Solid State NMR Investigation of the Local Environment of Cations in Apatites

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Introduction

Calcium hydroxyapatite, $Ca_{10}(PO_4)_6(OH)_2$, is the main inorganic phase of bone tissue, and an important material for bone substitution. In natural apatites, several ions, such as magnesium, enter the lattice. Despite their biological importance, the exact structural role of these ions is often unclear. The main objective of this work is thus to determine how the presence of substituting ions changes the local environment of calcium in apatites, using ^{43}Ca solid state NMR.

Experimental

Solid state NMR experiments were performed on a 19.6 T magnet (31 mm bore size), operating with a Bruker DRX console. The natural-abundance ^{43}Ca NMR spectra were recorded using a 7mm rotor homebuilt probe, spinning at 5kHz. Because of the low sensitivity of calcium, an "adiabatic pulse" signal-enhancement scheme was used (5 ms, 5 kHz CHIRP sweep, at ~250 kHz below the Central Transition frequency).

Results and Discussion

Natural abundance magic-angle spinning ^{43}Ca NMR spectra of various calcium phosphates and substituted apatites were recorded. As shown in Figure 1, the two distinct crystallographic sites of $Ca_{10}(PO_4)_6(OH)_2$ and α-$Ca_2P_2O_7$ were resolved at 19.6 T, with better resolution than at 18.8 T.[1,2] This proves that the experimental setup at NHMFL is well suited for performing natural-abundance ^{43}Ca NMR experiments on such materials.

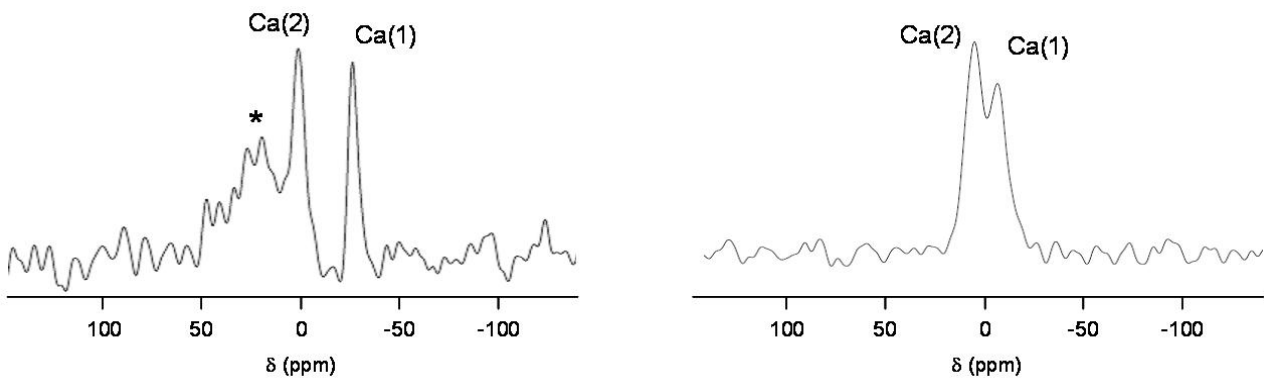

Figure 1. Natural abundance ^{43}Ca NMR spectra of α-$Ca_2P_2O_7$ (left) and $Ca_{10}(PO_4)_6(OH)_2$ (right).
(The * symbol corresponds to an impurity in the α-$Ca_2P_2O_7$ sample)

The NMR spectra of magnesium and sodium-substituted hydroxyapatites and of a cow's tooth sample were recorded and compared to that of $Ca_{10}(PO_4)_6(OH)_2$ (spectra not shown). This allows direct evidence to be obtained on the preferential location of the substituting cations in the lattice, and sheds light on the distribution in local environments around calcium.

Conclusions

This study shows that natural abundance ^{43}Ca solid state NMR at high magnetic fields can bring highly valuable information on the structure of calcium phosphates and substituted apatites, which complements well the Ca-Kedge EXAFS and XANES studies we have recently performed on these samples. As part of this work, further studies aiming at understanding better the role of magnesium in apatites have also been initiated, using ^{25}Mg NMR.

Acknowledgements

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References

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[2] Gervais, C., *et al*., Chem. Phys. Lett., **464**, 42-48 (2008).