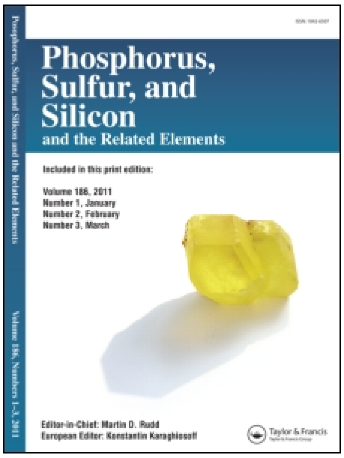

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The Investigation of the Spatial Distribution of F- in Fluoridated Hydroxyapatite by ^{31}P-^{19}F Rotational-Echo, Double-Resonance (Redor) NMR

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This work demonstrates the use of Rotational-Echo, Double-Resonance (REDOR) NMR to investigate the spatial distribution of spins in a heterogeneous system. In the study, ^{31}P-observed ^{31}P-^{19}F REDOR NMR was performed on F^--treated hydroxyapatite and 25% F^--substituted fluorohydroxyapatite. The ratios of REDOR difference to full-echo intensity with various dephasing times were measured and then compared to the simulated values for models with various fluoridation depths and orientations. The simulation involved calculating the dephasing of multiple ^{31}P's by multiple ^{19}F's and then summing over all the P-F spin clusters, weighted by the occurring probabilities. The data showed that the OH ions in the first unit cell on the (001) surface were replaced by F ions. This result suggested the fluoridation was via the ion-exchange process rather than by the diffusion or the dissolution and remineralization pathway.

Keywords: Rotational-Echo; Double-Resonance NMR; Phosphorus-31; Fluorine-19; Fluoridated apatite; Dipolar couplings; Spatial distribution

Introduction

Hydroxyapatite (HAP), $Ca_{10}(OH)_2(PO_4)_6$, is the major inorganic constituent of dental enamel and cortical bone. Incorporation of fluoride into HAP has been proven effective in preventing dental caries. The effects of fluoride on the mechanical properties of bone remain extremely controversial. In addition to identify the reactions products, a key question to understand fluoride and hydroxyapatite interaction is the spatial distribution of fluoride in apatite lattice. That is: are F ions uniformly distributed throughout apatite crystals or are they concentrated on the surface? On which crystal plane is the fluoridation preferred? Here we report our recent development of the use of P-F REDOR NMR to investigate the spatial distribution of F^- in apatite, which can provide detailed information on the history and mechanism of fluoride and HAP interactions.

Rotational-Echo, Double-Resonance (REDOR) NMR is a technique for retrieving information on weak heteronuclear dipolar coupling interactions (1). In a typical REDOR experiment, NMR signal is recorded under two different conditions: one with applying 180° pulses on dephasing nucleus and one without. The ratio of the REDOR difference signal (ΔS) to the signal without dephasing pulses (full echo, S_0) can be easily measured and translated into internuclear distances (2). For systems where an observed nucleus is dephased by more than one heteronucleus, the calculation requires the knowledge of the relative geometry of the nuclei. The calculated values for various dephasing cycles can be compared with experimental data.

Results and Discussion

FHAP was synthesized according to the method of McCann (3). A 25% F^--substituted sample (25% F^--substituted FHAP) was used in this study. For the fluoridation of hydroxyapatite, high surface area HAP was reacted with 0.016 M NaF solution at pH 7.1 for 5 minutes. The F content was determined by fluoride-selective electrode analysis to be 0.93% by weight, which is equivalent to 25% of the OH^- being substituted by F^- on average.

^{31}P-observed ^{31}P-^{19}F REDOR spectra of F^--treated HAP and 25% F^--substituted FHAP (Fig. 1) were obtained on a Bruker MLS-300 spectrometer. The recycle delay was 20 sec and magic-angle spinning rate was 9 kHz. The REDOR difference spectra (top) are the difference between rotational spin echo ^{31}P NMR with and without the ^{19}F 180° pulses. Due to the difference in F^- distribution,

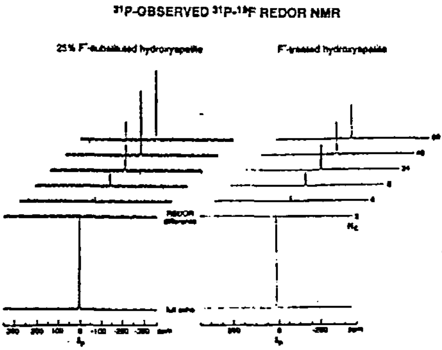

FIGURE 1

differences in the spinning sideband intensities as well as the REDOR difference signal intensities were observed between these two samples. For comparison, the experimental $(\Delta S/S_0)$'s with various dephasing cycles for are plotted in Fig. 2i and 2h.

The dephasing for ^{31}P-observed ^{31}P-^{19}F REDOR of several simple models which are important to understand the fluoridation mechanism was calculated: a) F ions are randomly distributed throughout the sample; b) OH ions of the first layer of the unit cell along the (001) plane are replaced by F ions; c) the OH ions of the first two layers of the unit cells along the (001) surface are replaced by F ions; d) the OH ions of the first three layers of the unit cells along the (001) surface are replaced by F ions; e) the OH ions of the first and the third layers of the unit cells along the (001) surface are replaced by F ions; f) the OH ions in the first layer of the unit cells along the (100) surface are replaced by F ions; and g) the OH ions in the first two layers of the unit cells along the (100) surface are replaced by F ions. The results of these calculations are plotted in Fig. 2.

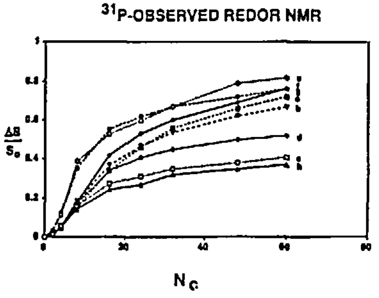

FIGURE 2

The experimental data for the 25% F$^-$-substituted FHAP (Fig. 2a) match the calculated values for the random distribution model (Fig. 2h). The data for the F$^-$-treated sample (Fig. 2i) fit best with models c and d, in which the OH ions in the first two or three layers of the unit cells along the (001) plane are substituted by F ions.

For models c and d, the fluoridation depth is 6.9 and 10.4 Å, respectively. These values are reasonable when compared with the 6.1 Å average fluoridation depth obtained from the calculation based on the surface area (128 m^2/g) and the average F^- substitution (25%), since the calculation assumes the fluoridation is isotropic in orientation. While it is true that needle-like crystallites are common in biological apatite, for synthetic HAP, when CO_3^{2-}content is less than 0.01%, the crystals formed are less structured or have hexagonal faces of {1,0,-1,0} with pyramidal faces of {1,0,-1,1} at both ends. Examination of the HAP by high-magnification light microscopy showed the majority of the HAP samples in our study were in a less-structured, non-needle crystal habit.

The depth of the F^- incorporation suggested that the fluoridation occurred via the ion-exchange process rather than by the diffusion or the dissolution and remineralization pathway (4). In our study, the five-minute treatment was too short for F ions to penetrate deeply into the crystal lattice. The ion exchange occurred preferentially on the (001) plane. This result is expected since F^- channels are exposed along the (001) surface. The exchange through the (100) or the (010) planes is hindered by Ca^{2+} and PO_4^{3-} ions. This conclusion can also be related to the dissolution study by Arends, et al. (5) of a single HAP needle-like crystal with hexagonal basal faces in acid, in which the acid attack or penetration starts with one etch pit in the (001) face and then forms a longitudinal hole parallel to the c-axis.

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