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Cassiterite precipitation from hydrothermal fluids: insight from thermodynamic modeling

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Cassiterite (SnO_2) is the main tin ore mineral in magmatic–hydrothermal tin deposits. Tin transport and cassiterite precipitation mechanisms from hydrothermal fluids remain poorly understood as a result of lacking reliable thermodynamic parameters of major aqueous tin species, such as $SnCl^+$, $SnCl_2(aq)$, and $SnCl_3^-$. We derived the revised Helgeson–Kirkham–Flowers model parameters of these three tin species and two tin ions (Sn^{4+} and Sn^{2+}) from the correlation algorithms among these parameters [1]. These thermodynamic parameters could reproduce the available solubility data of cassiterite in acidic solutions at 400–700 °C under oxygen fugacity levels (fo_2) buffered by hematite–magnetite (HM) or nickel–nickel oxide (NNO) (Fig. 1). These comparisons allow modeling chemical systems of SnO_2–NaCl–HCl–H_2O (liquid phase) to examine tin transport and cassiterite precipitation mechanisms under tin–mineralizing conditions : 300–500 °C, 50–150 MPa, 2 molal NaCl, and levels from QFM (quartz–fayalite–magnetite) to HM.

Sn(II) chloride complexes are commonly interpreted to dominate in aqueous tin speciation under = NNO, but our modeling results indicate that considerable contents of Sn(IV) chloride complexes also exist in these reduced fluids with high HCl contents (Fig. 2), consistent with recent in situ high–temperature experiments and molecular dynamic simulations. Furthermore, we find that the Sn(II)/Sn(IV) ratios in fluids can be affected by fo_2 levels, temperature, and HCl contents, so redox reactions are not as necessary to precipitate cassiterite as previously thought. This explains why cassiterite can precipitate in host rocks (e.g., sandstone or quartzite) that do not provide oxidizing agents. The influences of HCl contents on the valence of major tin species should be considered for previous hydrothermal experiments because experimental HCl contents are commonly considerably greater than those in natural hydrothermal systems [2]. Cassiterite solubility in oxidized acidic hydrothermal fluids (NNO <fo_2< HM) is high enough to account for the tin contents of fluid inclusions from typical tin deposits, but the mineralization potential of oxidized fluids is inferior to reduced fluids (fo_2≤NNO) under the same conditions.

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2. Piccoli, P.M., Candela, P.A. & Williams, T.J. E. (1999), *Lithos* **46**, 591-604.

