Speciation matters – views on iron and sulfur chemistry in geothermal waters, Iceland

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The geochemical behaviour of elements depends largely on their speciation (i.e. the actual form). Therefore, speciation is of outmost importance in processes including water-rock-microbe interaction, scaling, and environmental pollution in aqueous environments. Iron (Fe) and sulfur (S) are particularly important in environmental geochemistry, and the transformations between their dissolved, solid and colloidal forms play a key role in the release and sequestration of many trace elements and contaminants, in mineral formation and dissolution, and their availability to biota. Both Fe and S may be present at more than one oxidation state. Thus, in order to understand the (bio)geochemical processes involving Fe and S it is not sufficient to have chemical data on the total element concentrations only, but data on the chemical species concentrations (i.e. the individual oxidation states: SO_4^{2-}, $S_2O_3^{2-}$, $S_nO_6^{2-}$, SO_3^{2-}, H_2S, Fe(II), Fe(III)) are required. It is, however, not trivial to reliably measure the species concentrations due to difficulties of preserving the speciation for later laboratory analysis.

We have studied metal and sulfur geochemistry in active geothermal systems in Iceland, with special emphasis on understanding the S and Fe reactions in geothermal fluids. Such active geothermal systems are dynamic environments characterised by steep gradients in temperature, fluid composition and oxidation state. The geothermal waters considered in this study cover temperatures ranging from ambient to ~100°C, pH between <2 to 10 and a wide range of absolute and relative Fe(II), Fe(III), H_2S and SO_4^{2-} concentrations. In order to determine species concentrations in geothermal waters, we developed and applied sampling and analysis methods based on ion chromatography, spectrophotometry and voltammetry as well as size fractionation for geothermal waters. The analytical data on total element and species concentrations, combined with thermodynamic equilibrium constants and geochemical model calculations, were used to assess the most important reactions involving Fe and S in geothermal waters.