



New insights into cerium anomalies and mechanisms of trace metal enrichment in authigenic carbonate from hydrocarbon seeps



Yu Hu^{a,e}, Dong Feng^{b,*}, Jörn Peckmann^c, Harry H. Roberts^d, Duofu Chen^{a,b,**}

^a CAS Key Laboratory of Marginal Sea Geology, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou 510640, China

^b CAS Key Laboratory of Marginal Sea Geology, South China Sea Institute of Oceanology, Chinese Academy of Sciences, Guangzhou 510301, China

^c Department of Geodynamics and Sedimentology, Center for Earth Sciences, University of Vienna, 1090 Vienna, Austria

^d Coastal Studies Institute, Department of Oceanography and Coastal Sciences, Louisiana State University, Baton Rouge, LA 70803, USA

^e University of Chinese Academy of Sciences, Beijing 100049, China

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ABSTRACT

Authigenic carbonates that form at marine hydrocarbon seeps provide a unique geological archive of past local environmental conditions and pore fluid geochemistry. Recent work on such carbonates revealed variable cerium (Ce) anomalies and anomalous enrichments of certain trace metals. However, the mechanisms accounting for such anomalies remain poorly constrained. Here, we characterize the rare earth element (REE) patterns of carbonate phases and the trace metal patterns of bulk carbonate rocks sampled at three hydrocarbon seeps located at Congo Fan pockmarks (CF) and the Gulf of Mexico sites AC645 and GB425. The analyzed CF, GB425, and AC645 carbonates yielded different REE patterns, displaying positive, no, as well as negative Ce anomalies. The covariation of molybdenum (Mo) with uranium (U), including authigenic Mo (Mo_{auth}) and U (U_{auth}) enrichments as well as $(Mo/U)_{auth}$ ratios proved useful to obtain new insight into the applicability of Ce anomalies to constrain past redox conditions. Trace element patterns suggest that (1) CF carbonates formed in a restricted sulfidic environment, while (2) the AC645 site experienced intermittent oxygenation causing negative Ce anomalies, and (3) environmental conditions were variable at the GB425 mud volcano site. Interestingly, GB425 carbonates show significant Mo, arsenic (As), and antimony (Sb) enrichments with the enrichment factor of As (As_{EF}) correlating well with the authigenic Fe fraction. These results suggest that iron oxyhydroxides played an important role in the adsorption of Mo, As, and Sb in the water column and their transfer to the sediment. The combination of trace metal and REE geochemistry of authigenic carbonates used here is a promising tool to better assess past variability of redox conditions and biogeochemical processes at marine hydrocarbon seeps.

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1. Introduction

Seepage of hydrocarbon-rich fluids mainly consisting of methane out of the sedimentary column is a widespread phenomenon along continental margins worldwide (Campbell, 2006; Judd and Hovland, 2007 and references therein). Seafloor expressions of focused fluid seepage include a large range of geological structures such as gas chimneys, pockmarks, mud volcanoes, and brine pools (Judd and Hovland, 2007 and references therein). Modern marine hydrocarbon seeps are characterized by highly variable seepage intensity (Tryon et al., 1999; Klauke et al., 2010), resulting in significant changes of chemical and physical parameters and early diagenetic conditions within sediments (Tryon

et al., 1999; Tryon and Brown, 2004; Solomon et al., 2008). At seeps, methane is mostly consumed within sediments by sulfate-dependent anaerobic oxidation of methane (AOM) mediated by a microbial consortium (Hinrichs et al., 1999; Boetius et al., 2000). This process releases dissolved bicarbonate and hydrogen sulfide, thereby increasing pore water alkalinity, thus favoring precipitation of authigenic carbonate close to the seafloor (Berner, 1980). The resultant authigenic carbonates provide excellent geological and geochemical archives to evaluate the conditions of mineral formation, the evolution of pore fluids, and the biogeochemical processes at seeps (Roberts and Carney, 1997; Bohrmann et al., 1998; Greinert et al., 2001; Peckmann et al., 2001; Peckmann and Thiel, 2004; Roberts et al., 2010a).

Rare earth elements (REE) have been frequently used to trace changes in the composition of seep fluids and to assess redox conditions during the formation of seep carbonates (Chen et al., 2005; Feng et al., 2009a,b, 2010a; Ge et al., 2010; Himmler et al., 2010; Bayon et al., 2011; Birgel et al., 2011; Rongemaille et al., 2011; Kim et al., 2012; Bayon et al., 2013; Feng et al., 2013; Himmler et al., 2013). Some of

* Corresponding author. Tel.: +86 20 85290286; fax: +86 20 85290130.

** Correspondence to: D. Chen, CAS Key Laboratory of Marginal Sea Geology, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou 510640, China. Tel.: +86 20 85290286; fax: +86 20 85290130.

E-mail addresses: feng@scsio.ac.cn (D. Feng), cdf@gig.ac.cn (D. Chen).

the studies on the REE geochemistry of seep carbonates revealed varying redox conditions during mineral formation (Feng et al., 2009a, b; Birgel et al., 2011). In particular, Birgel et al. (2011) suggested that temporarily oxic conditions prevailed based on real negative Ce anomalies and the presence of molecular fossils of aerobic methanotrophic bacteria. However, highly alkaline, organic-rich pore fluids may also cause the generation of negative Ce anomalies (Pourret et al., 2008; Kim et al., 2012). To better constrain paleoenvironments and paleoredox conditions, trace metals, including redox-sensitive elements such as uranium (U) and molybdenum (Mo) that are strongly enriched under anoxic conditions, are commonly used (Algeo and Tribovillard, 2009; Tribovillard et al., 2012a,b). Uranium and Mo exhibit conservative behavior under oxic conditions and have long residence times in seawater (~450 kyr for U, ~780 kyr for Mo), while both elements are enriched in authigenic mineral phases under reducing conditions (Algeo and Tribovillard, 2009). In oxic seawater, U is present mainly as U(VI), forming $\text{UO}_2(\text{CO}_3)_3^{4-}$, and Mo is adsorbed onto manganese oxyhydroxides (Tribovillard et al., 2006). Under suboxic conditions close to the Fe(III)–Fe(II) transition, soluble U(VI) is reduced to insoluble U(IV), the uptake of which may be accelerated by the presence of organic substrates (Zheng et al., 2002; Tribovillard et al., 2006; Algeo and Tribovillard, 2009). Under such conditions, the rate of accumulation of authigenic U (U_{auth}) increases relative to that of authigenic Mo (Mo_{auth}), resulting in $(\text{Mo}/\text{U})_{\text{auth}}$ ratios of sediment that are below those of seawater (Algeo and Tribovillard, 2009). As the sedimentary environment becomes increasingly reducing with free hydrogen sulfide being generated, molybdate (MoO_4^{2-}) is converted to thiomolybdates ($\text{MoS}_4 - x\text{O}_x^{2-}$) that are scavenged from solution via organic material or via Mo capture by iron sulfide phases (Helz et al., 1996; Zheng et al., 2000; Tribovillard et al., 2006; Helz et al., 2011). Under such conditions, Mo_{auth} enrichment tends to exceed that of U_{auth} and $(\text{Mo}/\text{U})_{\text{auth}}$ ratios of sediment equal or exceed ratios of seawater (Algeo and Tribovillard, 2009). Therefore, authigenic U–Mo enrichment and their covariation patterns in marine sediments are a robust proxy for tracing variation of redox condition. The patterns of authigenic U–Mo covariation as a redox indicator have already been employed in the study of seep carbonates and sediments (Palomares et al., 2012; Sato et al., 2012). However, such trace-metal studies focusing on the reconstruction of the conditions during mineral formation at seeps have rarely been combined with REE geochemistry, yet, the combination of trace-metal and REE studies has great potential to shed new light on the causes of Ce anomalies and past environmental conditions.

Trace metals have the potential to serve as tracer for the source of seep fluids. For instance, Nath et al. (2008) reported elevated levels of arsenic (As) in mud volcano fluids. Similar As enrichment, as well as Mo and antimony (Sb) anomalies have been observed in seep sediments from an active mud volcano (Cangemi et al., 2010). The enrichments of trace metals have been attributed to the ascending fluids from deep sedimentary strata (Nath et al., 2008; Cangemi et al., 2010). Similarly, Mo, As, and Sb enrichments have also been found in ancient seep carbonates, however, the overlying seawater was considered to have been responsible for the trace-metal enrichments through a so-called iron–manganese–oxyhydroxide shuttle (Tribovillard et al., 2013).

Similar trace-metal enrichments are also present in some of the seep carbonates studied here, which were collected from an active mud volcano situated at Garden Banks block 425 (GB425, Gulf of Mexico), representing a good opportunity to explore possible enrichment mechanisms. Seep carbonates from two other sites (Congo Fan off western Africa and Alaminos Canyon block 645, Gulf of Mexico) were used to obtain new insight into the causes of Ce anomalies. Here, REE signatures of individual, authigenic carbonate phases as well as trace element compositions of bulk seep carbonate rocks are presented to explore the mechanisms that cause anomalies of certain elements, allowing to further constrain the formation conditions of seep carbonates and the involved geochemical processes.

2. Geological background

2.1. Congo Fan

The northern Congo Fan is located offshore western Africa on the Congo–Angolan margin, which is a passive continental margin resulting from the Early Cretaceous opening of the South Atlantic Ocean (130 Ma; Marton et al., 2000). After 1000 m thick evaporites accumulated in the Early Cretaceous, black shales and bituminous sandstones deposited during the middle Cretaceous (Droz et al., 1996). The terrigenous sediment input to the Atlantic Ocean increased strongly during the Cenozoic, resulting in the initiation of the huge Congo turbiditic sedimentation system and the formation of the Congo Fan (Droz et al., 1996). Numerous investigations on the Congo Fan revealed prominent features of focused upward fluid migration such as pockmarks (Charlou et al., 2004; Gay et al., 2006, 2007; Sahling et al., 2008; Haas et al., 2010; Nöthen and Kasten, 2011). Among other sites, the distribution of chemosynthesis-based communities, authigenic carbonates, and gas hydrates has been described from the Kouilou pockmarks located north of the Congo Fan (Sahling et al., 2008; Haas et al., 2010; Nöthen and Kasten, 2011).

2.2. Northern Gulf of Mexico

The northern Gulf of Mexico (GOM) is characterized by a column of over 10 km of Mesozoic–Cenozoic sediment that resulted in the generation and accumulation of large oil and gas reservoirs (Sassen and MacDonald, 1994). Extensive salt diapirism and related sediment deformation created faults, which provide efficient conduits for hydrocarbon fluid and gas migration from the deep subsurface petroleum systems into shallow sediments or to the seafloor (Sassen and MacDonald, 1994). Massive leakage of oil and gas from hydrocarbon traps manifests itself at the seafloor and in the water column as gas plumes, gas hydrate, oil-stained sediments, authigenic carbonates, and hydrocarbon-driven chemosynthesis-based communities (Roberts and Aharon, 1994; Aharon et al., 1997; Roberts and Carney, 1997; Sassen et al., 1999; Feng et al., 2009b). The Alaminos Canyon (AC) area is situated along a series of northeast–southwest trending salt-cored box folds of the Perdido fold belt located in the northwestern GOM (Trudgill et al., 1999). The AC645 site is a small mound surrounded by hemipelagic mud with no evidence of currently active hydrocarbon seepage; however, the mound is composed of imbricated slabs and blocks of seep carbonates (Roberts et al., 2010b). Garden Bank 425 (GB425) is a brine-charged site located in the northern GOM. Overpressured fluids migrating along faults above salt structures resulted in the formation of the GB425 mud volcanoes (Milkov and Sassen, 2000; Castellini et al., 2006), which is characterized by intense venting of hydrocarbon-rich brines (Joye et al., 2005) and the development of barite-rich carbonate nodules (Castellini et al., 2006).

3. Samples and methods

Considering different geological settings (e.g. pockmarks and mud volcanoes) and different, previously reported Ce anomalies (cf. Feng et al., 2010a; Birgel et al., 2011), authigenic carbonates from three seep sites on the Congo Fan and the GOM were chosen in this study (Fig. 1). Congo Fan (CF) carbonates were collected by TV-guided grabs from the Hydrate Hole and Diapir Field sites during RV METEOR Cruise M56. The AC645 carbonate samples were collected during dives with deep submergence vehicle (DSV) Alvin in 1990 (Dive 2209) and 2006 (Dives 4194 and 4197). The GB425 carbonates were collected from the southern venting sites of the mud volcano during an expedition with DSV Alvin (Dive 4645) in 2010. Location, geographical coordinates, water depth, $\delta^{13}\text{C}_{\text{carbonate}}$ values, and mineralogy of carbonate samples are listed in Table 1. Authigenic carbonates from the Congo Fan are mainly composed of aragonitic and high-Mg calcite associated with

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