

Fluid geochemistry and surface alteration associated with rhyolitic rocks, Torfajökull Iceland

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Studies of alteration mineralogy and fluid composition in many geothermal systems have indicated that equilibrium is closely approached between solution and the secondary minerals and that all major components except mobile elements like Cl are controlled by mineral buffers when temperatures are above 100°C. Boiling (phase separation and segregation), mixing and cooling are, however, active processes in such systems leading to very variable fluids at the surface including acid sulphate waters, carbon-dioxide waters, sodium-chloride waters and mixed waters. Re-equilibration between the gases, water and alteration minerals upon these changes is however unclear.

Samples of surface geothermal fluids and associated surface alteration mineralogy of rhyolitic rocks at the Torfajökull geothermal area, Iceland, were collected and analyzed for major and trace elemental composition as well as alteration mineralogy. Great variability was observed in surface water composition in the range of pH 2.14-9.77, Cl 0.3-602 ppm, SO₄ 2-884 ppm, CO₂ 0.5-530 ppm and metals in the range of 0.5-155 ppm in acid waters and 0.001-35 ppm in alkaline waters. The surface mineralogy is characteristic of argillic alteration with kaolinite, alunite, amorphous silica being abundant as well as hematite and goethite and pyrite above and below the oxidation front, respectively. All these fluids have a common deep source fluid, the very variable surface chemistry resulting from the boiling and phase separation, cooling and mixing upon ascend to the surface and surface oxidation.

The system is clearly open with the fluid chemistry at the surface depending on the mineral-water reaction as well as oxidation kinetics, fluid fluxes and mixing ratios. Nevertheless, thermodynamic modelling and mobility calculations clearly revealed a local re-equilibrium at least between some of the secondary minerals and the associated geothermal water and gases. Interestingly, the waters are commonly saturated with the surface alteration minerals, which in turns are often metastable with fast precipitation kinetics, for example amorphous silica and simple metal hydroxides.

Resolving equilibrium and kinetic Zn isotope fractionations

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Large fractionations in transition metal stable isotope systems may have a use as palaeoredox proxies and for monitoring the transport and deposition of metals in the environment. However, using stable isotope ratios to decipher these processes relies on an understanding of the underlying mechanisms controlling isotope partitioning. Here we use a combined theoretical and experimental approach to study how the competing rates of deposition and mass-transport affect the fractionation of zinc during a redox reaction ($Zn^{2+}_{(aq)} + 2e^- = Zn_{(s)}$). *Ab initio* and DFT calculations of aqueous zinc complexes of varying solvation indicate that aqueous Zn(II) would be ~2 ‰ ($\Delta^{66}Zn$) heavier in equilibrium with metallic Zn(0) (Fig. 1). The magnitude of these calculated fractionation factors decrease with increasing solvation and level of theory used. Experimental electrochemical studies show a much larger fractionation ($\Delta^{66}Zn_{(s)-(aq)} \sim -5.1$ ‰) associated with zinc deposits where charge-transfer kinetics are rate limiting, and smaller fractionations ($\Delta^{66}Zn_{(s)-(aq)} \sim -3.9$ ‰) where mass-transport to the electrode is rate limiting. Fig 1. summarizes these results with lines showing calculated equilibrium fractionation factors and markers for metallic zinc deposits plated as a function of overpotential voltage, temperature (increasing marker shade: 0°C, 25°C, 50°C) and solution chemistry.

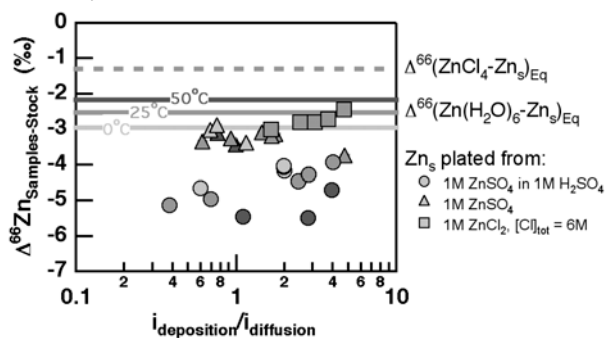


Figure 1: $\Delta^{66}Zn$ vs. deposition/diffusion current ratio.