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The imprint of methane seepage on the geochemical record and early diagenetic processes in cold-water coral mounds on Pen Duick Escarpment, Gulf of Cadiz

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ABSTRACT

The diagenetic history and biogeochemical processes in three cold-water coral mounds located in close proximity to each other on Pen Duick Escarpment in the Gulf of Cadiz were examined. The influence of ascending methane-rich fluids from underlying sediment strata delineated two mound groups: Alpha and Beta Mound showed evidence for the presence of a sulfate-methane transition zone (SMTZ) at shallow depth, whereas Gamma Mound appeared to lack a shallow SMTZ. In the methane influenced Alpha and Beta Mound, upward diffusion of hydrogen sulfide from the shallow SMTZ caused extensive pyritization of reactive iron phases as indicated by values for the degree-of-pyritization >0.7. This secondary pyritization overprinted the sulfur isotope composition of sulfides formed during organoclastic sulfate reduction. The almost complete consumption of reactive iron phases by upward diffusing sulfide limited dissimilatory iron reduction to the top layer in these mounds while organic matter in the pyritized zones below was primarily degraded by organoclastic sulfate reduction. Hydrogen sulfide produced during sulfate reduction coupled to the anaerobic oxidation of methane (AOM) diffused upward and induced aragonite dissolution as evidenced in strongly corroded corals in Alpha Mound. This mound has been affected by strong fluctuations in the depth of the SMTZ, as observed by distinct layers with abundant diagenetic high-Mg calcite with a ^{13}C-depleted carbon isotope composition. In the non-methane influenced Gamma Mound low sulfate reduction rates, elevated concentrations of dissolved iron, and solid-phase iron speciation indicated that organic matter mineralization was driven by dissimilatory iron reduction and organoclastic sulfate reduction coupled to oxidative sulfur cycling. The latter process led to ^{34}S-depletion in pyrite of up to 70‰ relative to pore-water sulfate.

1. Introduction

Cold-water coral ecosystems occur worldwide within a large bathymetric and temperature range on continental shelves, seamounts and ridge systems (Roberts et al., 2006; Wheeler et al., 2007). They represent a sink for inorganic carbon that has so far not been fully considered in global carbonate budget estimations (Lindberg and Mienert, 2005; Titschack et al., 2009). These ecosystems, formed predominately by the scleractinian corals *Lophelia pertusa* and *Madrepora oculata* occur as patches, reefs systems as well as cold-water coral mounds (Freiwald, 2002; Roberts et al., 2006). Mounds composed of cold-water coral fragments embedded in a loose matrix of hemipelagic sediments (Dorschel et al., 2007; Rüggeberg et al., 2007; Titschack et al., 2009) can form enormous carbonate build-ups of up to 300 m in height and of several kilometers in diameter (Mienis et al., 2007; Wheeler et al., 2007). Surveys on the NE Atlantic margin report their distribution from northern Norway to the continental slope off Morocco (e.g. Freiwald, 2002; Weaver et al., 2004; Roberts et al., 2006; Wheeler et al., 2007; De Mol et al., 2009). While morphology, growth history and environmental setting of individual mounds or mound provinces are often well-constrained (Huvenne et al., 2003; van Weering et al., 2003; De Mol et al., 2007; Mienis et al., 2007; Wheeler et al., 2007; Eisele et al., 2008), less is known about microbially-mediated early diagenetic processes in these large carbonate fabrics. Biogeochemical processes, however, might play

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an important role in syn-depositional mound stabilization and ultimately control coral skeleton preservation. A tight coupling between microbially-mediated organic matter degradation and carbonate-mineral diagenesis was proposed for the sediments of Challenger Mound, which was drilled during the Integrated Ocean Drilling Program (IODP) Expedition 307 (Ferdelman et al., 2006). A detailed microbiological survey of mound sediments suggests the presence of a significant and active prokaryotic community in this mound (Webster et al., 2009). The influence of cold-water coral ecosystems on biogeochemical processes and carbonate preservation in associated sediments at post-glacial reefs on the Norwegian shelf has been elucidated by Wehrmann et al. (2009).

In 2002, cold-water coral mounds were discovered in the Gulf of Cadiz, a tectonically active area characterized by gas seepage, fluid venting, and the occurrence of numerous mud volcanoes (e.g. Baraza and Ercilla, 1996; Gardner, 2001; Pinheiro et al., 2003; Somoza et al., 2003; Van Rensbergen et al., 2005; Niemann et al., 2006a). The discovery of cold-water coral mounds in an area of gas seepage is very intriguing as biogeochemical processes associated with the oxidation of methane can leave a fundamental diagenetic imprint in the sedimentary record, pore-water composition and isotopic signatures of pore-water and solid-phase constituents in marine sediments. Sulfate reduction coupled to the anaerobic oxidation of methane (AOM) proceeds according to the following net reaction (Valentine and Reeburgh, 2000; Nauhaus et al., 2002; Treude et al., 2003, and reference therein):

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

This process, apparently mediated by a consortium of anaerobic methane-oxidizing archaea and sulfate-reducing bacteria (Hinrichs et al., 1999; Boetius et al., 2000; Valentine and Reeburgh, 2000; Orphan et al., 2001; Michaelis et al., 2002; Knittel et al., 2003, 2005; Niemann et al., 2006b), can lead to a strong modification of the primary sediment composition by dissolution and precipitation of iron and sulfur bearing mineral phases, e.g. iron oxides, barite, and pyrite (Passier et al., 1998; Jørgensen et al., 2004; Neretin et al., 2004 Riedinger et al., 2005). The prominent role of these minerals as paleoceanographic and paleoclimatologic proxies demands a careful assessment of the mechanisms and extents of diagenetic alteration in the sedimentary record (Riedinger et al., 2005; Jørgensen and Kasten, 2006; März et al., 2008).

So far, little is known about the imprint of AOM coupled to sulfate reduction on the sedimentary record within a cold-water coral mound and how it affects modes of early diagenesis. Initial studies by Foubert et al. (2008) and Maignien et al. (in press) described the presence of a shallow sulfate-methane transition zone (3.0–3.5 m sediment depth) at Alpha Mound on Pen Duick Escarpment and suggest a possible link between methane-driven diagenetic processes and coral dissolution as well as carbonate production.

In the present study, we provide evidence that deep fluids and methane ascend to near surface sediments of three cold-water coral mounds, Alpha, Beta and Gamma Mound on the Pen Duick Escarpment. These mounds thus represent a model system for exploring the impact of fluid flow and methane seepage on coral-bearing, carbonate-rich siliciclastic sediments. The comparison of a non-methane influenced coral-framework mound, i.e. Gamma Mound and methane influenced structures such as Alpha and Beta Mound allows us to evaluate the imprint of methane cycling on recent early diagenetic processes and the geological record.

2. Regional setting

The study area Pen Duick Escarpment is located in the Gulf of Cadiz west of the Gibraltar Arc between the Iberian Peninsula and the Moroccan margin (Fig. 1a). The complex structural development of the Gulf of Cadiz is controlled by subduction associated to the westward motion of the Betic-Rifean orogenic arc, dextral strike–slip movement along the Azores-Gibraltar Plate Boundary, and the Africa-Eurasia plate convergence motion (Maldonado and Nelson, 1999; Gutscher et al., 2002; Medialdea et al., 2004, 2008; Zitellini et al., 2009). These processes led to the formation of a large allochthonous unit which is covered by an undeformed Late Miocene to Plio-Quarternary sedimentary pile (Maldonado and Nelson, 1999; Medialdea et al., 2004; Zitellini et al., 2009). Along the Moroccan margin, several sub-parallel ridges are located that represent large rotated blocks confined by lystric faults that formed Plio-Pleistocene centers of deposition including Renard Ridge and Vernadsky Ridge (Van Rensbergen et al., 2005). The Pen Duick Escarpment represents a NE–SW oriented fault-bounded cliff of 6 km length and 80 to 125 m height situated on the southeastern leg of Renard Ridge (Van Rooij et al., this issue). The nature of the substratum below Pen Duick Escarpment is largely unknown. On the northeastern site, the escarpment is underlain by a small subbasin which is suggested to host a discontinuous stratigraphic record with interference from adjacent mud volcanoes (Van Rooij et al., this issue). To the southwest, the escarpment flank descends into a depression with a maximal depth of 10–20 m (Van Rooij et al., this issue). Average slope gradients of the cliff are about 15 to 20° at the south–west facing part and up to 25° at the eastern edge (Foubert et al., 2008). Seismic profiles across Pen Duick Escarpment provide evidence for gas accumulation and features related to hydrocarbon (gas) seepage (Van Rooij et al., this issue). Renard and Vernadsky Ridges are located in the El Arraiche mud volcano field which consists of eight mud volcanoes that are situated around the ridges on top of normal faults which constrain the rotated blocks (Van Rensbergen et al., 2005). The onset of mud volcano activity in the El Arraiche mud volcano field is estimated at 2.5 Ma before present (Van Rensbergen et al., 2005). Pen Duick Escarpment is separated from its closest neighboring mud volcano, Gemini Mud Volcano, by an only 1 km wide moat feature (Fig. 1b; Van Rooij et al., this issue).

Fluid escape structures such as mud volcanoes, pockmarks and carbonate chimneys are widely distributed in the Gulf of Cadiz (e.g. Baraza and Ercilla, 1996; Díaz-del-Río et al., 2003; Pinheiro et al., 2003; Somoza et al., 2003; Van Rensbergen et al., 2005; Van Rooij et al., 2005; León et al., 2006; Niemann et al., 2006a; Medialdea et al., 2008; Stadnitskaia et al., 2008). The source of fluids migrating into the mud volcano systems on the Betic-Rifean margin is inferred to be the allochthonous unit. For mud volcanoes located on the lower continental slope it is suggested that they might be related to sources below this unit, probably of Mesozoic age (Fernández-Puga et al., 2007; Medialdea et al., 2008). Analyses of venting hydrocarbon gas composition at active mud volcanoes suggest a large thermogenic component (Niemann et al., 2006a,b; Stadnitskaia et al., 2006; Nuzzo et al., 2009). The extensional faulting of the ridges in the El Arraiche mud volcano field facilitates migration of overpressured fluid and mud-breccia flow, expressed in the formation of the mud volcanoes.

The Pen Duick Mound Province hosts a series of 15 identified cold-water coral mounds covering the cliff top and several smaller mounds at the base. Further small mound-like features have been discovered in the sedimentary sequences surrounding the escarpment and have been interpreted as buried mounds (Foubert et al., 2008). The 15 cold-water coral mounds are distributed in a water depth of 500–600 m and reach up to 60 m in height and about 500 m in diameter at the mound base (Foubert et al., 2008; Van Rooij et al., this issue). Seismic profiles suggest that the mound base is an erosional surface, interpreted as the outcropping basement that is forming Renard Ridge (Foubert et al., 2008).

In this study, three cold-water coral mounds were investigated, Alpha, Beta and Gamma Mound, which reside next to each other on the cliff top (Fig. 1b). Alpha Mound is located on the southeastern side of Pen Duick Escarpment close to Gemini Mud Volcano. The mound