Quantum mechanical predictions of thermodynamic mixing properties of alunite supergroup minerals

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In various geological settings, alunite supergroup minerals form extensive solid solutions that can accommodate a variety of elements. In this study, thermodynamic mixing properties of sulfate-chromate (S-Cr), sulfate-selenate (S-Se), and sulfate-phosphate-arsenate (S-P-As) solid solutions in the alunite supergroup minerals are investigated based on quantum-mechanical modeling and statistical analysis.

S-Cr and S-Se solid solutions in alunite and jarosite are due to the mixing of anions with the equivalent charges at the sulfate site. The enthalpy of mixing (ΔH_{mix}) is the lowest at 0 K and increases with increasing temperature; it is also dependent on the arrangement of atoms at the sulfate site (i.e., the ordering effect). S-Cr and S-Se solid solutions tend to be complete solid solution at room temperature and no ordering is acquired at or above ambient conditions. The Gibbs free energy of mixing (ΔG_{mix}) indicates that the jarosite structure is more flexible to accommodate chromate and selenate at the sulfate site than the alunite structure and that complete solid solution can be formed between jarosite and either of Se- and Cr-analogues at temperatures above -80 °C.

S-P-As solid solution is examined between alunite family minerals. Below 700 °C, ternary S-P-As mixing having alunite, crandallite and arsenocrandallite as end members shows large miscibility gaps at compositions close to the ratio of S:P:As = 4:1:1 and 1:1:1 at the TO_4 site. Ternary S-P-As mixing between woodhouseite, arsenowoodhouseite and one of alunite and natroalunite shows that arsenate is more compatible with sulfate in natroalunite than sulfate in alunite whereas substitution of sulfate with phosphate is energetically more favorable in alunite than natroalunite. Our computed phase diagrams of S-P-As mixing suggest that binary solid solutions between two of sulfate, phosphate, and arsenate in alunite family minerals scarcely occur below 100 °C, are limited at temperatures from 100 to 300 °C, and become extensive or complete above 300 °C.