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PhD Thesis abstract

New method for prediction of thermodynamic functions for apatites

The apatite supergroup is the second largest of all minerals and has been of interest to mineralogists, petrologists and materials engineers for decades. In the present study, experimental data on thermodynamic state functions (TSF) and molar volume were collected for phosphate, arsenate, and vanadate minerals and their synthetic analogs belonging to apatite supergroup containing Ca, Sr, Ba, Pb, and Cd in the Me^{2+} cationic position and F, OH, Cl, Br, and I in the X halide position. Based on this, a new method for predicting TSF for apatite was proposed. It was shown that the apatite supergroup splits into distinct subgroups (populations) constituted by $Me_{10}(AO_4)_6X_2$ with the same Me^{2+} cations and tetrahedral AO_4^{3-} anions but with different anions at the X position. Linear relationships between TSF and various physico-chemical parameters of element at X position within apatite subgroups are observed and have been investigated. The prediction method for molar volume V_m, enthalpy of formation from elements $\Delta H°_{f,el}$ and third-law standard entropy $S°$ is based on regression analysis of the linear correlations within the subgroups between TSF and e.g., ionic radii of element X, lattice energy of apatite or $\Delta H°_{f,el}$ of their anions AO_4^{3-} or X^-. This allowed the author to predict new TSF values for apatite endmembers and materials with an apatite structure so far unknown. The prediction precision is comparable to the experimental uncertainty obtained when reproducing experimental data using calorimetric measurements or dissolution experiments and can be applied to a wider range of apatite than other methods. Using the predicted data, the author calculated other useful TSFs such as the Gibbs free energy of formation from elements $\Delta G°_{f,el}$ and the solubility constant K_{sp} for investigated apatite endmembers. Based on the updated TSF database for the apatite supergroup, it was possible for the first time to discuss trends of variation within and between different apatite subgroups. The outcomes of this work are providing many new pathways e.g., experimental expanding the apatite supergroup with new compounds, or testing the presented method itself on other groups of minerals such as amphiboles or tourmalines.