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Thermodynamic sublattice model for the aqueous solubilities in the apatite solid-solution system $(Ca,Sr)_5[(P,V)O_4]_3(OH,F)$ with eight endmembers

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To understand the elevated vanadate concentrations in some aquifers, and the toxic effects of the oxyanion on the human skeletal system, solubility products of the solid solutions between phosphate and vanadate phases in the apatite supergroup system $(Ca,Sr)_5(PO_4,VO_4)_3(OH,F)$ were investigated. The solid solutions were synthesized at 200°C and characterized by using X-ray diffraction and chemical analysis. The dissolution of the synthetic solids was studied at 25°C in a series of aqueous batch equilibrium experiments starting at low pH 2 for up to two months. The pH values increased rapidly at the beginning of dissolution, remained constant after 24 h at a pH 5-8 depending on composition. The solute concentrations indicated stoichiometric cation and anion release. The solubility of the solid solutions increased with an increase in the mole fraction of vanadate, with orders of magnitude higher solubilities of the respective hydroxyl- or fluorapatite endmembers. The endmember thermodynamic constants thus derived were justified by theoretical evaluation based on the Simple Salt Approximation model. Further interpretation of the data was performed for the first time based on an advanced sublattice solid-solution aqueous-solution (SSAS) equilibrium thermodynamic model for the multicomponent apatite supergroup phase members. In such complex mineral structures, co-substitutions of ions may occur on structurally different sites simultaneously. A sublattice denotes a set of all possible substitutions of the same structural site. For example, if sole 1:1 substitution of oxyanions occurs on the tetrahedral sublattice positions and no substitutions occur in other sublattice sites (e.g., no hydroxyl by halogenides), then a simple single-site binary mixing model applies, which is also a common implementation for SSAS models in codes such as PHREEQC. However, a more complex sublattice SSAS model of mixing is necessary to predict solubility changes upon co-substitution in apatite-type minerals using the GEMS code. The experimental and model results show that even a trace Ca or phosphate substitution in the vanadate apatite endmembers decreased dramatically the V(5) solubility. This allows for predicting solubilities in any of the possible solid solution subsystems, which can easily be extended by including other endmembers of the apatite supergroup system.