Thermodynamics of tin perovskites of the schoenfliesite group $\square_2(B\mathrm{Sn}^{4+})$ $(\mathrm{OH,O})_6$ (B = Ca, Fe^{3+}, Mg, Mn^{2+}, Zn, Cu)

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The environmental mobility of elements in soils, sediments, and aquatic environments is commonly controlled by minerals, either by incorporation into the mineral structures or adsorption onto the surfaces. In this work, we investigated the thermodynamic properties of tin perovskites by a combination of acid-solution and high-temperature oxide-melt calorimetry. All phases were synthetic and their purity was established by powder X-ray diffraction, chemical analyses, thermogravimetric measurements, ^{119}Sn nuclear magnetic resonance spectroscopy and ^{57}Fe Mössbauer spectroscopy. Enthalpies of formation were determined with respect to $\mathrm{SnO_2}$ or $\mathrm{SnCl_4}$ and entropies were estimated. The resulting Gibbs free energies of formation were used to calculate solubility products. Calculations predict that these phases have a high solubility in acidic media but may form in mild to strongly alkaline systems. Burtite (B = Ca) could form in systems, where the activity of Ca^{2+} is buffered by calcite or gypsum at pH > 9. In cementitious systems with the dominant C-S-H phase, similar conditions for burtite formation can be expected. Jeanbandyite (B = Fe^{3+}) is predicted to be stabilized in Fe(III)-rich aqueous solutions, if the Fe(III) concentrations are buffered by ferrihydrite or other poorly crystalline iron oxides. pH-Eh phase diagrams were constructed for all investigated phases suggest similar formation conditions. Several measurements along the mushistonite-vismirnovite (B = Cu-Zn) solid solution show negative enthalpies of mixing, with a predicted minimum at $X_{\mathrm{Cu}} = X_{\mathrm{Zn}} = 0.5$ of -3.8 kJ·mol^{-1}. Modeling of mine drainage solutions confirmed the predictions and showed that under near-neutral or basic conditions, the tin perovskites can be more stable than cassiterite ($\mathrm{SnO_2}$) and act as the sinks of Sn in such environments.