Goldschmidt 2000
September 3rd–8th, 2000
Oxford, UK.

Journal of Conference Abstracts
Volume 5(2), 237

Lipid Biomarkers in Carbonate Crusts from mud Volcanoes of the Eastern Mediterranean Ridge: Implications for Methane Oxidation

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Methane seeps, authigenic carbonates and chemosynthetic benthic communities are common seabed features in the large mud volcanoes fields on the Eastern Mediterranean Ridge. In these settings, carbonates are a sink for methane carbon migrating from the depth or released from shallow gas hydrates and affect the carbon cycling at the benthic boundary.

During the Medinaut cruise (1998), submersible sampling allowed recovery of carbonate crusts from various mud-volcano settings. Significant ^{13}C-depletion of authigenic calcite/aragonite ($\delta^{13}C$ below 20 per mill) indicates incorporation of light CO_2 derived from methane oxidation. Furthermore, unusual ^{18}O enrichments suggest methane release from dissociation of shallow gas hydrates.

In order to investigate the role of micro-organisms in methane oxidation and in carbonate formation, the lipid composition of carbonate crusts was analysed. Emphasis was placed on the occurrence of distinctive biomarkers and on their carbon isotope composition for signifying processes mediated by micro-organisms.

Compounds characteristic of archaea, and specifically methanogens, are prominent among lipid constituents. The hydrocarbon fraction is dominated by the irregular C_{25}-isoprenoid 2,6,10,15,19-pentamethylicosane (PMI), a major component of most methanogens, along with several unsaturated counterparts with one to five double bonds (PMI:1-5), which have been so far reported only in cultures of *Methanosarcina mazeii* and *Methanolobus bombayensis* (Schouten et al., 1997). C_{20}-isoprenoids (crocetane and crocetene) are also abundant, accompanied by lesser amounts of saturated and unsaturated C_{30}- and C_{35}-isoprenoids, presumably derived from archaeabacteria.

Archaeol, a most common lipid of archaeabacteria and prominent in methanogens, is among the dominant polar lipids along with lesser amounts of hydroxyarchaeol, which typifies methanogens of the orders of Methanosarcinales and Methanococcales. Co-occurrence of C_{20}-/C_{25}-isoprenoids and archaeol/hydroxyarchaeol has not been reported previously in cold seeps (Thiel et al., 1999; Hinrichs et al., 1999 ; Elvert et al.,1999) other than those found in our study area (Pancost et al., 2000).

Overall, lipids identified in carbonate crusts point to a pronounced methanogenic activity. Nevertheless, their strong ^{13}C depletion (archaeol/hydroxyarchaeol : $\delta^{13}C$ from - 112 to -84 per mill, PMIs: $\delta^{13}C$ from -91 to -69 per mil) is not consistent with production by CO_2-reducing methanogens. This suggests that methanogenic archaea assimilate rather than produce ^{13}C-depleted methane. No conclusive evidence of aerobic methanotrophy supplying substrates for methanogenesis was found, diagnostic biomarkers being absent or at trace levels. Hopanoid alcohols, which are non-specific bacterial biomarkers, have $\delta^{13}C$ values consistent with an aerobic methanotroph source. Their low abundance, however, indicates that aerobic methanotrophy, if active, is of secondary importance in this setting.

Laboratory and field studies have proposed that methane oxidation under anaerobic conditions is carried out by methanogens operating in reverse although the responsible organisms have not been identified (Hohler et al., 1994). Reverse methanogenesis can account for the dominance of strongly ^{13}C-depleted methanogen biomarkers in the crust samples. In this process, sulphate-reducing bacteria act as hydrogen scavengers maintaining low hydrogen concentrations and favouring net methane oxidation (Hohler et al., 1994). Significant amounts of iso- and anteiso-C_{15} and C_{17} fatty acids, compounds abundant in sulphate-reducing bacteria, occur in crust samples. They are generally ^{13}C-depleted, albeit less than the archaeal biomarkers, suggesting that sulphate-reducing bacteria may thrive on substrates derived from methanogen biomass. Net anaerobic methane oxidation by methanogen and sulphate reducing assemblages in this setting would be further favoured by CO_2 removal during carbonate precipitation and by excess methane supply. Recent biomarker investigations indicated that this process is widespread in Mediterranean mud volcano sediments (Pancost et al., 2000).

An intriguing feature of crusts from all sites is the occurrence of abundant ^{13}C-depleted glycerol diethers containing C_{14} to C_{17} alkyl moieties, which are absent in nearby seep sediments and have not been previously reported in similar settings. This could suggest the presence of a consortium of prokaryotes specific to carbonate crusts, possibly containing species directly involved in carbonate precipitation.

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Ongoing geochemical and phylogenetic investigations are expected to provide further insight on processes, environmental conditions and prokaryotic assemblages involved in methane oxidation, as suggested by the variability of the lipid composition and carbon isotope signature in different crusts and sediment samples. This would also test a recent hypothesis that methane oxidation can be carried out by a new group of archaeabacteria phylogenetically distinct from known methanogens (Hinrichs et al., 1999).

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