https://doi.org/10.46427/gold2026.37816

DFT-based thermodynamic prediction of iodine retention in $Me_5(AO_4)_3I$ apatites under repository conditions

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Radioactive iodine-129 (half-life 1.57×10^7 years) is one of the most critical safety-relevant radionuclides in deep geological repositories due to its high mobility and long-term radiological impact. Mineral-based immobilization strategies therefore require phases capable of structurally incorporating iodide while maintaining low aqueous iodine concentrations under repository boundary conditions. We investigate iodine-bearing apatites of general formula $Me_5(AO_4)_3I$, where Me = Ca, Sr, Ba, Cd, Pb and A = P, As, V. These phases belong to the apatite supergroup and accommodate iodide within structural channels, while cationic and tetrahedral substitutions allow systematic tuning of thermodynamic stability.

Density functional theory (DFT) calculations were performed using CASTEP code [1]. Structural optimizations employed the LDA functional with ultrasoft pseudopotentials (plane-wave cutoff 380 eV; k-point spacing 0.04 $Å^{-1}$). Vibrational properties and temperature-dependent heat capacities were obtained from phonon calculations within GGA (700 eV cutoff). Standard entropies and enthalpy corrections at 298.15 K were derived from numerical integration of phonon-derived heat capacities. Formation enthalpies of $Me_5(AO_4)_3I$ were calculated via internally consistent oxide-iodide reactions by combining total DFT energies with reference thermodynamic data for binary oxides and iodides.

Temperature-dependent Gibbs free energies were then calculated and converted into solubility constants for the dissolution reaction of $Me_5(AO_4)_3I$ into aqueous metal cations, tetrahedral oxyanions, and iodide. The resulting $\log K_{sp}(T)$ dataset was implemented into PHREEQC to simulate equilibrium iodine concentrations under repository-relevant porewaters, including alkaline cement-influenced conditions (pH 12.5-13.2, ionic strength 0.3-1.0 M, reducing environment) and clay/bentonite-buffered conditions (pH 7-9, ionic strength 0.1-0.7 M) for temperatures between 25 and 90 °C.

The results demonstrate strong compositional control on iodine retention, with Pb-bearing apatites exhibiting the lowest predicted aqueous iodine concentrations across the investigated temperature-pH space. This DFT-constrained thermodynamic framework provides quantitative stability envelopes for iodine-bearing apatites and supports their evaluation as reactive mineral barriers for long-term nuclear waste immobilization.

[1] Benisek, A., & Dachs, E., 2018. The accuracy of standard enthalpies and entropies for phases of petrological interest derived from density-functional calculations. *CMP*, 173, 1-11. https://doi.org/10.1007/s00410-018-1514-x,,

Financial support for BP was provided by the National Science Center, Poland [Grant No. 2025/57/B/ST10/02894]