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Solubility at 5 - 75 °C and thermodynamic parameters of halogenated mimetites $Pb_5(AsO_4)_3X$

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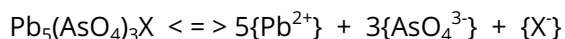
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Mimetite $Pb_5(AsO_4)_3Cl$, apatite supergroup member, is a mineral of very low solubility. A very flexible structure of apatite allows for substitution of Cl by F, OH, Br, or even I. Due to lack of solubility constants K_{sp} , and other thermodynamic parameters (enthalpy of formation ΔH_f° , specific heat capacity C_p° , entropy of formation S_f° , Gibbs free energy of formation ΔG_f°), it is unclear which of the investigated phases is the most soluble or most stable. Answers to these questions have multiple environmental and technological consequences.

The objective of this study was to run dissolution experiments of synthetic halogenated analogs of mimetite: $Pb_5(AsO_4)_3F$, $Pb_5(AsO_4)_3OH$, $Pb_5(AsO_4)_3Cl$, $Pb_5(AsO_4)_3Br$, and $Pb_5(AsO_4)_3I$, and determine their solubility at 5 - 75 °C which allows to calculate thermodynamic functions of state.

Pure phases have been successfully synthesized by precipitation from aqueous solutions. Batch dissolution and dissolution–recrystallization experiments were conducted for up to 9 months in triplicates at 5, 15, 25, 35, 45, 55, 65 and 75 °C, at pH = 3.5 (to avoid crystallization of secondary phases during dissolution), in a 0.05 M NH_4NO_3 background electrolyte. A plateau in the [Pb] evolution patterns was used to determine equilibrium. The ion activity products (IAP) of the mimetites were calculated based on the dissolution reaction:



where the brackets denote activity and X means F⁻, OH⁻, Cl⁻, Br⁻ or I⁻. The new, experimentally determined values of logK_{sp} at 25 °C for mimetites are: -76.45±0.72; -77.71±0.38; -76.82±0.55; -76.13±0.54 and -72.48±0.45 respectively. The logK_{sp} of Pb₅(AsO₄)₃Cl determined here is in very good agreement with the logK_{sp} determined by Bajda, 2010 (the discrepancy equals to 0.62%). The nonlinear regression of logK_{sp} versus temperature allowed for calculation of ΔH^o_f, C_p^o, S^o_f and ΔG^o_f. The calculated ΔG^o_f for mimetites increases linearly with the increase of ionic radius of X⁻. Thus, the most stable phase is F-mimetite while the least stable, in terms of Gibbs free energy of formation, is I-mimetite. The thermodynamic data reported in this study supplement existing databases used in geochemical modeling.

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Bajda T. (2010) Solubility of mimetite Pb₅(AsO₄)₃Cl at 5–55 °C. *Environ. Chem.* 7, 268–278.