Formation of modern and Paleozoic stratiform barite at cold methane seeps on continental margins

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ABSTRACT

Stratiform (bedded) Paleozoic barite occurs as large conformable beds within organic- and chert-rich sediments; the beds lack major sulfide minerals and are the largest and most economically significant barite deposits in the geologic record. Existing models for the origin of bedded barite fail to explain all their characteristics: the deposits display properties consistent with an exhalative origin involving fluid ascent to the seafloor, but they lack appreciable polymetallic sulfide minerals and the corresponding strontium isotopic composition to support a hydrothermal vent source. A new mechanism of barite formation, along structurally controlled sites of cold fluid seepage in continental margins, involves barite remobilization in organic-rich, highly reducing sediments, transport of barium-rich fluids, and barite precipitation at cold methane seeps. The lithologic and depositional framework of Paleozoic and cold seep barite, as well as morphological, textural, and chemical characteristics of the deposits, and associations with chemosymbiotic fauna, all support a cold seep origin for stratiform Paleozoic barite. This understanding is highly relevant to paleoceanographic and paleotectonic studies, as well as to economic geology.

Keywords: barite, Paleozoic deposits, sulfur isotopes, chemosynthetic fossils, cold seeps, strontium isotopes.

INTRODUCTION

Stratiform (or bedded) barite is the dominant source of industrial barite, commonly used as a weighting agent in drilling fluids by the oil and gas industry. Large Paleozoic deposits in Nevada, Arkansas, Mexico, south China, and elsewhere can be described as comprising meter-scale layers and lenses of barite conformably hosted within organic- and chert-rich sedimentary rocks and deficient in metal sulfides (Maynard and Okita, 1991). Understanding the origin of this stratiform barite can have a significant impact on the study of paleoceanography, paleotectonics, and economic geology; however, the mechanism leading to its formation remains controversial after a few decades of research (e.g., Papke, 1984). Proposed genetic mechanisms include precipitation in three settings: at or near low-temperature hydrothermal vents (e.g., Dubé, 1988; Poole, 1988); biogenically from sulfate-deficient ocean waters (e.g., Clark, 1988; Jewell, 2000); and from submarine discharge of fluids at continental margins (Hanor and Baria, 1977). Although Paleozoic deposits display features consistent with an exhalative origin, including localized fossil remains of chemosymbiotic organisms, they lack appreciable polymetallic sulfide to support a hydrothermal source.

Discoveries of massive barite deposits associated with nonhydrothermal methane seeps along present-day continental margins reflect barite remobilization in sulfate-depleted sediments, subsurface transport of Ba^{2+} by hydrotectonic processes, and barite reprecipitation at sites of cold fluid discharge on the seafloor (e.g., Torres et al., 1996a). Here we summarize the occurrence and characteristics of these modern deposits, which clearly support a cold seep origin for Paleozoic stratiform barite lacking polymetallic sulfides.

BARITE IN THE MODERN OCEAN

Marine barite has been recovered from pelagic, hydrothermal vent, and continental margin settings. The term ''biogenic barite'' is used to designate barite deposition in pelagic sediments underlying high-productivity waters, which are thought to result from biologically mediated precipitation of barium sulfate within the water column (e.g., Bishop, 1988; Dehairs et al., 1991; Paytan et al., 1993). Deposits formed by direct precipitation from a barium-enriched hydrothermal fluid are known as hydrothermal barite; they are restricted to the vicinity of seafloor venting and are commonly associated with anhydrite and polymetallic sulfides (e.g., Koski et al., 1985, 1988). During the past two decades, a third type of barite deposit has been documented along continental margins, in association with submarine venting of cold fluids enriched in hydrocarbons and barium (Fig. 1). The size and extent of these deposits of cold seep barite are significant. Barite pillars along the San Clemente fault can reach 10 m in height (Lonsdale, 1979), and local sites of barite deposition were observed along a 3 km survey of the fault (Torres et al., 2002). Similarly, observations on the Sea of Okhotsk documented massive barite deposits scattered along 3.5 km (Greinert et al., 2002). A 6-m-long core re-

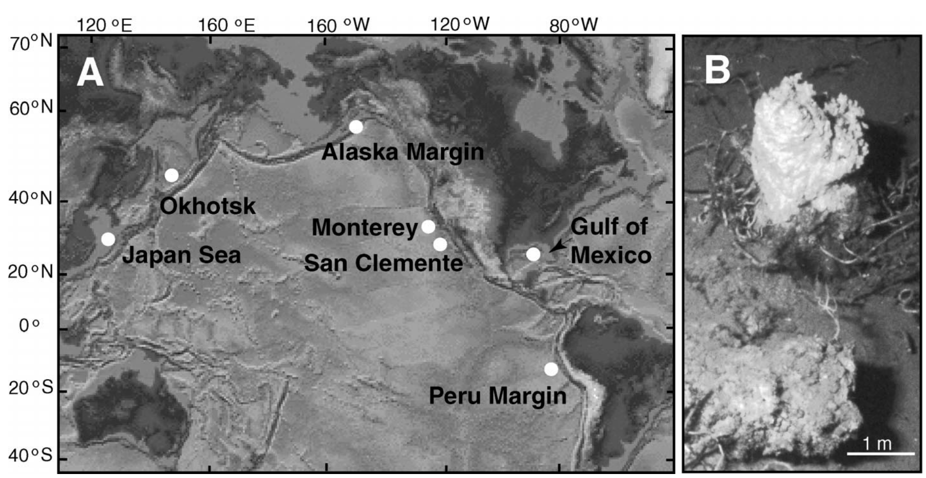

Figure 1. A: Locations of cold seep barite deposits. B: Barite columns (3 m high) on seafloor at sites of fluid seepage along San Clemente fault.

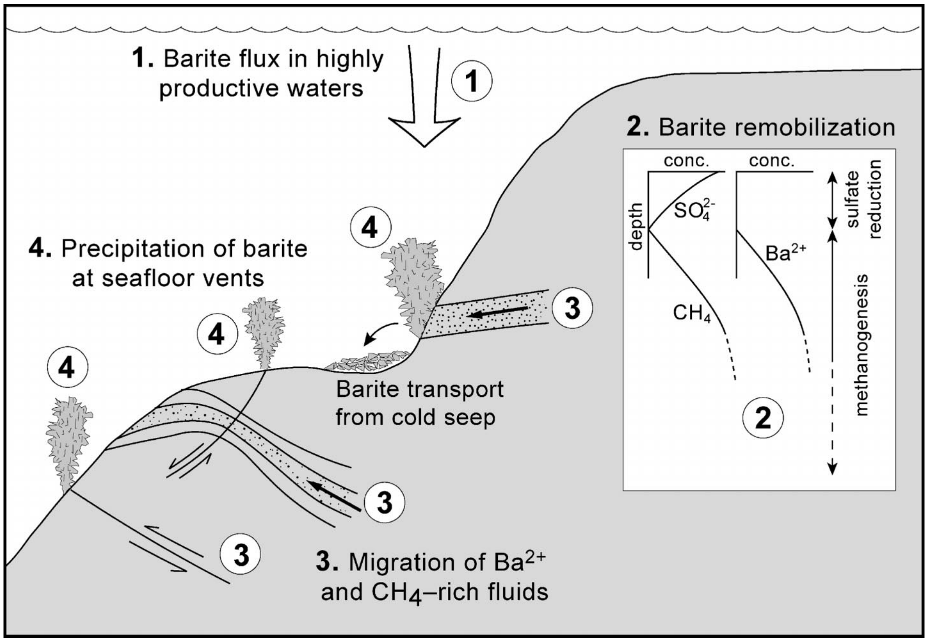

Figure 2. Processes leading to formation of cold seep barite. 1: Enhanced barium flux to sediments in high-productivity regions. 2: Remobilization of barite in zones of sulfate depletion. 3: Transport of fluids rich in methane and barium. 4: Precipitation of barite at cold methane seeps.

covered from this area consisted of intercalated diatomaceous mud with nearly pure finely crystalline barite in horizons to 1 m thick, in which Greinert et al. (2002) observed cemented tubeworms and clam valves of *Calyptogena*.

COLD SEEP MODEL

Biogenic barite accumulates beneath areas of high productivity in organic-rich, and commonly opal-rich, sediments. Upon burial, microbial degradation of organic carbon in these environments leads to methanogenesis, and pore-water sulfate is consumed by oxidation of both organic carbon and biogenic methane (e.g., Suess and Whiticar, 1988). In spite of its low solubility, barite dissolves under conditions of sulfate depletion, leading to high barium concentrations in pore fluids (e.g., Torres et al., 1996b), and thus coupling the methane, sulfur, and barium cycles (Dickens, 2001). Within continental margin sediments, prevalent fluid migration transports the chemically altered fluids, which upon discharge at the seafloor result in barite deposition at cold methane seeps (Fig. 2). We contend that massive barite deposits along structurally controlled sites of cold fluid seepage in continental margins represent modern analogues to stratiform, metal-deficient barite from the Paleozoic.

GEOLOGICAL EVIDENCE

Barite crystal morphology is controlled by the chemical and physical environment of precipitation, and is primarily a function of saturation state (Shikazono, 1994). Surface ocean waters are undersaturated with barite; and in both open ocean and anoxic basin waters, biogenic barite occurs as poorly crystalline particles, with a predominant crystal size of 10^{-4} to 10^{-3} mm (e.g., Bertram and Cowen, 1977; Paytan et al., 1993; Falkner et al., 1991). Cold seep barite ranges from rhomboid crystals (Greinert et al., 2002) indicative of low supersaturation, to dendritic and concentric growth patterns (Fu et al., 1994; Aquilina et al., 1997; Torres et al., 1996a, 2002) that characterize precipitation from highly supersaturated solutions. These well-defined crystalline structures range in size from 0.01 to 0.3 mm (Fig. 3). Paleozoic stratiform barite also has well-defined crystals, generally ranging from 0.01 to 0.15 mm (Hanor and Baria, 1977; Dubé, 1988; Graber and Chafetz, 1990; Wang and Li, 1991).

Barite textures that characterize the modern cold seep deposits (e.g., Torres et al., 1996a; Greinert et al., 2002) are also observed in Paleozoic stratiform barite, including rosettes, nodular, laminated, and finely crystalline deposits, as well as turbiditic barite sandstones and conglomerates (e.g., Poole, 1988; Poole et al., 1991; Wang and Li., 1991). Modern cold seep barites are very porous; similarly, microscopic vugs in Nevada barite are common enough to significantly decrease its specific gravity (Papke, 1984).

Barite distributions of both modern cold seep and Paleozoic deposits are limited to stratigraphically defined areas and are often associated with faults or are adjacent to steep slopes. A tectonic setting, similar to that of modern sites of fluid seepage along subduction zones, has been postulated for some Antler-age barite deposits of Nevada (Dubé, 1988). The depositional settings proposed for Paleozoic barite in central Sonora, Mexico (Poole et al., 1991), and in Arkansas (Hanor and Baria, 1977), are remarkably similar to the modern barite setting along the San Clemente fault (Torres et al., 2002).

Host-rock lithology of modern cold seep barite is analogous to that of the Paleozoic deposits, which occur within organic-rich shales that may contain chert and phosphorite. Large carbon fluxes, common along ocean margins where modern cold seep barite forms, are needed to support the barium flux to the sediments, as well as barite remobilization and Ba^{2+} transport within chemically reduced pore fluids (Fig. 2). Along the Peru margin, cold seep barite occurs within extremely organic-rich facies associated with coastal upwelling (e.g., Reimers and Suess, 1983), and is associated with aphanitic carbonate, phosphorite, mudstone, and chert (Kulm et al., 1984). Other cold seep barite localities that show a high organic-carbon flux include the California margin, Sea of Okhotsk, and Gulf of Mexico. Cold seep barite cooccurs with minor amounts of detrital silicates and pyrite, whereas the amount of carbonate varies from minor (San Clemente sites) to very abundant (Peru margin and Sea of Okhotsk). Such mineral assemblages are similar to those observed in Paleozoic barite deposits, which also contain abundant organic carbon.

Paleontologic data also support a cold seep origin for the Paleozoic barite. *Dzieduszyckia* brachiopod valve impressions in Devonian barite from Nevada and Sonora reflect an indigenous fauna related to seafloor vents (Fig. 3). In addition, these deposits contain well-preserved tubeworm remains, which are strictly limited to the barite bodies (Dubé, 1988; Poole, 1988; Poole et al., 1991). At modern cold seeps, the discharging fluids are highly enriched in methane and other reduced chemical species that support chemosynthetic-based communities (e.g., Southward, 1989). All cold seep barite deposits described to date are associated with macroinvertebrate communities of tubeworms and vesicomyid clams. These chemosymbiotic organisms are not found in hemipelagic or pelagic settings, because they are dependent on the localized discharge of reducing fluids at the seafloor (Southward, 1989).

GEOCHEMICAL EVIDENCE

Strontium isotope data from Paleozoic barite were used by Maynard et al. (1995) to dis-

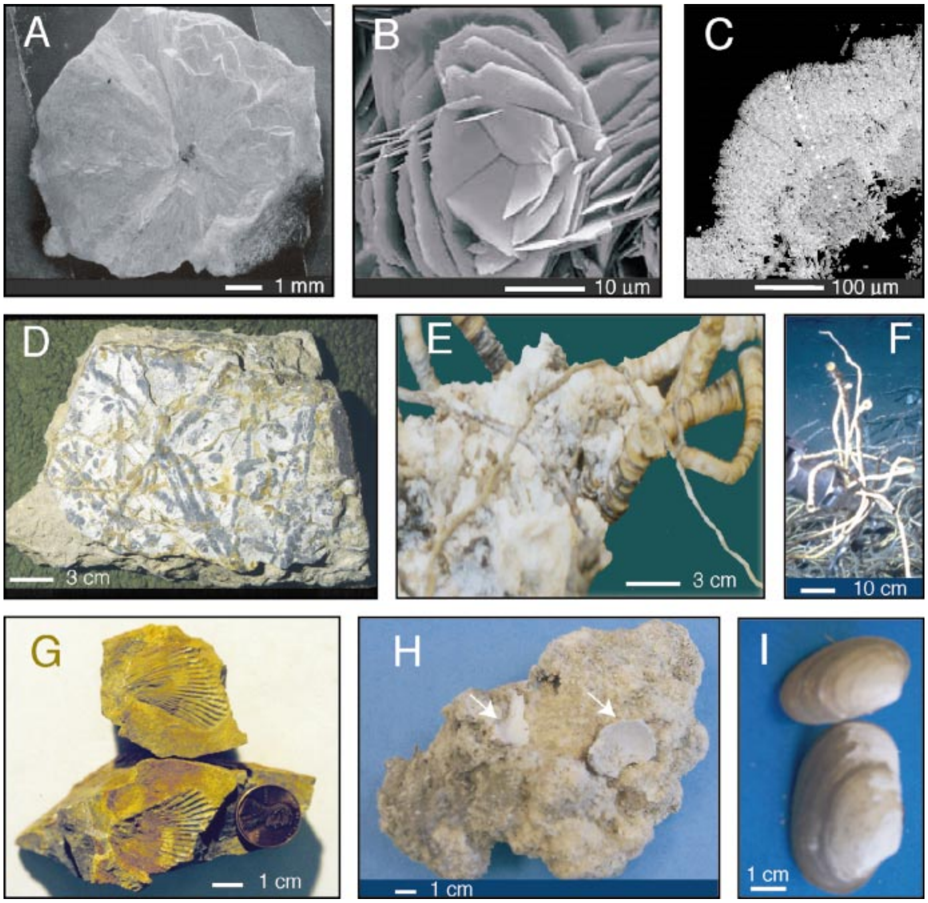

Figure 3. Comparison of Paleozoic and modern barites. Scanning electron microscope (SEM) image of rosette from Nevada deposits (A), which is similar to modern cold seep barite from Peru margin, illustrated by SEM (B) and electron microprobe (C) images. Fossil tubeworm in Devonian barite from Nevada (D), compared with modern barite from San Clemente fault (E). Modern deposits are associated with large tubeworm colonies (F). Molds of brachiopod *Dzieduszyckia* in massive barite from Nevada (G), and modern barite from San Clemente: arrows point to *Calyptogena* valves within its matrix (H). *Calyptogena* clams from San Clemente cold seeps (I).

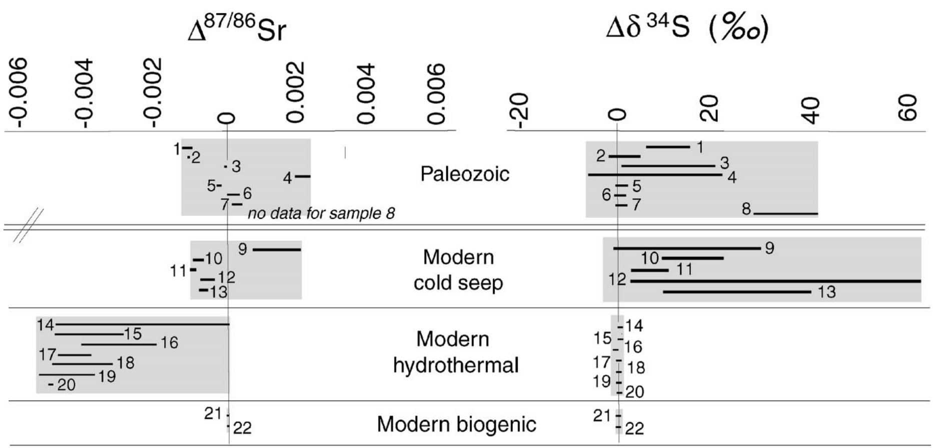

Figure 4. $^{87}Sr/^{86}Sr$ and $\delta^{34}S$ composition of barite expressed as difference from coeval seawater (Δ). Paleozoic deposits originating in continental margin setting include barite from Jiangnan (1) and Qinling (2) in China; East Northumberland Canyon (3), Argenta (4), and Queen Lode (5) in Nevada; Fancy Hills (6) and Millchem deposits (7) in Arkansas; and (8) Jixi deposits from South China. $^{87}Sr/^{86}Sr$ data for Paleozoic deposits were compiled by Maynard et al. (1995); and $\delta^{34}S$ data were compiled by Jewell (2000), Laney (1980), and Wang et al. (1993). $^{87}Sr/^{86}Sr$ and $\delta^{34}S$ data for modern cold seep barite from Peru margin (9) are from Aquilina et al. (1997) and Paytan et al. (2002); San Clemente fault (10) data are from Torres et al. (2002); Monterey Canyon (11) data are from Naehr et al. (2000); Sea of Okhotsk (12) data are from Greinert et al. (2002); and Gulf of Mexico (13) data are from Paytan et al. (2002). Data for hydrothermal barite from Juan de Fuca Ridge (14–17); Mid-Atlantic Ridge (18), Mariana backarc (19), and East Pacific Rise (20) are from Paytan et al. (2002). Data for modern biogenic barite in core tops (21) and sediment traps (22) are from Paytan et al. (1993).

tinguish continental-margin barite from cratonic-rift deposits. The $\Delta^{87}Sr/^{86}Sr$ values (Δ defined as the deviation from contemporaneous seawater values) of Paleozoic continental-margin barite vary by as much as ± 0.002 (Fig. 4). Paytan et al. (1993) showed that biogenic barite reliably records both present and past variations in seawater strontium compositions within the analytical precision of the measurements (± 0.000024). These relationships show that Paleozoic barite did not form by biogenic precipitation in the water column. Hydrothermal barite is highly depleted in ^{87}Sr ($\Delta^{87}Sr/^{86}Sr \leq -0.006$, Fig. 4), reflecting hydrothermal fluid interaction with oceanic basement (Paytan et al., 2002). The Paleozoic barite is not so depleted in the heavy strontium isotope, thus precluding a hydrothermal origin for the ancient deposits. The isotopic compositions of fluids discharging at cold seeps, however, are significantly different from that of the overlying seawater, and have $\Delta^{87}Sr/^{86}Sr$ values that are of the same magnitude as those reported for the Paleozoic deposits (Fig. 4). The $\Delta^{87}Sr/^{86}Sr$ of cold seep barite reflects the interaction of fluids with various types of rock and sediment before venting at the seafloor (e.g., Naehr et al., 2000).

Sulfur isotope data support the $^{87}Sr/^{86}Sr$ observations. Paleozoic barite shows a wide range of values, with $\Delta\delta^{34}S$ similar in magnitude to those of modern cold seep deposits (Fig. 4). The enrichment in ^{34}S of modern cold seep barite reflects a component of isotopically heavy sulfate derived from microbial processes in anoxic sediments or at cold seep sites (e.g., Naehr et al., 2000; Greinert et al., 2002). In contrast, biogenic barite accurately records the seawater composition (Paytan et al., 1998), and barite from modern hydrothermal settings does not deviate from seawater values by more than 2‰.

SUMMARY AND IMPLICATIONS

Tectonic and depositional considerations, in addition to textural, faunal, and geochemical associations, provide compelling evidence that the extensive deposits of barite at cold methane seeps on continental margins represent modern analogues to stratiform, metal-deficient barite from the Paleozoic. Thus the ancient deposits reflect remobilization of barite in sulfate-depleted, methane-rich sediments, and transport of methane- and barium-enriched fluids by hydrotectonic processes. This genetic mechanism satisfies the conundrums facing biogenic and hydrothermal scenarios of massive barite deposition, and provides a consistent model to aid reconstruction of tectonic and oceanographic conditions operating in the Paleozoic. For example, our genetic model indicates that the $\Delta\delta^{34}S$ values of the Paleozoic stratiform deposits reflect mixing of fluids affected by microbial processes in anoxic sediments or at cold methane seeps on the seafloor, rather than a change of $\delta^{34}S_{SO_4}$ in the water column. Furthermore, the massive Paleozoic barite deposits must represent large-scale submarine venting of not only barium, but also of methane, which would have affected the Paleozoic carbon cycle, and could perhaps have modified ancient climate.

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