



## Rare earth elements of seep carbonates: Indication for redox variations and microbiological processes at modern seep sites

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### ABSTRACT

At marine seeps, methane is microbially oxidized resulting in the precipitation of carbonates close to the seafloor. Methane oxidation leads to sulfate depletion in sediment pore water, which induces a change in redox conditions. Rare earth element (REE) patterns of authigenic carbonate phases collected from modern seeps of the Gulf of Mexico, the Black Sea, and the Congo Fan were analyzed. Different carbonate minerals including aragonite and calcite with different crystal habits have been selected for analysis. Total REE content ( $\Sigma$ REE) of seep carbonates varies widely, from 0.1 ppm to 42.5 ppm, but a common trend is that the  $\Sigma$ REE in microcrystalline phases is higher than that of the associated later phases including micospar, sparite and blocky cement, suggesting that  $\Sigma$ REE may be a function of diagenesis. The shale-normalized REE patterns of the seep carbonates often show different Ce anomalies even in samples from a specific site, suggesting that the formation conditions of seep carbonates are variable and complex. Overall, our results show that apart from anoxic, oxic conditions are at least temporarily common in seep environments.

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### 1. Introduction

Methane is partially bound in gas hydrates in the subsurface seafloor within the gas hydrate stability zone (Chen and Cathles, 2003; Chen et al., 2004, 2005; Chi et al., 2006; Huang et al., 2006; Yang et al., 2006; Wang et al., 2006). Upon seepage, methane is partially oxidized to bicarbonate, resulting in the deposition of carbonate minerals due to the admixture of seawater-derived calcium and magnesium close to the seafloor. This oxidation is performed by the combined metabolisms of methane oxidizing archaea (MOA) and sulfate reducing bacteria (SRB; Peckmann and Thiel, 2004). Thereby, sulfate in pore waters is reduced to hydrogen sulfide, which may lead to the formation of iron sulfides (Valentine and Reeburgh, 2000; Lin et al., 2006). As a consequence of sulfate-dependant methane oxidation, redox conditions in the sediment at seeps change significantly.

Seafloor observations at seeps reveal that chemical and physical parameters, such as fluid flux of gas and water, temperature, thermal diffusivity, pH, alkalinity, and element concentrations (e.g., Li, Ca, Mg, B, Cl, S) are highly variable with time and space (Linke et al., 1994; Tryon et al., 1999, 2001, 2002; Washburn et al., 2001; Carson et al., 2003; Leifer et al., 2004; Tryon and Brown, 2004; MacDonald et al., 2005; Leifer and Boles, 2005; Brown et al., 2005; Yang et al., 2006; Vardaro et al., 2006; Oung et al., 2006; Chuang et al., 2006, 2010; Chao and You, 2006; Chen and Tseng, 2006; Birgel et al., 2011; Lim et al., 2011). However, up to now, it is difficult to trace redox variations induced by microbial processes at recent and ancient seep sites.

REE exhibit generally similar geochemical behavior. In an anoxic environment, Ce occurs as  $Ce^{3+}$  like other REE elements, whereas under oxic conditions, the soluble  $Ce^{3+}$  is oxidized to insoluble  $Ce^{4+}$  (De et al., 1988; German and Elderfield, 1989). This behavior can result in a marked fractionation of REE. Therefore, Ce anomalies of authigenic mineral phases are an effective indicator of redox variations (McArthur and Walsh, 1984; Wright et al., 1987; German and Elderfield, 1990; Chen et al., 2003; Shields and Webb, 2004; Feng et al., 2008, 2009a,b, 2010; Birgel et al., 2011).

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Aragonite, calcite, and dolomite are common authigenic minerals that precipitate at cold seeps. They have the potential to preserve primary REE signatures, reflecting the chemical environment during precipitation. In order to test the potential of REE as palaeoenvironmental indicators at seeps, we analyzed REE patterns of modern seep carbonates.

## 2. Samples and analytical methods

Carbonate samples were collected from seep sites in the Gulf of Mexico (GOM), the Congo Fan, and the Black Sea (Fig. 1). All samples were crushed to small pieces, and thoroughly cleaned in an ultrasonic bath using double distilled de-ionized water. Microcrystalline phases, later cements, and bivalve shells were selected under a microscope, and then were milled to powder passing through a sieve with a mesh size of 200 using an agate mortar and pestle. The XRD analyses show that all seep carbonates mainly consist of calcite and aragonite with few detrital minerals (Table 1).

About 0.5 g of sample powder was treated with 50 ml of 5% HNO<sub>3</sub> in a centrifuge tube for 3 h to separate the carbonate phase from the residue. At the same time, 2500 ng of rhodium was added as an internal standard for calculating the concentration of the REE in the 5% HNO<sub>3</sub> solution. 5 ml of this solution were diluted 10 times for analysis with a VG Plasma-Quad Excell ICP-MS at the University of Hong Kong. Precision of the REE analysis was checked by multiple analyses of carbonate standard samples CAL-S. The ICP multi-element standard solution from AccuStandard Inc. (USA) was used to prepare a variety of calibration solutions. 100 ng/ml single standard solution: Ba and Pr were used to correct the interference of BaO<sup>+</sup> on Eu and PrO<sup>+</sup> on Gd, respectively. The average standard deviations are less than 10%, and average relative standard deviations are better than 5%. For the detail of ICP-MS analysis see Qi and Gregoire (2000), Chen et al. (2003, 2005), and Qi et al. (2005). The Ce/Ce\* denotes  $3Ce_N / (2La_N + Nd_N)$ , Eu/Eu\* denotes  $Eu_N / (Sm_N \times Gd_N)^{0.5}$ , where N refers to normalization of concentrations against the standard Post Archean Australian Shale (McLennan, 1989).

## 3. Results and discussion

### 3.1. Seep carbonate of the Gulf of Mexico

The GOM seep carbonates were collected from the Bush Hill site, Alaminos Canyon, and Green Canyon Block 238 (Table 1). The Bush Hill (BH) seep carbonates were collected in 1997 and 1998 during the Johnson-Sea-Link I manned submersible dives 2904, 4061 and 4063 using the robot arm of the submersible at a water depth of ~540 m. The bottom water temperature was ~7 °C. The Alaminos Canyon (AC) seep carbonates were collected during submersible cruise with DSV Alvin in 1990. Water depth of the site was 2200 m. Seep carbonate S-4 from Green Canyon Block 238 (GC 238) were sampled during dive 4398 using the robot arm of Johnson-Sea-Link II submersible in 2002. The temperature was ~6 °C and the water depth was ~700 m. All seep carbonates were slabs and blocks, displaying gray white or gray yellow colors.

The BH seep carbonates and the AC seep carbonates mainly consist of bioclasts and a matrix of microcrystalline and acicular aragonite, with fossilized tube worms, foraminifera, and bivalve shells materials. The S-4 seep carbonate mainly consists of microcrystalline calcite with minor foraminifera. The δ<sup>13</sup>C values of the BH and AC carbonates range from -29.4‰ to -15.1‰ and -33.9‰ to -20.4‰, respectively, clearly indicating that the carbon was derived from hydrocarbons (Feng et al., 2008, 2009a). The δ<sup>13</sup>C values of the S-4 carbonates are lower ranging from -52.3‰ to -52.0‰, suggesting that their carbon was derived mainly from biogenic methane (Chen et al., 2005).

The ΣREE of the microcrystalline matrix samples vary from 7.1 ppm to 20.8 ppm, these values are much higher than those of cement samples and bivalve shells, which are from 0.4 ppm to 3.1 ppm (Table 2). The ΣREE is exclusively from carbonate phases with no contribution from detrital minerals that usually contain much higher ΣREE. Therefore, the ΣREE in samples of microcrystalline matrix, in cement, and bivalve shells suggest that the ΣREE of seep carbonates is mainly a function of phases.

Fig. 2 shows the shale-normalized REE patterns of the BH seep carbonate samples. The microcrystalline matrix and the cement samples of the BH-C and BH-D show pronounced negative Ce anomalies, suggesting oxic formation conditions. The microcrystalline matrix, the cement, and the bivalve shell samples of other seep carbonates, however, all show no or weak Ce anomalies, indicating anoxic formation conditions. This pattern implies that redox variations in the Bush Hill sampling area may reflect differences in sampling sites rather than different carbonate phases.

The shale-normalized REE pattern of the microcrystalline matrix of the S-4 seep carbonate from GC238 shows no negative Ce anomaly (Fig. 2c), indicating reducing formation conditions. The shale-normalized REE patterns of the microcrystalline matrix, cement, and bivalve shell samples of the AC seep carbonate, however, all show pronounced negative Ce anomalies (Fig. 2c), suggesting that the AC seep carbonates were precipitated under oxic formation conditions.

All seep carbonates from the GOM were collected with the robot arm of the Johnson-Sea-Link submersible using a clamshell sampler. The clamshell scoop collected a ~30 cm swath of sediment to a depth of approximately 10 cm, revealing that the carbonate samples were originally located on or near the seafloor. The GOM seep carbonates, collected from upper slope (Bush Hill) to the lower slope (Alaminos Canyon), show a spectrum from negative Ce to no Ce anomalies. This variability in the GOM seep carbonates indicates that the redox conditions varied between sampling areas, but also between individual sampling sites in a specific area.

Similarly, the compositions of seeping gas sampled at the Bush Hill site over the last decade varied between sampling sites,

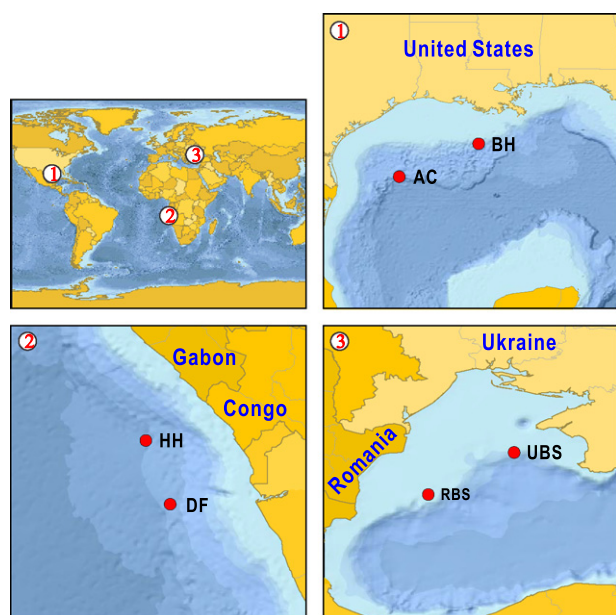


Fig. 1. Global map showing the study areas: (1) Gulf of Mexico, (2) Congo Fan, and (3) Black Sea. BH, Bush Hill; AC, Alaminos Canyon; HH, Hydrate Hole; DF, Diapir Field; RBS, Romanian Shelf of the Black Sea, UBS, Ukrainian Slope of the Black Sea.

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