

In Pursuit of Safe Water in East Africa: Bringing Together Advanced Spectroscopy and Microscopy Techniques to Solve a Longstanding Mystery

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High fluoride (>2 mg/L) in drinking water causes chronic fluorosis. Many groundwater aquifers around the world contain toxic fluoride levels that disproportionately affect poor, rural populations who lack access to technically involved, financially prohibitive, or otherwise inappropriate treatment technologies. As of 2008, it is estimated that 200 million people worldwide have or risk incurring fluorosis because they consume water above the World Health Organization's recommended level of 1.5 mg-F/L^{1,2}.

Calcium hydroxyapatite (HAP, Ca₅(PO₄)₃OH), synthesized via an aqueous precipitation route, is a promising ionic nanocrystal (NC) technology that is easy to use, highly selective in removing fluoride, and a cost-effective treatment option. Moreover, there is significant room for enhancing HAP's effective sorption capacity by understanding its structure-property relationships with regards to fluoride removal mechanisms. To date, these fundamental mechanistic aspects have remained elusive³. Given that fluorapatite (FAP, Ca₅(PO₄)₃F) has a significantly higher thermodynamic stability than HAP, and that the large phosphate anions conserve the apatite NC framework (a well-studied phenomenon in ionic NC systems^{4, 5}), anion exchange of aqueous fluoride with host lattice hydroxide ions ought to result in full, facile conversion to FAP⁵. In this work, we use quantitative ¹H and ¹⁹F as well as 2D ¹H solid-state nuclear magnetic resonance spectroscopy (ssNMR) in conjunction with bench-scale batch testing and conventional characterization techniques to show that host-guest lattice ion exchange does indeed occur (see Figure 1). However, the rate of uptake is significantly hampered by the loss of structural or lattice water, which can be controlled by heating the material up to 300 °C without incurring any other structural changes. We show for the first time that this structural water exists in close proximity (~2 Å) to lattice OH ions located along a 1-dimensional column in the crystallographic [001] direction (see Figure 2). This evidence suggests that structural water fills OH vacancies and facilitates the transport of OH lattice ions along the channel for exchange with F ions at the solid-water interface.

Until recently, microscopy techniques could not provide adequate information to bolster these findings because: (1) HAP NCs degrade quickly under typical e-beam intensities, making high-resolution transmission electron microscope (TEM) imaging and elemental mapping practically impossible; and (2) other microscopy techniques like atom-probe tomography (APT) lacked preparation techniques for atomically resolving nanoparticles at the nano-scale. State-of-the-art TEM and APT instruments (e.g. FEI Themis Z advanced TEM and CAMECA LEAP 4000X SI Atom Probe) and techniques⁶ now exist that should render atomic resolution HAP NC images and 3D elemental maps. In this presentation, we will convey our current findings as well as describe how these techniques (to be performed at Prof. Julie Cairney's Advanced Microscopy and Microanalysis Centre at the University of Sydney from 09.2018 - 05.2019) will provide unique locational, structural, and chemical information that will both confirm and clarify how HAP removes fluoride.

[1] Fawell, J. et al. *Fluoride in drinking water*. World Health Organization: London, UK, 2006. [2] Amini, M. et al. *Environ. Sci. Technol.* **2008**, *42*, 3662-3668. [3] Sternitzke, V. et al. *Environ. Sci. Technol.* **2012**, *46*, 802-809. [4] Meir, N. et al. *Chem. Mater.* **2016**, *28*, 7872-7877. [5] Koscher, B.A. et al. *J. Am. Chem. Soc.* **2016**, *138*, 12065-12068. [6] Felfer, P. et al. *Angew. Chem. Int. Ed.* **2014**, *53*, 1190-1193.

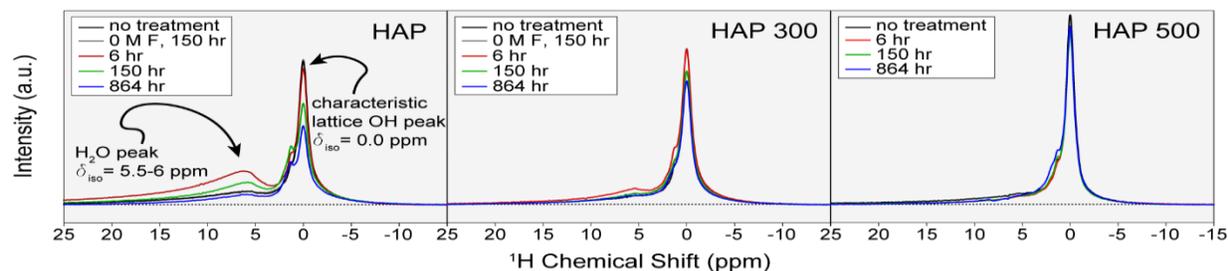


Figure 1. 1D ^1H direct polarization ssNMR of HAP in a 300 MHz instrument, with magic angle spinning (MAS) at 10 kHz in a 4 mm rotor. Samples were used as synthesized or heated at 300 or 500 °C and then treated with 30 mg/L of fluoride aqueous solution at pH 8 in batch tests for various times. All samples were vacuum dried at 160 °C and packed in airtight rotors under a N_2 atmosphere. A decrease in peak area is quantitatively proportional to the loss of protons in that distinct chemical environment.

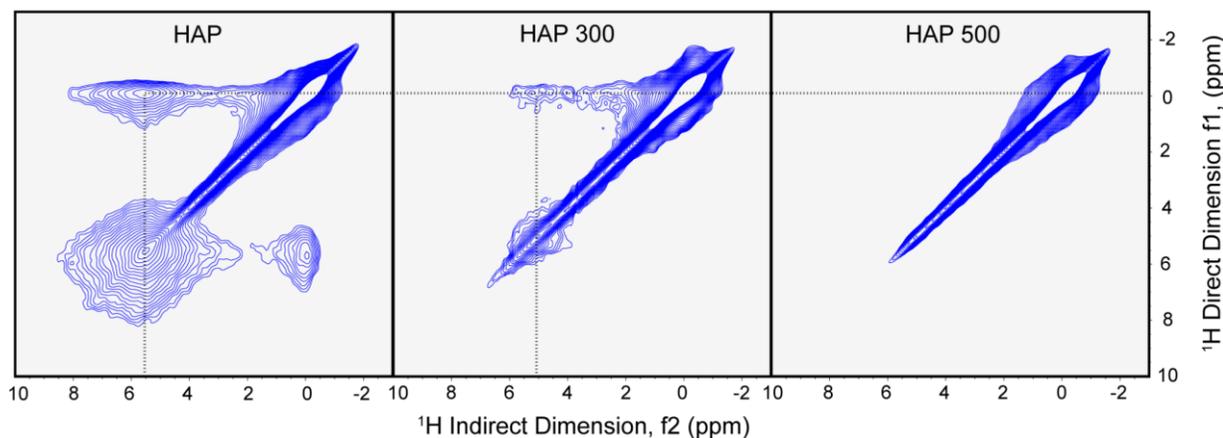


Figure 2. 2D ^1H NOESY ssNMR spectra of HAP vacuumed for >24-hr in a 600 MHz instrument, at 40 kHz MAS and 100-ms mixing time. Nuclear Overhauser effects (NOEs), that is, through-space interactions between two nuclear magnets (e.g. ^1H - ^1H spin diffusion and chemical exchange) are only significant over short distances of 2 - 4 Å and manifest as cross peaks in NOESY spectra (as indicated).