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Arsenate substitution in hydroxylapatite: Structural characterization of the Ca₅(P_xAs_{1-x}O₄)₃OH solid solution

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ABSTRACT

Arsenate (As^{5^+}) substitution in the hydroxylapatite structure was examined using a combination of crystallographic and spectroscopic techniques. Samples of hydroxylapatite, the As^{5^+} -substituted analog (synthetic johnbaumite), and five intermediate compositions were synthesized from solution. Synchrotron X-ray diffraction data show that all samples are single-phase, confirming complete substitution. No evidence is found for lowering of symmetry below $P6_3/m$. Rietveld structure refinements show progressive expansion of the unit cell with increasing As substitution, which can be accounted for primarily by an average expansion of the tetrahedral site. Sizes of Ca polyhedra show little variation as a result of As substitution. NMR results show no evidence for local clustering of PO₄ tetrahedra. EXAFS confirms that the size of As-centered tetrahedra remains constant across the solid-solution series.

Keywords: Apatite, hydroxylapatite, johnbaumite, arsenic, arsenate, NMR, EXAFS