

Experimental determination of the solubility constant of kurnakovite, $\text{MgB}_3\text{O}_3(\text{OH})_5 \cdot 5\text{H}_2\text{O}$

YONGLIANG XIONG^{1,*,\dagger}

¹Nuclear Waste Disposal Research & Analysis, Sandia National Laboratories, 1515 Eubank Boulevard SE, Albuquerque, New Mexico 87123, U.S.A.

ABSTRACT

In this study, I present experimental results on the equilibrium between boracite [$\text{Mg}_3\text{B}_7\text{O}_{13}\text{Cl}(\text{cr})$] and kurnakovite [chemical formula, $\text{Mg}_2\text{B}_6\text{O}_{11} \cdot 15\text{H}_2\text{O}(\text{cr})$; structural formula, $\text{MgB}_3\text{O}_3(\text{OH})_5 \cdot 5\text{H}_2\text{O}(\text{cr})$] at 22.5 ± 0.5 °C from a long-term experiment up to 1629 days, approaching equilibrium from the direction of supersaturation, $\text{Mg}_3\text{B}_7\text{O}_{13}\text{Cl}(\text{cr}) + \text{H}^+ + 2\text{B}(\text{OH})_4^- + 18\text{H}_2\text{O}(\text{l}) \rightleftharpoons 3\text{MgB}_3\text{O}_3(\text{OH})_5 \cdot 5\text{H}_2\text{O}(\text{cr}) + \text{Cl}^-$.

Based on solubility measurements, the 10-based logarithm of the equilibrium constant for the above reaction at 25 °C is determined to be 12.83 ± 0.08 (2σ).

Based on the equilibrium constant for dissolution of boracite, $\text{Mg}_3\text{B}_7\text{O}_{13}\text{Cl}(\text{cr}) + 15\text{H}_2\text{O}(\text{l}) = 3\text{Mg}^{2+} + 7\text{B}(\text{OH})_4^- + \text{Cl}^- + 2\text{H}^+$ at 25 °C measured previously (Xiong et al. 2018) and that for the reaction between boracite and kurnakovite determined here, the equilibrium constant for dissolution of kurnakovite, $\text{MgB}_3\text{O}_3(\text{OH})_5 \cdot 5\text{H}_2\text{O}(\text{cr}) = \text{Mg}^{2+} + 3\text{B}(\text{OH})_4^- + \text{H}^+ + \text{H}_2\text{O}(\text{l})$ is derived as -14.11 ± 0.40 (2σ).

Using the equilibrium constant for dissolution of kurnakovite obtained in this study and the experimental enthalpy of formation for kurnakovite from the literature, a set of thermodynamic properties for kurnakovite at 25 °C and 1 bar is recommended as follows: $\Delta H_f^\circ = -4813.24 \pm 4.92$ kJ/mol, $\Delta G_f^\circ = -4232.0 \pm 2.3$ kJ/mol, and $S^\circ = 414.3 \pm 0.9$ J/(mol·K). Among them, the Gibbs energy of formation is based on the equilibrium constant for kurnakovite determined in this study; the enthalpy of formation is from the literature (Li et al. 1997), and the standard entropy is calculated internally with the Gibbs-Helmholtz equation in this work. The thermodynamic properties of kurnakovite estimated using the group contribution method for borate minerals based on the sums of contributions from the cations, borate polyanions, and structural water to the thermodynamic properties from the literature (Li et al. 2000) are consistent, within their uncertainties, with the values listed above.

Since kurnakovite usually forms in salt lakes rich in sulfate, studying the interactions of borate with sulfate is important to modeling kurnakovite in salt lakes. For this purpose, I have re-calibrated our previous model (Xiong et al. 2013) describing the interactions of borate with sulfate based on the new solubility data for borax in Na_2SO_4 solutions presented here.

Keywords: Pitzer model, nuclear waste management, borate deposits, actinide-borate aqueous complex, borate minerals, salt lakes, hydrofracking materials, solution chemistry; Lithium, Beryllium and Boron: Quintessentially Crustal