Geophysical Research Abstracts
Vol. 19, EGU2017-5392, 2017
EGU General Assembly 2017

Hydrothermal fluoride and chloride complexation of indium: an EXAFS study

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Indium (In) is one of the geochemically lesser studied ore metals, and the factors that control the hydrothermal transport and deposition are largely unknown. It has no ore deposits of its own and is commonly mined as a by-product of Zn ores, and there are very few minerals that contain In as an essential structural component. Recently, industrial application of In in touch screen devices has drastically increased demand, which is projected to exceed supply from the current sources in the near future. Since the most relevant In sources are hydrothermal sphalerite ores and to a lesser extent hydrothermal greisen-type deposits in evolved granitic plutons, the aqueous geochemistry of In is of particular interest for understanding its ore forming processes.

As a first step towards a comprehensive model for hydrothermal In solubility and speciation, we have studied In speciation in fluoride and chloride bearing solutions at 30-400˚C and 500 bar using X-Ray Absorption Spectroscopy (XAS) measurements. The experiments were conducted in a unique hydrothermal autoclave setup at beamline BM30B–FAME at the European Synchrotron Radiation Facility (ESRF) in Grenoble, France. Our results show that the complexation of In changes dramatically between 30 and 400˚C. Below ca. 200˚C, fluoride complexes are the most stable ones, but they break down at higher temperatures. Chloride complexes on the other hand become increasingly stable with increasing temperature. This behavior has interesting consequences for natural ore forming systems. In Cl-rich systems (e.g. massive sulfide ores formed in sea floor environments), cooling can be an effective precipitating mechanism. In F-rich systems, fluoride complexation can extend In mobility to low temperatures and In will only precipitate when F is effectively removed from the fluid, e.g. by mixing with a Ca-rich fluid and precipitation of fluorite (CaF_2) as is commonly observed in skarn or greisen-type deposits. Due to In complexing with both F and Cl, depending on temperature, In distribution also has great potential as a fluid chemistry/temperature indicator in a wide range of different hydrothermal ore-forming systems.