INTEGRATED STUDIES OF CARBONATE CRUSTS FORMED THROUGH MICROBIAL ACTIVITY ON SUBMARINE MUD VOLCANOES

Giovanni Aloisi[1],*, Ioanna Bouloubassi[2], Sander K. Heijs[3], Richard D. Pancost[4], Catherine Pierre[1], Jaap S. Sinninghe Damsté[5], Jan C. Gottschal[3], Larry J. Forney[6], Jean-Marie Rouchy[7] and the MEDINAUT shipboard scientific party

[1] Laboratoire d'Océanographie Dynamique et de Climatologie, Université Pierre et Marie Curie, Paris, France - vanni@lodyc.jussieu.fr
[2] Laboratoire de Physique et Chimie Marines, Université Pierre et Marie Curie, Paris, France
[3] Department of Microbiology, Centre for Ecological and Evolutionary Studies (CEES), University of Groningen, The Netherlands
[4] Organic Geochemistry Unit, School of Geochemistry, University of Bristol, Bristol BS8 1TS
[5] Netherlands Institute for Sea Research, Department of Marine Biogeochemistry and Toxicology, Den Burg (Texel), The Netherlands
[6] Department of Biological Sciences, University of Idaho, Moscow, Idaho, USA
[7] Laboratoire de Géologie (CNRS-ESA 7073). Muséum National d'Histoire Naturelle, Paris, France

Abstract

Authigenic carbonate crusts formed through microbial methane oxidation are widespread at seafloor cold seeps. They are a sink for methane carbon migrating from depth or being released from shallow gas hydrates and thus, partly regulate ocean atmosphere carbon fluxes. To investigate their formation we conducted an integrated microbial, mineralogical and organic geochemical study of authigenic carbonate crusts recovered from mud volcanoes of the eastern Mediterranean. Our results show that carbonate crusts are formed in an anaerobic environment through anaerobic methane oxidation. This process is mediated by diverse consortia of prokaryotes which include previously uncharacterised methanotrophic archaeabacteria.

Keywords : Eastern Mediterranean, Mud volcanoes, Bacteria, Geochemistry, Mineralogy

Introduction

In the Eastern Mediterranean, mud volcanoes form when tectonically over-pressured and methane-charged mud is extruded at the seafloor and re-deposited as mud breccia. Seven such structures at depths between 1600 and 2000 m were explored with the *Nautile* submersible during the Medinaut cruise in 1998. An important discovery was that the central parts of the mud volcanoes actively seep methane to the bottom waters and are covered by carbonate crust pavements formed by precipitation of aragonite and lesser quantities of high-Mg calcite and dolomite in the shallow pore water of mud breccia deposits (1,2).

Materials and Methods

In order to understand the geochemical and microbiological processes that lead to carbonate crust formation, two carbonate crusts recovered with the *Nautile* submersible from the Napoli and Amsterdam mud volcanoes were investigated. We combined mineralogical (X-Ray diffraction) and stable isotope studies of the authigenic carbonate phase (2) with lipid biomarker analysis (GC, GC-MS, HPLC), compound-specific carbon isotope measurements (3) (GC-irm-MS) and 16SrRNA gene surveys conduced on the organic matter extracted from the crusts.

Results and discussion

The carbonate cements have unusually low concentrations of ^{13}C indicating methane as the major source of carbon. Measured velues of $\delta^{18}O$ of the Eastern Mediterranean crusts are considerably higher than those expected for carbonates precipitating from modern eastern Mediterranean bottom waters. Although this could reflect precipitation at lower temperatures, no significant temperature anomaly was measured during the Medinaut cruise. The ^{18}O-enrichment is possibly due to precipitation from ^{18}O-rich water derived from the decomposition of gas hydrates that are present in the studied mud volcanoes (1). Other possible sources of ^{18}O are the seepage of relic brines of Messinian age that are present in the sedimentary succession of the eastern Mediterranean and high temperature fluid-rock interactions.

Prior to carbonate crust formation, methane is oxidised and, at cold seeps, this process is mediated by aerobic and/or anaerobic chemosynthetic microorganisms. Simple chemical considerations predict that aerobic methane oxidation produces acidity, favouring the dissolution of carbonates, rather than their precipitation. Furthermore, pore water chemical profiles in marine sediments suggest that most of the rising methane could be consumed in the absence of oxygen. Knowledge of the nature of the microorganisms which are involved in methane consumption in anoxic environments, however, is incomplete (3,4).

No evidence for the occurrence of aerobic bacteria performing methane oxidation was found in the crusts, relevant diagnostic biomarkers being virtually absent among lipids. In contrast, abundant and highly diverse ^{13}C-depleted biomarkers specific of archaeabacteria indicate that methane is assimilated by a diverse community of archaea. Organic geochemical analyses also indicate that methane oxidation is mediated by sulfate reducing bacteria.

Bacterial 16S rRNA gene surveys confirmed the absence of aerobic methanotrophic bacteria. Archaeal 16S rRNA gene surveys identified a great diversity of archaeal lineages, most of which are novel and previously uncharacterised. In agreement with lipid analyses, bacterial 16S rRNA gene surveys identified sequences of sulphate^reducing bacteria. These observations are consistent with the presence of a consortium of prokaryotes composed of methane-consuming archaea and sulphate reducing bacteria which is held responsible for the anaerobic oxidation of methane in a variety of marine settings (5).

Conclusion

Recent studies show that gas hydrate destabilisation following bottom water temperature increase had profound effects on past global climate. Authigenic carbonates formed through anaerobic methane oxidation at cold seeps have the potential of recording such events. The microbial processes we describe provide the easiest explanation of their formation and could dominate at cold seeps worldwide. Highly diverse microbial communities are involved supporting recent propositions that microorganisms play a fundamental role in mineral precipitation.

References

1. MEDINAUT/MEDINETH Shipboard Scientific Parties, 2000. Linking Mediterranean brine pools and mud volcanism. EOS, *Transactions* 81: 631-633.
2. Aloisi G., Pierre C., Rouchy J.-M. and the MEDINAUT scientific party, 2000. Methane-related authigenic carbonates of Eastern Mediterranean Sea mud volcanoes and their possible relation to gas-hydrate destabilisation. *Earth. Planet. Sci. Lett.* 184 : 321-338. 3.
3. Pancost R.D., Sinninghe Damsté J. S., de Lint S., van der Maarel M.J.E.C., Gottshall J.C. and the Medinaut Shipboard Scientific Party, 2000. Biomarker evidence for widespread anaerobic methane oxidation in Mediterranean sediments by a consortium of methanogenic archaea and bacteria. *Appl. Environ. Microbiol.* 66: 1126-1132.
4. Hinrichs K.-U., Hayes J.M., Sylva S.P., Brewer P.G. and DeLong E.F., 1999. Methane-consuming archaeabacteria in marine sediments. *Nature* 398: 802-805.
5. Thiel V., J. Peckmann H.H. Richnow U. Luth J. Reitner and W. Michaelis, 2001. Molecular signals for anaerobic methane oxidation in Black Sea seep carbonates and a microbial mat. *Mar. Chem.* 73: 97-112.