## Diffusive reequilibration of quartz hosted silicate melt and fluid inclusions: Are all metal concentrations unmodified?

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We conducted experiments to determine the extent and mechanism by which the composition of quartz-hosted silicate melt inclusions (SMI) and aqueous fluid inclusions (FI) can undergo post-entrapment modification via diffusion. Quartz slabs containing assemblages of SMI and FI were reacted with synthetic HCl-bearing and metalliferous aqueous fluids at T=500-720°C and P=150-200 MPa. SMI from single inclusion assemblages were analyzed by laser ablation inductivelycoupled plasma mass spectrometry (LA-ICPMS) and electron probe microanalysis (EPMA) before and after the experiments. Analyses revealed that rapid diffusion of the univalent cations Na<sup>+</sup>, Li<sup>+</sup>, Ag<sup>+</sup>, Cu<sup>+</sup> and H<sup>+</sup> occurred through the quartz from the surroundings, resulting in significant changes in the concentrations of these elements in the inclusions. As these elements diffuse as univalent cations, their mobility is limited by the necessity to maintain charge balance. The concentration of Cl (sensu lato salinity) cannot be modified in fluid inclusions, but the relative proportions of H, Na, Li, Cu and Ag can easily reequilibrate with subsequent generations of fluids, silicate melts, sulfide liquids, or precipitated sulfide minerals that come into contact with the host quartz. Concentrations of other elements with an effective ionic radius larger than that of Ag<sup>+</sup>, or multiple valence states were not modified in the inclusions during the experiments. Our results warn inclusion researchers that the interpretation of Na, Li, Cu and Ag concentrations from quartz-hosted SMI and FI should be treated critically.

## XPS study of stibnite (Sb<sub>2</sub>S<sub>3</sub>) oxidation

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To properly understand many physical and chemical properties of an important antimony-containing mineral, stibnite, and its geochemical cycle, the stibnite surface should be understood and the nature of stibnite-fluid interfaces should be documented. Recent progress in X-ray Photoelectron Spectroscopy (XPS) technology makes it possible to obtain high-resolution core-level and valence band spectra of many minerals which are semiconductors with large band gaps and non-conductors. This can be used to study mineral surfaces and their reactivity in much greater detail [1,2 and references therein].

We will present our study of the surface chemical species formed upon cleavage of stibnite [1] and upon its reaction with air (days), air-saturated distilled water (days) and 1-3% hydrogen peroxide solutions (minutes and days). The survey, Sb 4d, Sb 3d, and S 2p spectra were collected. The data provide good evidence for the existence of the reduced antimony at the pristine (vacuum cleaved) stibnite surface as a mechanism of the surface relaxation [1]. The stibnite surface reacted with air and hydrogen peroxide undergoes extensive oxidation to give Sb<sub>2</sub>O<sub>3</sub> and Sb<sub>2</sub>O<sub>5</sub>, when reacted with air, and mixed Sb oxide/hydroxide compound when reacted with hydrogen peroxide.

[1] Zakaznova-Herzog *et al.* (2006) High resolution XPS study of the large-band-gap semiconductor stibnite  $(Sb_2S_3)$ : Structural contributions and surface reconstruction. *Surface Science*, **600/2**, 348-356. [2] Zakaznova-Herzog *et al.* (2008) Characterization of leached layers on olivine and pyroxenes using high resolution XPS and density functional calculations. *GCA* **72**, 69-86.