

Arsenate substitution in hydroxylapatite: Structural characterization of the $\text{Ca}_5(\text{P}_x\text{As}_{1-x}\text{O}_4)_3\text{OH}$ solid solution

**YOUNG J. LEE,¹ PETER W. STEPHENS,² YUANZHI TANG,³ WEI LI,³ BRIAN L. PHILLIPS,³
JOHN B. PARISE,^{3,4} AND RICHARD J. REEDER^{3,*}**

¹Department of Earth and Environmental Sciences, Korea University, Seoul 136-701, Korea

²Department of Physics and Astronomy, Stony Brook University, Stony Brook, New York 11794, U.S.A.

³Department of Geosciences and Center for Environmental Molecular Science, Stony Brook University, Stony Brook, New York 11794, U.S.A.

⁴Department of Chemistry, Stony Brook University, Stony Brook, New York 11794, U.S.A.

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 PO_4 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