Abiotic synthesis of methane from biomolecules under ambient conditions

FREDERIK ALTHOFF[1] AND FRANK KEPPLER[2]

[1]Max-Planck-Institute for Chemistry, Joh.-Joachim-Becher-Weg 27, 55128 Mainz; (Frederik.althoff@mpic.de)
[2]Max-Planck-Institute for Chemistry, Joh.-Joachim-Becher-Weg 27, 55128 Mainz; (frank.keppler@mpic.de)

The formation of methane can be classified in biotic and abiotic reactions. While biotic methanogenesis is related to anaerobic microorganisms, abiotic methane formation requires high pressure and/or temperature. Such conditions can be found for instance during biomass burning or serpentinisation of olivine, under hydrothermal conditions in the deep ocean or below tectonic plates [1].

The bio available substances ascorbic acid, iron and hydrogen peroxide were used in aqueous solution to perform an abiotic methane formation under ambient conditions [2]. In a further step to this reaction other important biomolecules were added which are known from methylation reaction in biosystems, e.g. methionine, or expose a possible methane precursor methyl groups, such as choline or leucine.

Furthermore, the reaction was carried out using different iron species, such as Fe^{2+}, Fe^{3+}, ferrihydrite and other iron hydroxides.

Methionine was found to produce the highest amount of methane. Stable isotope analysis in combination with ^{13}C labelling of methionine confirmed the assumption of sulphur bond methyl group as methane precursor. Moreover, a linear increase of the generated methane with the amount of added methionine could be found.

The investigation of the iron species basically showed a conversion to methane, however, methane formation is significantly higher using iron minerals in comparison to free Fe ions. By analysing the remaining products within the solution a reaction scheme was created.

The results of these experiments show the possibility of an abiotic aerobe methane formation using biomolecules under ambient conditions.

[1] Sherwood Lollar *et al*. (2002), *Nature* **416**, 522-524. [2] Althoff *et al*. (2010), *Chemosphere* **80**, 286-292.

The correlation between iodide sorption capacity and microbial enzyme activity in soils

S. AMACHI[1]* AND Y. MURAMATSU[2]

[1]Chiba Univ., 648 Matsudo, Matsudo-shi, Chiba 271-8510, Japan (*corespondence: amachi@faculty.chiba-u.jp)
[2]Gakushuin Univ. Mejiro 1-5-1, Toshima-ku, Tokyo 171-8588, Japan (yasuyuki.muramatsu@gakushuin.ac.jp)

Iodide (I^-) sorption on soils is strongly inhibited by autoclaving, reducing agents, common enzyme inhibitors (NaN_3 and KCN), and anaerobic incubation of soils. These suggest that the sorption of iodide is influenced by the soil redox potentials, and that microbial oxidation of iodide might play a role in the process. Recently, we found that bacterial iodide-oxidizing enzyme is a laccase-like enzyme, since it oxidized not only iodide but also phenolic compounds such as ABTS, syringaldazine and 2,6-dimethoxy phenol. Laccases are copper-containing enzymes that are secreted into soils by soil fungi and bacteria.

To understand possible participation of microbial enzymes in iodide sorption, we examined the correlation of iodide sorption rate with laccase activity in several soils. Laccase activity was assayed colorimetrically with ABTS as a substrate. As have been observed in iodide sorption, laccase activity in soils was also inhibited by autoclaving, reducing agents, enzyme inhibitors, and anaerobic incubation. The calculated iodide sorption rate [$(1-C/C_0)$/h/g dry soils]and laccase activity (Unit/g dry soils) showed significant positive correlation. Furthermore, addition of bacterial iodide-oxidizing enzyme to autoclaved soil allowed it to adsorb iodide again. From these results, it is possible that iodide in soils is oxidized by laccase (or laccase-like enzyme) to I_2 or HIO, and that these oxidized iodine species are incorporated into soil organic matters.