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Methane-derived authigenic carbonates along the North Anatolian fault system in the Sea of Marmara (Turkey)

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A B S T R A C T

The Marnaut cruise (May–June 2007) investigated the submerged part of the North Anatolian fault system, an active tectonic area in the Sea of Marmara. Already known and new fluid venting sites along the fault system were visited by submersible diving. Cold seeps present a considerable diversity of geochemical background associated with occurrences of authigenic carbonate crusts outcropping at the seafloor. Buried carbonate concretions were also recovered by coring within the sediments of the Tekirdağ Basin and of the Western-High ridge that separates the Tekirdağ and Central Basins. Interestingly, numerous of these early diagenetic carbonates were found within the transitional sediments from lacustrine to marine environment deposited after the late glacial maximum. The authigenic carbonates are mainly composed of aragonite, Mg-calcite and minor amounts of dolomite, and are often associated with pyrite and barite. The carbon isotopic compositions of carbonates present a wide range of values from −50.6‰ to +14.2‰ V-PDB indicating different diagenetic settings and complex mixtures of dissolved inorganic carbon from different sources. The low $\delta^{13}C$ values of the seafloor crusts and of most buried concretions indicate that the carbon source was a mixture of microbial and thermogenic methane and possibly other hydrocarbons that were oxidized by anaerobic microbial processes. The positive $\delta^{13}C$ values of a few buried concretions from the Western-High ridge reflect the mineralization of heavy CO_2, which is thought to represent the residual by-product of oil biodegradation in a subsurface petroleum reservoir that migrated up with brines. Most of the oxygen isotopic compositions of seafloor carbonates are close to the isotopic equilibrium with the present-day bottom water conditions but a few values as low as −1.9‰ V-PDB indicate precipitation from brackish waters. In buried carbonate concretions, $\delta^{18}O$ values as high as +4.9‰ V-PDB reflect the contribution of water enriched in ^{18}O. The results support the hypothesis that after the late glacial/Holocene transition, precipitation of authigenic carbonates, now buried within the sediments of the Western-High mound structures, was promoted due to enhancement of anaerobic oxidation of methane, possibly from massive methane release by gas hydrate dissociation, and by sulfate rich Mediterranean water incursion.

1. Introduction

Natural escapes of fluids and gas from seafloor margins are widespread manifestations called "cold seeps" found all over the world's oceans (Campbell, 2006; Judd and Hovland, 2007; Tyler et al., 2003) in specific geological environments such as convergent plate boundaries (Kulm et al., 1986; Sibuet et al., 1988), passive continental margins (Kennicutt et al., 1985; Paull et al., 1984) and active fault systems (Moore et al., 1990) that allow ascending migration of gas-rich fluids throughout the sediments.

Typically, these vents release fluids rich in methane and other hydrocarbons that are produced by the degradation of organic matter by microbial or thermogenic processes (Whiticar, 1999). Seafloor discharge of these fluids enriched in reduced compounds, such as methane and hydrogen sulfide, feeds chemosynthetic benthic communities (Sassen et al., 1993; Sibuet and Olu, 1998). Methane is mostly consumed within sediments by the anaerobic oxidation of methane (AOM) mediated by a microbial consortium

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that oxidizes methane generally via sulfate reduction and produces hydrogen sulfide (Boetius et al., 2000; Orphan et al., 2001; Reeburgh, 1976; Valentine and Reeburgh, 2000).

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

This reaction occurs mainly at the sulfate-methane transition zone (SMTZ) between the upward advecting methane-rich fluid and sulfate-rich bottom seawater that either diffuses or is advected through the sediment (Borowski et al., 2000; Borowski et al., 1996; Wallmann et al., 1997). Production of bicarbonate ions increases pore water alkalinity, which combined with dissolved Ca^{2+} and other divalent cations promotes precipitation of authigenic carbonates in shallow subsurface sediment according to the reaction:

$$2HCO_3^- + Ca^{2+} \rightarrow CaCO_3 + CO_2 + H_2O$$

Microbial and thermogenic methane is characterized by low $\delta^{13}C$ values ranging from $-110‰$ to $-50‰$, and $-50‰$ to $-20‰$, respectively (Whiticar, 1999). The mineralization of oxidized methane is recorded in carbonates presenting low $\delta^{13}C$ values (Aloisi et al., 2000; Bahr et al., 2009; Feng et al., 2010; Gontharet et al., 2007; Kulm et al., 1986; Mazzini et al., 2004; Naehr et al., 2007; Paull et al., 1992; Peckmann et al., 2001; Pierre and Fouquet, 2007). Production of a ^{13}C-rich CO_2 pool in methanogenic sediments by organic-matter fermentation or by CO_2 reduction contributes to the formation of ^{13}C-rich carbonates (Boehme et al., 1996; Claypool and Threlkeld, 1983; Irwin et al., 1977; Kopf et al., 1995).

In a low temperature and high-pressure regime, water and methane can combine to form gas hydrates within the sediments. These crystalline structures consist of cages formed by water molecules entrapping molecules of light gases such as methane, ethane, carbon dioxide or hydrogen sulfide (Kvenvolden, 1993; Sloan, 2003). Methane hydrates contained in the sediments of continental margins represent a large carbon reservoir sensitive to fluctuations of temperature and pressure. Massive episodic releases of methane to the atmosphere from dissociation of marine gas hydrates are thought to have played a significant role in the past climatic system as this gas contributes to increase the greenhouse effect (Kennett et al., 2000; Kvenvolden, 1988; MacDonald, 1990). Past events of huge and abrupt methane release due to decomposition of marine gas hydrates were inferred from low $\delta^{13}C$ values of diagenetic carbonates as well as foraminifers in marine sediments (Bohrmann et al., 1998; Dickens et al., 1995; Garidel-Thoron et al., 2004; Katz et al., 1999; Kennett et al., 2000; Matsumoto, 1989; Pierre et al., 2002).

One of the main purpose of the Marnaut cruise (2007) in the Marmara Sea was to understand the relationships between active faults, fluid emissions and biogeochemical processes in the deep-sea sediments (Henry, 2007). Authigenic carbonates were recovered by submersible dives and in piston cores along the North Anatolian fault network. In this study, we report petrographical, mineralogical and scanning electron microscopy (SEM) observations coupled with stable isotopes analysis of diagenetic carbonates. This paper discusses about the variability of the processes that controlled the carbonate diagenesis, in the local context of the North Anatolian fault system. For the buried concretions retrieved down to 4.8 m below the seafloor (mbsf) at the Western-High ridge located between the deep Tekirdağ and Central Basins, we discuss their occurrence in the stratigraphic record, their possible relationship with the presence of gas hydrates, and we propose a link with the paleoceanographic history of the Sea of Marmara during the late glacial/Holocene transition.

2. Background informations

2.1. Geological setting

The Sea of Marmara is an intra-continental basin located in the northwestern part of Turkey between the Mediterranean Sea and the Black Sea. Seafloor morphology (Fig. 1(B)) is characterized by three deep basins (from west to east: Tekirdağ, Central and Çinarcik Basins) reaching a maximum depth of 1273 m, which are separated by two transpressional push-up structures (Western High and Central High).

The Sea of Marmara presents a long term history of large earthquakes (e.g., Ambraseys and Finkel, 1991). The North Anatolian fault accommodates about 25 mm/year of strike slip motion between the Anatolian block and the Eurasian plate (Fig. 1(A)) (Armijo et al., 1999; Armijo et al., 2002; McClusky et al., 2000; Reilinger et al., 1997). The northern branch of the North Anatolian fault crosses the Sea of Marmara, where it further divides in main and secondary fault branches (Armijo et al., 2002; Becel et al.,

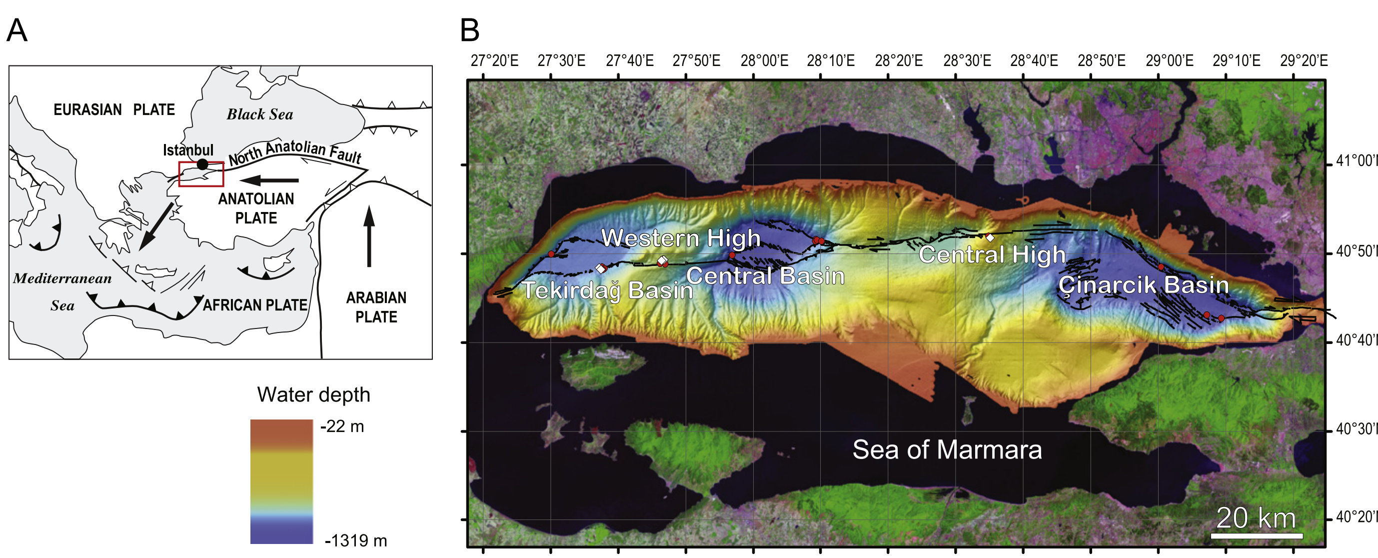

Fig. 1. (A) Regional setting of the tectonic framework in the eastern Mediterranean modified from Okay et al. (2000). (B) Bathymetric map of the Sea of Marmara with the location of studied dives (red dots) and coring sites (white diamonds) along the main Marmara fault (Bathymetry after Rangin et al. (2001) and land from Landsat Msrid, NASA: https://zulu.ssc.nasa.gov/mrsid/). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)