METHANE-RELATED CARBONATES FROM COLD SEEPS OF EASTERN MEDITERRANEAN AND MARMARA SEA

C. Pierre [1]*, M. Blanc Valleron [2], I. Bouloubassi [1], N. Cagatay [3], J. Foucher [4], P. Henry [5], J. Mascle [6] and T. Zitter [5]
[1] Université Pierre et Marie Curie- LOCEAN - catherine.pierre@locean-ipsl.upmc.fr
[2] MNHN-CR2P
[3] Istanbul Technical University
[4] Ifremer-Centre de Brest
[5] Université Aix-Marseille-CEREGE
[6] Geoazur, Villefranche-sur-mer

Abstract

Active methane seeps are present at the sea floor in the Eastern Mediterranean and Marmara Sea. The flow rate, temperature and chemistry of venting fluids differ largely from one site to another, depending on the source and depth of fluids. We present here the mineralogical and stable isotope compositions of carbonate crusts and concretions that were precipitated at or close to the sea floor and have registered the great variability of the fluids from the Mediterranean Ridge, Nile Deep Sea Fan and Marmara Sea cold seeps.

Keywords: Bacteria, Eastern Mediterranean, Marmara Sea, Deep Sea Processes, Mud Volcanoes

Active cold seeps in the Eastern Mediterranean were described since years 80's and their study was completed by deep-sea observations and sampling during oceanographic cruises using submersibles (MEDINAUT in 1998, NAUTINIL in 2003, MEDECO in 2007). In the Marmara Sea, cold seeps were observed in 2002 during the MARMARASCARPS cruise with ROV dives [1] and they were sampled using the submersible Nautile during the MARNAUT cruise in 2007. A few articles refer to the carbonate crusts from the MEDINAUT and NAUTINIL cruises [2],[3],[4].

Methane-rich fluids venting at sea-floor through geological structures as mud volcanoes, pockmarks and faults support specific chemosynthetic ecosystems where the microbial communities are particularly active in the carbon and sulfur cycles. The most important microbial process involved in these environments is the Anaerobic Oxidation of Methane (AOM) that is coupled with Bacterial Sulfate Reduction (BSR). During this process, the methane contained in the advected fluids is oxidized by the sulfate ions provided either by diffusion from bottom seawater or by advection of sulfate-rich brines.

The overall reaction describes the transfer of oxidized and reduced carbon and sulfur components:

$3CH_4 + 3SO_4^{2-} + Ca^{2+} \longrightarrow 3HS^- + CO_2 + HCO_3^- + 4H_2O + CaCO_3$

Carbonate and sulfide minerals are the two most important by-products of this reaction; their mineralogy may vary, depending on the cations and metal elements that are available in the fluids. Calcium carbonates (aragonite, calcite and magnesian calcite) dominate, especially in the upper sediments whereas magnesium-rich and iron-rich carbonates (dolomite, ankerite, siderite) increase progressively at depth.

The oxygen and carbon isotopic compositions of the diagenetic carbonates display very wide ranges that define three groupings :

1] The Mediterranean Ridge: the carbonate crusts are characterized by $\partial^{13}C$ values mostly in the range from -15 to -30‰ and more rarely down to -45‰; they include the highest $\partial^{18}O$ values (from 2.4 to 7.1‰).

2] The Nile Deep Sea Fan : the carbonate crusts display generally lower $\partial^{13}C$ values than the previous grouping, from -25 to -41‰; the range of $\partial^{18}O$ values is relatively narrow (2.4 to 4.8‰), except rare outlier lower values (-0.5 to 1‰).

3] The Marmara Sea : the carbonate crusts show the largest range of $\partial^{13}C$ values from -13 to -47.6‰ ; the range of $\partial^{18}O$ values is shifted to negative values (3.6 to -2.1‰).

The very low $\partial^{13}C$ values of diagenetic carbonates at all cold seep sites confirm that they are methane derived; the close association of carbonate with pyrite in the diagenetic crusts as well as biomarker proxies indicate that AOM was operating in conjunction with BSR.

The $\partial^{18}O$ values of carbonates mostly reflect isotopic equilibrium with the present-day bottom sea water; the heaviest $\partial^{18}O$ values from the Mediterranean Ridge are explained by the contribution of 18O-rich fluids originating from clay mineral dehydration at great burial depth; the lowest $\partial^{18}O$ values are due either to high heat flow in Amon mud volcano or to the contribution of brackish fluids in the Marmara sea.

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