



High Resolution Solid State NMR Studies of Biomaterials at 35.2 T: Analysis of Calcium and Oxygen Local Environments

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Introduction

A large diversity of calcium-containing biominerals are present within living organisms, including pathological calcifications belonging to the family of calcium oxalates ($\text{CaC}_2\text{O}_4 \cdot x\text{H}_2\text{O}$, $x = 1, 2, 3$) and Ca-pyrophosphates ($\text{Ca}_2\text{P}_2\text{O}_7 \cdot x\text{H}_2\text{O}$, $x = 1, 2, 4$). Understanding the structure of these materials has been the object of much interest, and solid state NMR has been shown to be a very valuable technique for this. However, the vast majority of NMR studies have concerned the spin-1/2 isotopes (^1H , ^{31}P and ^{13}C), due to their higher sensitivity and more straightforward investigation. *A contrario*, investigations on ^{43}Ca and ^{17}O have been much scarcer, especially on samples of biological origin, due to the difficulties related to the study of these poorly-receptive quadrupolar nuclei. In this report, we demonstrate the interest of performing experiments on the Series Connected Hybrid (SCH) magnet at the NHMFL, due to the significant gains in sensitivity and resolution.[1]

Experimental

^{43}Ca and ^{17}O MAS NMR spectra of a series of oxalate and pyrophosphate phases (including glasses) were acquired at 101 and 203 MHz (respective Larmor frequencies at 35.2 T field), using a Bruker NEO NMR console and a 3.2mm magic-angle spinning probe developed at the NHMFL. The spinning speed was set between 10 and 18 kHz, depending on the sample. The magnetic field was regulated using the Bruker field-frequency lock on ^7Li signal of an external paramagnetic doped LiCl solution sample [2].

Results and Discussion

For ^{43}Ca NMR samples were analyzed at natural abundance, while for ^{17}O NMR the samples were labeled in ^{17}O (with moderate enrichment levels ($< 10\% \text{ }^{17}\text{O}$)). In both cases, the use of the SCH magnet was a major asset, allowing 1D MAS spectra to be recorded in just a few hours, with a significantly higher resolution than at lower fields. This is illustrated in Figure 1 for the crystalline phase $\text{Ca}_2\text{P}_2\text{O}_7 \cdot 4\text{H}_2\text{O}$, which presents two different Ca sites. ^{43}Ca NMR analyses were also extended to the study of amorphous pyrophosphates, the structure of which is still unclear, and the data was used to discuss the quality of the computational models (developed using Molecular Dynamics & Density Functional Theory). In conclusion, these investigations have provided direct evidence of the added value of performing ^{17}O and ^{43}Ca NMR studies of biomaterials at ultra-high fields.

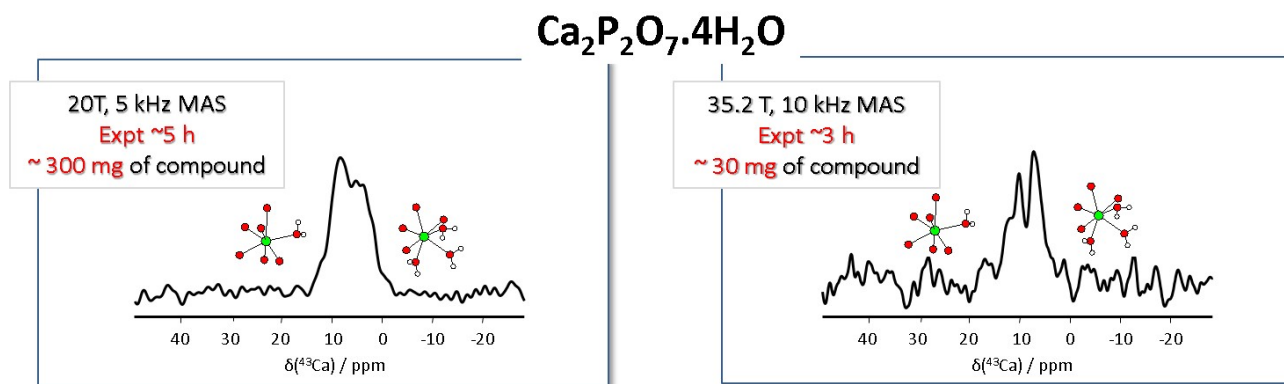


Fig 1 Comparison of natural abundance ^{43}Ca MAS NMR spectra of crystalline $\text{Ca}_2\text{P}_2\text{O}_7 \cdot 4\text{H}_2\text{O}$ recorded at 20.0 T (left) and 35.2 T (right), showing the gains in both sensitivity and resolution on the SCH magnet.

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References

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- [2] Gan, Z., *et al.*, J. Magn. Reson., **284**, 125-136 (2017).