

MICROFRACTURE GEOCHEMISTRY AS AN INDICATOR OF TERMINAL ELECTRON ACCEPTING PROCESSES IN TCE-CONTAMINATED BEDROCK

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A TCE-contaminated competent bedrock site in Portsmouth, NH was used to determine if a relation exists between microfracture (MF) surface geochemistry and the ecology and metabolic activity of attached microbes relative to terminal electron accepting processes (TEAPs) and trichloroethene (TCE) biodegradation. The bedrock is metasandstone and metashale of the Kittery Formation. Eleven microfractures (MF 01-11) in the competent rock were extracted from cores of two boreholes (BBC5 and BBC6) at depths > 21.3 m (70 ft) below ground. The host rock (HR) had three nominal pore throat sizes (131.1, 1.136, and 0.109 μm), a porosity of 0.8%, and a permeability of < 1 ud. Petrography, SEM-EDAX, XRD and XPS were used to characterize the HR and MF surface precipitates. Carbonate minerals and quartz were the dominant MF surface precipitates. Likely oxidized and reduced iron species were identified with XPS on the MF precipitate surfaces. Carbon functional groups characteristic of NOM were also identified with XPS. Static SIMS mass fragment fingerprints suggested that TCE, PCE and/or VC were present and possibly adsorbed to NOM on the MF surfaces. Straddle packer samples from intervals where MF were located were alkaline (131-190 mg/L as CaCO_3 , pH 8.8 to 9.6), mildly reducing (Eh of -208 to 160 mV, DO of 0.4 to 2.5 mg/L), with low NPDOC values (0.8 to 1.7 mg/L), and measurable Fe (II) (0.1 mg/L) and Fe (III) (0.02 to 0.3 mg/L). Sulfate was the dominant anion in the packer sample water (110-120 mg/L). No sulfide was detected. H_2 was present in a number of the BBC wells at the site (2.2 – 7.3 nM). Amplification of 16S rDNA specific primers of adherent microbes identified bacteria and potential methanogens (*Archaea*) in all of the BBC5 MF samples. Positive results were also observed for dehalorespirers (*Dehalococcoides* sp.), sulfate reducing bacteria (SRB), and potential iron reducing bacteria (IRB, *Geobacteraceae*). The MF network was likely more reducing than the open fracture system based on the preponderance of primer data. The borehole water H_2 values observed for BBC6 suggested sulfate reduction was the dominant TEAP in the open fracture system. However, high levels of sulfate and the absence of sulfide in the packer water samples suggested that sulfate reduction was not the dominant TEAP. The levels of Fe(II) and Fe(III) in the packer samples, the spatial prevalence of Fe on the MF surfaces as well as its situation in top few nm of the MF surface suggested that Fe (III) was available for IRB. The spectroscopic characterization of the MF surfaces points to Fe (III) reduction as perhaps a dominant TEAP in the MF network. The presence of daughter products of dehalorespiration as well as H_2 concentrations supported the role of *Dehalococcoides* sp. in dehalorespiration in the MF network under conditions where Fe (III) reduction was strongly correlated to the presence of oxidized iron species on the microfracture surfaces. Other means of TCE biodegradation, including aerobic and anaerobic respiratory and cometabolic processes, can not be excluded.

Biographical Sketches

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