Microbially mediated geochemical iron and carbon cycling in a cold mineral spring

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We are investigating the highly mineralized, iron-rich, micro-oxic Fuschna spring, which is an excellent model site for studies on coupled carbon and iron cycling in surface environements at near neutral pH. The spring offers oxic-anoxic gradients, is accessible at the surface and the carbon cycle is linked to inorganic carbon stemming from subsurface dissolution of rock minerals.

The spring emerges from a fractured aquifer consisting of layers of slightly metamorphic, pelagic sediments (Bündner shale). It is located in the Lower Engadin Window, an erosion opening into the penninic layers near Ftan (Swiss Alps). During percolation the water gets enriched with HCO_3^- and H_2CO_3. It is characterized as an Fe(II)-rich Ca-Mg-SO_4-HCO_3 spring (TDS ≈ 4.4 g/l, > 70% HCO_3^-; pH ≈ 6.3; dissolved Fe^{2+} ≈ 8.5 mg/l. Bissig, P. 2004, Bull. angew. Geol, 9/2, 39-47).

Dissolved CO_2 escapes from the spring-water at the surface, thereby creating oversaturation with regard to calcium carbonate. So called “carbonate ice” precipitates as a thin film on water surfaces or forms carbonate terracettes.

Once the dissolved oxygen concentration increases in the outflow water, dissolved ferrous iron gets oxidized and precipitates along the flow channels as ferric iron oxides. These oxides contain large numbers of microorganisms.

We have isolated an anoxigenic, phototrophic, Fe(II)-oxidizing bacterium and characterized the microbial community composition genotypically, employing 16S rRNA phylogeny. Besides clones of filamentous *Cyanobateria* related to *Phormidium* spp*.*, *Tychonema* spp. and *Lyngbya* spp., and of *Synechocystis* sp. we also detected clones of *alpha* and *beta-Proteobacteria* that are closely related to *Rhodoferax* spp*., Gallionella* spp*., Iodobacter* spp. and *Rhodobacter* spp.

The geochemical conditions of the Fuschna spring and the kind of microorganisms detected indicate that the carbon and iron cycles are coupled via biotic and abiotic redox-reactions and acid-base equilibria. Organic carbon from phototrophic primary production fuels the reductive part of the redox cycle.

Reduction of aqueous hexavalent chromium by steel slag

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Trivalent chromium, Cr(III), is an essential element for humans, while hexavalent chromium, Cr(VI), is an established *human carcinogen. In situ* remediation of groundwater contaminated with hexavalent chromium can be achieved by reduction of Cr(VI) to barely soluble Cr(III) with a reducing agent, such as zero-valent iron, and its subsequent precipitation as stable hydroxides.

Millions of tons of steel slag is produced annually as a by-product of steel industry. For this reactive, alkaline material new environmental applications have recently been developed. Due to the presence of Mn(II) and Fe(0,II,III), steel slag is a strong reductant. To test steel slag’s capacity to reduce aqueous hexavalent Cr to a trivalent form and its potential use in treating Cr(VI)-contaminated land, we have performed laboratory batch (24 h) and kinetic experiments using slag samples from the Rautaruukki Co., Finland. Total chromium in water samples was analysed with ICP-OES, and hexavalent chromium was separated using ion exchange columns and determined spectrophotometrically.

As a comparative material we employed agricultural soil, which did not show any significant uptake (reduction) of dissolved Cr(VI). Steel slag instead was effective in chromate reduction. The percentage of reduction was dependent on the solid/liquid ratio (L/S) and initial Cr(VI) concentration. Using L/S = 20, more than half of hexavalent chromium was converted to trivalent even with high initial Cr(VI) contents of up to 45 mg/L and the reducted fraction was 90% or more when the initial Cr(VI) concentration was 1.0 mg/L or less. Increasing L/S to 500 did not remove the reduction capacity as the adsorption percentage was still >50% if the initial Cr(VI) was 1.0 mg/L (note that EPA’s max. contaminant level for total Cr in drinking water is 0.1 mg/L). The obtained reduction (adsorption) pattern follows a Langmuir-type isotherm model. The reduction rate in the experiments was fast as a 90% removal of chromate from the solution took place within a shaking time of 2 minutes (L/S 20, initial Cr(VI) 5 mg/L). Our results demonstrate that steel slag can provide a low-cost material for remediation of contaminated land containing hexavalent chromium.