An easy-to-use method to predict the K_{sp} and thermodynamic functions of state for apatites

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Although apatites, a huge supergroup of minerals including phosphates, arsenates, vanadates and many others with general formula $Me_5(AO_4)_3Z$, have been intensively studied for years, many thermodynamic constants are still missing, in particular K_{sp} and ΔG°_f, ΔH°_f, ΔS°_f. Knowledge of these constants is important because of the widespread occurrence of apatites in the lithosphere and biosphere and because of the huge application of various apatites in practice. We propose a new, relatively easy to use method of estimating predicted values of thermodynamic functions for apatites on the basis of existing data and systematic relationships between them.

Thermodynamic data for apatites have been reviewed and evaluated and systematic relationships with ionic substitutions were tested and evaluated. The best, close to linear correlations for K_{sp}, ΔG°_f, ΔH°_f and ΔS°_f were selected: A) correlation with electronegativity of Me cation (Me= Ca^{2+}, Pb^{2+}, Ba^{2+}, Sr^{2+}, Mg^{2+}, Zn^{2+}, Cd^{2+}, Cu^{2+}); B) correlation with mass of the Z anion (Z= OH-, F-, Cl-, Br-, I); and C) correlation with the ionization energy of the Z anion. Based on these strong correlations, more than 40 new thermodynamic data not yet determined experimentally were predicted and estimated. The accuracy of these predictions was confirmed experimentally by the synthesis and direct experimental determination of thermodynamic constants for several arsenic apatites, for which they were so far unknown. The comparison of new experimental data with predictions showed a discrepancy of less than 1%. This work is funded by (NCN) grant No. 2017/27/N/ST10/00776.