

AEROBIC METHANOTROPHY AT ANCIENT METHANE-SEEPS – A REVIEW

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The inventory of lipid biomarkers of a number of ancient methane-seep deposits has been studied over the last decade (for a review see Peckmann and Thiel, 2004). The authigenic carbonates at seeps that form due to an increase in alkalinity result from microbial activity. The molecular fingerprints of the chemosynthesis-based microbial communities tend to be extremely well-preserved in these seep carbonates. The key process is the anaerobic oxidation of methane, which is performed by consortia of sulphate-reducing bacteria and methanotrophic archaea. Typically, compounds preserved within modern and ancient seep settings comprise ^{13}C -depleted archaeal isoprenoidal (e.g. PMI, archaeol) and bacterial *n*-alkyl lipids (e.g. *anteiso*- C_{15} fatty acid). Besides the occurrence of ^{13}C -depleted isoprenoids and *n*-alkyl-chains in seep settings, ^{13}C -depleted hopanoids have been reported from modern seeps. They have been interpreted to be derived from aerobic methanotrophic bacteria (e.g. Elvert et al., 2000), or from unknown anaerobic bacteria (Thiel et al., 2003). The potential of seep-dwelling anaerobic bacteria to synthesise hopanoids has now been confirmed by Blumenberg et al. (2006), who cultured sulphate-reducing bacteria from a microbial mat from the Black Sea and found abundant hopanoids.

Here, lipid biomarker data are presented from two ancient methane-seep limestones embedded in Miocene strata in Italy and one in Late Cretaceous strata in Colorado, USA. These examples provide strong evidence that methane was not solely oxidized by an anaerobic process. Structural and carbon isotope data reveal that aerobic methanotrophy is more common at ancient methane-seeps than previously noticed. In one Miocene setting, abundant $3\beta\text{-Me-}17\beta(\text{H}),21\beta(\text{H})\text{-dihomohopanoic}$ acid was found ($\delta^{13}\text{C} -100\text{‰}$). Most likely, 3β -methylated hopanepolyols, prevailing in aerobic methanotrophs (e.g. *Methylococcus capsulatus*; Summons et al., 1994), were the precursor lipids of this compound. Moreover, more common hopanoids with very similar $\delta^{13}\text{C}$ values (e.g. $17\beta(\text{H}),21\beta(\text{H})\text{-pentakishomohopanoic}$ acid methylester; -97‰) have been found in this location as well. A series of isotopically depleted C-4-methylated steranes (lanostanes; -90 to -72‰) in another Miocene seep deposit has been attributed to aerobic methanotrophs (Peckmann et al., 2004). Lanosterol is the most likely precursor of C-4-methylated steranes. These compounds are known to be produced by aerobic methanotrophs, some of which are outstanding among

Bacteria in having the capacity to produce steroids (e.g. Summons et al., 1994). In a Late Cretaceous seep-limestone a suite of conspicuous 8,14-secohexahydrobenzohopanes (–110 to –107‰) has been described (Birgel et al., 2006). These hopanoids have been interpreted as early degradational products of precursor lipids locally produced by seep-endemic aerobic methanotrophs. This interpretation is supported by the presence of ‘regular’ hopanoids that can be discriminated from the unusual 8,14-secohexahydrobenzohopanes by only moderately low ^{13}C -values (–49 to –42‰).

Aerobic methanotrophy is more common at methane-seeps than previously recognised. Our data indicate that anaerobic and aerobic oxidation of methane at ancient seeps occurred in the same setting, probably in close proximity to each other.

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