American Mineralogist, Volume 99, pages 1109–1118, 2014

In situ Raman spectroscopy identification of the S_3^- ion in S-rich hydrothermal fluids from synthetic fluid inclusions

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Abstract

The chemical forms of sulfur in geological fluids control the behavior of this element and associated base and precious metals in magmatic, hydrothermal, and metamorphic environments. However, these forms are insufficiently known at elevated temperature (*T*) and pressure (*P*). In this study, sulfur speciation in model aqueous solutions of thiosulfate and sulfur (~3 wt% of total S) was examined by in situ Raman spectroscopy on synthetic fluid inclusions at *T*-*P*-pH-redox conditions typical of porphyry Cu-Au-Mo deposits. Fluid inclusions were entrapped at 2 kbar and 600 or 700 °C in quartz that served as a container for the high *T*-*P* fluid. Then, the inclusion-bearing quartz samples were re-heated and examined by Raman spectroscopy as a function of *T* and *P* (up to 500 °C and ~1 kbar). At $T < 200$ °C, all fluid inclusions show sulfate ($SO_4^{2-} \pm HSO_4^-$) and sulfide ($H_2S \pm HS^-$) in the aqueous liquid phase and elemental sulfur (S_8) in the solid/molten phase; these results agree both with thermodynamic predictions of sulfur speciation and the common observation of these three S forms in natural fluid inclusions. At $T > 200$–300 °C, in addition to these S species, the S_3^- ion was found to appear and grow with increasing temperature to at least 500 °C. The formation of S_3^- is rapid and fully reversible; its Raman signal disappears on cooling below 200 °C, and re-appears on heating. These new data confirm the recent findings of S_3^- in similar aqueous solutions at *P* of 5–50 kbar and $T > 250$ °C; they suggest that S_3^- may account for some part of dissolved sulfur and serve as a ligand for chalcophile metals in fluids from subduction zones and related Cu-Au-Mo deposits. This work demonstrates that in situ approaches are required for determining the true sulfur speciation in crustal fluids; it should encourage future spectroscopic investigations of natural fluid and melt inclusions at high temperatures and pressures close to their formation conditions.

Keywords: Hydrothermal fluid, Raman spectroscopy, sulfur, sulfate, sulfide, trisulfur ion, fluid inclusion