



Anaerobic oxidation of methane in evaporitic settings: An example from the Messinian in Sicily

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Sulphate-dependent anaerobic oxidation of methane (AOM) is known to induce the precipitation of secondary, authigenic carbonates with extreme ^{13}C -depletions at cold seeps (e.g., Thiel et al., 1999, Naehr et al., 2007). AOM has also been documented in marine anoxic sediments (Knittel and Boetius, 2009 and references therein). In modern hypersaline or evaporitic settings, however, AOM appears to be inhibited (Joye et al., 2009).

In Sicily, evaporitic carbonates and secondary carbonates containing native sulphur (the so-called 'Calcare solfifero') occur below a thick succession of gypsum that was deposited during the Messinian salinity crisis. Some of the secondary carbonates are characterized by pseudomorphs after lenticular gypsum and high $\delta^{18}\text{O}$ values (as high as +9‰ vs. V-PDB), confirming formation under evaporitic conditions. Low $\delta^{13}\text{C}$ values (as low as -52‰ vs. V-PDB) reveal that the carbonate formed as a consequence of the oxidation of biogenic methane.

The presence of ^{13}C -depleted molecular fossils in these carbonates including pentamethylcosane (PMI; $\delta^{13}\text{C}$: -92‰), hydroxyarchaeol (-79‰), as well as archaeal tetraether-derived biphytanes (-97 to -83‰) demonstrates that methanotrophic archaea oxidized methane under evaporitic conditions. ^{13}C -depleted *iso*- and *anteiso*- $\text{C}_{15:0}$ and $\text{C}_{17:0}$ fatty acids (-78 to -59‰), as well as mono- and dialkylglycerolethers (-84 to -53‰) prove that sulphate reducing bacteria were involved in AOM. This study provides the first evidence that sulphate-dependent AOM was not confined to normal marine environments in the past, having been a dominant process during the onset of the desiccation of the Mediterranean Sea in the Messinian.

References:

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