

Fluorine and Proton Environments in Fluoridated Calcium Hydroxyapatite

Mosiman, D.S., Mariñas, B.J. (U. of Illinois at Urbana-Champaign, Civil & Environmental Engineering) and Fu, R. (NHMFL)

Introduction

Calcium hydroxyapatite (HAP) is used to lower fluoride in water to levels healthy for consumption, as many aquifers contain toxic levels¹. There is potential to increase HAP's sorption capacity, yet, little understanding of how HAP removes fluoride from water². We need to understand the removal mechanism(s) in order to rationally synthesize more effective materials. The strength of ssNMR for this project is its sensitivity to both ¹H and ¹⁹F nuclei to help quantify and distinguish their chemical states and their connectivity within or on HAP nanoparticles.

Experimental

MAS ssNMR Experiments were conducted at the NHMFL's headquarters in Tallahassee, FL using the Bruker 600 MHz 89 mm magnet system #2. ¹⁹F DP 40 kHz MAS experiments, which employed an in-house developed, multi-acquisition technique with small flip angle pulses³, were performed on three variations of HAP (as precipitated, and heat treated to 300 and 500 °C) after being fluoridated at increasing times from 1 hr up to 864 hr. Additionally, ¹H NOESY experiments at 40 kHz MAS were conducted on the three un-fluoridated HAP variations with mixing times of 1, 50, and 100 ms. Larmor frequencies of 564.69 and 600.13 MHz were used for ¹⁹F and ¹H, respectively.

Results and Discussion

The ¹⁹F FastMAS measurements (figure 1) allowed for identification and quantification of fluoride environments in and at the surface of fluoridated HAPs due to the suppression of spinning side bands (FastMAS) and of any artifacts (multi-acquisition). The strongest ¹⁹F environment over the range of fluoridation times is that of Fluorapatite ($\delta_{FAP} = -101$ to -104 ppm), the fluoridated form of HAP. A smaller, unassigned peak at $\delta = -89$ to -92 ppm (not CaF₂, which has a chemical shift of $\delta_{CaF_2} = -110$ ppm) is also consistently present at anywhere from 15 – 30% of the total F⁻ amount, depending on the fluoridation time. Deconvoluted and mass normalized spectra are quantified and agree with fluoride uptake measured during fluoridation with an ion selective electrode; specifically, that F⁻ uptake increases with time and is systematically lower with heat treated HAP variants. ¹H NOESY spectra were utilized to determine associations between the subsurface bulk OH⁻ ($\delta = 0.0$ ppm) ions and molecular water ($\delta = 5.5 - 6.5$ ppm). Cross peaks were strongest in un-heat-treated HAP at a mixing time of 100 ms. They disappeared in HAP 500 and at a mixing time of 1 ms, although some water is still present. The ¹H NOESY experiments established two important findings: (1) that some water in HAP exists in close spatial proximity to lattice OH⁻ ions at around 4-5 Å and are thus likely located near or within the OH channels as has been postulated⁴; (2) that the presence of this 'structural' water is highly correlated with the uptake ability of HAP after accounting for other factors like particle size, morphology, and crystallinity.

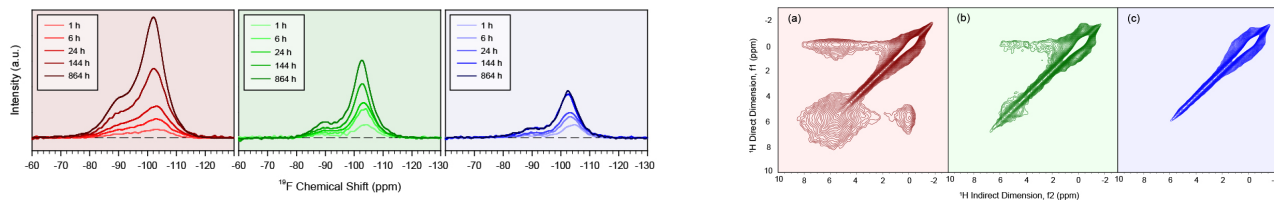


Figure 1. (LEFT) Mass normalized spectra of un-heat-treated HAP (red), HAP 300 (green), and HAP 500 (blue) over increasing fluoridation times.

Figure 2. (RIGHT) ¹H NOESY spectra of non-fluoridated samples at 100 ms mixing time, same colors apply.

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