Solid State NMR: a Pertinent Tool of Investigation for Calcium Derivatives. The Study Case of Randall’s Plaque.

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Background: The fine structure of calcium oxalates and phosphates (including Randall’s plaques) is revealed by the implementation of the ultra-sensitive NMR (Nuclear Magnetic Resonance) DNP (Dynamic Nuclear Polarization) MAS (Magic Angle Spinning) methods.

Materials and methods: A large panel of synthetic (carbonate and sodium substituted hydroxyapatite, HAp, and hydrated calcium oxalates, CaC₂O₄.nH₂O, n = 0, 1, 2, 3 – crystalline or amorphous) and natural (kidney stones, Randall’s plaques) samples were systematically studied by multinuclear (¹H, ¹³C, ²³Na, ⁴³Ca, ³¹P) multidimensional fast/ultra-fast MAS NMR at high/ultra-high magnetic fields. Besides standard NMR techniques operated at room temperature, DNP MAS experiments were implemented at 100 K involving the saturation of the EPR transitions of biradicals and the subsequent transfer of polarization to the nuclei of interest with huge gain in sensitivity.

Results: We demonstrate here that MAS NMR techniques are fully adequate for the fine and detailed characterization of synthetic and natural samples in terms of: (i) chemical composition, (ii) structure of interfaces between minerals and organic moieties such as triglycerides and proteins, (iii) local dynamics, (iv) quantification of the involved phases.

In the case of Randall’s plaques, the spectroscopic challenge in terms of NMR sensitivity is huge as one is dealing with samples characterized by a very small mass (< 100 μg). We demonstrate that this drawback can be elegantly circumvented by implementing DNP MAS NMR. The gain in nuclear magnetization is estimated to 25 leading to a reduction of the experimental time by a factor of 625!

Conclusions: DNP MAS spectroscopy offers unique perspectives for new insights in the detailed structure of calcium derivatives even in the case of situations related to severe sensitivity issues (i.e. Randall’s plaques).