The speciation of sulfur in magmatic-hydrothermal fluids

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Sulfur compounds are major constituents of volcanic gases and magmatic-hydrothermal fluids. They are responsible for the climatic effect of major volcanic eruptions as well as for the transport and precipitation of metals during the formation of magmatic-hydrothermal ore deposits. Up to now, it was usually assumed that SO_2 and H_2S are the only important sulfur species occuring in high-temperature magmatic fluids.

The speciation and oxidation state of sulfur in aqueous fluids was studied using synthetic fluid inclusions in quartz cores generated in rapid-quench autoclaves under controlled oxygen fugacity and variable pressures and temperatures (500 – 950 ˚C; 500 – 3000 bar). Run durations lasted up to several weeks. The sulfur speciation in the fluid inclusions was determined by Raman spectroscopy. Raman spectra were calibrated against standard solutions.

At Ni-NiO buffer conditions, H_2S was the dominant sulfur species in the fluid, coexisting with small amounts of SO_2. At Re-ReO_2 buffer conditions, the quenched fluid contained a mixture of SO_2, SO_4^{2-} and HSO_4^-. Our data therefore suggest that under oxidizing conditions as they may prevail in many magmatic systems in subduction zone settings, aqueous fluids contain abundant species of hexavalent sulfur (see Fig. 1).

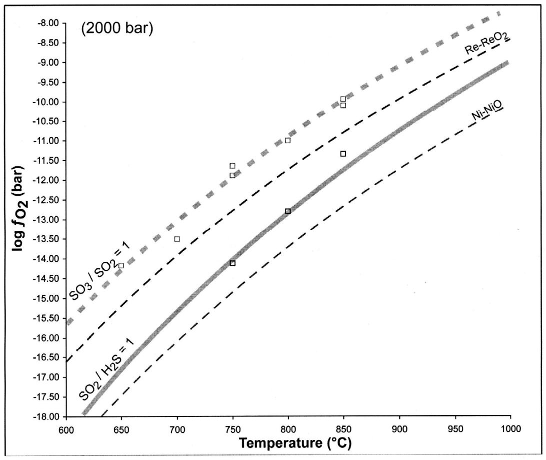

Figure 1: Experimentally determined sulfur speciation in aqueous fluids. Shown are the conditions under which the molar fraction of SO_2 equals that of H_2S and under which SO_2 is equally abundant as species of hexavalent sulfur (“SO_3”).

REE enrichment in authigenic and biologically mediated minerals of phosphate rocks

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The geochemical behavior of the REE under the influence of chemical and microbial activity is still insufficiently explored issue. REE significant bioaccumulation and fractionations was recently reported by many authors in plant organs (Ding *et al*., 2005) and with microbial activity (Bishay, 2005).

The REE are accommodated in minute authigenic minerals in the phosphate rocks which reach to about 12.65% ΣREEs. The NASC normalized REE pattern of these minerals are nearly flat with occasional distinct -ve Eu anomaly suggesting fluctuations in the redox environment during their formation (Fig.1). The mobilization and enrichment of the REE is evidenced by both abiotic and biotic laboratory experiments. It is indicated that under controlled boundary conditions, some organic acids as well as biological mediation of the phosphate rocks influence the redistribution and enrichment of REE.

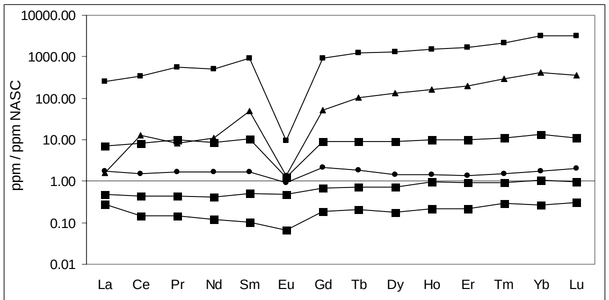

Fig.(1): NASC REE diagram of some authigenic minerals showing Eu anomaly.

References

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Ding, S., Liang, T., Zhang, C., Yan, J. and Zhang, Z. (2005): *Journal of Experimental Botany*, **56** (420): 2765–2775.