

Aqueous solubilities in the apatite solid-solution system with double co-substitution on both Ca-Sr cation and OH-F anion sublattice positions

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To investigate the potential for Sr-90 sequestration by apatite phases in contaminated soils and aquifers, the solubility products of solid solutions in the apatite supergroup system $(\text{Ca,Sr})_5(\text{PO}_4)_3(\text{OH,F})$ were studied [1]. Binary hydroxyl- and fluorapatite solid solutions of varying compositions were synthesized hydrothermally at 200°C and characterized by using Rietveld and chemical analysis. The lattice parameters exhibited a linear increase with increasing Sr content, adhering to Vegard's law and indicating mixing without mixing gaps in the solid-solution system. Dissolution studies were conducted at 25°C through aqueous batch equilibrium experiments. Aqueous solubility increased with the Sr mole fraction. However, batch equilibration over weeks led to a stoichiometric rather than a true thermodynamic equilibrium state. Such stoichiometric dissolution of a solid solution is commonly observed in low-solubility phases such as apatite minerals [2]. Stoichiometric saturation for solid solutions corresponds to equal molar Gibbs energy functions of the solid and aqueous phases, which can be represented by an "equal-G curve" (EGC) in Lippmann diagrams. Stoichiometric solubility constants K_{st} were calculated from the solute activities in the dissolution experiments. These constants align along the straight EGC line connecting the endmember solubility products. The excess Gibbs energy of mixing in the solid phase is therefore zero indicating formation of an ideal solid solution system. Correct binary Lippmann phase diagrams were successfully plotted for the first time for substituting cations with stoichiometric factors greater than unity. These diagrams allows for the prediction of solubilities across any solid solution composition, including co-substitutions in both the cation and anion sublattices as represented for the first time by a quaternary Lippmann diagram. The *solidus* plane of the quaternary Lippmann diagram is shown in Figure 1a and the *solutus* plane in Figure 1b below. The results illustrate that substitution of Ca by Sr increases the solubility of the resulting solid solutions under both short-term metastable and long-term thermodynamic equilibrium conditions. These findings provide significant environmental implications for Sr-90 radionuclide immobilization using apatite.

[1] Kersten (2025), *Applied Geochemistry* 182, 106323.

[2] Solecka, Puzio, Kersten, Topolska, Manecki & Bajda (2025), *Chemical Geology* 675, 122609.

