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Geochemical characteristics of the barite deposits at cold seeps from the northern Gulf of Mexico continental slope

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ABSTRACT

Although less common than the occurrence of authigenic carbonate, barite has been observed frequently at cold seeps on continental margins worldwide. It is understood that barite forms by the interaction of barium-rich and sulfate-free seeping fluids with dissolved sulfate of pore water near the seafloor, but questions remain about the geochemical processes and mode(s) of the barite formation. Here, we report geochemical characteristics of barite deposits at 11 cold seep locations from the northern Gulf of Mexico continental slope. Samples from these sites of fluid and gas expulsion provide environmental information on barite formation. Seafloor observations and samples acquired indicate that barites occur as chimneys, cones, crusts, irregular mound-like buildups up to 2-meters high, and as a material disseminated in host sediment. Most barite samples are white-to-gray and usually have a porous fabric and layered internal structure. Mineralogically, samples of barite may contain a significant amounts of carbonate minerals, such as calcite and dolomite, but aragonite is absent in all samples analyzed in this study. Negative $\delta^{13}C$ values (as low as −46.4‰ V-PDB) of the associated carbonates strongly suggests that methane is the primary carbon source. The $\delta^{34}S$ and $\delta^{18}O$ values of the barites have large variations, ranging from 18‰ to 80.4‰ V-CDT, and 7.5‰ to 26.7‰ V-SMOW, respectively. On $\delta^{34}S$ versus $\delta^{18}O$ plots, many barite deposits show a linear trend that projects down toward the isotopic composition of seawater sulfate. The trend suggests that barite formed from seawater sulfate that has been isotopically modified to varying degrees by biological sulfate reduction. The $\delta^{34}S/\delta^{18}O$ ratios vary between 2.4 and 4.1. The variations are interpreted to reflect local controls on the flux of barium-rich seep fluids, changes in the rate of bacterial sulfate reduction, and/or the openness of pore fluid system. The $^{87}Sr/^{86}Sr$ values of the barites indicate that within-site variation is small (<0.00026) although there is a considerable range of Sr isotopic variations across multiple geographic sites (from 0.70782 to 0.71005). The observed variations probably reflect local controls on the source(s) and diagenetic evolution of seeping fluids. Strong deviation of the Sr isotope ratios of barites from coeval seawater ($^{87}Sr/^{86}Sr = 0.70917$) is interpreted as the modification of the strontium from less radiogenic sources like older marine sediments or more radiogenic terrigenous material such as basinal brine and/or meteoric water. The new results further offer a better understanding of the origin and geochemical history of barite deposits that occur in geological record on the basis of $\delta^{34}S$ and $\delta^{18}O$ compositions.

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1. Introduction

The anaerobic oxidation of methane and sulfate reduction are the dominant biogeochemical processes at cold seeps in marine settings worldwide (e.g. Boetius et al., 2000). These processes lead to an increase of carbonate alkalinity by the production of bicarbonate [HCO_3^-]:

$$CH_4 + SO_4^{2-} \leftrightarrow HCO_3^- + HS^- + H_2O \quad (1)$$

favoring the precipitation of authigenic carbonates:

$$2HCO_3^- + Ca^{2+} \leftrightarrow CaCO_3 + CO_2 + H_2O \quad (2)$$

However, depending on the chemistry of cold seep fluids, mineral species other than carbonates, such as barite, may form on the seafloor if the fluids expelled contain high amounts of dissolved barium (e.g. Aloisi et al., 2004; Aquilina et al., 1997; Castellini et al., 2006; Greinert et al., 2002; Hanor and Mercer, 2010; McQuay et al., 2008; Torres et al., 1996a, b, 2002). It is known that barite deposits form by the interaction of barium-rich and sulfate-free seeping fluids with dissolved sulfate at relatively low-to-moderate flux fluid expulsion regimes (Aloisi et al., 2004; Roberts and Carney, 1997):

$$Ba^{2+} + SO_4^{2-} \leftrightarrow BaSO_4 \quad (3)$$

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Seep-related barites were first discovered on the California margin at the San Clemente Fault Zone in 1979 (Lonsdale, 1979), although they were thought to be hydrothermally-related at the time. Since then, seep-related barites have been found in other parts of the world's oceans, for example, the Alaska margin (Suess et al., 1998), the Gulf of Mexico (Castellini et al., 2006; Fu and Aharon, 1997; Fu et al., 1994; Joye et al., 2005; Roberts and Carney, 1997), the Peru Margin (Aquilina et al., 1997; Torres et al., 1996a), the Sea of Japan (Torres et al., 1996b), the Monterey Canyon (Naehr et al., 2000), the Sea of Okhotsk (Greinert et al., 2002), Blake Ridge (Snyder et al., 2007), and the Southern California Continental Borderland (Hein et al., 2007). Such barite deposits can be quite large. For instance, seafloor observations illustrate that barite build-ups up to 10 m high were scattered over the seafloor along a 3.5 km long track from the Sea of Okhotsk with several single barite blocks larger than 40 cm in diameter (Greinert et al., 2002). Barite chimneys in the San Clemente Fault Zone reach up to 10 m in height (Lonsdale, 1979), and sites of barite deposition were observed over 3 km along the fault (Torres et al., 2002). These observations indicate that barite deposition might be an important process along many continental margins and may have affected the global marine barium cycle in the geological past (e.g. Castellini et al., 2006; Dickens, 2001; Dickens et al., 2003; McQuay et al., 2008; Snyder et al., 2007; Torres et al., 1996a,b, 2002, 2003).

Although the precipitation of seep-related barite deposits is now known to form where barium-enriched fluids discharge at the seafloor, questions remain about the characteristics of such barites and geochemical processes that control their formation. Both sulfur (S) and oxygen (O) isotopes of barite have been used as indicators of the origin and geochemical history of the sulfate associated with precipitation of barite (e.g. Claypool et al., 1980). In addition, the $\delta^{34}S/\delta^{18}O$ ratios of barite serve as a promising tool for assessing the variability and diversity of sulfate reduction during the precipitation of barite (cf. Aharon and Fu, 2000). However, studies that include both $\delta^{34}S$ and $\delta^{18}O$ values of seep-related barites are rare, and there is disagreement on explanation of the data. For example, Aquilina et al. (1997) reported a $\delta^{34}S/\delta^{18}O$ ratio of 1.5 in barite from cold seeps at the convergent margin of Peru. The low $\delta^{34}S/\delta^{18}O$ ratio was explained to be caused by an ^{18}O enrichment on SO_4^{2-} resulting from equilibrium isotope exchange between SO_4^{2-}—H_2O at high temperature (>100 °C), although there is no evidence of heat anomalies in their study area. Furthermore, seep-related barites from the Gulf of Mexico and the Sea of Okhotsk have a $\delta^{34}S/\delta^{18}O$ ratio between 1.0 and 5.3 (cf. Fu and Aharon, 1997; Greinert et al., 2002), but no explanation for their developments were given.

The source of the barium in the seeping fluids is still controversial (see Judd and Hovland 2007 and references therein). Fu et al. (1994) suggested a link with underlying salt deposits. Greinert et al. (2002) proposed that barium may come from a depth of 900 m to 1800 m below seabed in the Derugin Basin. Similarly, remobilization of pelagic barite is suggested as the main source for elevated dissolved barium in the shallow subsurface of the seafloor (Torres et al., 1996a, 2002). The authors suggested that biogenic $BaSO_4$ was remobilized by sulfate depletion, coupled with a low-temperature hydrodynamic regime of fluid flow through the sediments to the seafloor. Strontium (Sr) isotopes of the barite are excellent tracers for barium-bearing fluid sources and transport history of barium in deposits (e.g. Paytan et al., 2002).

Here, we present a geochemical study of the barite deposits from 11 cold seeps from the northern Gulf of Mexico (GOM) continental slope. The barite samples were collected from early 1990s to 2007 at water depths between 510 m and 2230 m (Table S1; Fig. 1). The barites were analyzed using a combination of petrography, mineralogy, and sulfur, oxygen, and strontium isotopes. This study aims at creating a first-order assessment of precipitation processes and sources of sulfate and barium in barite at cold seeps of the modern GOM continental slope.

2. Geological setting and sampling

The northern GOM continental slope is characterized by numerous ridges, domes, and basins resulting from the interplay between intense periods of sedimentation, largely at times of fall-to-low sea

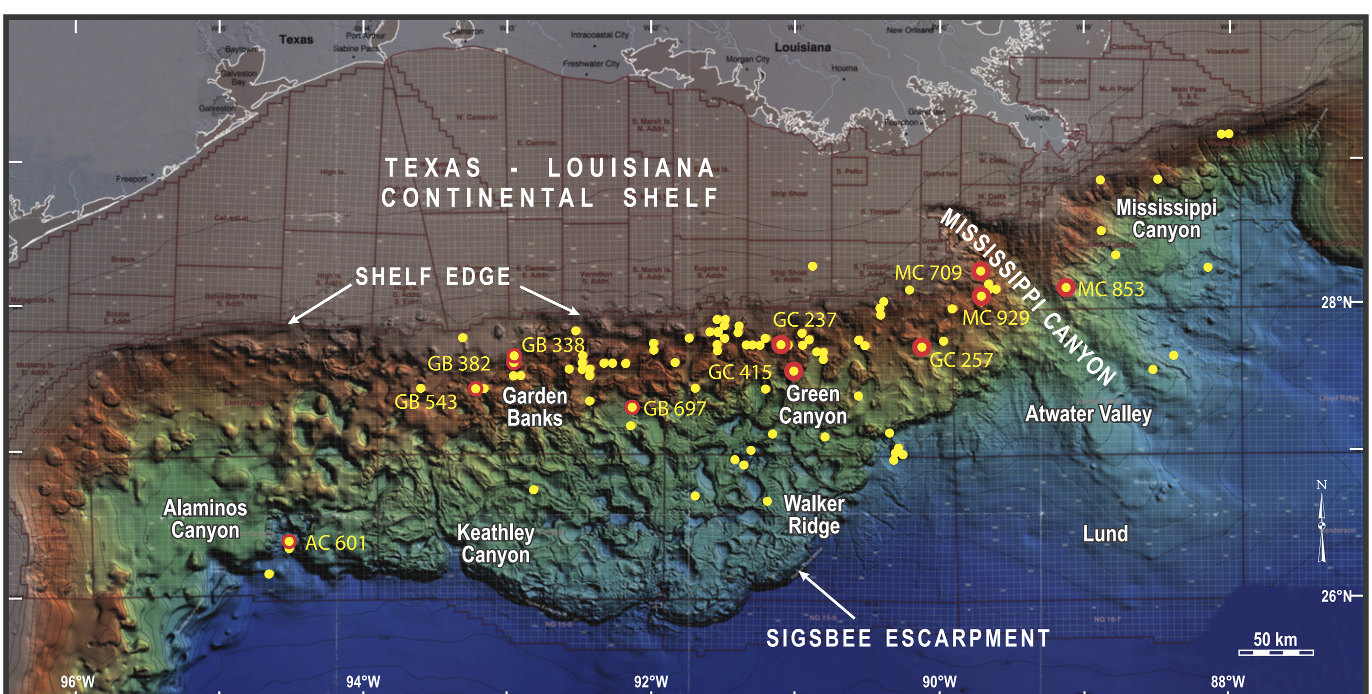

Fig. 1. Multibeam bathymetric image of the northern Gulf of Mexico showing the locations of all hydrocarbon seeps that have been confirmed by DSV and ROV dives (yellow dots). The locations of the barite samples in this study are illustrated (red circles).