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Redox controls on the solubility of SnO_2 cassiterite and the speciation of tin in crustal fluids

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Tin (Sn) is a critical metal commodity with very high industrial demand. Understanding the conditions of Sn transport and deposition in the crust is thus of crucial economic relevance. More than 95% of the world's Sn-production comes from Sn-W deposits related to granitic intrusions where primary Sn mineralization is dominated by SnO_2 cassiterite. While the role of chlorinated fluids in the transport of Sn in crustal setting is well recognized, little is known about the actual atomic-scale mechanisms that controls the mobilization of Sn and the physical-chemical conditions for SnO_2 cassiterite precipitation. Information on the identity and stability of Sn species has been indirectly obtained from solubility experiments and extrapolations of low pressure thermodynamic models. However, the dominant Sn-Cl remain unconstrained and therefore, the qualitative understanding of Sn transport and related ore-forming processes is limited. Here we report *in situ* investigations of SnO_2 cassiterite solubility and Sn speciation in saline magmatic-hydrothermal fluids at crustal conditions, i.e. 20 – 500 °C and 30 – 1000 bar, by means of synchrotron X-ray absorption spectroscopy (XAS) in a hydrothermal autoclave. The measurements were performed over a broad range of fluid compositions and redox states. The investigated fluid compositions represent natural magmatic fluids with variable salinities (2 - 5 m NaCl), acidities (0.1 - 1 m HCl) and silica contents. Redox buffer assemblages were employed to control the oxygen fugacity. The analysis of the XAS spectra reveal that Sn speciation in hydrothermal solutions is largely dominated by Sn^{2+} as $SnCl_4^{2-}$ complexes, while oxidized Sn^{4+} is only detected in fluids buffered by the hematite-magnetite assemblage. Further, we will discuss the redox controls on the dissolution/precipitation of SnO_2 cassiterite and the implications for the genesis of Sn-W deposits.