ABSTRACT

Barite can precipitate in microenvironments in the water column (marine barite), from supersaturated pore fluids at the oxic-anoxic boundary within marine sediments and where Ba-rich pore fluids are expelled and come into contact with sulfate-rich seawater (diagenetic barite), or from hydrothermal solutions (hydrothermal barite). Barite is relatively resistant to alteration after burial and has been used in paleoceanographic studies to reconstruct seawater chemistry and productivity through time. For such applications it is very important to determine the origin of the barite used, because both diagenetic and hydrothermal barite deposits may not accurately record the open-ocean contemporaneous seawater chemistry and productivity. We show here that it is possible to distinguish between the different types of barite by using Sr and S isotopes along with crystal morphology and size characteristics.

Keywords: barite, sulfur isotopes, strontium isotopes, paleoceanography.

INTRODUCTION

Barite in marine sediments is frequently used as a paleoproductivity proxy (Schmitz, 1987; Dymond et al., 1992; Gingele and Dahmke, 1994; Paytan et al., 1996a; Dean et al., 1997) as well as to reconstruct the seawater Sr isotope curve (Paytan et al., 1993; Martin et al., 1995), to determine the S isotope ratio of marine sulfate (Cecile et al., 1983; Goodfellow and Jonasson, 1984; Strauss, 1997; Paytan et al., 1996a; Dean et al., 1997) as well as to reconstruct seawater chemistry and productivity through time. For such applications it is very important to determine the origin of the barite used, because both diagenetic and hydrothermal barite deposits may not accurately record the open-ocean contemporaneous seawater chemistry and productivity. We show here that it is possible to distinguish between the different types of barite by using Sr and S isotopes along with crystal morphology and size characteristics.

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RESULTS AND DISCUSSION

The S and Sr isotope ratios of barite samples collected from different oceanic environments are given in Table 1 and Figure 1. Barite
samples cluster into three groups depending on their origin. The first very tight cluster (represented by one green diamond in Fig. 1) includes barite samples separated from core-top sediments in the Pacific, Atlantic, and Indian Oceans (30 samples) and barite crystals separated from sediment-trap samples (9 samples). These barite samples have precipitated from seawater (marine barite) and record present-day seawater Sr and S isotope ratios. These results, as determined in our laboratory, are consistent with previous studies (Elderfield et al., 1980; 14, Lonsdale (1979); 15, Lonsdale and Becker (1985); 16, Naehr et al. (2000); 17, Fu and Aharon (1997).

Because the seawater Sr and S isotope ratios have not remained constant over time, the combination of Sr and S isotope ratios represents contemporaneous seawater values that are different for different environmental conditions. Accordingly, the isotope ratios for any given barite sample of known age (independently derived) should be compared to the well-known seawater Sr and S isotope values (plotted as one point). Accordingly, the isotope values for all core-top and sediment-trap samples (excluding Juan de Fuca Ridge [JDFR] trap) (i.e., marine barite). Blue circles—diagnostic barite samples. Red circles—hydrothermal barite samples. Black dots within diamond—barite in <8 μm fraction of Juan de Fuca Ridge trap. Dotted lines pass through present-day seawater Sr and S isotope ratios. CDT—Canyon Diablo tuff (S isotope standard).

The second category (blue circles in Fig. 1) includes barite samples with S isotope ratios higher than contemporaneous seawater values. For example, a recent massive barite deposit dredged in Baja California (Lonsdale, 1979; Table 1) has a δ34S isotope value of 29.0‰, and an Sr isotope ratio of 0.708 701, clearly different from those expected for present-day seawater. These samples have precipitated from fluids that had some degree of sulfate loss due to bacterial sulfate reduction (diagenetic barite). Sulfate reduction leads to enrichment of the heavy S isotope (34S) in the residual sulfate in these fluids (Harrison and Thode, 1958). Barite precipitation may occur within the sedimentary column when Ba-rich fluids (from barite dissolution by the sulfate-reduction process or from continental sources) migrate by diffusion or advection toward sulfate-rich sediments in the sediment, typically at oxic-anoxic fronts (Dean and Schreiber, 1977; Kastner et al., 1990; Elderfield et al., 1990). Alternatively, barite could form at the sediment-water interface where these Ba-rich fluids are discharged through seeps or faults into sulfate-rich seawater, and barite saturation is exceeded (Torres et al., 1996a, 1996b; Naehr et al., 2000).

The Sr isotope ratio of these diagenetic barites depends on the Sr isotope ratio of the water at the site of precipitation. The Sr could have less 87Sr than the Sr that is typical of contemporaneous seawater if the pore fluids have been modified by Sr from less radiogenic sources like older marine sediments or the oceanic crust (as in San Clemente Basin and Monterey Canyon); the Sr could have more 87Sr relative to contemporaneous seawater if the pore-fluid Sr was derived from alteration of radiogenic terrigenous material in the sediment or meteoric water (Torres et al., 1996a; Kastner et al., 1990; Elderfield et al., 1990) (as in Peru Margin and Ocean Drilling Program Site 765C samples). A third group is composed of barite samples (red circles in Fig. 1) characterized by Sr isotope ratios that are between the modern seawater value and the Sr isotope ratio of pure (mantle derived) hydrothermal fluids (estimated to be 0.703 50; Albarède et al., 1981). These hydrothermal barite samples precipitate from fluids influenced by hydrothermal processes. Nonradiogenic Sr as well as Ba are leached from samples cluster into three groups depending on their origin. The first very tight cluster (represented by one green diamond in Fig. 1) includes barite samples separated from core-top sediments in the Pacific, Atlantic, and Indian Oceans (30 samples) and barite crystals separated from sediment-trap samples (9 samples). These barite samples have precipitated from seawater (marine barite) and record present-day seawater Sr and S isotope values (plotted as one point). Accordingly, the isotope values for all core-top and sediment-trap samples (excluding Juan de Fuca Ridge [JDFR] trap) (i.e., marine barite). Blue circles—diagnostic barite samples. Red circles—hydrothermal barite samples. Black dots within diamond—barite in <8 μm fraction of Juan de Fuca Ridge trap. Dotted lines pass through present-day seawater Sr and S isotope ratios. CDT—Canyon Diablo tuff (S isotope standard).

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most likely from hydrothermal solutions. However, in this sediment-covered ridge system, the fluids are expelled into marine-sediment sections where sulfate reduction takes place, depleting the pore-water sulfate from the light S isotope and resulting in barite with S isotope ratios slightly greater than seawater (Elsgaard et al., 1994).

In addition to the characteristic isotopic signatures of barite deposited in the different marine settings already described, the size and morphology of barite crystals formed by those different precipitation modes are distinct. Figure 2 shows SEM micrographs of typical barite crystals separated from the different depositional environments. Marine barite crystals precipitated in the water column and extracted from sediment-trap samples (including the <8 μm barite fraction from the Juan de Fuca Ridge black smoker) or from marine sediments that have not undergone extensive sulfate reduction are smaller than 5 μm and are typically ellipsoidal in shape (Fig. 2, A–C). Hydrothermal barite crystals are larger, 20–70 μm, and are typically precipitated as cross-cutting tabular crystals commonly forming rosettes (Fig. 2, D–F). The >8 μm barite crystals from the sediment trap above the Juan de Fuca Ridge, as expected, have morphological features typical of hydrothermal precipitates. Diagenetic barite crystals are also large (20–700 μm), flat, tabular-shaped crystals and appear as barite beds in the sedimentary column. Diagenetic barite crystals that precipitate at the sediment-water interface form mounds of highly porous barite with the layered appearance of platy crystals that form diamond-shaped clusters (Fig. 2, G–H).

CONCLUSIONS

On the basis of crystal size and morphology and the Sr and S isotope ratios of barite deposits, it is possible to distinguish between the depositional environments and thus the origin of this mineral if the age of the barite sample is independently determined. Careful examination of barite samples used for paleoceanographic studies would eliminate any questions with respect to the authenticity of marine barite origin and its fidelity in recording the seawater characteristics (productivity and/or chemistry).

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