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, $CaC_2O_4.nH_2O$, n = 0, 1, 2, 3 – crystalline or amorphous) and *natural* (kidney stones, Randall's plaques) samples were systematically studied by multinuclear (^{1}H, ^{13}C, ^{23}Na, ^{43}Ca, ^{31}P) 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).