

In-situ spectroscopy of sulfur and critical metals in fluid-mineral-melt systems at high temperatures and pressures

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Our understanding of geological processes in the Earth's interior involving fluids and magmas, such as chemical element cycling and fractionation, magma generation and degassing, volcanic activity and ore deposit formation, to name a few, all require knowledge of metal and sulfur solubility, partitioning, and chemical speciation at depth. This knowledge generally comes from analyses of products brought to the Earth's surface and cooled down or quenched in laboratory experiments, and thus lacks direct data at elevated temperatures (T) and pressures (P).

In this contribution, I overview recent advances of in-situ spectroscopic approaches such as Raman spectroscopy and X-ray absorption spectroscopy (both XANES and EXAFS) for studies of sulfur speciation and partitioning in fluid-melt systems and the effect of sulfur on the solubility and transport of critical metals (gold and platinum) by geological fluids and formation of their economic resources. These spectroscopic data, combined with complementary thermodynamic and molecular modeling methods, reveal the formation, both in fluids and melts together with traditional sulfate and sulfide, of previously overlooked S chemical forms, the trisulfur and disulfur radical ions $S_3^{\cdot-}$ and $S_2^{\cdot-}$. These particular S species are stable at elevated T - P but cannot be preserved in quenched products due to their extremely fast breakdown to sulfate, sulfide and/or molecular sulfur on cooling. The radical ions have specific properties that distinguish them from traditional sulfur forms. The radical ions partition 10 to 1000 times more than sulfate and sulfide from silicate melts into the volatile aqueous phase, thereby enhancing sulfur degassing and transfer during magma generation in subduction zones. Furthermore, these species have an exceptionally high affinity for binding "chalcophile" metals such as Au, Pt or Mo in the fluid phase and thus greatly enhance these metals transfer across the lithosphere, from magmas to hydrothermal ore deposition sites.

These findings highlight the necessity of using in-situ spectroscopic approaches for studying high T - P "fugitive" fluid and melt phases inaccessible to direct observation or sampling; they thus open large perspectives for probing these "extreme" geological *milieux* using cutting-edge synchrotron techniques. Among these perspectives are, for example, the use of high-resolution XAS (using crystal analyzer spectrometers) for quantifying redox and structural state of critical trace metals in complex fluids and their host minerals; the design of novel diamond-anvil cells that would enable direct XANES measurements at the S K-edge of the identities and amounts of different S species in fluids, melts and minerals at high T - P ; and the rapidly growing progress in development of laser-heated diamond-anvil cells that will open the door to a host of both laboratory and synchrotron in-situ studies of fluid-mineral-melt systems far beyond the T - P conditions of the lithosphere.