



## Research paper

# Tracing the composition, fluid source and formation conditions of the methane-derived authigenic carbonates in the Gulf of Cadiz with rare earth elements and stable isotopes



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## ABSTRACT

The mineral composition, stable carbon and oxygen isotopes, and rare earth element (REE) concentrations in methane-derived authigenic carbonates collected from the Gulf of Cadiz were used to trace fluid sources and examine the controlling factors on REE composition during carbonate formation. These authigenic carbonate samples are composed of a detrital fraction (mainly quartz and clay) cemented by authigenic carbonate minerals: aragonite and Mg-calcite, pure Mg-calcite, or dolomite and Mg-calcite. The  $\delta^{13}\text{C}$  values of the whole rock samples vary between  $-45.8\text{‰}$  and  $-9.7\text{‰}$  VPDB and  $\delta^{18}\text{O}$  values range from  $3.7\text{‰}$  to  $6.9\text{‰}$  VPDB. The  $\delta^{13}\text{C}$  values are indicative of a methane-derived source for these carbonates, most likely resulting from thermogenic gas or a mixture of thermogenic and biogenic gas. The total REE content ( $\Sigma\text{REE}$ ) of these authigenic carbonate minerals range from 13 to 31 ppm; all but four of the subsamples are lower than a typical marine carbonates ( $\sim 28$  ppm). This suggests that the REE composition of methane-derived authigenic carbonates is controlled primarily by the methane-rich fluids. The results also show that the REE contents in carbonate mineral subsamples containing dolomite and Mg-calcite is higher than those subsamples with aragonite, suggesting that the authigenic mineral composition and the formation environment are important factors. The shale-normalized REE patterns of the seep carbonates show no or slightly positive Ce anomalies, suggesting that the formation of these seep carbonates occurred under anoxic conditions and associated with rapid fluid seepage. The correlation results of  $\text{Ce}/\text{Ce}^*$  and  $\text{La}_\text{N}/\text{Sm}_\text{N}$ ,  $\text{Ce}/\text{Ce}^*$  and  $\text{Dy}_\text{N}/\text{Sm}_\text{N}$ , and  $\text{Ce}/\text{Ce}^*$  and  $\Sigma\text{REE}$  suggest that the REE characteristics of most seep carbonate samples preserve the original redox conditions of their formation. Late diagenesis or post-oxidation of the samples by their exhumation from the sediments into seawater has little effect on REEs. Therefore, it can be assumed these methane-derived authigenic carbonates represent primary carbonate phases; they have not undergone significant diagenesis and their geochemical and isotopic signatures mainly reflect their formation processes.

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## 1. Introduction

Cold seeps are ubiquitous features of many active and passive continental margins, where hydrocarbon-rich fluids and gases

migrate to the shallow subsurface environment and emerge at the sediment–water interface (Roberts et al., 2010). Methane is the dominant component of the rising fluids expelled at these seepage sites (Campbell, 2006; Judd and Hovland, 2007) and the most important biological sink for methane in the sea bed globally is AOM (anaerobic oxidation of methane) with sulfate as the electron acceptor (Boetius et al., 2000). Authigenic carbonates have been widely reported both at modern and fossil venting sites of methane-rich fluids (Peckmann et al., 2001; Han et al., 2004;

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Bayon et al., 2007; Gontharet et al., 2007; Paull et al., 2007; Wang et al., 2014a,b), and they can be used to identify past fluid circulation events on continental margins as well as provide information about the geochemical composition of the fluids from which they precipitated (Bohrmann et al., 1998; Naehr et al., 2000). In most sedimentary environments, all REEs exhibit similar geochemical behavior and the REE pattern tends to be relatively stable in the course of carbonate diagenesis (Shields and Webb, 2004) so that their patterns are useful for reconstructing environmental conditions in early diagenetic settings, including the formation of authigenic carbonates (Webb et al., 2009). It is well known that REE geochemical properties are powerful tracers of chemical processes in the marine environment (Haley et al., 2004). The distribution of these elements is very sensitive to water depth, salinity and oxygen level (Frimmel, 2009). In an anoxic environment, Ce occurs as  $Ce^{3+}$ , similar to other REEs, whereas under oxic conditions, soluble  $Ce^{3+}$  is oxidized to insoluble  $Ce^{4+}$ . This behavior can result in a marked fractionation of the REEs between fluid and precipitating mineral phases (Elderfield and Greaves, 1982; German and Elderfield, 1990; Klinkhammer et al., 1994; Birgel et al., 2011). The natural REE abundances in seawater can vary by orders of magnitude as a function of atomic number. The common practice in marine geochemistry is to normalize measured REE concentrations to REE values of average shale (Post Archean Australian Shale-PAAS; Taylor and McLennan, 1985). This normalization removes the odd-even effect of elemental distributions and produces curves, defined as REE patterns, where subtle REE enrichments or depletions are readily apparent (Rongemaille et al., 2011). The seep carbonate REE characteristics can reflect formation conditions, but the degree of REE fractionation is dependent on carbonate mineral composition (Rongemaille et al., 2011). Dolomite, aragonite and calcite are common authigenic minerals that precipitate at cold seeps and have the potential to preserve primary REE signatures, which would reflect the chemical environment during precipitation (Feng et al., 2013). Therefore, the REE concentrations, shale-normalized REE patterns, and Ce anomalies have been extensively studied to assess the redox conditions during carbonate precipitation (Sarkar et al., 2003; Feng et al., 2008, 2009a, 2009b, 2010; Frimmel, 2009; Ge et al., 2010; Himmler et al., 2010; Feng et al., 2013). There have been only a few studies on the REE distribution in pore waters from marine sediment cores (Elderfield and Sholkovitz, 1987; Sholkovitz et al., 1989; Haley et al., 2004). These studies clearly showed that REEs were significantly enriched in pore waters relative to bottom waters. In addition, marked REE variations in concentration and shale-normalized patterns were reported down core with changing oxic to anoxic conditions, which indicated that the REE distribution in pore waters was controlled by early diagenetic processes (Elderfield and Sholkovitz, 1987; Sholkovitz et al., 1989; Haley et al., 2004). However, limited attention has been paid to REE patterns in the geochemical characterization of cold seep carbonates, and published studies are scarce: northern South China Sea, Gulf of Mexico, Black Sea and Niger delta (Feng et al., 2008, 2009a, 2009b, 2010; Ge et al., 2010; Birgel et al., 2011; Rongemaille et al., 2011; Feng et al., 2013; Wang et al., 2014a,b). These studies showed that  $\Sigma$ REE concentrations of these cold seep carbonates are lower than typical marine carbonate except for the southwestern Dongsha area of the northern South China Sea and the redox conditions (oxic and anoxic) are variable during carbonate formation. These studies also showed that variable REE contents,  $\Sigma$ REE and Ce anomalies in cold seep carbonates may reflect their variable and complex formation conditions. Thus, evaluation of REE concentrations in fluids or in authigenic carbonate phases at cold seeps provides additional constraints for biogeochemical processes related to methane-rich

fluids circulations on continental margins (Rongemaille et al., 2011).

Authigenic carbonate occurrences extend for several square kilometers in the Gulf of Cadiz (Magalhães et al., 2012). These methane-derived authigenic carbonates occur from the upper continental slope to ~4500 m water depth on the lower continental rise. The carbonate distribution in the Gulf of Cadiz is much more extensive and widespread than previously reported in other cold seepage regions (Díaz-del-Río et al., 2003; Gonzalez et al., 2009; León et al., 2010; Magalhães et al., 2012). They are associated with mud volcanoes, mud diapirs, diapiric ridges or deep routed faults (Pinheiro et al., 2003) represent evidence of fluid migration and can be used to understand the circulation of methane-rich fluids in the Gulf of Cadiz (Magalhães et al., 2012). The REE content and relative authigenic carbonate indices have not previously been reported from the Gulf of Cadiz cold seeps. This study's objectives are to improve knowledge of the redox implications of REEs and the carbon source implications of stable carbon and oxygen isotopes in the cold seeps from this area, to investigate the viability of using of authigenic carbonate REEs and stable isotopes to trace fluid sources, and to better understand the impact of the mineral composition, redox conditions and diagenesis on REE characteristics during the formation of authigenic carbonates. We provide new evidence that the aerobic oxidation of methane is the most significant process responsible for the formation of these cold seep carbonates in the Gulf of Cadiz. We found very limited diagenesis, which indicates the carbonate geochemical and isotopic characteristics reflect the conditions of their formation rather than post-formation diagenetic evolution or late seawater alteration. These research results have very important significance to understand fluid characteristics and authigenic carbonates formation process in the Gulf of Cadiz.

## 2. Geological setting

The Gulf of Cadiz comprises the southern Iberian continental margin and the northern African Atlantic margin. The regional geodynamics is dominated by the slow convergence (~4 mm/year) of the African and the Eurasian plates (Argus et al., 1989). The study area (between 34°45'N and 36°45'N, and 6°25'W and 10°W) corresponds to the south Portuguese margin and the Gulf of Cadiz (Fig. 1). The water depth in the study area ranges from 200 to 4000 m, corresponding to the upper and lower continental slopes and the continental rise of the southwest Iberia margin and the Atlantic Moroccan margin.

The upper slope (130–400 m water depth) is narrow and characterized by: (1) depositional processes related to the prograding edge of the continental shelf break, (2) erosive processes related to the canyons and channels, (3) gravitational structures related to slumping, (4) tectonic processes revealed by recent fractures and diapiric processes, and (5) the presence of gas-charged sediments and fluid escape structures, such as pockmarks (Baraza and Ercilla, 1996). The middle slope (400–1200 m water depth) is extensive, except in the area of the Portimão and Faro Canyons (South Portuguese margin), where it is narrower. The central part of this area is characterized by the presence of important ridge systems associated with NE–SW trending diapiric structures and by the frequent occurrence of mud volcanoes and other fluid escape structures. The lower slope (1200–4000 m water depth) corresponds to the accretionary/olistostrome domain. West of Faro (south Portuguese margin), the lower slope is narrower and dominated by the presence of canyons; the middle slope is also narrower. The dominant seafloor morphology within the accretionary domain is characterized by the presence of small-scale

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