1.00	1.00
$\text{Sr}^{2+}$	1.16	0.95
<b><math>\text{Ba}^{2+}</math></b>	<b>1.36</b>	<b>0.89</b>
$\text{Ra}^{2+}$	1.43	0.90
$\text{Pb}^{2+}$	1.18	2.33
$\text{La}^{3+}$	1.05	1.10
$\text{Ce}^{3+}$	1.01	1.12
$\text{Lu}^{3+}$	0.85	1.27
$\text{Eu}^{2+}$	1.17	1.20

phase, but rather as solid solutions. However, Monnin & Cividini (2006) found that the saturation state of ocean waters with respect to barite as a regular solid solution is very close to that of pure barite.

Barite forms over a relatively large range of pressures ( $P$ ) and temperatures ( $T$ ) (0 to 400°C and 1 to 2000 bars) in many different geological settings, but it is mostly formed by precipitation from aqueous solution (Hanor, 2000). Equilibrium constants ( $K_{\text{BaSO}_4}$ ) calculated over the broad

spectrum of  $P$ - $T$ , show a range of several orders of magnitude (Hanor, 2000). Barite solubility ( $K_{\text{BaSO}_4}$ ) increases with increasing pressure and temperature, up to 100°C, then it progressively decreases with increasing temperature. The lowest values for  $K_{\text{BaSO}_4}$  are at very high- $T$ , low- $P$  conditions. The wide range of kinetics and conditions of barite crystallization results in a variety of crystal sizes, morphologies and textures ranging from sub-micron to several millimetres in size and including tabular and euhedral crystals (Fig. 2).

## BARIUM AND SULPHATE IN THE MARINE ENVIRONMENT

The major constituents of barite are  $\text{Ba}^{2+}$  and S in its oxidized state  $\text{SO}_4^{2-}$ . Although Ba and S are relatively abundant and widely distributed elements in Earth's crustal rocks (Faure, 1998), most naturally occurring fluids are undersaturated with respect to barite (Chow & Goldberg, 1960; Church & Wolgemuth, 1972; Monnin *et al.*, 1999; Rushdi *et al.*, 2000). Therefore, for barite to precipitate, the interaction between distinct sources of Ba and  $\text{SO}_4$  is necessary, and saturation with respect to barite should be maintained for the mineral to be preserved after precipitation.

Most Ba in the Earth's crust exists in association with K-bearing minerals, such as K-feldspars and K-micas, because its geochemistry is similar to the major rock-forming cation,  $\text{K}^+$  (Table 1). A lesser amount substitutes for  $\text{Ca}^{2+}$  in Ca-silicates. Typical Ba concentrations in the open ocean vary from 20 nmol  $\text{kg}^{-1}$  in surface waters to 150 nmol  $\text{kg}^{-1}$  in the deep Pacific (Bacon & Edmond, 1972; Church & Wolgemuth, 1972; Li *et al.*, 1973; Chan *et al.*, 1976, 1977). High concentrations, up to 460 nmol  $\text{kg}^{-1}$ , are found in marine anoxic basins, such as the Black Sea, at water depths below 100 m (Falkner *et al.*, 1993). In coastal systems and estuaries, input from terrestrial sources (for example, river water and ground water) may increase the Ba concentrations relative to open ocean settings because ground water and river waters are enriched in Ba relative to surface ocean water (Hanor & Chan, 1977; Edmond *et al.*, 1979; Shaw *et al.*, 1998; Hanor, 2000).

Hydrothermal vents are also a source of Ba to the ocean. The estimate for the hydrothermal contribution of Ba is between 1/10 to 1/3 of the total input of Ba to the ocean (Edmond *et al.*, 1979; von Damm *et al.*, 1985; Elderfield & Schultz, 1996) with concentrations in these fluids

ranging from 10 to 40  $\mu\text{mol kg}^{-1}$  (von Damm *et al.*, 1985). In marine sediments, Ba is associated with various particulate phases, including carbonates, organic matter, opal, ferromanganese oxyhydroxides, terrestrial and marine silicates, detrital material and barite (Dehairs *et al.*, 1980; Dymond *et al.*, 1992; Schroeder *et al.*, 1997; Gonneea & Paytan, 2006). The major carrier of particulate Ba in the water column is the mineral barite (Collier & Edmond, 1984; Bishop, 1988; Dymond *et al.*, 1992).

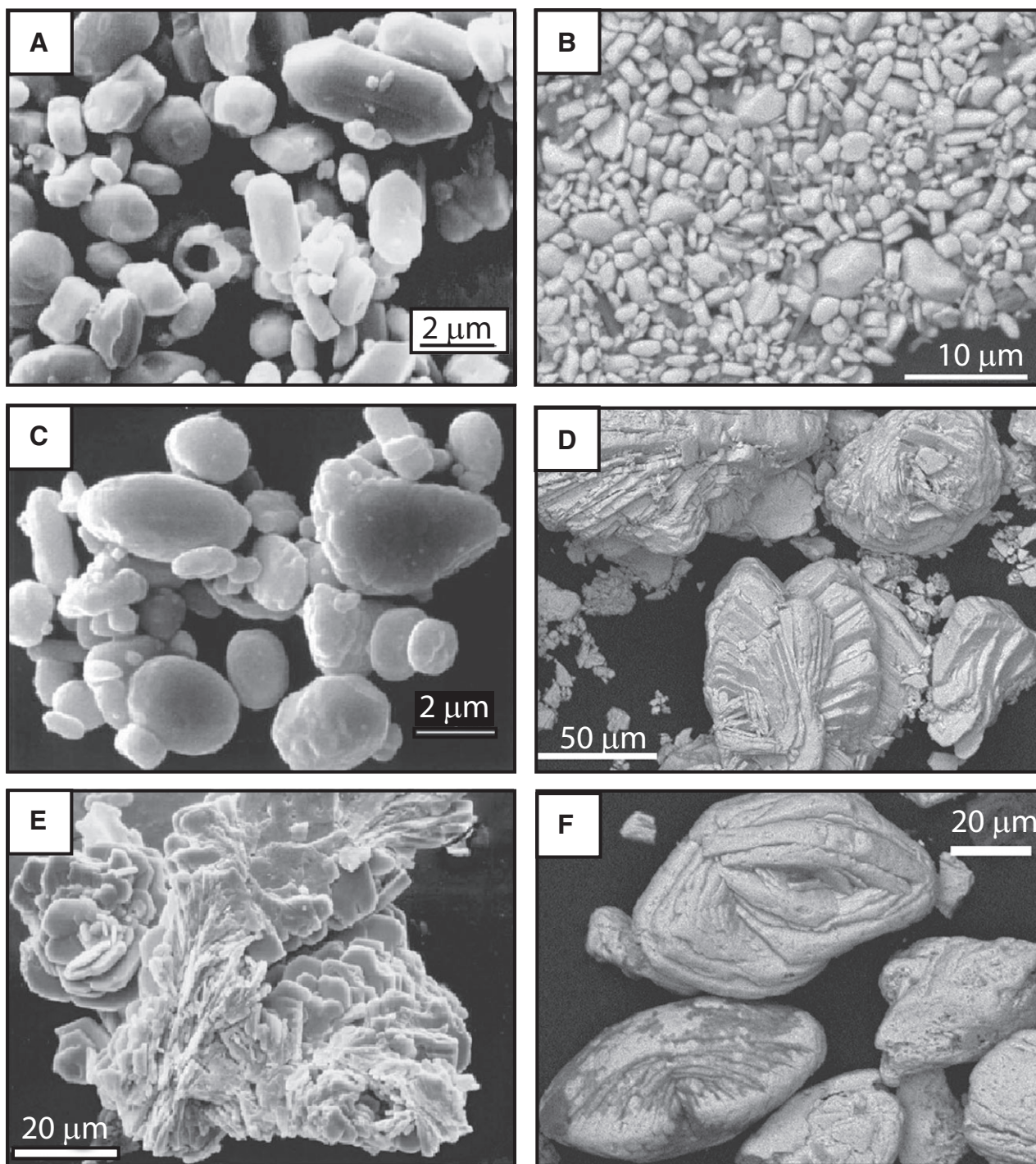
The geochemistry of sulphur in the Earth's crust is controlled largely by redox state, existing primarily as sulphide ( $\text{S}^{2-}$ ), sulphate ( $\text{SO}_4^{2-}$ ) and as native sulphur ( $\text{S}^0$ ). Sulphate is the second most abundant anion in modern sea water with an average concentration of 28 mmol  $\text{kg}^{-1}$ . It has a conservative distribution with uniform  $\text{SO}_4$ /salinity ratios in the open ocean and a very long residence time of close to 10 Myr (Chiba & Sakai, 1985; Berner & Berner, 1987). In contrast, the residence time of Ba in open sea water is approximately 8 kyr (Broecker & Peng, 1982).

The mineral barite has extremely low solubility ( $\text{ca } 10^{-10}$  at 25°C, 1 atm; Church & Wolgemuth, 1972), such that natural solutions can maintain high concentrations of either dissolved Ba or  $\text{SO}_4$ , but not both. Today, sea water is  $\text{SO}_4$ -rich and Ba-poor, providing important solution chemistry constraints on conditions and settings where barite may precipitate in the ocean. In the past, however, when the ocean contained little free oxygen and was  $\text{SO}_4$ -poor, sea water could have been enriched in Ba (Hanor, 2000); this has implications for the conditions for barite precipitation in the geological past, see discussion in Jewell (2000) and Huston & Logan (2004).

## MECHANISMS OF BARITE FORMATION IN THE OCEAN

In the modern marine environment, there are several distinct modes of barite formation, all of which require interaction between Ba and  $\text{SO}_4$ -rich fluids that result in supersaturation within the formation environment. The origin of the fluids (sea water, pore fluids or hydrothermal solution) and the location of precipitation (water column, sea floor, sedimentary column, cold seep or hydrothermal settings) impact the chemistry and morphology of the barite crystals. Four general modes of precipitation of barite are distinguished (Paytan *et al.*, 2002; Hein *et al.*, 2007).





**Fig. 2.** Scanning electron micrographs of barite crystals, some images are adapted from Paytan *et al.* (2002). (A) Euhedral to sub-spherical marine barite, core-top sediments, Pleiades expedition, core 77, 1°03'N, 119°55'W. (B) Euhedral marine barite, Deep Sea Drilling Project Site 366, 35 Ma. (C) Sub-spherical to elliptical marine barite, sediment trap, <8 μm fraction from Juan de Fuca Ridge black smoker. (D) Platy tabular diagenetic barite, Baja California, Ensenada dredged sample. (E) Rosette structures of hydrothermal barite, Mid-Atlantic Ridge, chimney at Lucky Strike, ALV 2602-3. (F) Platy tabular diagenetic barite, San Clemente Sea Cliff 355. Images (A), (C) and (E) were taken in secondary electron mode. Images (B), (D) and (F) were taken in back scatter mode.

## Marine or pelagic barite

Barium released during degradation of organic material can create micro-environments that are supersaturated with respect to barite, inducing the precipitation of barite in the water column (Goldberg & Arrhenius, 1958; Bishop, 1988; Bernstein *et al.*, 1992, 1998; Ganeshram *et al.*, 2003). This type of authigenic barite is referred to as marine or pelagic barite. The Ba content of many different marine organisms is considerably higher than sea water concentrations (Fisher *et al.*, 1991), providing a potential source of Ba to the micro-environments within the water column in which marine barite is thought to precipitate (Goldberg & Arrhenius, 1958; Bishop, 1988; Bernstein *et al.*, 1992, 1998).

Acantharia (protozoan zooplankton) and bacteria have also been proposed as mediators of marine barite formation (Bernstein *et al.*, 1992; González-Muñoz *et al.*, 2003; González-Muñoz *et al.*, 2012). Acantharia shells are made of celestine ( $\text{SrSO}_4$ ), which typically contains Ba at concentrations of thousands of ppm, and readily dissolve in sea water potentially providing both Ba and  $\text{SO}_4$  to promote barite supersaturation (Bernstein *et al.*, 1992, 1998; Bernstein & Byrne, 2004). Using the non-carbonate Sr content in suspended particles to track the presence of acantharia, van Beek *et al.* (2007) suggest that acantharian dissolution does contribute significantly to barite formation in the upper 500 m of the water column. However, the lack of a clear correlation between barite concentration in the water column or in marine sediment and acantharian abundance indicate that these organisms are not required for the formation of barite in the water column (Bertram & Cowen, 1997). In addition, Ganeshram *et al.* (2003) formed barite in mesocosm decay experiments with natural coastal plankton and laboratory-cultured diatoms and coccolithophorids. The plankton decomposed in dark oxic conditions and barite, which was absent in the initial sea water solution, and precipitated and increased in abundance with time. These experiments provided direct evidence to support the water column micro-environment mechanism of marine barite formation and to verify that barite can form in the absence of acantharia. This study also showed that living plankton indeed contains a relatively large pool of labile Ba, which is readily released during decomposition. Ganeshram *et al.* (2003) further suggested that Ba enrichment (rather than  $\text{SO}_4$ ) induced barite precipitation.

This process of barite precipitation is thought to occur mainly in the upper water column where most of the organic matter is regenerated (Chow & Goldberg, 1960; Dehairs *et al.*, 1980; Bishop, 1988; Stroobants *et al.*, 1991). This observation is also supported by the depth distribution of particulate barite in the water column (Dehairs *et al.*, 1980, 1991). This mechanism of barite precipitation could potentially operate at any water depth where organic aggregates exist and decompose, including at the sediment-water interface. Recent work by van Beek *et al.* (2007) suggests that marine barite production is not restricted to shallow water but may occur at greater depths as well.

## Biogenic precipitation of barite

In addition to marine barite formation in sinking particulate matter, certain protozoa and algae are thought to precipitate barite intracellularly to serve as statoliths to maintain orientation and depth by adjusting their density (Arrhenius & Bonatti, 1965; Tendal, 1972; Gooday & Nott, 1982; Swinbanks & Shirayama, 1986). In the marine environment, barite crystals have been found inside of the cells of the benthic protozoan *Xenophyophores* (deposit feeders), but it is not clear whether these organisms actively precipitate barite or selectively retain it in their cells during filter-feeding (Fresnel *et al.*, 1979; Gooday & Nott, 1982). Bertram & Cowen (1997) described mostly benthic 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 for the contribution of direct barite precipitation within living organisms to the total barite budget, it is most likely to be insignificant. So far, no abundant living marine planktonic organism with intra-cellular barite crystals has been identified.

Bacterially induced barite precipitation has also been documented by González-Muñoz *et al.* (2003). This work was done with bacterial cultures using a broad array of bacteria strains including marine bacteria. These results support the hypothesis that bacteria may mediate the precipitation of barite by providing nucleation sites and enhancing crystal growth. Bacterial mediation of barite precipitation is consistent with the distribution of barite in the water column because bacterial abundance is high in organic-rich sinking aggregates. However, direct evidence from observations of sinking particulate matter in the water column are still lacking and much more work is needed to determine the exact



role of bacteria in the oceanic Ba cycle and to elucidate their involvement in barite formation in the ocean.

### Hydrothermal barite

Hydrothermal barite precipitates from Ba-rich fluids formed in association with volcanic hydrothermal activity ascending from depth and mixing with sea water near the sea floor. Extensional faults and fractures focus hydrothermal fluids upward onto the sea floor, where they mix with sea water – the primary source of  $\text{SO}_4$  for barite precipitation. The main Ba source to hydrothermal fluids is from the leaching of oceanic or continental rocks driven by heat from magmatic activity. Hydrothermal leaching of pelagic sediments enriched in Ba is another potential source of Ba to these fluids (Murchey *et al.*, 1987). Barite solubility decreases during the lowering of pressure at any temperature, and with decreasing temperature, below 100°C (Hanor, 2000), further enabling the precipitation of barite from hydrothermal solutions.

The geochemistry of the hydrothermal fluid, and thus the size and composition of the barite deposit, is determined by the type and amount of host volcanic rocks and the sediments through which the fluid has passed (Hanor, 2000). The temperature of the hydrothermal fluid further distinguishes between the different environments where ‘hydrothermal’ barite forms. Barite can precipitate from low-temperature (<120°C) hydrothermal fluids around ‘warm-springs’ at the sea floor. Barite may also precipitate at intermediate temperatures (150 to 250°C) in continental margin hydrothermal settings where fluid circulation driven by high heat flow is common (Hein *et al.*, 2007; and references therein). This mode of precipitation occurs either at the sea floor near hydrothermal plumes and forms chimneys and mounds, or within sediments as dispersed crystals in basement fractures at oceanic back-arc basin spreading centres, fracture zones and volcanic arcs (for example, East Pacific Rise 21°N, Haymon & Kastner, 1981; Tonga arc, south-west Pacific, Stoffers *et al.*, 2006; the Kurile and western Aleutian island arcs, north-west Pacific, Glasby *et al.*, 2006; Okinawa and Mariana Troughs, Japan, Lüders *et al.*, 2001; Noguchi *et al.*, 2011).

### Cold seeps barite

Barite that precipitates in association with fluid flow and expulsion at the sediment-water inter-

face is referred to as cold seeps barite. Cold seeps barite precipitates when Ba-rich fluids are driven out of the sediment by tectonic and hydrological processes not related to volcanic or hydrothermal activity. Sedimentary loading formed from lateral compressive tectonic and/or high sedimentation rates causes fluids to become over-pressured and migrate vertically. As these fluids ascend from depth, barite can precipitate at or near the sea floor where fluids mix with sulphate-rich sea water. This type of barite is found along transform faults and at both passive and active margins. Salt tectonics can also control fluid emission inducing barite precipitation, such as that along the passive continental Nile margin (Gontharet *et al.*, 2007).

Several sources of Ba to fluids associated with cold seeps barite formation have been proposed, including the remobilization of pelagic barite deposited in sulphate reducing sediments along the continental margin (Torres *et al.*, 1996), leaching of Ba from mainly continental sources (Aquilina *et al.*, 1997) and expulsion of brines rich in Ba, sourced from the migration of fluids through salt deposits at depth (Manheim & Biscchoff, 1969; Kharaka *et al.*, 1987; Macpherson, 1989; Sassen *et al.*, 2004).

The chemistry of the expelled fluids, in addition to the seepage rate, affect the amount and mineralogy of cold seeps barite precipitates (Aloisi *et al.*, 2004). In general, at high methane to barium ( $\text{CH}_4/\text{Ba}^{2+}$ ) ratios (>4 to 11) carbonates will dominate, while at lower ratios barite dominates (Aloisi *et al.*, 2004). At slow seepage rates (< ca 5 cm a<sup>-1</sup>), barite precipitation occurs throughout the top few metres of the sedimentary column, producing microcrystalline phases and concretions (Aloisi *et al.*, 2004). However, when seepage rates exceed 100 cm a<sup>-1</sup>, barite precipitation occurs at the sea floor and is so rapid that barite chimneys form in the water column (Aloisi *et al.*, 2004).

Modern examples of environments where cold seeps barite forms include the San Clemente Fault (Torres *et al.*, 2002), the Gulf of Mexico (Fu *et al.*, 1994), the Peru Margin (Dia *et al.*, 1993; Torres *et al.*, 1996), Monterrey Bay (Naehr *et al.*, 2000), the sea of Okhotsk (Greinert *et al.*, 2002), the Nile deep-sea fan (Gontharet *et al.*, 2007) and the Gulf of Guinea.

### Diagenetic barite

Barite may precipitate from pore fluids within the sediment column during post-deposition diagenetic processes (referred to as diagenetic barite).

In some systems, tectonic advection can lead to over-pressured rock units and sediment dewatering which can induce fluid flow that is enriched in Ba or  $\text{SO}_4$  and can result in precipitation of diagenetic barite within sediments (Hein *et al.*, 2007). Alternatively, barite precipitation within sediments can be induced by a decrease in solubility resulting from changes in fluid pressure and temperature (Hanor, 2000). Interestingly, Stamatakis & Hein (1993) reported diagenetic barite occurring within plankton tests found in Tertiary marine sedimentary rocks. These authors speculate that these crystals precipitated diagenetically in the sediment following decomposing organic matter within the tests after burial. However, the most common way for diagenetic barite to form is through barite dissolution mediated by sulphate reduction in sediments followed by re-precipitation of barite when Ba-rich pore fluids interact with pore water rich in sulphate at the redox boundaries within the sediment.

When pore waters become anoxic and  $\text{SO}_4$  reduction rates are faster than the rate of  $\text{SO}_4$  replenishment into pore fluids, barite will not be preserved as  $\text{SO}_4$  concentrations decrease and drop below those required for barite saturation. This dissolution will typically result in an increase of Ba concentrations in the pore water associated with a depletion of  $\text{SO}_4$  and loss of particulate barite (Brumsack & Gieskes, 1983; Breheret & Brumsack, 2000; Dickens, 2001). Barium may then diffuse within the sediment and could interact with solutions containing  $\text{SO}_4$ , resulting in the precipitation of diagenetic barite within the sedimentary column, often at the oxic-anoxic boundary (Bolze *et al.*, 1974; Dean & Schreiber, 1977; Brumsack & Gieskes, 1983; Cecile *et al.*, 1983; Breheret & Brumsack, 2000). It has been suggested that this process may also occur in some sub-oxic sediments where  $\text{SO}_4$  reduction takes place but pore fluids are not devoid of  $\text{SO}_4$  (McManus *et al.*, 1998). Analysis of pore water chemistry (for example,  $\text{SO}_4$  concentration), abundance of redox-sensitive trace metals in the sediments (for example, authigenic U, Fe, Mn, Mo and I) or occurrence of pyrite can be used to decipher whether  $\text{SO}_4$  reduction has taken place within the sedimentary column (at present or in the past) and could have mobilized Ba in the pore water (Chun *et al.*, 2010).

The thermodynamic stability of barite depends not only on its solubility in aqueous solutions (for example, sea water and pore water), but also on the presence or absence of other reactive compo-

nents that can combine with Ba and  $\text{SO}_4$ , as well as the carbonate- $\text{SO}_4$  and  $\text{SO}_4$ -silicate equilibrium within the environment. Work by Monnin *et al.* (2003) illustrates the importance of the dissolution of other minerals, specifically anhydrite ( $\text{CaSO}_4$ ), to the preservation and precipitation of barite. Upon dissolution of anhydrite, pore water  $\text{SO}_4$  concentrations may increase, thus inducing the precipitation of diagenetic barite and the loss of Ba from solution (the common ion effect) (Monnin *et al.*, 2003). For a general review of this process, see Hanor (2000) and references therein.

## BARITE CRYSTAL MORPHOLOGY

### Crystal morphology and size

The various environments of formation result in a range of saturation conditions and precipitation rates, thus resulting in differences in crystal sizes and morphologies of barite which appear distinct for the different modes of precipitation (for example, marine, hydrothermal, cold seep and diagenetic; Paytan *et al.*, 2002; Fig. 2). Crystal morphology and size are dependent largely on the growth conditions of the crystal which depends on the temperature, pressure, composition of fluids and the availability of surface area for crystal growth.

Marine (pelagic) barite has been found in aggregates of sub-micrometre grains (typically  $<5\ \mu\text{m}$ ) with or without a crystalline habit, sub-spherical particles and particles with a distinct crystalline habit (Dehairs *et al.*, 1980; Bishop, 1988; Bertram & Cowen, 1997). Stroobants *et al.* (1991) found marine barite in the upper 10 to 20 m of the water column in the Southern Ocean, in bioaggregates as amorphous entities without a distinct crystalline habit, while below this surface layer barite existed in bioaggregates as micro-particles with a more defined crystalline habit. Although some of the marine barite formed in the water column dissolves at depth due to the undersaturation of the water column with respect to barite, much of it does reach the sea floor because of its low solubility and common packaging in fast settling faecal pellets (Paytan & Kastner, 1996). However, dissolution also continues at the sediment-water interface (Paytan & Kastner, 1996). Marine barite crystals found in sediments are similar to those seen in the water column – small sized ( $\mu\text{m}$  in range) and euhedral, elliptical or spherical crystals (Fig. 2).

Hydrothermal, cold seep and diagenetic barite crystals vary widely in size and morphology; they are generally large crystals, but can range from tens of microns to up to 5 mm in size. The morphology of the crystals is determined largely according to where they precipitate, for example, on the sea floor or within the sedimentary column. Diagenetic barite formed in the sedimentary column typically consists of flat, tabular-shaped crystals found in beds composed primarily of barite (Dean & Schreiber, 1977) or as nodules in sedimentary layers (Breheret & Brum-sack, 2000). However, at the sediment-water interface, diagenetic or cold seep barite can form mounds of highly porous crystals which exhibit a layered appearance of platy crystals in diamond-shaped clusters (Torres *et al.*, 1996, 2002; Paytan *et al.*, 2002).

Descriptions of hydrothermal barite crystals include well-formed polyhedra to euhedral lath-like crystals, often found in radiating bundles or sector-zoned euhedral minerals that project into open vugs (Haymon & Kastner, 1981; Hanor, 2000). Both hydrothermal and cold seep barite can form cross-cutting tabular crystals that commonly form rosette structures (Haymon & Kastner, 1981; Fu *et al.*, 1994; Paytan *et al.*, 2002).

### Fluid inclusions

Fluid inclusions can occur in large coarse-grained barite (Chang *et al.*, 1996; Hanor, 2000). The heating and freezing behaviour of primary fluid inclusions could provide information on the temperature of fluid entrapment and on fluid salinity. Chemical analysis of the fluids in the mineral provides a direct measure of the chemistry of the solution from which they precipitated (Roedder, 1972). However, many fluid inclusions in barite stretch when heated, leading to inference of anomalously high fluid pressures and temperatures (Ramboz & Charef, 1988; Ulrich & Bodnar, 1988). Lüders *et al.* (2001) estimated maximum formation temperatures of barite-hosted fluid inclusions from the JADE active hydrothermal field in the Central Okinawa Trough (Japan) of between 150°C and 200°C. This massive sulphide deposit is of interest because it is suggested as a modern analogue of volcanogenic Kuroko-type massive sulphide ore deposits (Lüders *et al.*, 2001). Barite veins of several districts of the Cuddapah Basin (India) have been correlated by their barite fluid inclusion data, including the composition, salinity, density, pressure, depth of entrapment and temperature

of homogenization (Mukherjee & Prabhakar, 2006). More recently, analysis of fluid-inclusions in barite-rich quartz hydrothermal veins, associated with 3.47 byr old algal mats and stromatolites in the North Pole Dome of Western Australia, aided in reconstructing the temperature and composition of hydrothermal fluids in this environment (Harris *et al.*, 2009).

## BARITE GEOCHEMISTRY

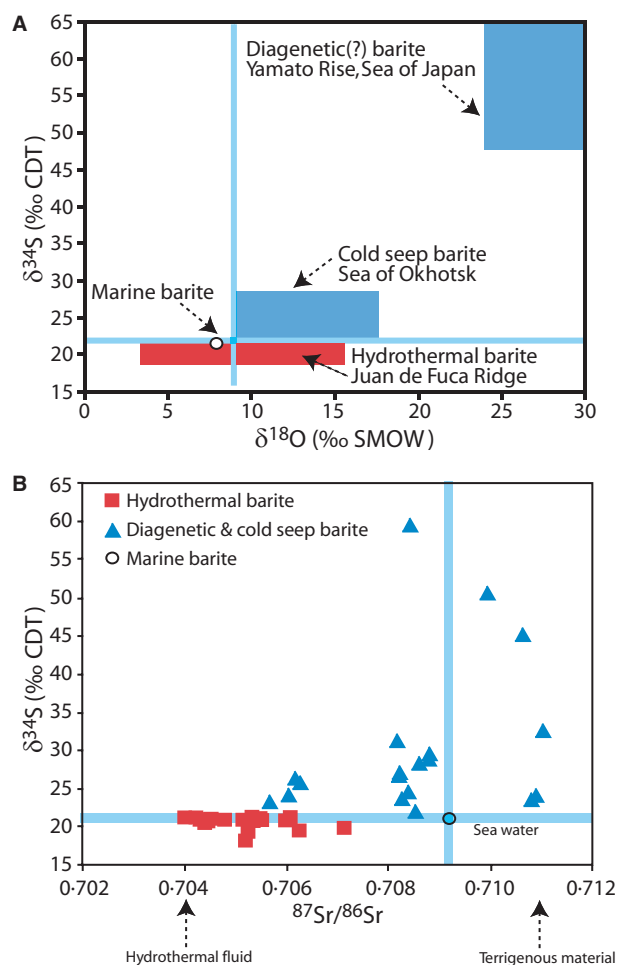
Isotopic and chemical signatures of major (for example, S, O, Ba and Sr) and trace elements (for example, Ca, REE and Pb) in barite are indicative of the source(s) of the fluids from which it precipitated. Therefore, the origin of a particular barite sample can often be constrained by the isotopic analyses of its major elemental components. The chemical and isotopic composition recorded in barite may, in turn, provide information on the chemistry of formation fluids and specifically could be used to reconstruct changes in sea water chemistry over time.

### Sulphur isotopes

The sulphur isotopic composition ( $\delta^{34}\text{S}$ ) of barite is quite similar to the  $\text{SO}_4$  from which it precipitated (<0.4 per mil difference) (Kusakabe & Robinson, 1977). Accordingly, barite  $\delta^{34}\text{S}$  will record the sulphur isotopic composition of the formation fluids. Depending on the mode of barite formation, several potential sources of  $\text{SO}_4$  may be available for barite precipitation, including sea water  $\text{SO}_4$  ( $\delta^{34}\text{S} = +21\text{‰}$  in the modern ocean), magmatic sulphate ( $\delta^{34}\text{S} = +1$  to  $2\text{‰}$ ), pore water  $\text{SO}_4$  modified by microbial reduction,  $\text{SO}_4$  from calcium sulphate minerals and  $\text{SO}_4$  produced by the oxidation of reduced sulphur species.

The sulphur isotopic signature in barite can be used to distinguish the mode of barite formation (Paytan *et al.*, 2002). Marine barite records contemporaneous sea water sulphur isotope values. Diagenetic barite typically precipitates from fluids that have undergone some degree of  $\text{SO}_4$  loss due to bacterial sulphate reduction (BSR), the precipitated barite is expected to have high sulphur isotope ratios similar to those in the residual  $\text{SO}_4$  of these fluids (Fig. 3). In the Peru margin and in the Japan Sea, Torres *et al.* (1996) measured highly enriched sulphur isotope ratios in barite ( $\delta^{34}\text{S}$  up to  $+84\text{‰}$ ). Torres *et al.* (1996) suggested that these barites formed as a result of sulphate reduction of marine barite, its





**Fig. 3.** (A) Plot of the sulphur and oxygen isotopic composition of barite. Juan de Fuca O and S isotope data are from Goodfellow *et al.* (1993) and Paytan *et al.* (2002), respectively. Sea of Okhotsk data are from Greinert *et al.* (2002) and Sea of Japan data are from Sakai (1971). Marine barite S isotope data are from Paytan *et al.* (1998) and O isotope data are from Turchyn & Schrag (2004). The reason for the apparent offset between marine barite and sea water  $\delta^{18}\text{O}_{\text{SO}_4}$  compels further investigation. (B) Plot of the S and Sr isotopic composition of barite. All data are from Paytan *et al.* (2002). Light blue lines designate the modern sea water isotopic composition of each element.

remobilization and subsequent reprecipitation as a diagenetic barite front.

In hydrothermal barites, the relative amount of sulphur incorporated from sea water  $\text{SO}_4$  (+21‰ at present) or from the oxidation of hydrothermal  $\text{H}_2\text{S}$  with an isotopic signature of about +1 to 2‰ results in the sulphur isotope ratio equal to or slightly less than contemporaneous sea water (Fig. 3). Bacterial sulphate reduction of sea water

can also occur in hydrothermal settings, resulting in a high sulphur isotope ratio in some hydrothermal barite deposits. Lüders *et al.* (2001) explained the range of sulphur isotope values in barites found in stockwork, smokers and mounds on the sea floor in the Central Okinawa Trough of Japan to suggest mixing of hydrothermal solutions with sea water to form the barites. Locally heavy  $\delta^{34}\text{S}$  of barite was related to partial  $\text{SO}_4$  reduction as well (Lüders *et al.*, 2001).

Cold seeps barite sulphur isotope values represent a mixture of sea water and pore fluid signatures. For example, in the California continental margin, Naehr *et al.* (2000) interpreted systematic changes in S isotope ratios of barite samples precipitated on the sea floor to reflect changes in the relative contribution of  $\text{SO}_4$  from pore fluids and sea water resulting from changes in pore water flow rates. Detailed  $\delta^{34}\text{S}$  analyses suggest that most massive bedded (stratiform) barite deposits have a sea water sulphate source and thus probably formed from rapid Ba-rich fluid flow to the sea floor (Jewell, 2000).

Marine barite which precipitates in the water column records changes in oceanic sulphate  $\delta^{34}\text{S}$  through time (Paytan *et al.*, 1998, 2004). Because sulphur has a long residence time in the ocean [ $>10$  Myr; (Walker, 1986)], the isotopic composition of sea water sulphate is uniform throughout the oceans at any given time (Rees *et al.*, 1978). The oceanic sulphate  $\delta^{34}\text{S}$  at any given time is controlled by the relative proportion of sulphide and sulphate input and removal from the oceans and their isotopic compositions and this, in turn, influences the oxygen content of the atmosphere (Holland, 1973; Berner & Canfield, 1989; Berner, 1999; Paytan & Arrigo, 2000). In addition, knowledge of the  $\delta^{34}\text{S}$  of sea water can shed light on potential changes in the S sources to the ocean such as river runoff, volcanism and hydrothermal activity (Paytan *et al.*, 2004), and the size of the oceanic sulphur reservoir (Wortmann & Chernyavsky, 2007). The use of barite for the reconstruction of sea water  $\delta^{34}\text{S}$  increased the temporal resolution and uncertainty associated with records based on evaporites (Holser & Kaplan, 1966; Claypool *et al.*, 1980) and revealed previously unrecognized fine structure in the record. Paytan *et al.* (1998, 2004, 2011) found several large fluctuations in oceanic sulphate  $\delta^{34}\text{S}$  recorded in marine barite over the past 130 Myr implying considerable changes in the rate of pyrite burial and the size of the sea water sulphate reservoir (DeBond *et al.*, 2012). In addition, these signatures could be used for

stratigraphic correlations when other more traditional tools cannot be applied (Paytan & Gray, 2012).

### Oxygen isotopes

In hydrothermal barite, formed at temperatures above 150°C and near-neutral pH, the oxygen isotopic composition of  $\text{SO}_4$  is in isotopic equilibrium with environmental water (Chiba & Sakai, 1985). The oxygen isotopic fractionation factor of the  $\text{SO}_4\text{-H}_2\text{O}$  system is temperature dependent and can therefore be used as a geothermometer to infer the conditions under which  $\text{SO}_4$  formed (Ohmoto & Lasaga, 1982). For example, the  $\text{SO}_4$  oxygen isotope analyses of barite confirmed a magmatic origin for the pore fluids for the Yauricocha copper deposit in Peru (Kusakabe & Robinson, 1977).

Diagenetic barite formed at an oxic/anoxic interface is thought to have anomalously high  $\delta^{18}\text{O}_{\text{SO}_4}$  due to barite dissolution associated with bacterial sulphate reduction, oxygen isotope exchange reactions associated enzymatically-activated sulphate reactions and subsequent re-precipitation within the pore fluids (Turchyn & Schrag, 2006; Wortmann *et al.*, 2007). Bacterial sulphate reduction will increase the  $\delta^{18}\text{O}_{\text{SO}_4}$  by preferentially reducing the  $\text{SO}_4$  of light oxygen isotopes leaving a heavy residual  $\text{SO}_4$  pool, although the exact parameters affecting this  $^{18}\text{O}$  fractionation are not known (Knoller *et al.*, 2006). Pore water profile measurements suggest that the fractionation during BSR is typically between 2‰ and 10‰ (Aharon & Fu, 2000). Oxygen isotope exchange reactions associated with enzymatically-activated sulphate seem to be associated with an oxygen isotope equilibrium fractionation factor of about 30‰ also resulting in pore water sulphate oxygen isotope enrichment (Wortmann *et al.*, 2007). The combination of the  $\delta^{34}\text{S}$  and  $\delta^{18}\text{O}$  of  $\text{SO}_4$  can aid in distinguishing the sulphur transformation processes that have occurred in the environment (Fig. 3A).

In the present day ocean, the  $\delta^{18}\text{O}_{\text{SO}_4}$  is about +9.3‰ VSMOW (Vienna Standard Mean Ocean Water) which is well out of equilibrium with the  $\delta^{18}\text{O}$  of ocean water, +0‰ VSMOW (Lloyd, 1968). This difference has been explained as resulting from isotopic non-equilibrium which persists due to the slow kinetics of isotopic exchange between oxygen in  $\text{SO}_4$  and sea water at most oceanic conditions of temperature and pH (Chiba & Sakai, 1985). Equilibrium is not expected to occur within the estimated oceanic residence time of

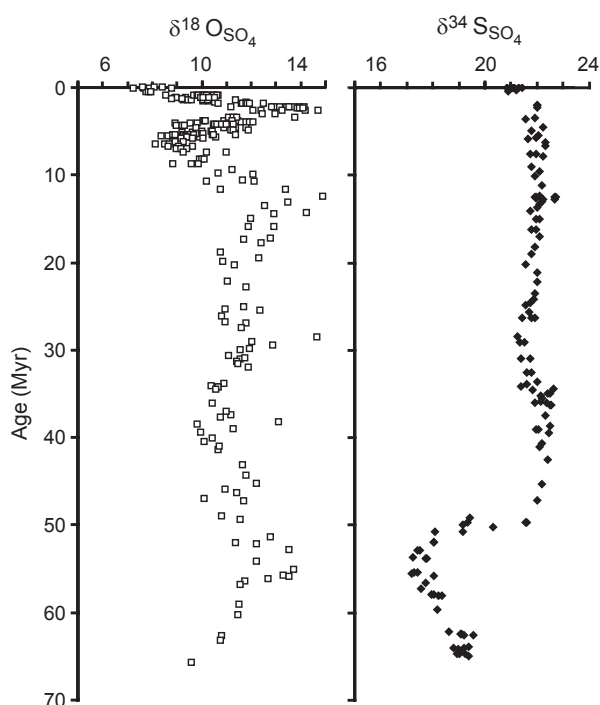
sea water  $\text{SO}_4$  (>10 Myr). Therefore, the sea water  $\delta^{18}\text{O}_{\text{SO}_4}$  will reflect the source of  $\text{SO}_4$  to the ocean (weathered evaporites +11 to +13‰ and oxidative pyrite weathering -4 to +2‰), the biogeochemical cycling of  $\text{SO}_4$  in the ocean (for example,  $\text{SO}_4$  reduction and sulphide oxidation) and the sinks of  $\text{SO}_4$  from the ocean (for example, gypsum, anhydrite and pyrite burial) (Claypool *et al.*, 1980).

Marine barite should reflect the contemporaneous marine  $\text{SO}_4$  isotopic composition and thus will also not record equilibrium values (Fig. 3A). The record of  $\delta^{18}\text{O}_{\text{SO}_4}$  in marine barite has provided valuable insight into the marine sulphur cycle which appears to be more dynamic than previously thought (Turchyn & Schrag, 2004, 2006; Turchyn *et al.*, 2009) (Fig. 4). In addition, the  $\delta^{18}\text{O}_{\text{SO}_4}$  signature of barite can be used to distinguish sea water non-equilibrium conditions from high temperature precipitates where equilibrium is expected to be obtained. For example, non-thermally equilibrated  $\text{SO}_4$  ( $\delta^{18}\text{O}_{\text{SO}_4}$  and  $\delta^{34}\text{S}$ ) in barite from the Derugin Basin (Sea of Okhotsk) suggests precipitation at ambient bottom water temperatures (cold seep), challenging a hydrothermal origin which is commonly assumed for most massive barite deposits (Greiner *et al.*, 2002).

### Strontium Isotopes

Barite is ideal for Sr isotope work because of the high concentrations of Sr in the crystal structure (up to 3 mol%; Monnin & Cividini, 2006) and low rubidium (Rb) in barite, which eliminates any need for correcting the measured  $^{87}\text{Sr}/^{86}\text{Sr}$  for the *in situ* production of radiogenic  $^{87}\text{Sr}$  from Rb. Barite will record the Sr isotopic composition of the formation fluids, thus the origin of barite can often be constrained by its Sr isotopic composition (Reesman, 1968; Paytan *et al.*, 2002). Sources of Sr include sea water ( $^{87}\text{Sr}/^{86}\text{Sr} = 0.70917$  at present) and fluids influenced by Sr sources that are less radiogenic than modern sea water, such as low-Rb oceanic crust (for example, mantle derived hydrothermal fluid,  $^{87}\text{Sr}/^{86}\text{Sr} = 0.70350$ ; Albarède *et al.*, 1981), older marine sediments (representing a range of values depending on sediment age; see McArthur *et al.*, 2001) or from more radiogenic sources such as terrigenous material ( $^{87}\text{Sr}/^{86}\text{Sr} = 0.711$ ) (Fig. 3B).

Complications can exist however in interpreting the Sr isotopic composition of barite. Specifically, two possible origins exist for barite with a low  $^{87}\text{Sr}/^{86}\text{Sr}$ . Barite could be precipitated from formation fluids with Sr derived from older



**Fig. 4.** Oxygen and sulphur isotopic composition of marine barite over the past 65 Myr. All the S and O isotopic ratios are reported in per mil relative to the Canyon Diablo Troilite (CDT) and standard mean ocean water (SMOW) standards, respectively, as reported by Paytan *et al.* (1998) and Turchyn & Schrag (2006).

marine rocks with low  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios (cold seep or diagenetic barite) or from mantle fluids (hydrothermal barite). For example, old marine sedimentary rocks are suspected to be the origin of low  $^{87}\text{Sr}/^{86}\text{Sr}$  in cold seep barite deposits in Monterey Bay that are not sourced from volcanic rocks (Naehr *et al.*, 2000). In contrast, large barite deposits at the northern Peru convergent margin have radiogenic Sr isotopic ratios that preclude a hydrothermal origin (Dia *et al.*, 1993). It is thought that the source of the fluid originated from the continent or from reaction of sea water with the underlying continental metamorphic basement (Dia *et al.*, 1993). Because Sr isotope signatures are not completely unique for each mode of barite precipitation, it is important to analyze multiple geochemical characteristics of a barite with an unknown origin in order to accurately describe the environment of its formation.

Barite precipitated in the water column records the contemporaneous sea water Sr isotopic composition (Goldberg *et al.*, 1969; Paytan *et al.*, 1993). The Sr isotopic composition in sea water is uniform throughout the ocean at any particular time due to the long residence time of Sr in sea

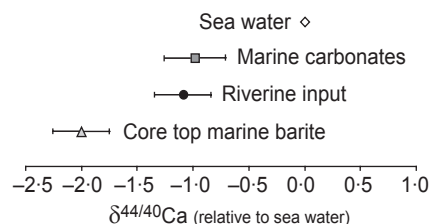
water (2 to 3 Ma). The sea water  $^{87}\text{Sr}/^{86}\text{Sr}$  history has been determined for the past 500 Myr primarily from measurements of carbonates (e.g. Burke *et al.*, 1982; McArthur *et al.*, 2001). Variations through time reflect changes in weathering and hydrothermal activity as they relate to changes in climate and tectonics. The sea water Sr isotope curve is also useful for stratigraphic correlation and dating (McArthur *et al.*, 2001). Marine barite is a particularly useful alternative for dating carbonate-poor or diagenetically altered sedimentary sections (Paytan *et al.*, 1993; Mearon *et al.*, 2003). For example, Mearon *et al.* (2003) used the Sr isotopic composition of marine barite in Cretaceous marine sediments to refine the biostratigraphic age models for several sites where carbonates were diagenetically altered. This record was also used to reaffirm the composite Cretaceous strontium curve of McArthur *et al.* (2001).

### Calcium isotopes

Griffith *et al.* (2008b) reported results from core-top samples of the Ca isotopic composition of marine barite. The fractionation of Ca during precipitation of barite is larger than that for calcium carbonate (Fig. 5; Griffith *et al.*, 2008b). The Ca isotopic composition of marine barite in core-top samples has a constant fractionation from sea water and does not appear to be dependent on any environmental parameter (Griffith *et al.*, 2008b). Such a record will provide a valuable insight into changes of the marine Ca cycle in the past (Skulan *et al.*, 1997). The use of marine barite eliminates complications related to biological fractionation associated with records based on biologically precipitated phases such as biogenic calcium carbonate (De La Rocha & DePaolo, 2000; Fantle & DePaolo, 2005; Heuser *et al.*, 2005; Sime *et al.*, 2005; Hippler *et al.*, 2006; Farkas *et al.*, 2007). Combining marine barite and carbonate records could be useful to define both the  $\delta^{44}\text{Ca}$  of sea water and the fractionation factor associated with carbonate sedimentation to gain insight into changes in the cycling of Ca (and C) in the ocean and the various influences on biogenic sea water Ca isotope records (Fantle, 2010; Griffith *et al.*, 2011).

A record over the past 28 Myr of variations in sea water  $\delta^{44}\text{Ca}$ , inferred from marine barite, identified a period of pronounced change in the cycling of sea water Ca corresponding to major climate change at the middle Miocene (Griffith *et al.*, 2008a). At this time, following a period of





**Fig. 5.** Calcium isotopic composition of core top marine barite (Griffith *et al.*, 2008b) compared with average biogenic marine carbonates, riverine calcium input and sea water (Heuser *et al.*, 2005).

climate warmth, the Earth cooled making the final transition into an ‘icehouse’ world with expansion of the ice sheet on East Antarctica. Another time period when Earth’s climate cooled from a ‘greenhouse’ to an ‘icehouse’ state occurred at the Eocene–Oligocene boundary (*ca* 34 Ma). Calcite sedimentation in the open ocean changed dramatically, but dissolved calcium in the oceans remained stable as documented by marine barite (Griffith *et al.*, 2011). The response of ocean chemistry to climate change thus depends upon the composition of sea water and the rate of change. Furthermore, calcite precipitated by marine micro-organisms showed variations inconsistent with the marine barite, demonstrating that the biogenic calcite records not only changes in the sea water isotope ratio of calcium, but also changes in temperature and/or the assemblages of such organisms, which are sensitive to climate change (Griffith *et al.*, 2011).

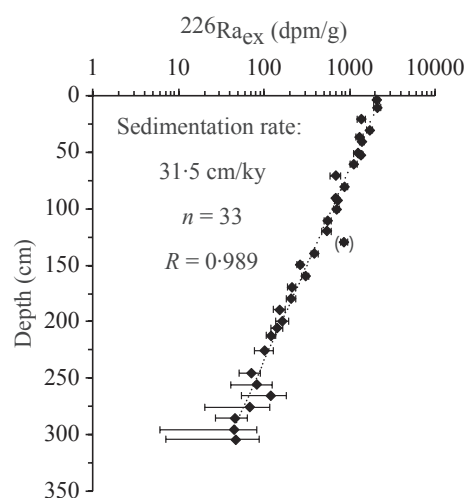
### Radium, thorium and lead

Radium ( $\text{Ra}^{2+}$ ) is close in ionic radius to  $\text{Ba}^{2+}$ , and its detection in barite [along with other products of the uranium (U) decay series] has been used to determine the age of recent cold seep and hydrothermal deposits of barite (Kadko & Moore, 1988; Moore & Stakes, 1990; Reyes *et al.*, 1995; Naehr *et al.*, 2000; Noguchi *et al.*, 2004), the sedimentation rates of recent marine sediments (Paytan *et al.*, 1996; van Beek & Reyss, 2001; van Beek *et al.*, 2004) and the surface water reservoir age for the Antarctic zone of the Southern Ocean (van Beek *et al.*, 2002). Paytan *et al.* (1996) measured an exponential decrease in  $^{226}\text{Ra}$  of marine barite in the upper 25 cm of the sediment, suggesting that barite behaves as a closed system and is not affected by exchange or recrystallization. The lack of detectable  $^{226}\text{Th}$ ,  $^{228}\text{Ra}$  and  $^{224}\text{Ra}$  activities in any of the marine barite samples indicates that no significant barite growth is occurring below the

bioturbated zone (Paytan *et al.*, 1996). These results demonstrate the utility of marine barite to calculate sedimentation rates in recent sediments.

The  $^{226}\text{Ra}$  decay in marine barite separated from Southern Ocean pelagic sediments (Fig. 6) was used to determine the absolute age of the sediments for the Holocene (van Beek *et al.*, 2002). Van Beek *et al.* (2002) compared these ages with  $^{14}\text{C}$  ages measured on planktonic foraminifera to reconstruct the sea-surface reservoir age in the Antarctic zone of the Southern Ocean and estimate the reservoir correction for radiocarbon dating. A change in reservoir age during this time period suggests a major change in circulation in the Southern Ocean during the Holocene (van Beek *et al.*, 2002).

Concentrations of U in marine barite are less than 0.5 ppm, negligible in comparison to the concentrations of thorium (Th), indicating that essentially all the  $^{230}\text{Th}$  in marine barite is unsupported (Paytan *et al.*, 1996). The  $^{230}\text{Th}/^{232}\text{Th}$  activity ratios are consistent with the bulk sediment ratio, with a mean of *ca* 100, ranging between 20 and 190 (Paytan *et al.*, 1996). These results were in contrast to the previous work by Church & Bernat (1972) and Borole & Somayajulu (1977) who reported results of Ra, Th, U and lead (Pb) in barite samples and suggested rapid exchange and remobilization of



**Fig. 6.** Excess  $^{226}\text{Ra}$  activity normalized to marine barite content in a core from the Southern Ocean (modified from van Beek *et al.*, 2002). Van Beek *et al.* (2002) calculated the sedimentation rate of  $31.5 \text{ cm ky}^{-1}$  (error of  $1.0 \text{ cm ky}^{-1}$ ) from the exponential decay with sediment depth. Data point out of trend was ignored in the calculation.

these elements after burial. Paytan *et al.* (1996) attributed these previous results to the use of milder sequential leaching procedures that did not remove all detrital material from the sample and left oxyhydroxide coatings on the marine barite.

The  $^{210}\text{Pb}/^{226}\text{Ra}$  activity ratios of several active cold seep barite samples in the Monterey Canyon along the California continental margin were measured by Naehr *et al.* (2000) to determine the age of the barite crust and to assess its growth rate. The age of the barite precipitates suggest that the site could be as young as 100 years and its growth rate in the order of 1 cm per year (Naehr *et al.*, 2000). Noguchi *et al.* (2004) calculated the precipitation age of the hydrothermal barite deposit in the Okinawa Trough (Japan) by the  $^{210}\text{Pb}/^{226}\text{Ra}$  method. The range of ages of the hydrothermal barite calculated were five to 88 years and showed a relationship with the Sr/Ba ratio in the samples, suggesting a possible alteration of the hydrothermal activity in the field (Noguchi *et al.*, 2004).

### Neodymium isotopic composition and rare earth elements

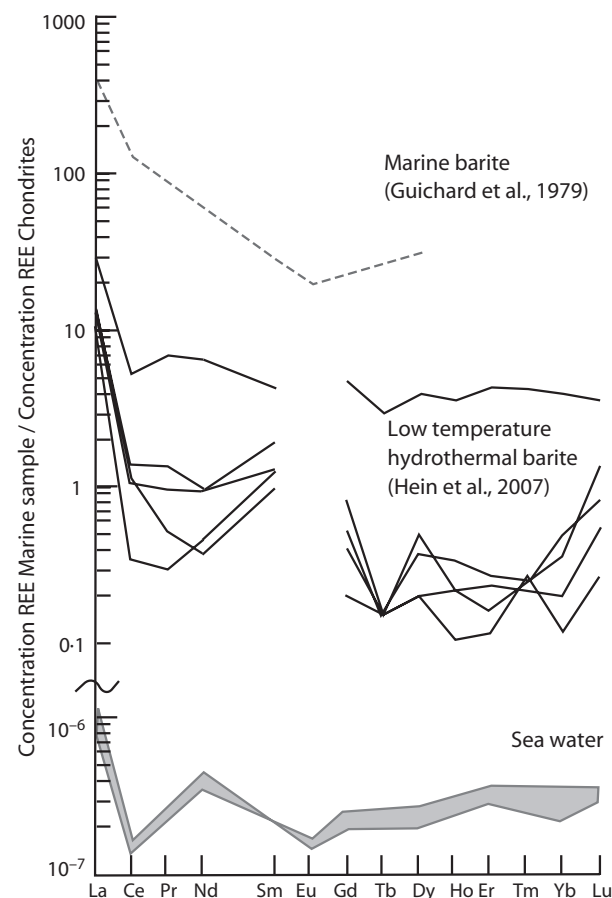
Relatively high neodymium (Nd) concentrations (5 to 100 ppm) were reported by Guichard *et al.* (1979) for marine barite, potentially making it a useful mineral for sea water Nd-isotope studies. However, Martin *et al.* (1995) measured much lower Nd concentrations and Nd-isotope ratios of marine barite that were significantly different from contemporaneous sea water, concluding that the samples were contaminated by an unidentified aeolian contaminant having a high Nd concentration and low  $^{143}\text{Nd}/^{144}\text{Nd}$  ratios. Thus, although marine barite could be a potential recorder of palaeo-sea water, Nd isotopes and rare earth elements (REE), its utility is complicated by the presence of various refractory sources (for example, rutile, anatase and zircon) that are not easily removed using standard chemical separation techniques (Martin *et al.*, 1995). More work on complete separation of marine barite from potential sources of contaminants or selective dissolution of this barite is needed in order to resolve these questions and to provide reliable measurements of trace components of marine barite.

Rare earth elements of hydrothermal barite along with co-existing hydrothermal minerals (for example, anhydrite, siderite and galena) could potentially reveal the REE content and

temperature of the parent hydrothermal fluid when combined with appropriate experimental data (Morgan & Wandless, 1980). When normalized to 'crustal' abundances, a linear function of the ionic radius of major cations to the ionic radius of REE exists in barite (Morgan & Wandless, 1980; Ehya, 2012) (Fig. 7).

### Strontium/barium elemental ratios

The Sr/Ba ratio of marine barite in the water column encompasses a wide range (e.g. Bertram & Cowen, 1997). In contrast, the Sr/Ba ratio in deep-sea marine barite has a much smaller range (Averyt & Paytan, 2003, 2007; van Beek *et al.*, 2003); this suggests preferential dissolution of Sr-rich barite in the water column and sediment. Reconstruction of sea water Sr concentrations from marine barite Sr/Ba was proposed by Averyt & Paytan (2003) using empirically determined



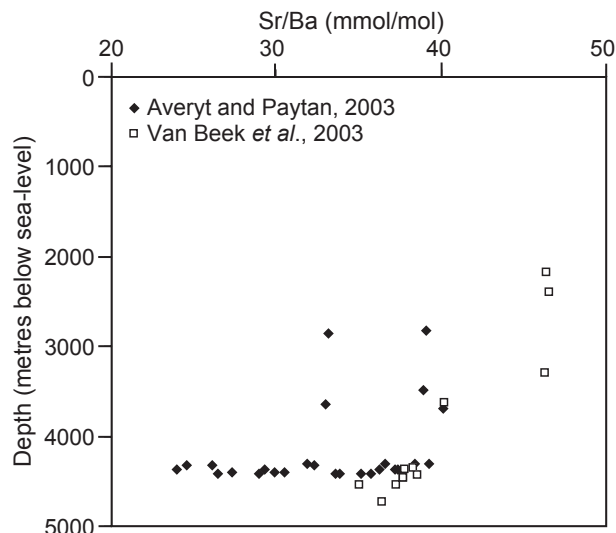
**Fig. 7.** The distribution of rare earth elements (REE) in barite (marine and low temperature hydrothermal) compared with sea water, data from Guichard *et al.* (1979) and Hein *et al.* (2007).

partition coefficients for Sr in marine barite. Averyt (2005) found fluctuations in Sr/Ba ratios of marine barite at the 100 kyr periodicity coherent with global records of sea-level change. These fluctuations might be related to the increased delivery of Sr at low sea-level stands. Furthermore, Averyt (2005) highlights the importance of further constraining the processes affecting Sr substitution in marine barite in order to be able to determine absolute sea water Sr concentrations from the  $[\text{Sr}/\text{Ba}]_{\text{barite}}$ .

Van Beek *et al.* (2003) alternatively suggested that the Sr/Ba ratio of marine barite in pelagic sediments could be used as a proxy for marine barite preservation, which these authors propose is a function of depth and sea water Ba concentrations. The preliminary work found that mean Sr/Ba ratios in several cores decreased with increasing water depth, potentially related to preferential dissolution of Sr-rich barite during settling to the deep-sea floor and/or at the sediment-water interface (van Beek *et al.*, 2003). Additionally, thermodynamic models suggest that the degree of barite saturation in the water column at these sites decreased with increasing water depth (van Beek *et al.*, 2003). If this preliminary work is confirmed, it has implications for the use of Sr content in marine barite for reconstructing changes in sea water Sr concentrations. However, combined results from van Beek *et al.* (2003) and Averyt & Paytan (2003) suggest that there is no strong relationship with water column depth (Fig. 8).

## BARITE AND OCEAN PRODUCTIVITY

The fraction of marine barite that is preserved in the sedimentary column is expected to be related directly to the amount of barite arriving at the sediment (for example, export production), the degree of undersaturation at the sediment-water interface and the exposure time of marine barite in the uppermost sediments to undersaturated conditions (Goldberg *et al.*, 1969; Dymond *et al.*, 1992; Francois *et al.*, 1995). Although little research has been done so far to quantitatively determine the various parameters influencing barite preservation (for example, deep water saturation state, sedimentation rates, sediment properties and barite rain rate to the sediment; Schenau *et al.*, 2001), existing data suggest that, at least in some pelagic settings of the present day ocean, the fraction of marine barite preserved could reach up to 30% of the rain rate (Paytan &



**Fig. 8.** A plot of the Sr/Ba molar ratio in coretop marine barite versus the depth of the coretop from sea-level. Data from Averyt & Paytan (2003) and van Beek *et al.* (2003).

Kastner, 1996). However, in other settings, such as in low productivity regions where barite production is low and sedimentation rates are also low, barite is exposed to undersaturated water for an extended time, resulting in very low preservation and little or no barite accumulation (i.e. Eagle *et al.*, 2003). Understanding the controls on barite preservation is important for quantitative reconstructions of export production across ocean basins in Earth's past (Eagle *et al.*, 2003). In oxic pelagic environments, it is expected that the fraction of marine barite that has not dissolved in the water column, at the sediment-water interface, or within the upper few centimetres of sediment will be preserved in the sedimentary record as long as pore fluids remain  $\text{SO}_4$ -rich (i.e. saturation with respect to barite is maintained). A detailed review on the use of marine barite for palaeoproductivity reconstruction, which includes a discussion on barite preservation, has been published by Paytan & Griffith (2007).

## CONCLUDING REMARKS

The high preservation potential of barite and its resistance to diagenetic alteration after burial in oxic settings make this authigenic mineral favourable for studies of the origin of formation fluids and past sea water chemistry. Geochemical analysis of elemental and isotopic composition of



barite can give invaluable information on the origin of the sample (hydrothermal, diagenetic, cold seep or marine). This research has led to dramatic changes in models describing the formation of massive barite deposits and the biogeochemical cycling of major elements in the ocean. Continued research on the modes of barite formation and its preservation will lead to advances in understanding its application in many areas including palaeoceanographic, hydrogeological, sedimentological and geochemical research. Some key areas for future work include: fully characterizing the mechanisms of precipitation of marine barite in the water column; understanding the role and potential significance of bacteria in barite precipitation; quantifying parameters controlling barite export and preservation in sediments and the influence of diagenesis on barite geochemistry; and investigating the utility of additional trace components in barite.

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