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Paleo-environmental controls on cold seep carbonate authigenesis in the Sea of Marmara

Antoine Crémière [a,*], Germain Bayon [b], Emmanuel Ponzevera [b], Catherine Pierre [a]

[a] Université Pierre et Marine Curie, LOCEAN, UMR 7159, Paris, France
[b] IFREMER, Unité de Recherche Géosciences Marines, Plouzané, France

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A B S T R A C T

The factors controlling fluid emission dynamics at ocean margins are poorly understood. In particular, there are significant uncertainties on how fluid seepage at cold seeps may have responded to abrupt environmental changes in the geological past. This study reports on a detailed geochemical investigation of seafloor carbonate crusts sampled at cold seeps along the submerged part of the North Anatolian Fault system in the Sea of Marmara – an inland sea, which has experienced major paleo-environmental changes over the last deglaciation period. We also analyzed a series of authigenic carbonate concretions recovered from two sediment cores at the Western-High ridge, an active fluid venting area.

The ages of seafloor carbonate crusts derived from isochron U–Th dating cover the last 7 kyr, suggesting that fluid activity along the fault system remained continuous over that time interval. In the sediment cores, carbonate concretions are concentrated at the lacustrine-to-marine transition, which corresponds to the period when Mediterranean waters flowed into the Marmara Basin about 12–14 kyr ago. U–Th isotopic data indicate that most of these concretions formed later during the Holocene, around 9–10 kyr ago, a period coinciding with an important anoxic event that led to the deposition of a sapropel layer in the Sea of Marmara.

Based upon these results, we suggest that the absence of carbonate concretions in the lacustrine sediment unit indicates that dissolved sulfate concentrations in the Marmara lake pore waters during glacial time were too low to promote significant anaerobic methane oxidation, thereby preventing sedimentary carbonate authigenesis. In contrast, the progressive inflow of Mediterranean waters into the glacial Marmara lake after 15 ka provided a source of dissolved sulfate that allowed anaerobic oxidation of methane to proceed within the anoxic sediment. Importantly, the synchronism between the main phase of authigenic carbonate precipitation at the studied sites (average 9.4 ± 1.8 ka, $n = 16$) and the regional anoxic sapropel event support the idea that the drop in bottom water dissolved oxygen content was probably a key factor to enhance microbial activity and associated carbonate precipitation at that time. Overall, these results provide straightforward evidence that fluid emission dynamics and hydrocarbon oxidation at cold seeps can be directly related to changing environmental conditions through time.

1. Introduction

Since their first discovery in the Gulf of Mexico (Paull et al., 1984), hydrocarbon-rich fluid discharges on the seafloor have been widely reported at ocean margins, often in association with chemosynthetic communities and authigenic carbonate deposits (for reviews see Campbell, 2006; Judd and Hovland, 2007; Sibuet and Olu, 1998). Substantial amounts of methane and other hydrocarbons transit in cold seep areas, which represent a significant component of the marine carbon cycle. In these environments, the mineralization of methane-derived authigenic carbonates represents a major sink for carbon. Despite this significance, the global factors driving fluid seepage activity at ocean margins through time remain poorly understood. In particular, it is still unclear how cold seeps may respond to large-scale environmental changes, such as those that have been induced in the recent geological past by the alternance between glacial and inter-glacial periods. These considerations could have major implication in the understanding of the paleo-biogeochemical fluxes at ocean margins, with possible significance in the context of the foregoing climate change.

At cold seeps, authigenic carbonate precipitation is induced by the anaerobic oxidation of methane (AOM) coupled with reduction of dissolved sulfate in pore waters. This reaction generally takes place in sub-surface sediments at the so-called sulfate–methane transition zone (SMTZ) and is mediated by a consor-

* Corresponding author at: LOCEAN, Université Pierre et Marie Curie, Tour 45-55, 5ème étage, Case 100, 4 place Jussieu, 75252 Paris Cedex 05, France. Tel.: +331 44 27 84 79; fax: +331 44 27 71 59.

E-mail address: antoine.cremiere@locean-ipsl.upmc.fr (A. Crémière).

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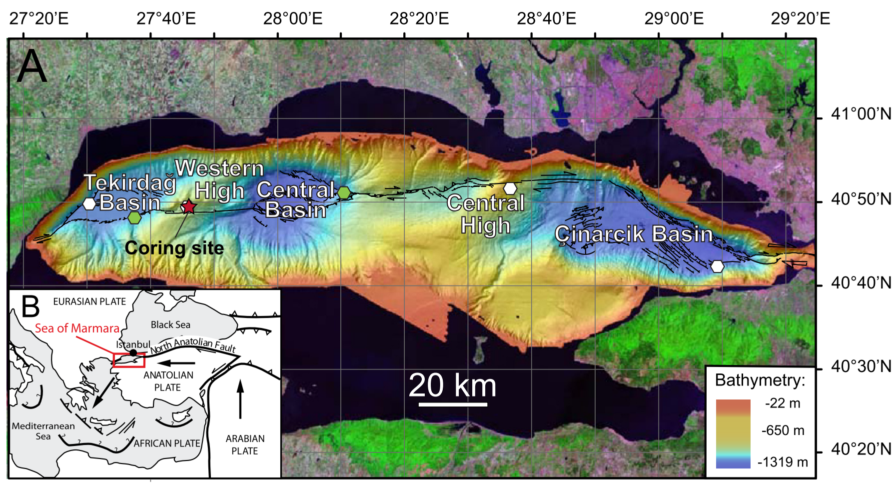

Fig. 1. (A) Bathymetry of the Sea of Marmara with sampling locations (white hexagons: seafloor carbonate crusts, green hexagons: carbonate chimneys expelling glacial brackish water, red star: coring site). (B) Tectonic setting of the eastern Mediterranean region. Arrows indicate relative plate motion and red box shows study area of the Sea of Marmara. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

tium of methane oxidizing archaea and sulfate reducing bacteria (Boetius et al., 2000; Hinrichs et al., 1999; Knittel et al., 2005; Orphan et al., 2001; Reeburgh, 1976; Valentine, 2002; Valentine and Reeburgh, 2000), following the chemical reaction:

$$CH_4 + SO_4^{2-} \rightarrow HCO_3^- + HS^- + H_2O$$

The production of bicarbonate and hydrogen sulfide at the SMTZ induces precipitation of carbonate minerals and pyrite (e.g. Peckmann et al., 2001; Ritger et al., 1987; Sassen et al., 2004).

Because authigenic carbonates are usually preserved within the geological record, they represent reliable archives of paleo-cold seep activity and related environmental parameters. For instance, the carbon isotopic composition ($\delta^{13}C$) of carbonates represents a complex mixture of different carbon pools that possibly feeds carbonate precipitation and indirectly helps identifying the source of fluids from which they have precipitated. In addition, the oxygen isotopic composition ($\delta^{18}O$) can provide information on both the temperature and the isotopic composition of fluids in equilibrium during carbonate formation (e.g. Aloisi et al., 2000; Feng et al., 2010a; Gontharet et al., 2007; Greinert et al., 2001; Han et al., 2004; Magalhães et al., 2012; Peckmann and Thiel, 2004; Ritger et al., 1987; Stakes et al., 1999; Vanneste et al., 2012). In comparison, the temporal evolution of fluid dynamics at cold seeps is generally poorly constrained, mainly because authigenic carbonate minerals incorporate a substantial amount of dead carbon that makes conventional radiocarbon dating unsuitable. To date, uranium–thorium dating methods represent the most suitable technique to constrain the temporal activity of cold seeps (Aharon et al., 1997; Bayon et al., 2009; Feng et al., 2010b; Kutterolf et al., 2008; Lalou et al., 1992; Liebetrau et al., 2010; Teichert et al., 2003; Watanabe et al., 2008).

This study reports absolute U–Th ages for a series of authigenic carbonate samples, together with more conventional stable carbon and oxygen isotopic data. The authigenic carbonates studied here were collected both at the seafloor and within sediments at various locations along the submerged fault system in the Sea of Marmara (northeastern Anatolia area; Fig. 1). The Sea of Marmara has experienced large environmental changes since the last glacial maximum (i.e. the last 20 kyr), which makes it a well suited natural laboratory for investigating the response of fluid seepage to changes of various environmental parameters, such as dissolved sulfate and oxygen concentrations in bottom waters.

2. Background

2.1. Geological setting

Located at the intersection between four tectonic plates, the Anatolian region is one of the seismically most active zone in the world. In its northwestern part, the inland Sea of Marmara pull-apart basin (Armijo et al., 1999) is crossed east-to-west by the western extension of the North Anatolian Fault (Fig. 1). This strike-slip fault is the expression of the transform plate boundary between the Eurasian plate and the Anatolian block, which accommodates motion of 20–25 mm/yr (Armijo et al., 1999; Armijo et al., 2002; McClusky et al., 2000; Reilinger et al., 1997). Along its submerged segment, the fault divides into a complex system of main and secondary branches (Bécel et al., 2010; Carton et al., 2007; Hergert and Heidbach, 2010). Extensive seafloor gas flares are associated with the fault network, as inferred from the occurrence of acoustic anomalies in the water column (Géli et al., 2008).

2.2. Late Quaternary oceanographic evolution

A major environmental change occurred in the Sea of Marmara during the Last Glacial Maximum (LGM) when the global sea level was approximately 120 m lower than today (Yokoyama et al., 2000). This event resulted in the isolation of the Sea of Marmara from the Mediterranean Sea via the Dardanelles sill. At that time, the Sea of Marmara became a large brackish water lake (Aksu et al., 2002; Çağatay et al., 2000; McHugh et al., 2008; Stanley and Blanpied, 1980). From ~ 14.7 ka before present (BP), and for about 2 kyrs, the marine transgression accompanying the onset of the deglaciation led to the progressive reconnection of the Sea of Marmara to the Mediterranean Sea (Vidal et al., 2010). During this transition episode, a thin layer of authigenic calcite was deposited from 13 to 11.5 cal kyr BP, interpreted as a result of the mixing between oxic and salty Mediterranean waters and the brackish (mainly anoxic) lake waters (Reichel and Halbach, 2007). The Holocene period recorded in Marmara Sea sediments is characterized by the onset of two anoxic events, inferred from the presence of sapropel deposits. The first sapropel event occurred between 11.5 to 7 cal kyr BP, mainly associated with an enhancement of the primary productivity possibly sustained by the reorganization of phytoplankton populations, whereas the second one, less prominent, took place between 4.7 and 3.5 cal kyr BP (Aksu et al., 2002;