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Research paper

Authigenic minerals from the Paola Ridge (southern Tyrrhenian Sea): Evidences of episodic methane seepage

F. Franchi [a, b, *], M. Rovere [b], F. Gamberi [b], H. Rashed [c], O. Vaselli [c, d], F. Tassi [c, d]

[a] Department of Earth and Environmental Science, Botswana International University of Science and Technology (BIUST), Private Bag 16, Plot 10071, Palapye, Botswana
[b] ISMAR-CNR, U.O.S. Bologna, Via Gobetti 101, 40129 Bologna, Italy
[c] Department of Earth Sciences, University of Florence, Via G. La Pira, 4, 50121 Florence, Italy
[d] IGG-CNR, U.O.S. Florence, Via G. La Pira, 4, 50121 Florence, Italy

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ABSTRACT

Paola Ridge, along the NW Calabrian margin (southern Tyrrhenian Sea), is one of the few reported deep sea sites of precipitation of authigenic carbonates in the Tyrrhenian Sea. Here, the changing composition of the seeping fluids and the dynamic nature of the seepage induced the precipitation of pyrite, siderite and other carbonate phases. The occurrence of this array of authigenic precipitates is thought to be related to fluctuation of the sulfate-methane transition zone (SMTZ).

Concretions of authigenic minerals formed in the near sub-bottom sediments of the Paola Ridge were investigated for their geochemical and isotopic composition. These concretions were collected in an area characterized by the presence of two alleged mud volcanoes and three mud diapirs. The mud diapirs are dotted by pockmarks and dissected by normal faults, and are known for having been a site of fluid seepage for at least the past 40 kyrs. Present-day venting activity occurs alongside the two alleged mud volcanoes and is dominated by CO_2-rich discharging fluids. This discover led us to question the hypothesis of the mud volcanoes and investigate the origin of the fluids in each different domed structure of the study area.

In this study, we used stable isotopes (carbon and oxygen) of carbonates coupled with rare earth element (REE) composition of different carbonate and non-carbonate phases for tracing fluid composition and early diagenesis of authigenic precipitates. The analyses on authigenic precipitates were coupled with chemical investigation of venting gas and sea-water.

Authigenic calcite/aragonite concretions, from surficial sediments on diapiric structures, have depleted ^{13}C isotopic composition and slightly positive $\delta^{18}O$ values. By contrast, siderite concretions, generally found within the first 6 m of sediments on the alleged mud volcanoes, yielded positive $\delta^{13}C$ and $\delta^{18}O$ values. The siderite REE pattern shows consistent LREE (light REE) fractionation, MREE (medium REE) enrichment and positive Gd and La anomalies. As shown by the REE distribution, the ^{13}C-depleted composition and their association with chemosymbiotic fauna, calcite/aragonite precipitated at time of moderate to high methane flux close to the seafloor, under the influence of bottom seawater. Authigenic siderite, on the other hand, formed in the subseafloor, during periods of lower gas discharges under prolonged anoxic conditions within sediments in equilibrium with ^{13}C-rich dissolved inorganic carbon (DIC) and ^{18}O-rich water, likely related to methanogenesis and intermittent venting of deep-sourced CO_2.

1. Introduction

Submarine seepage areas originate from the migration of methane-rich fluids and their discharge at the seafloor through peculiar morphologic features such as mud volcanoes (e.g., Krastel et al., 2003; Løseth et al., 2009), pockmarks (e.g., Hovland et al., 2002; Sultan et al., 2014) and mud diapirs (e.g., Rovere et al.,

* Corresponding author. Department of Earth and Environmental Science, Botswana International University of Science and Technology (BIUST), Private Bag 16, Palapye, Botswana.
E-mail address: franchif@biust.ac.bw (F. Franchi).

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2014). In such areas, faults may act as plumbing systems, favoring the uprising of fluids from deep-seated sources, which can affect at different degrees the diagenesis of marine sediments (e.g., Hein et al., 2006). The fluids often sustain complex ecosystems with a high degree of biodiversity (e.g., Levin et al., 2016) and significant chemosynthetic biomass, which may drive anaerobic oxidation of methane (AOM) and trigger carbonate mineral precipitation (Boetius and Suess, 2004). In such environments, methane is thought to be mostly consumed by sulfate-dependent AOM mediated by microbial consortia in the sulfate-methane transition zone (SMTZ) (Boetius et al., 2000). The AOM-related processes increase bicarbonate and hydrogen sulfides. This, in turns, increases the pore water alkalinity and favors the precipitation of authigenic carbonates. It has been proved that the discontinuous seepage of methane may influence the overall geochemical composition of the authigenic carbonates affecting both stable isotope composition of carbon and oxygen (Birgel et al., 2011; Hu et al., 2014) and REE distribution (Solomon et al., 2008; Kim et al., 2012; Hu et al., 2014).

Whether cold seeps are by definition sites of active or extinct fluid escape dominated by dissolved methane, hydrothermal vents are normally considered as result of volcanic activity and characterized by higher temperatures and dominated, among the others, by dissolved CO_2 and H_2S (Joseph, 2017 and references therein). While hydrothermal vents were first discovered in 1977 along the Galápagos Rift, a spur of the East Pacific Rise (Corliss et al., 1979), the first finding of cold seeps occurred in the Gulf of Mexico (Paull et al., 1984). The term cold seep soon became popular to identify seafloor sites where hydrocarbon-rich fluids are released, and have temperatures comparable with that of the surrounding seawater. Here, we abide to the aforementioned definitions and therefore refer to sites dominated by dissolved methane as ‘seeps’, and sites dominated by CO_2 with the term ‘vents’.

The eastern Mediterranean Sea and the eastern part of the central Mediterranean Sea have extensively been investigated for the occurrence of mud volcanism and cold seeps related to the presence of collision zones (Ceramicola et al., 2014; Lykousis et al., 2009; Mascle et al., 2014). In the western part of the central Mediterranean Sea, the Tyrrhenian Sea, evidences of fluid seepage are limited to the Adriatic Sea (Geletti et al., 2008), Strait of Sicily, Sardinian Margin (Dalla Valle and Gamberi, 2011) and Malta Plateau (Savini et al., 2009; Micallef et al., 2011; Taviani et al., 2013), mostly in the form of pockmarks, occasionally associated with methane-imprinted carbonates (Capozzi et al., 2012; Cangemi et al., 2010; Angeletti et al., 2015; Taviani et al., 2015). In the westernmost part of the Central Mediterranean Sea, the Tyrrhenian Sea, little evidence of past and present fluid circulation was found in the deep sea, except for the Paola Ridge, along the NW Calabrian margin (Fig. 1). This area, surrounded by hydrothermally active vent sites (Peters et al., 2011; Passaro et al., 2016), has been described as a site of seepage, gas venting at the seafloor and precipitation of methane-related authigenic carbonates (Gamberi and Rovere, 2010; Rovere et al., 2014, 2015).

Although authigenic calcite and aragonite have commonly been used for geochemical characterization of seeping fluids and paleoenvironmental reconstruction at recent (e.g., Himmler et al., 2010; Peckmann et al., 2001; Peckmann and Thiel, 2004; Capozzi et al., 2012; Magalhães et al., 2012) and fossil (e.g., Blumenberg et al., 2015; Cau et al., 2015; Viola et al., 2015) methane seeps, the occurrence of authigenic siderite at seepage sites is less documented (Fritz et al., 1971; Curtis et al., 1972; Mozley and Wersin, 1992; Rongemaille et al., 2011). Siderite nodules have been reported in modern settings associated with methane seepage (Niger delta; Rongemaille et al., 2011) or methane hydrate decomposition (Black Outer Ridge; Matsumoto, 1989), and with highly ferruginous, low-sulfate, anoxic lake waters (e.g., Wittkop et al., 2014). Despite the wide occurrence of sedimentary siderite little is known about the chemical conditions in which siderite forms in deep marine settings. Siderite is a common early diagenetic mineral that likely records the chemistry of the mineralizing fluids providing insights into the characteristics of the depositional environments (Mozley and Wersin, 1992). Pioneering studies of deep marine sediments, argued that the isotopic composition of siderite might be the result of the incorporation of deep circulating fluids (Clayton and Epstein, 1961; Muehlenbachs and Hodges, 1978; Cocker et al., 1982).

To characterize the pattern of fluid seepage that has triggered the precipitation of authigenic minerals at Paola Ridge, whole rock geochemistry (REE) and stable isotope (carbon and oxygen) composition were investigated. REE composition of carbonates has successfully been applied to the reconstruction of seeping fluids composition and redox conditions in both recent (e.g., Himmler et al., 2010; Hu et al., 2014) and ancient (e.g., Nothdurft et al., 2004; Feng et al., 2009; Franchi et al., 2015, 2016) settings. The variation of the REE pattern from the standard seawater composition (e.g., Zhong and Mucci, 1995; Zhang and Nozaki, 1998) is related to either mixing processes between methane-rich and hydrothermal fluids (e.g., Kamber et al., 2004; Feng et al., 2009) or modification of pore water redox conditions (Kim et al., 2012; Hu et al., 2014).

Although extensive literature deals with the characterization of authigenic precipitates at methane seeps, few cases are known where pyrite, siderite, dolomite and calcite/aragonite concretions occur in the same setting. The presence of siderite concretion alongside with pyrite concretion and the occurrence of calcite/aragonite concretions lined by dolomite crusts make the Paola Ridge an unparalleled laboratory for marine and petroleum geologists interested in the study of the interaction between mineralizing fluids and sub-bottom sediments.

Starting from the assumption that authigenic pyrite, siderite and calcite precipitate under different chemo-physical conditions, this paper aims at unraveling the dynamic processes occurring in the sub-bottom sediments of Paola Ridge (southern Tyrrhenian Sea) and provides an alternative interpretation of peculiar domed morphologies hitherto considered as mud volcanoes (Gamberi and Rovere, 2010; Rovere et al., 2014, 2015). By coupling trace elements and REE distributions and the $\delta^{13}C$ (‰ V-PDB) and $\delta^{18}O$ (‰ V-PDB) values, the source of the seeping fluids and redox condition during carbonate precipitation have been defined. This work aims at providing for the first time a detailed genetic scenario for the formation of diverse authigenic products precipitated under different chemo-physical conditions considering the dynamism at methane seepage sites. These consist of CO_2 venting, intermittent methane seepage and migration of the SMTZ for the formation of authigenic minerals along the Paola Ridge.

2. Geological setting

The Paola Ridge is a NNW-SSE 60-km-long and ca. 500-m-high anticline that confines the Paola Basin westward along the continental slope of the NW Calabrian margin (Fig. 1). The Paola Basin lies at the rear of the Calabrian Arc (inset of Fig. 1) in the upper plate of the Ionian subducting system (Faccenna et al., 2011). The Paola Basin, along with other basins along the Italian margins, originated from the extensional tectonics connected to the southeast migration of the Apennine Thrust Belt, this led to the opening of the Tyrrhenian Sea back arc basin, (see Milia et al., 2009; Gutscher et al., 2015 and references therein).

Cold seeps were first identified between 700 and 900 m water depth along the Paola Ridge with the aid of full-ocean depth multibeam and backscatter data (Gamberi and Rovere, 2010). The cold seeps are located on 2 structures initially defined as mud volcanoes