

## Sulfur speciation in aqueous solution and its consequences for metal transport by hydrothermal fluids

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Sulfur is a ubiquitous element in magmatic-hydrothermal-volcanic settings, occurring in a variety of valences (from -2 to +6) and chemical forms, which may act as efficient complexing agents for many metals of economic concern (e.g. Au, Ag, Cu, Pt), and thus impact their transport by fluid and vapor phases and the formation of metal resources [1]. The major obstacle for quantifying the effect of different sulfur ligands on the metal behavior in geological fluids is the paucity of high temperature-pressure (*T-P*) data on the speciation of sulfur itself. With the exception of sulfide and sulfate ( $S^{2-}$ :  $H_2S/HS^-$ ,  $S^{+6}$ :  $HSO_4^-/SO_4^{2-}$ ), for which limited experimental data are available to  $\sim 300^\circ\text{C}$ , our current knowledge of other important aqueous sulfur forms (e.g. sulfite, thiosulfate, polysulfides, molecular sulfur) is based exclusively on extrapolations of data obtained below  $100^\circ\text{C}$ , inevitably resulting in large uncertainties when estimating sulfur species concentrations in high *T-P* magmatic-hydrothermal fluids. The major difficulty in studying sulfur speciation at elevated *T* is the rapid recombination of most sulfur forms on cooling, thus requiring *in situ* spectroscopic methods or special sampling devices.

Here we combined *in situ* Raman spectroscopy in a hydrothermal diamond-anvil cell and batch-reactor measurements using an ultra fast sampling technique, on model solutions  $H_2O+S\pm NaOH\pm Na_2S_2O_3$  of total dissolved S content 0.5-5.0 wt% and  $pH=2-8$ , to assess the identities and amounts of sulfur species and their effect on chalcophile metals (Cu, Au, Pt) solubilities in aqueous fluids at  $T=200-500^\circ\text{C}$  and  $P=0.3-30$  kbar. The results obtained, along with a revision of literature data, indicate the dominant formation of polysulfide (e.g.  $H_{0-2}S_3$ ) and/or polythionate (e.g.  $H_{0-2}S_2O_5$ ) species, in marked contrast with thermodynamic predictions based on low *T-P* data, of sulfide and sulfate as the major forms in solution. These new species, far more abundant than believed, together with other high-*T* sulfur forms (e.g.  $SO_2$ , COS), might enhance the chalcophile metal transfers in subduction-zone settings that host many magmatic-hydrothermal deposits of base and noble metals.

[1] Pokrovski *et al.* (2008) *Earth Planet. Sci. Lett.* **266** 345-362.

## Evidences of crustal contamination and magma mixing at Taapaca Volcanic Complex, Central Andes

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Taapaca Volcanic Complex (TVC:  $18^\circ 06'S$ ,  $69^\circ 30'W$  and 5,850 m a.s.l., Late Pliocene to Holocene) is an active eruptive center of ca. 35 km<sup>3</sup> that is located in the Central Andes in the Altiplano of northern Chile. TVC is mainly composed by lavas, domes, block-and-ash flow, blasts and debris avalanche deposits. Clavero *et al.* [1] indicate that the volcanic activity (stages I to IV) is characterized by 4-5 km SW vent migration and short cycles of intrusion and extrusion dacitic domes associated with block-and-ash flows and blasts and several sector collapses; followed by long periods of quiescence. Its products are mainly dacitic in composition, as most of the volcanoes of the Central Andes [2], with ubiquitous mafic inclusions and characteristic sanidine megacrysts.

The samples collected and analysed (whole-rock, minerals and isotope geochemistry) correspond to high-K (2.6-3.5%, m/m) calc-alkaline dacites and subordinated andesites, typical of subduction settings [2]. The data have high incompatible mobil elements (Sr and Ba: 715-1059 and 791-1707  $\mu\text{g/g}$ ) and show Nb anomaly. Also, REE patterns have LREE very enriched and relative low Pb isotopic composition, indicating that the crustal contamination and assimilation processes are important in the evolution of the TVC magmas, consistent with the  $>70$  km crustal thickness of this segment of the Andes. In addition, the Nd and Sr ratios are identical to values of other volcanoes of this volcanic zone [2]. However, the mafic inclusions, the reabsorption textures (mainly in plagioclase and quartz) and oscillatory zoned plagioclases are evidences of the occurrence of magma mixing processes where pulses of new less evolved (and hot) magma input into the shallower magmatic chamber of TVC. Probably, the later process triggered the successive eruptive cycles.

This work is a contribution of Project ASH (CGL2008-00099) (Spain) and Project FONDECYT 1040137 (Chile), and the PEGEFA Research Group (2005SGR-00795).

[1] Clavero *et al.* (2004) *J Soc Geol London* **161**, 603-618. [2] Stern *et al.* (2007) *Geology of Chile*, 147-178.