



Anaerobic methane oxidation and carbonate precipitation in the carbonate crusts from The Gulf of Cádiz

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Carbonate "chimneys", concretions, crusts and slabs from the Gulf of Cádiz record very low $\delta^{13}\text{C}$ values (up to - 45 permil V-PDB) indicating the inflow of CO_2 derived from the oxidation of methane during carbonate precipitation. $\delta^{18}\text{O}$ values are very high (up to $\approx + 7$ permil V-PDB in dolomite concretions) pointing to the inflow of deep-seated fluids. Most carbonate cements (calcite and dolomite) consist of micrite and microspar (calcite and / or dolomite) and thus it is very difficult to microsample and isolate the cements from the original marine sediments with a hand-held dentist drill. The interpretation of the source of methane (biogenic vs. thermogenic) becomes very difficult.

An integrated study in one selected crust from Hespérides mud-volcano was carried in order to: 1) better constrain the possible sources of methane, 2) establish the origin and paragenetic evolution of cements present in these samples and 3) evaluate mixing with original marine sediments vs. fractionation effects as a possible cause of the dispersion in $\delta^{13}\text{C}$ values obtained in microsamples. The studied crust has calcite mineralogy and consists of mudstones-wackestones with micrite to microspar calcite cements. Patches with peloids and microspar cements are frequent. Open vugs of mostly ellip-

soidal to elongated shapes are rimmed with bright luminescent concentrically zoned sparry calcite cement. The isotopic composition has been determined in microsamples obtained with a computer-monitored micromill in specific areas previously differentiated through conventional and cathodoluminescence petrography. The samples analyzed consist of isolated cements. The small amounts of sample required for analyses ($\approx 60 \mu\text{g}$) has ensured minor contamination with the original sediment. The $\delta^{13}\text{C}$ of the peloidal areas with microspar cement ($\delta^{13}\text{C} = -23.5$ permil V-PDB), and the concentrically zoned bright luminescent cements ($\delta^{13}\text{C} = -12.3$ permil V-PDB), cannot differentiate the source of CO_2 as derived from bacterial sulphate reduction and organic matter oxidation, or from the oxidation of thermogenic methane. The $\delta^{18}\text{O}$ values ($+4 < \delta^{18}\text{O} \text{ permil V-PDB} < +4.8$) of both types of isolated microsamples plot in the range of values obtained in "bulk" microsamples microdrilled with a hand-held dentist drill. These $\delta^{18}\text{O}$ values suggest parental fluids enriched in ^{18}O .

The presence of archaeol, hydroxyarchaeol and glycerol dibiphytanyl glycerol tetraethers with very low $\delta^{13}\text{C}$ values (-104 to -114 permil V-PDB) confirms that, at least partially, CO_2 used for carbonate precipitation derived from the anaerobic oxidation of methane by methanotrophic archaea possibly in a consortium with sulphate-reducing bacteria. The results obtained from this pilot integrated study are still not conclusive. However, our current interpretations suggest that the range of $\delta^{13}\text{C}$ values recorded in "bulk" microsamples do not only reflect mixtures of authigenic carbonate derived from CH_4 oxidation with different proportions of the original marine sediment; but either different sources of methane (thermogenic vs. biogenic) and/or variations in CH_4 - CO_2 fractionation related to vital effects of methane oxidizers. It is expected that current integrated studies in all available samples from cruises ANASTASYA 00/09 and ANASTASYA 01/09 (years 2000 and 2001) will help to constrain the source of CO_2 and to better understand the causes for $\delta^{13}\text{C}$ dispersion of values in the carbonate concretions from the Gulf of Cádiz.

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