

The chemistry of sulfur in volcanic geothermal fluids

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Sulfur compounds are among the major components in volcanic geothermal systems, playing an important role in the transport and precipitation of many metals. Aquifer geothermal fluids are reduced with hydrogen sulfide (H₂S) and sulfate (SO₄) predominating. Sulfur dioxide (SO₂) may also be degassed from a magma source into the geothermal system. Upon ascending to the surface the composition of the deep geothermal fluid may change due to cooling, boiling and mixing with shallow ground- and surface waters. These processes result in steam fumaroles, alkaline hot springs and acid-sulfate springs and mud pots at the surface and oxidation of hydrogen sulfide to sulfate via series of complex reactions and formations of metastable sulfur species including thiosulfate (S₂O₃²⁻) and polythionates (S_xO₆²⁻).

Samples of volcanic and non-volcanic geothermal waters were collected from several locations in Iceland and analyzed for sulfur species concentration on site and major and trace elemental content. The waters include samples of well discharges, alkaline hot springs, acid-sulfate mud pots and springs. The measured surface temperature were 7-100°C and the pH was 1.83- 9.71 (at 25°C). The waters are of NaCl and acid sulfate type with molal SO₄/Cl ratio between 0.05 and 2813. The concentration of the main sulfur species were SO₄ = 0.02-106 mM, S₂O₃ = 1.7-394 μM and H₂S = 0.3-2160 μM. Metastable sulfur species were only detected in surface geothermal waters whereas H₂S and SO₄ are the only forms found in well waters discharging aquifer fluids. The formation of thiosulfate and polythionates is considered to result from oxidation of hydrogen sulfide and hydrolysis of sulfur. The associated major and trace elemental chemistry in the geothermal waters is largely influenced by the sulfur chemistry, both due to changes in water pH and redox state and by complexing the metal cations. Acid-sulfate waters are often enriched in trace metals, these being transported as free ions and sulfate complexes, whereas alkaline NaCl waters have very low metal concentrations with ions, hydroxo and carbonate complexes predominating.

Isotopic systematic of the In'Teria lithospheric mantle (Hoggar, SE Algeria)

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The Hoggar massif (SE Algeria) is located above an E-W trending belt of anomalously high heat flow [1]. The maximum heat flow (100-120 mW.m⁻²) has been recorded at the northern margin of the Hoggar swell, near In'Teria district. The volcanic In'Teria district is composed of melilite pipe, which contains xenoliths of spinel and garnet peridotite, pyroxenite, and mega-crystals of pyroxene and amphibole. Spinel peridotites record two metasomatism events before their entrainment by melilitic magmas: (1) injection of alkali silicated magmas (basaltic or kimberlitic); (2) carbonatitic metasomatism possibly related to the partial melting of a volatile enriched garnet bearing peridotite.

Nd and Pb isotope analyses were performed on all lithologies. The Pb isotopic ratios range from 18.4 to 19.9, 15.60 to 15.68, and 38.2 to 39.5 for ²⁰⁶Pb/²⁰⁴Pb, ²⁰⁷Pb/²⁰⁴Pb and ²⁰⁸Pb/²⁰⁴Pb, respectively. In the ²⁰⁷Pb/²⁰⁴Pb- ²⁰⁶Pb/²⁰⁴Pb space the samples report into two distinct domains. A first one carried by spinel peridotites and pyroxenites shows a clear himu affinity, signature which seems to be characteristic of the rejuvenated North African lithosphere [2]. This composition is also expressed in the melilitites from In'Teria and from recent alkaly magmatism [3]. The Garnet bearing peridotites (± spinel peridotites) show high ²⁰⁷Pb/²⁰⁴Pb (15.6) for a given ²⁰⁶Pb/²⁰⁴Pb (18.5) and form a second domain close to the EM1 pole.

The data suggest (1) an isotopic stratification of the Lithosphere, (2) an evolution through time of the source of magmatism and (3) intricate interaction between those reservoirs via melting and metasomatism reactions. The In'Teria peridotites sample thus a more complex possibly more ancient (or preserved) lithosphere than in the central Hoggar. This is suggested by the "persistence" of EM1 signature not registered in the Central Hoggar.

[1] Takherist & Lesquer (1989) *Can J Earth Sci.* **26**, 615-626.

[2] Beccaluva *et al.* (2007) *Earth Planet Sci Lett.* **260**, 482-

494. [3] Aït-Hamou *et al.* (2000) *C R Acad Sc Paris* **330**, 829-836.