Sulfur speciation and metal transport in surface geothermal waters

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Geothermal waters are generally reduced with elevated hydrogen sulfide concentrations. When these waters assent to the surface sulfide mineralization occurs upon cooling, mixing and boiling (phase separation) as well as oxidation. The oxidation of hydrogen sulfide proceeds through a series of complex reactions with the formation of metastable sulfur species including sulfur (S^0), polysulfides (S_nS^-), thiosulfate ($S_2O_3^{2-}$), polythionates ($S_xO_6^{2-}$) and sulfite (SO_3^{2-}) and eventually to sulfate, often resulting in acid waters. The associated metal speciation and transport is largely influenced by the redox chemistry of sulfur.

We have developed methods for on-site determination and/or sample preservation and lab determination of the concentrations of redox sensitive sulfur and selected metal species in geothermal waters using both ion chromatographic and spectrophotometric techniques. In geothermal surface waters associated with basaltic and rhyolitic rocks in Iceland, H_2S, S_2O_3 and SO_4 are found to be the dominant forms of sulfur with concentrations up to 73, 22 and 5060 mg/L, respectively, and H_2S:S_2O_3:SO_4 molar ratios between 0:0:1 to 1.2:0.7:1. These waters are often enriched in trace elements like Al, Fe, Mn, Cr, V, Zn, Ni and As with concentrations in the range <1-390 mg/L, <1-756 mg/L, 0.04-4.64 mg/L, <0.01-754 µg/L, 7-890 µg/L, 1-698 µg/L, 0.06-1004 µg/L and 0.2-258 µg/L, respectively. The dissolved metals are predominantly transported in the reduced form as simple ions and hydroxide complexes or as sulfur containing species.

Combined field and modeling study indicates that the main processes governing the chemistry of sulfur species are H_2S discharge (flux), H_2S oxidation via S_2O_3, SO_4 reduction, and native sulfur hydrolysis. These reactions are sometimes catalyzed by metals and metal surfaces as well as bacteria. Further, the sulfur redox chemistry and metal transport and precipitation are closely linked together.

Trace element composition of metasomatic reaction zones: Insights into the evolution of the slab-mantle interface

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The peridotite-gneiss reaction zone may be regarded as a natural window on the processes affecting crust-mantle interaction. A spectacular outcrop of the contact between garnet-peridotite and gneisses is located in the northern side of Mt. Hochwart (Ulten Zone, Italy). The ultramafic body consists of strongly serpentinized metaperidotites associated to monomineralic zones that developed at the contact between the peridotite body and the garnet gneiss country rocks. The composition of monomineralic zones records an order of metasomatic zoning formed by phlogopite-rich to tremolite-anthophyllite-rich rocks from the host gneiss towards the peridotite. Phlogopite aggregates (phlogopitite) with accessory zircon, tourmaline and Cl-apatite also occur.

Whole-rock geochemistry and trace element (LA ICP-MS) composition of hydrous phases (phlogopite and amphibole) in different metasomatic zones indicate mobility of many elements, including elements such as Ta which are considered to have scarce mobility in fluids. Trace element composition of accessory minerals in the phlogopite-rich zone suggests that the trace element signature of subduction zone fluids may be fractionated in this zone. The progressive depletion in some trace elements (LREE) and enrichment in LILE and Li from the peridotite towards the gneiss suggests a strong influence of bulk composition on the trace element budget of hydrous minerals.

The reaction between mantle and gneissic rocks was enhanced by considerable influx of H_2O-B-Cl-rich fluids, causing crystallization of hydrous phases and release of a trondhjemitic residual melt. We interpret fluid flow responsible for metasomatism at the peridotite-gneiss contact to have occurred at ≈700-800°C, after the migmatization of crustal rocks and incorporation of the peridotite inside the slab. In this contribution we highlight that the chemical composition of fluids in collisional settings can be substantially modified by metasomatic reactions occurring in the mantle wedge.