Lipid biomarkers in methanogenic sediments of the alpine Lake Bled (SW Slovenia)

N. OGRINC[1]*, M. PETRIŠIČ[1], I. MANDIČ-MULEC[2], K. GORENC[2] AND J. FAGANELI[3]

[1]Dept. of Environ. Sci., J. Stefan Institute, 1000 Ljubljana, Slovenia (*correspondence: nives.ogrinc@ijs.si)
[2]Biotehnical Faculty, University of Ljubljana, 1000 Ljubljana, Slovenia
[3]Marine Biological Station, National Institute of Biology, 6330 Piran, Slovenia

Combined molecular, biogeochemical and organic geochemical data are presented that enable determination of the methanogenic pathway in sediments of dimictic Lake Bled (NW Slovenia), which has a developed anoxic hypolimnion most of the year. Methane concentrations in sediment pore waters where rather low, averaging 114 μM. The average $\delta^{13}C$ value of methane was −69.5 ± 1.2‰ indicating that methane was predominantly formed hydrogenotrophically. Methanogenic achaea are shown to constituite 73% of the total population of archaea at the surface, where fresher organic matter accumulates, and hydrogenotrophs, mostly *Methanomicorbiaceae*, were dominant (56%). Deeper in sediments, there were 27% of *Euryachaeota* archaea with unknown affiliation, 24% of *Thermoplasmatales* and related linkages and only 21% of hydrogenotrophic methanogenic archaea. A similar percentages (about 17%) of sequences representing acetotrophic archaea (*Methanosaetaceae*) were present in both layers. Lipid biomarkers, comprising aliphatic hydrocarbons, aliphatic alcohols, sterols and fatty acids, decreased nearly exponentially with depth. Lipids of bacterial origin constitute 5% of total lipids and do not change significantly with depth. Diploptene, which is an unsaturated terpene, was also identified with isotopic composition of -67.5‰ inferred a methanotrophic bacterial source. C_{27} sterols were the dominant sterols in the surface sediments, and the presence of cholesterol, as the major sterol indicated the important contribution of aquatic algae to sedimentary organic carbon. It was noteworthy that the $C_{29}\Delta^5$ sterol (24-ethylcholest-5-en-3β-ol), which has been commonly associated with terrestrial sources, showed $\delta^{13}C$ values similar to those of other planktonic sterols confirming their autochtonous origin. The longer chain n-alkanes, n-C_{25} to n-C_{33}, showed $\delta^{13}C$ values between -34.0 and -37.0‰, confirming their terrestrial origin. Similar to the n-alkanes, the longer chain *n*-alcohols exhibited $\delta^{13}C$ between -35.0 and -36.0‰ indicating terrestrial sources.

Surface-catalyzed peptide formation on sulfide minerals

S. OHARA* AND G.D. CODY

Geophysical Laboraroty, Carnegie Institution of Washington, Washington, DC 20015, USA
(*correspondence: sohara@ciw.edu)

The formation of peptide from amino acids in dilute solutions on the early Earth remains an enigma for the origins of life. Hypotheses by Wächtershäuser [1, 2] and Russell and Hall [3] propose that sulfide minerals could catalyze the production of the first peptides. It has been shown that dipeptides form in the presence of a (Ni, Fe)S precipitate with CO and H_2S (or CH_3SH) at 100ºC [4]. However, the formation of COS, has been shown to be a condensation agent for peptide formation [5]. Consequently, a special role of sulfide minerals for peptide formation has not been demonstrated. We present results that show that peptide formation is significantly enhanced in the presence of pyrite (FeS_2), chalcopyrite ($CuFeS_2$) or sphalerite (ZnS) and in the absence of condensation reagents. That the peptization reaction is surface catalyzed is supported by the fact that the yield of peptides strongly correlates with mineral surface area. Metal sulfides in aqueous solution are expected to develop four different functional groups ($\equiv$Me-OH, $\equiv$Me-OH_2^+, $\equiv$S-H and $\equiv S^-$) [6]. Amino acids exist as unreactive zwitterions in neutral solution. The pair of acidic ($\equiv$Me-OH_2^+) and basic ($\equiv S^-$) sites of metal sulfides could activate the carboxyl (-CO_2^-) and amino (-NH_3^+) groups of amino acid zwitterions. The yield of peptides with sphalerite was much higher than with pyrite or chalcopyrite under the same surface-area condition. It is known that the oxidation of surface iron and reaction with water forms hydroxyl radicals ($^\bullet$OH) [7]. Zinc is incapable of oxidation and, thus peptides formed on the surface of ZnS would not be subjected to decomposition by $^\bullet$OH. Sphalerite may have been a useful catalyst for the promotion of prebiotic peptide formation.

[1] Wächtershäuser (1988) *System. Appl. Microbiol.* **10**, 207–210. [2] Wächtershäuser (1990) *Proc. Natl. Acad. Sci. USA* **87**, 200–204. [3] Russell & Hall (1997) *J. Geol. Soc.* **154**, 377–402. [4] Huber & Wächtershäuser (1998) *Science* **281**, 670–672. [5] Leman *et al.* (2004) *Science* **306**, 283–286. [6] Rönngren *et al.* (1991) *J. Colloid Interface Sci.* **145**, 396–404. [7] Cohn *et al.* (2004) *EPSL* **225**, 271–278.