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## Hydrogen formation from organic matter mediated redox reactions at silicate mineral surfaces

A. Kassahun (1), M. Hoffmann (1), N. Hoth (2)

(1) Dresden Groundwater Research Centre, Dresden, Germany, (2) University of Mining and Technology, Freiberg, Germany

(akassahun@dgfz.de / Phone: +49-351-4050672)

The formation of molecular hydrogen was observed in closed anoxic test systems containing sedimentary rock silicates, water of varying DOC and nitrogen gas headspace. Both pure silicate minerals (quartz, chlorite, albite, kaolinite) and sandstone rock samples were tested in potassium phthalate solution, humic acid and aqua dest. In all test systems using potassium phthalate solutions, hydrogen formed at considerable amounts (~500 nmol H<sub>2</sub> per g mineral). Hydrogen formation was one to two orders of magnitude smaller in test systems using humic acid and aqua dest., respectively. The measured H<sub>2</sub> formation at sedimentary rock minerals equals or exceeds the hydrogen formation levels of olivine minerals [1]. While  $H_2$  levels stayed constant over time in sterile test systems, non sterile test systems show decline in  $H_2$  by microbial  $H_2$ consumption upon CH<sub>4</sub> formation. Moreover, hydrogen formation was stimulated by the exchange of the headspace gas. NaOH extraction and subsequent HPLC analysis of the extracts revealed the presence of adsorbed phthalates in the chlorite and albite samples, both most effective in  $H_2$  formation even in aqua dest. Consequently, tests with NaOH-washed chlorite and albite showed smaller H<sub>2</sub> formation as compared to tests with untreated chlorite and albite in aqua dest. Since phthalates are common environmental substances (e.g. building blocks of humic substance, gas field water DOC components), their reaction capacity at silicate surfaces yielding the formation of molecular hydrogen could be an important factor causing microbial colonization of silicate mineral surfaces and subsequent biofilm formation.

[1] T.O. Stevens, J.P. McKinley: Abiotic controls on  $H_2$  production from basalt – water reactions and implications for aquifer biogeochemistry, Environ. Sci. Technol. 2000, 34, 826-831