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Authigenic barite records of methane seepage at the Carlos Ribeiro mud volcano (Gulf of Cadiz).

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ABSTRACT

Submarine mud volcanoes (MVs) are dynamic features that episodically expel gas-charged fluids and mud onto the seafloor, transferring various chemical constituents into the overlying water column. The temporal variability in MV activity is, however, poorly understood, so their importance as a source of methane (CH_4) and higher hydrocarbons for the oceanic carbon budget, although thought to be significant, cannot be properly constrained. In this study, the history of fluid and gas seepage at the Carlos Ribeiro MV (Gulf of Cadiz) is assessed via geochemical analyses and transport-reaction modelling of pore fluids and barium (Ba) rich layers (Ba fronts) in sediment cores, recovered along a transect from the eye to the periphery of the MV. X-ray fluorescence data reveal that Ba fronts are absent at the eye, while a single front (with up to 1740 ppm Ba) is present at the margin of the summit. Three Ba fronts occur at 45, 85 and 130 cm depth within a mudflow to the southeast of the crater. Spectrometric analyses indicate that barite is the Ba-rich mineral in these layers. Upward advecting pore fluids are enriched in barium but depleted in calcium (Ca^{2+}) relative to seawater. Modelling of the Ba^{2+} and Ca^{2+} pore fluid profiles indicates that the positions of the Ba fronts reflect both the present-day hydrodynamic conditions as well as higher fluxes of methane in the past. Fluid advection appears to have decreased since 340 cal yr before present, but degassing of the mudflow is ongoing and is potentially an important source of CH_4.

1. Introduction

Submarine mud volcanoes (MVs) have been extensively described and studied across the globe (e.g. MacDonald et al., 1994; Gardner, 1999; Graue, 2000; Hensen et al., 2004; Omoregie et al., 2009; Chao et al., 2011) as they are extremely efficient in transporting hydrocarbons (especially methane) from deeply buried sediments, to shallow sediments, to the overlying water column (Dimitrov, 2002), and potentially to the atmosphere (e.g. Dimitrov, 2003; Sauter et al., 2006). Quantifying methane fluxes from MVs has proven to be a real challenge, not only because MVs are extremely dynamic, but also because methane fluxes are modified by a number of biogeochemical processes, such as anaerobic oxidation within the sediments (Boetius et al., 2000) and aerobic oxidation in the water column (Higgins and Quayle, 1970). Most MV studies focus on their contribution to the present-day oceanic methane budget (e.g. Mau et al., 2006; Sauter et al., 2006; Wallmann et al., 2006), yet mud volcanism is known to be episodic (Kopf, 2002; Lykousis et al., 2009; MacDonald and Peccini, 2009). Hence, there is a need for more information on how hydrocarbon emissions have varied in the past, to understand the true impact of methane venting at MVs on the global carbon cycle.

Authigenic barite ($BaSO_4$) is considered to be a useful proxy for assessing past fluxes of methane gas on continental margins (Dickens, 2001). This is because gas-charged fluids generally lack sulphate (SO_4^{2-}) but contain elevated concentrations of dissolved barium (Ba^{2+}) (Torres et al., 1996b). During the ascent of the fluids through the sediment column, barite precipitates on contact with downward-diffusing seawater sulphate close to or even at the seafloor (Eq. (1); Aquilina et al., 1997; Fu et al., 1994; Gingele and Dahmke, 1994; Kasten et al., 2003; Torres et al., 1996a):

$$Ba^{2+}(aq) + SO_4{}^{2-}(aq) \leftrightarrow BaSO_4(s). \qquad (1)$$

The pore water sulphate gradient at MVs is typically regulated by the methane flux from depth via the anaerobic oxidation of methane (AOM; $CH_4 + SO_4{}^{2-} \rightarrow HCO_3{}^- + HS^- + H_2O$) at the sulphate–methane transition (SMT; e.g. Aloisi et al., 2002; Bohrmann et al., 2003; Borowski et al., 1999; de Beer et al., 2006; Haese et al., 2003; Niemann et al., 2006; Werne et al., 2004). As authigenic barite builds up just above the depth of sulphate depletion, its presence records the depth of the SMT (Von Breymann et al., 1992; Dickens, 2001; Kasten et al., 2003; Snyder et al.,

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2007a) and thus, can be used to document the history of gas seepage on continental margins.

Depending on the availability of sulphate and barium, barite precipitates at cold seep sites vary from microcrystalline phases that form within the sediment column (e.g. Peru Margin; Torres et al., 1996a) to blocks and columns up to 10 m high scattered over the seafloor (e.g. Sea of Okhotsk; Greinert et al., 2002). At MVs, barite tends to be present as a minor authigenic phase coexisting with the more widespread and abundant calcium carbonate concretions, slabs and chimneys e.g. in the Gulf of Cadiz (Díaz-del-Río et al., 2003; Vanneste et al., 2012) and in the Nile deep-sea fan (Gontharet et al., 2007). Although the Ba cycle is well documented at localities characterised by diffuse and/or advective methane flow (e.g. Torres et al., 1996a; Aquilina et al., 1997; Naehr et al., 2000; Dickens, 2001; Greinert et al., 2002; Torres et al., 2002; Riedinger et al., 2006), studies of authigenic barite layers and their linkage to methane venting in mud volcano settings, are limited to two MVs in the Gulf of Mexico (Castellini et al., 2006).

In this study, we investigate the history of venting activity at the Carlos Ribeiro MV, which is located on the Portuguese margin of the Gulf of Cadiz. The majority of the mud volcanoes in the Gulf of Cadiz are considered to be in a dormant stage, however mud volcanism has been estimated to be active since 2.4–2.6 Ma on for instance the Moroccan margin (Van Rensbergen et al., 2005; Perez-Garcia et al., 2011). To date mainly geophysical tools have been applied to investigate the episodic nature of MVs in this area. Here we use an ITRAX XRF core scanner to locate authigenic mineral fronts in sediment cores recovered from four sites along a transect from the centre to the periphery of the MV. Chemical analyses of the solid phase and pore fluids are used together with a numerical 1-D transport-reaction model to estimate past variations in methane fluxes. Finally, radiocarbon dating of hemipelagic sediments on top of the MV is used to provide an absolute chronology of the mud extrusion history of the mud volcano.

2. Geological setting

The Gulf of Cadiz is located in the North Atlantic Ocean on the European continental margin, west of the Gibraltar Strait (Fig. 1A).

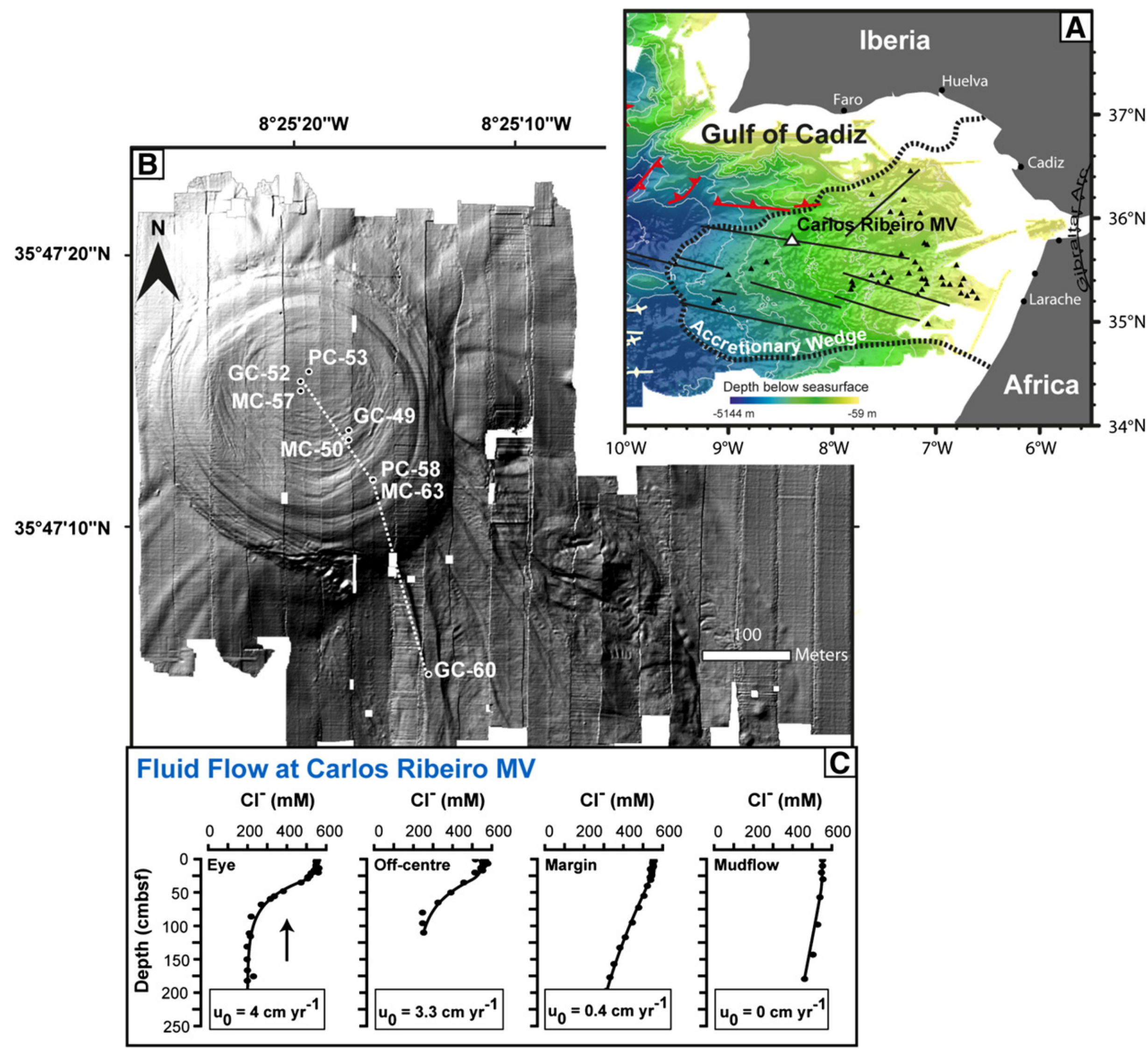

Fig. 1. A. Bathymetric map of the Gulf of Cadiz (modified from Zitellini et al., 2009) showing the position of the Carlos Ribeiro mud volcano and the main geological structures. Black triangles: mud volcanoes; black dotted line: external boundary of the accretionary wedge; black lines: deep rooted faults that affect the seafloor; red lines with triangles: active reverse faults; yellow lines with rhombuses: axis of inactive anticline (Medialdea et al., 2009; Zitellini et al., 2009). B. Shaded relief map of the Carlos Ribeiro MV, showing the location of the core sites. C. Fluid flow regime at the present-day at the MV (u_0 = upward fluid flow velocity). Measured data are shown by the black dots while the solid lines represent the best fit between the model simulated chloride (Cl^-) pore fluid profiles and measured data (after Vanneste et al., 2011).