Mimetite Pb₅(AsO₄)₃X, 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: Pb₅(AsO₄)₃F, Pb₅(AsO₄)₃OH, Pb₅(AsO₄)₃Cl, Pb₅(AsO₄)₃Br, and Pb₅(AsO₄)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 NH₄NO₃ 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:

\[
Pb_5(AsO_4)_3X \rightleftharpoons 5\{Pb^{2+}\} + 3\{AsO_4^{3-}\} + \{X\}
\]
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 Pb_{5}(AsO_{4})_{3}Cl 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}^{r}, C_{p}^{o}, S_{o}^{r} and ΔG_{o}^{r}. The calculated ΔG_{o}^{r} 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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