Sulfur speciation in natural geothermal fluids, Iceland – Kinetically or thermodynamically controlled?

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General redox dis-equilibrium often prevails in natural geothermal waters [1]. Sulfur has a complex redox chemistry and is among the major components in geothermal fluids. Its most common redox states are sulfate (VI) and sulfide (-II), but metastable species with intermediate oxidation states have been found to be sometimes present in significant concentrations in contrast to thermodynamic considerations in surface geothermal waters. The concentrations and origin of the intermediate species are not well understood and so far unknown for the deeper parts of geothermal systems.

Sulfur chemistry was studied in surface geothermal waters such as hot springs, acid-sulfate pools and mud pots as well as deep aquifer fluids discharged by sub-boiling and two-phase wells in Iceland. The speciation of aqueous dissolved sulfur (sulfide, sulfate, sulfite, thiosulfate and polythionates) was determined on-site or after sample stabilization in more than 60 samples. Sulfate was identified in all samples in concentrations between 0.2 to 53 mmol kg^{-1}, and sulfide in most waters with few exceptions ranging between 0.3 to 4100 μmol kg^{-1}. Sulfite was not detectable in most samples, but was found in some surface geothermal waters associated with high sulfide concentrations. Thiosulfate was detected in most samples in concentrations ranging from 1.2 to 394 μmol kg^{-1}. Thiosulfate and sulfite were not present in the deeper parts of subboiling systems and in low concentrations (<10 μmol kg^{-1}) in higher temperature systems. Polythionates were not detected.

The results indicate that the sulfur speciation in natural geothermal waters is kinetically and/or source controlled rather than thermodynamically. In the deeper parts of volcanic geothermal areas, the sulfur redox equilibrium is more closely approached. The aqueous speciation of sulfur is very complex and dynamic, and can not be estimated from bulk analysis and measurements of a given redox state. This has implications also on the chemistry of other elements associated with sulfur species.

[1] Stefánsson et al. 2005. Chem. Geol. **221**, 289–311.

The influence of irradiation and aging on nano-iron versus its bulk analogue in natural seawater

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Engineered nano-iron is widely used in bioremediation and also in the food industry. Experiments were designed to expose organisms to equimolar "surfce-bound" Fe^{3+} from both the nano-form (Fe_2O_3) and its bulk analogue ($FeCl_3$), to study the impact on early life stage development of marine invertebrates. The influence of the aging of particles and elevated UV-B on suspensions in seawater were studied. Iron nano particles were characterised using an array of techniques including dynamic light scattering (DLS), X-ray diffraction (XRD), nanoparticle tracking analysis (NTA), filter-fractionation followed by inductively coupled plasma optical emission spectrometry (ICP-OES), atomic force microscopy (AFM), transmission electron microscopy (TEM), scanning electron microscopy (SEM), etc.

Preliminary results obtained when comparing the two forms of the metal indicate clear differences in particle aggregation behaviour, hydrodynamic diameter, polydispersity index, zeta potential and particle surface topography. Results are valuable to explain differences observed in biochemical responses in test organisms.

This work aimed to differentiate between nano-form related biochemical responses as compared to effects from bulk analogues, and thus generates much needed risk data to support evidence based nanoparticle regulation.