Isotopic labeling of inorganic compounds in oxygen-17 using mechanochemistry: towards new opportunities for materials chemistry and NMR

Context:
Oxygen is among the most abundant elements on Earth. It is thus no surprise that early on, chemists have tried to probe the local structure around this element using Nuclear Magnetic Resonance (NMR) spectroscopy. However, the only stable isotope of oxygen which can be studied by NMR is oxygen-17, which has a very weak natural abundance (0.04%). This implies that $^{17}$O NMR spectroscopy is a poorly sensitive technique, which requires in most cases enriching in oxygen-17 the compounds of interest. Unfortunately, the majority of the synthetic routes reported in the literature for $^{17}$O-isotopic labeling are too expensive and/or too constraining experimentally for most research groups, thereby preventing the development and use of this technique by a broad research community. Implementing new $^{17}$O-enrichment protocols which are efficient, affordable and versatile, is thus a major goal to achieve.

One of the synthetic procedures which had not been looked into until very recently is mechanochemistry, which consists in using mechanical forces to perform chemical reactions. Mechanochemistry has several major advantages over more traditional solution-based synthetic routes (reduction or suppression of solvent, improved yield and selectivity, accelerated reaction rates, no solubility issues), and it meets most of the key criteria of « green chemistry ». In 2017, for the first time, we were able to demonstrate that it is possible to use mechanochemistry to enrich organic and inorganic precursors in oxygen-17, by establishing protocols which surpass in cost and efficiency those available in the literature.

Objectives:
Our first results show that mechanochemistry can be used to enrich in oxygen-17 metal hydroxides like Ca(OH)$_2$, Mg(OH)$_2$ and Al(OH)$_3$. However, many other inorganic precursors commonly used in materials synthesis contain oxygen (e.g. metal oxides, carbonates or phosphates). Thus, the main objective of this project will be to explore the potential of mechanochemistry as a new synthetic route for labeling a variety of inorganic precursors. Particular attention will be paid to the characterization of the labeled compounds, using in particular the latest high resolution $^{17}$O solid state NMR techniques, in order to broaden the scope of data accessible by this spectroscopy for the study of metal-(hydr)oxide bonds, and more importantly to determine the mechanisms of isotopic enrichment. Finally, the possibility to transpose some of the enrichment protocols to functional materials (e.g. mixed metal oxides, heterogenous catalysts and biomaterials) will also be looked into.

Keywords:
Inorganic synthesis, mechanochemistry, NMR, oxygen-17, isotopic labeling
Practical details:
This PhD research project will be performed at the University of Montpellier within the Institut Charles Gerhardt (ICGM, Danielle Laurencin & Bruno Alonso), and in close collaboration with the Institut des Biomolécules Max Mousseron (IBMM, Green Chemistry & Innovative Technologies team, Thomas-Xavier Métro). This will provide the candidate with an ideal environment for the syntheses and the characterizations, as (s)he will have direct access to the analytical platforms of the Institut Charles Gerhardt and the University of Montpellier (multinuclear solid state NMR, X-ray diffraction, electron microscopy...). Complementary high resolution $^{17}$O solid state NMR experiments on the high field instruments of IR-RMN national network will also be planned during the course of the PhD.

The project will begin on October 1st 2018, and will be funded by a European contract (ERC Consolidator grant – MISOTOP project) for a duration of 3 years. With this PhD thesis, the candidate will develop skills in both inorganic synthesis (notably by mechanochemistry), and in solid state NMR. Moreover, during the project, (s)he will have the possibility to interact not only with the research team directly associated to the project, but also with other researchers at the local, national and European levels, which will allow him (her) to develop a scientific network both nationally and internationally. Finally, (s)he will also have the opportunity to present his (her) results at conferences, and to publish them in high-impact scientific journals.

Profile:
This PhD offer is open to candidates with a Masters degree in Inorganic Chemistry or Materials Chemistry. The candidate must have a high interest not only for materials synthesis, but also for the technological aspects of the enrichment process which will be used here, and for advanced characterization methodologies. In particular, a sound knowledge in the different techniques available for the structural analysis of materials, notably solid state NMR and XRD, will be seen as a major advantage.

The candidate will have to demonstrate a high motivation for the project, and prove his (her) capacity to work in an autonomous and rigorous manner. (S)he will also have to show that (s)he will be able to integrate a multidisciplinary research team, and have excellent communication skills (both oral and written), notably in English.

Application procedure:
This offer is open to both national and international candidacies.

To apply to the position, please send a CV, a motivation letter, your Masters grades & ranking, as well as the names of 2 external contacts (for recommendation) to:

danielle.laurencin@umontpellier.fr

and

- Dr Thomas-Xavier Métro (http://www.greenchem.um2.fr/English/page32/page36/Metro.html):
thomas-xavier.metro@umontpellier.fr

and

bruno.alonso@enscm.fr

The deadline to apply to this position is March 15th 2018.

References: