Europium (II) and Europium (III) in hydrothermal fluids: new insight from in-situ XAS experimental results

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Knowledge of the mobility of europium and other Rare Earth Elements (REE) in hydrothermal fluids is important for understanding both the formation of REE deposits and REE geochemistry in general. Many REE deposits are considered to be of hydrothermal origin, and some magmatic REE deposits have undergone hydrothermal alteration. In geochemistry, the redox changes during magmatichydrothermal processes can be fingerprinted by observing the variation in the so-called "europium ', because Eu has both di- and trivalent anomaly' oxidation states in hydrothermal fluids, and thus behaves differently to other trivalent REE elements.

We have conducted in situ synchrotron X-ray absorption spectroscopy (XAS) experiments to investigate the oxidation state and speciation of europium in hydrothermal chloride solutions at temperature from 35-400°C, 600 bar. Our data show that Eu(II) species become stable with increasing temperature relative to Eu(III) in our experimental solutions. For Eu(III) chloride species, the number of water ligands around Eu(III) decreases with increasing temperature, and the number of chloride ligands increases. For example, in 4.5 m NaCl solution, there is approximately two chloride ligands around Eu(III) in the first coordination shell at 400°C, consistent with the speciation model from recent experimental solubility results (Migdisov et al., 2009, GCA 73, 7087-7109). For the Eu(II) system, our data confirm Sverjensky's (1984, EPSL 67, 70-78) theoretical predictions that Eu(II) species become more stable than Eu(III) at elevated temperatures; however the new data indicate that complexation between Eu(II) and chloride is much weaker than Haas's (1995, GCA 59, 4329-4350) theoretical estimations. A new model for the speciation of Eu(II) in hydrothermal fluids is proposed.