

Oxidation of organics under hydrothermal conditions: Implications for the evolution of methane on Mars

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To assess the effect of strong oxidants on the evolution of organics on Martian environments, a series of experiments have been conducted involving decomposition of dissolved $\text{HCOOH}_{(\text{aq})}$ utilizing $\text{H}_2\text{O}_2_{(\text{aq})}$ at low temperature hydrothermal conditions (80-150°C, 25 MPa). Results clearly indicate the significantly enhanced kinetic rate of decarboxylation process relative to the homogeneous $\text{HCOOH-H}_2\text{O}$ system, with even greater oxidation effects imposed when Fe-oxides (e.g. Fe_3O_4) catalyze the reaction. The later might be closely related to formation of metastable hydroxyl radicals through Fenton type reactions enforced by H_2O_2 decomposition in presence of Fe^{+2} phases. Moreover, the $\delta^{13}\text{C}$ isotopic composition of the evolved $\text{HCOOH}_{(\text{aq})}$ shows a kinetic isotope effect that could be used as a proxy to distinguish low-temperature abiotic oxidation from biotic or other abiotic processes occurring at higher temperatures.

To further evaluate $\text{CH}_4_{(\text{aq})}$ oxidation processes, we have also investigated the kinetic rate of abiotic methane oxidation in the $\text{CH}_4\text{-O}_2\text{-H}_2\text{O}$ system at subseafloor hydrothermal conditions (200-350°C, 30 MPa). Results indicate that complete CH_4 oxidation to CO_2 proceeds in significantly lower kinetic rate than the decomposition rates of intermediate carbon species (e.g. HCHO , CH_3OH , HCOOH). Experimental results also reveal formation of metastable species such as dissolved $\text{CO}_{(\text{aq})}$ and $\text{H}_2_{(\text{aq})}$. Thus, it appears that partial $\text{CH}_4_{(\text{aq})}$ oxidation might occurred leading to release of $\text{H}_2_{(\text{aq})}$ which is incorporated into the water-gas-shift reaction to form metastable $\text{CO}_{(\text{aq})}$. Both species are present only at the very early stages of the experiments suggesting that strongly disequilibria conditions might be responsible for triggering partial $\text{CH}_4_{(\text{aq})}$ oxidation. Most importantly, our data suggest that the rates of oxidation process approximate the extent of $\text{CO}_2_{(\text{aq})}$ conversion to $\text{CH}_4_{(\text{aq})}$ even when it's Fischer-Tropsch catalyzed at an ultimate rate by Ni-Fe alloy under highly reducing conditions. This has important implications on carbon cycling and the habitability of hydrothermal environments associated with the anoxic/oxic boundaries established during hydrothermal circulation especially within the highly oxidizing Martian upper crust.

Fe(II) uptake and transformation on uranium contaminated sediment from the Rifle IFRC field site

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In the course of biostimulation experiments designed to remediate subsurface uranium contamination through the creation of reducing conditions at the Rifle IFRC site, iron reduction by native bacteria produces large quantities of Fe (II) in the aquifer. Dissolved Fe (II) concentrations typically reach levels of 50-100 μM before the onset of sulfate reduction. The goals of our experiments were to investigate the degree and mechanism of Fe (II) uptake on Rifle sediments and the possibility of abiotic U (VI) reduction in the Rifle aquifer. Results from a tracer test in which Fe (II) amended groundwater was injected into multi-level sampling wells in the Rifle aquifer indicated that Fe (II) uptake by the sediments is extensive. In addition, decreases in dissolved U (VI) were observed in the aquifer after injection of a pulse of pH 8.4 groundwater, but not at the ambient pH value of 7.2, indicating that abiotic U (VI) reduction in the presence of Fe (II) may be important at higher pH. Results from a series of laboratory experiments performed over a range of chemical conditions (Fe (II) concentration and pH) are presented along with Mossbauer data collected on selected sediment samples. Mossbauer results indicate that a fraction of the Fe (II) added to sediments is oxidized to Fe (III) on mineral surface. Results from these field and laboratory experiments indicate that the sediment can take up very large quantities of Fe (II), and thus the dissolved Fe (II) represents only a fraction of the pool of Fe (II) in the aquifer. In addition, abiotic U (VI) reduction may be more favorable in the Rifle aquifer at higher pH values.