Thermodynamic characterization of synthetic lead-arsenate apatites with different halogen substitutions

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ABSTRACT

Thermodynamic parameters have been measured for synthetic analogs of the mimetite-group minerals Pb₅(AsO₄)ₓX (X = OH, Cl, Br, I) belonging to the apatite supergroup. Phases precipitated from aqueous solutions under ambient conditions with well-characterized structures and compositions were studied. For each phase, dissolution enthalpy was determined by oxide melt drop solution calorimetry in a molten solvent of sodium molybdate (3Na₂O·4MoO₃) at 976 K. The enthalpy of formation from the elements ΔH°f was calculated using thermochemical cycles and was −3030.6 ± 11.5, −3026.6 ± 15.8, −2967.6 ± 25.0, and −2993.1 ± 12.2 kJ/mol for Pb₅.₀₀(AsO₄)₁.₀₀OH₃.₀₀(CO₃)₀.₁₀, Pb₅.₀₀(AsO₄)₁.₀₀Cl₃.₀₀(CO₃)₀.₁₀, Pb₅.₀₀(AsO₄)₁.₀₀Br₃.₀₀(CO₃)₀.₁₀, and Pb₅.₀₀(AsO₄)₁.₀₀I₃.₀₀OH₃.₀₀(CO₃)₀.₁₀, respectively. These ΔH°f values exhibit typical trends for apatites: they increased (were less negative) with the increasing molar mass and ionic radius of X and decreased with the electronegativity and ionization energy of X. The compilation and comparison of data for Ca-, Pb-, P-, and As-apatites revealed correlations indicating that thermodynamic enthalpic stability is largely influenced by chemical factors (e.g., differences in electronegativities of the elements, ionization energy, or ionic characteristics of the bonds) and to a lesser extent by physical and geometric parameters in the crystal structure related to the mass and size of the X anion. Using the correlations, it was possible to estimate the value of hitherto unknown ΔH°f for Pb₅(AsO₄)₃F, −3144.3 ± 66.5 kJ/mol. The observed relationships apply to the entire apatite supergroup and can be used to predict the values of ΔH°f for phases that have not been studied experimentally. The new data on environmentally significant phases will contribute to the modeling of mineral-water interactions, particularly for potential use in the remediation of soils and wastes contaminated with Pb and As and in the immobilization of radioactive waste containing I-129.

Keywords: Lead apatite, lead arsenates, calorimetry, enthalpy, mimetite, iodoapatites

INTRODUCTION

Pyromorphite Pb₅(PO₄)₃Cl and mimetite Pb₅(AsO₄)₃Cl are the most stable lead apatites in the environment (Manecki 2019). With the capacity to hold more than half of the long-lived radioactive elements of the periodic table in its structure (Hughes and Rakovan 2015) and a structure that allows both cationic and anionic solid solutions and substitutions, apatite is also a versatile material for application in the field of environmental remediation (Rakovan and Pasteris 2015). The formation of these minerals in contaminated areas of mine dumps significantly reduces Pb and As bioavailability and improves ecosystem health (e.g., Nriagu 1974, Comba 1987, Ruby et al. 1994; Laperche et al. 1997, Manecki et al. 2006, 2019; Chappell and Scheckel 2007; Karna et al. 2018). Apatites are also used in permeable reactive barriers (PRBs), e.g., to isolate groundwater from radionuclides or as a form of processed waste in planned nuclear waste repositories (Conca et al. 2000; Rigali et al. 2016).

The thermodynamic stability of pyromorphite has been extensively studied (see, e.g., Nriagu 1974; Manecki et al. 2006, 2009 and the literature therein). However, little is known about the thermodynamic properties of mimetite-group minerals. To date, only one study has reported calculations of the enthalpy of formation for Pb₅(AsO₄)₃Cl from dissolution experiments (Bajda 2010). No calorimetric measurements have been reported to date. In addition, there are no thermodynamic data for other phases in this group where Cl is replaced by OH, F, Br, or I, and general information on these phases is scarce (Flis et al. 2011; Cao et al. 2014). This limits understanding of the properties of apatite as a group and prevents the thermodynamic modeling of mineral-water interactions in Pb- and As-bearing systems of high environmental importance (Twidwell et al. 1994; Liu et al. 2009; Nordstrom et al. 2014; Topolska et al. 2014).

The synthetic analogs of apatites have been of interest to environmental mineralogists and materials science engineers for decades. Attempts to synthesize and characterize mimetites with various halide substitutions were made as early as 1959 (Merker and Wondratschek 1959). Currently, research on iodine varieties has become particularly important because of their ability to incorporate radioactive fission products such as I-129 and Cl-36 (Lei et al. 2020). The immobilization of I-129, one of the problematic fission products, has been particularly chal-