Determination of Anion Order in F-Cl Apatite via Multinuclear Solid-State NMR & X-ray Crystallography

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Anion (F, OH, Cl) arrangements in apatite are critical to an understanding of its mineral chemistry, relevant not only to the geological sciences but also to numerous technological applications in materials science and biomedical engineering. Although the anion positions in endmember compositions are well described, there exist substantial gaps in our understanding of the anion environments in mixed binary and ternary compositions. Progress in this area has been inhibited due to crystallographic disorder or reversals in the anion column and synthesis problems such as control of composition and growth of sufficiently large crystals for X-ray diffraction analysis.

Recently[1] our group reported the crystallographic anion positions in synthetic fluor-chlorapatite $\{Ca_5(PO_4)_3(F_{0.5}Cl_{0.5})\}$ using single-crystal XRD. A new fluorine site was identified at (0,0,0.167), which yields acceptable F-Cl interatomic distances along the c-axis column, while retaining overall endmember $P6_3/m$ crystal symmetry. Successful structure analysis required exceptionally low OH-component, which was achieved by high-temperature (1200°C) synthesis under vacuum. Nominal OH occupancy was estimated via solid-state NMR using $^{31}P\{^1H\}$ cross-polarization, which indicates ca. 0.5% of P occur in hydroxylapatite-like local environments. Results from $^1H\{^{31}P\}$ REDOR showed the presence of two OH environments, giving chemical shifts near 1.6 and 0.2 ppm consistent with OH in mixed-anion and OH-rich local column arrangements, respectively. Only a small fraction of the H in the bulk sample occurs in the apatite structure. We are currently investigating the fluorine environments along the fluor-chlorapatite binary. ^{19}F spectra for the 50/50 F/Cl sample shows two main peaks, indicating distinct F environments and which are being investigated by $^{19}F/^{31}P$ and $^{19}F/^{35}Cl$ double resonance methods to provide the local structural relationships to adjacent chlorine sites and nearby phosphate groups. These methods combined with the atomic positions and occupancies from XRD will provide a comprehensive picture of the chemistry in the c-axis column and its variation across the fluor-chlorapatite binary.

[1] Hughes, J. M., Vaughn, J. S. *et al Am. Mineral.* In press.