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Enthalpy of formation and heat of dissolution for halogenated mimetites $Pb_5(AsO_4)_3X$

Bartosz Puzio (1), Lei Zhang (2), Peter C. Burns (2,3), and Maciej Manecki (1)

(1) AGH University of Science and Technology, Geology, Geophysics and Environmental Protection, Mineralogy, Petrography and Geochemistry, Kraków, Poland (bpuzio@agh.edu.pl), (2) Department of Civil and Environmental Engineering and Earth Sciences, University of Notre Dame, Notre Dame, IN 46556, USA, (3) Department of Chemistry and Biochemistry, University of Notre Dame, Notre Dame, IN 46556, USA

Mimetite $Pb_5(AsO_4)_3Cl$ 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. Halogenated mimetites are also quite insoluble. Due to lack of thermodynamic data it is unclear whether dissolution of these phases is exothermic or endothermic which has multiple environmental and technological consequences. The objective of this study was direct calorimetric measurement and calculation of the enthalpy of formation (ΔH_f^o) of 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 calculation of the heat of their dissolution in water. Pure phases have been synthesized by precipitation from aqueous solutions. A direct oxide melt solution calorimetric measurement procedure has been developed and the enthalpies of dissolution (ΔH_{diss}^o) were determined using Setaram AlexSys calorimeter. Based on ΔH_{diss}^o and specific thermochemical cycles for investigated apatites the ΔH_f^o were calculated. The ΔH_f^o equals to (in kJ/mol): -3019.48±11.48 for OH, -2882.36±16.10 for Cl, -2770.79±24.62 for Br, and -2709.9±11.71 for I-bearing mimetite. Direct calorimetric measurement for $Pb_5(AsO_4)_3F$ was impossible for technical reasons. However, the values of ΔH_f^o for halogenated mimetites strongly and linearly correlate with ΔH_f^o of aqueous ions: OH^-, Cl^-, Br^-, and I^-. This linear relationship allowed for extrapolation. The calculated ΔH_f^o for $Pb_5(AsO_4)_3F$ equals to -3150 kJ/mol. The new, calorimetrically determined value of ΔH_f^o for mimetite $Pb_5(AsO_4)_3Cl$ differs from the enthalpy determined by dissolution of mimetite in water at various temperatures: -2965.9±4.7 kJ/mol (Bajda 2010). The discrepancy equals to 82 kJ/mol (2.8%). This is quite significant since the discrepancy is at the order of variation within the series. The reason for this feature is unclear. These newly determined data allow for calculation of the enthalpy of dissolution in water ΔH_r^o based on the reaction:

$$Pb_5(AsO_4)_3X <=> 5Pb^{2+} + 3AsO_4^{3-} + X^-$$

where X denotes F^-, OH^-, Cl^-, Br or I^-. The calculated values indicate that dissolution of mimetite analogs containing light anion is endothermic: enthalpy of dissolution at normal conditions equals to 154.8, 129.65, and 56.1 kJ/mol for F, OH and Cl mimetite. However, dissolution of mimetite analogs containing Br or I is exothermic: ΔH_r^o equals to -10.4 and -6.7 kJ/mol, respectively. The reason for this transition from endothermic to exothermic reaction is unknown and heats of dissolution of solid solutions (containing mixed halogens) await investigation.

Bajda T. (2010) Solubility of mimetite $Pb_5(AsO_4)_3Cl$ at 5–55 ˚C. Environ. Chem. 7, 268–278.

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