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Microbial Reduction of Iron(III) Minerals by Natural Organic Matter

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The redox state of shallow groundwater is maintained by the relative rates of atmospheric O_2(g) and soil organic carbon inputs, carbon respiration and the oxidative weathering of sulphide and ferrous minerals. Higher valent iron and manganese minerals can provide significant oxidative capacity with respect to the respiration of organic carbon, and can thus buffer groundwater quality against the input of organic carbon in the absence of molecular oxygen. This study reports results from a large international field project on the redox biogeochemistry of groundwater in the vicinity of the Äspö Hard Rock Laboratory (HRL) in Sweden. The site is a full scale prototype repository for research and development of the geological disposal of spent nuclear fuel. Repository safety issues relevant to this study include the possible corrosion of the engineered barriers and the higher solubility and thus mobility of some long-lived radionuclides (particularly Np, Tc) under oxic conditions. The field site comprises a vertical, hydraulically-transmissive fracture zone in the granite bedrock, that was intercepted at a depth of 70 m during construction of the entrance tunnel to the HRL. Groundwater flow, water quality, microbiology, fracture mineralogy and stable isotope geochemistry were subsequently studied over a three year period. Although tunnel construction caused a 50-fold increase in recharge rates to the fracture zone, there was not significant intrusion of dissolved oxygen with the groundwater sampled within the fracture zone (Banwart et al.,1999a). Rather, a large increase in the transport of soil organic carbon (identified as fulvic acids) occurred. This subsequently stimulated anaerobic respiration within the fracture zone, yielding greatly elevated levels of dissolved carbon dioxide and in some cases, methane. Microbiological studies of the site showed significant populations of iron reducing bacteria (Pedersen et al.,1996) but no evidence for sulphate reducing populations. Recent results from modelling these reactive processes show that carbon turnover is rapid, exhibiting an apparent first-order decay constant of 3.7 ± 2.6 yr^{-1} (Banwart,1999b). Although iron reduction appears to be the dominant pathway for carbon respiration, there is not a stoichiometric increase in dissolved iron concentrations. Rather, total dissolved iron concentrations are limited in the range 0.3-0.5 mg L^{-1}. Geochemical modelling of groundwater speciation, and theoretical calculation of the solubility of the abundant iron-rich clay minerals found within the fracture zone, suggest that these phases are in equilibrium with the groundwater. In this case, such minerals can provide a solubility limitation on the iron(II) produced by microbial iron reduction. Although iron oxide phases are observed in drill cores taken from the fracture zone, there is also an abundance of Fe(III) present in the silicate minerals observed as well; iron-bearing primary silicates, hydrothermally-altered wall rock and the clay minerals. Two possible pathways thus exist for accumulation of ferrous iron within fracture minerals; direct microbial reduction of structural iron(III) or incorporation of biogenic Fe(II) into clay minerals in a subsequent reaction. The in situ production of reduced iron silicates, particularly clay minerals, is an important conclusion regarding the redox performance of the geological barrier. Accumulation of such phases increases the reducing capacity of the fracture; helping to buffer future intrusions of O_2 from the surface and thus protecting the engineered barriers against corrosion and maintaining anoxia regarding radionuclide solubility. An additional important conclusion is the observation that microbial iron reduction has provided a rapid pathway for complete oxidation of complex organic carbon to carbon dioxide, and with a characteristic reaction time scale that is characteristic for carbon turnover in soils rather than anoxic groundwater environments.

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