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Deciphering the Role of Organic Matter in the Biomineralization Process of Marine Sponge Spicules: A Solid-State NMR Investigation



Sylvie MASSE¹, Guillaume LAURENT¹, Thibaud CORADIN¹ and Andrzej PISERA²

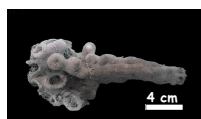
1. Laboratoire de Chimie de la Matière Condensée de Paris, Sorbonne Université, CNRS, Paris, France
2. Institute of Paleobiology, Polish Academy of Sciences, Warsaw, Poland

1 - Materials Preparation



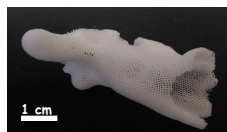
Living sponge collection:
Pr Hab. A. Pisera on board of the IRD ship for an expedition in New Caledonia

Roughly cleaning with water and drying in air



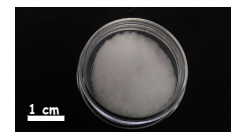
Raw APHRO specimen after collection (Hexactinellida, Hexactinosa, Aphrocallistes, Norfolk Ridge, New Caledonia)

Cleaning with HNO₃ and rinsing with water



Cleaned APHRO specimen after chemical cleansing

Grinding as a fine powder in a mortar



Ready to pack APHRO sample after grinding as a powder

(Supported by NSC, Grant No. 2016/21/B/ST10/02332)

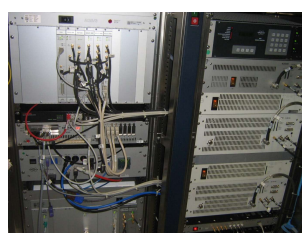
2 - Solid-State NMR Spectroscopy



NMR Facility Sorbonne University Faculty of Science and Engineering Campus Pierre et Marie Curie



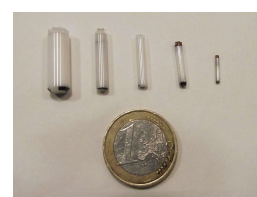
Ultraspeed 300WB Avance III Bruker ssNMR magnet



Electronic cabinet, generating radiofrequency pulses, and pneumatic unit, equilibrating bearing and driving air flows



¹H-X CP-MAS Bruker ssNMR probehead suitable for 7mm rotors



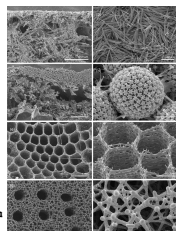
Zirconia ssNMR rotors range going from 7mm to 1.3 mm diameter (corr. to spin rate from 5kHz to 30kHz)

3 - Materials Characterization

Phylum: **2 main Classes:**

- Demospongiae
 - PETRO *Petrosia* sp., Demospongiae
 - GEODIA *Geodia* sp., Demospongiae
- Hexactinellida
 - APHRO *Aphrocallistes* sp., Hexactinellida
 - LAOCO *Laocoetis perion* sp., Hexactinellida (also known as *Carticularia*)

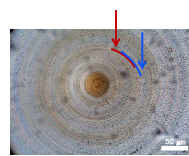
Siliceous Sponge Spicules



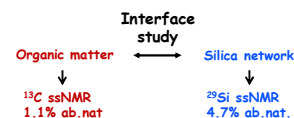
SEM pictures S. Masse et al, Minerals, 6 (1), 2016, 21

Various morphologies:

- Loose spicules (oxeas)
- Spherical star-like spicules (sterrasters)
- Honey-comb structure of fused-together spicules (hexactines)
- Fused, strongly modified and ornamented spicules (hexactines) with regularly organised canal openings

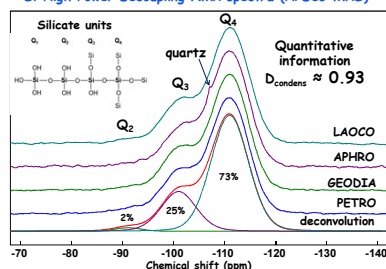


Transmitted light image in cross-section of the concentric layered structure of the giant basal spicule of the glass sponge *Monorhaphis chuni*, showing the axial cylinder at the centre (A. Pisera et al, Front. Zool, 18, 2021, 58)

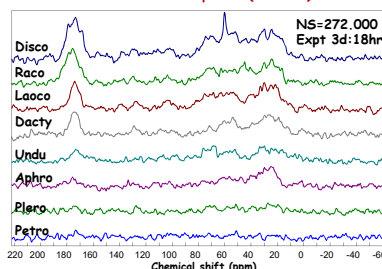


- Specific limitations of our system:
- Only < 1 wt% C into acid-cleaned samples
 - No isotopic enrichment possible
 - Only methodological and instrumental developments could help to get the signal faster

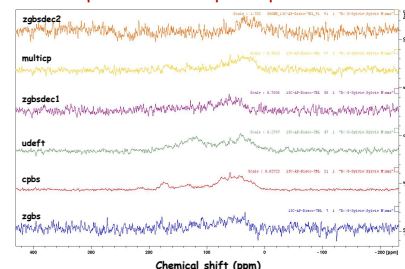
²⁹Si High Power Decoupling NMR spectra (HPDec-MAS)



¹³C Cross-Polarization NMR spectra (CP-MAS)



¹³C NMR spectra with various pulse sequences on DISCO



4 - Conclusion and Outlook

- Sponge spicules are biocomposite materials composed of a siliceous skeleton embedded in an organic matrix
- Inner skeleton is of various shapes depending on the taxon, but surprisingly ²⁹Si HPDec ssNMR signature is quite ever the same and a condensation degree of ca. 0.93 is usually observed
- ¹³C CP-MAS ssNMR should be more promising to discriminate the samples but due to the low abundance of ¹³C and low content of carbon into the cleaned samples, the signal is too poor to get detailed assignment and to explore the organic-mineral interface through 2D heterocorrelation NMR mapping
- Dynamic Nuclear Polarization (DNP-enhanced ssNMR) should be a helpful technique to go further in the comprehension of the biomineralization process of sponges