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Sylvie Masse, Guillaume Laurent, Thibaud Coradin, Andrzej Pisera. New Expectation from DNP-Enhanced SS-NMR to figure out the Role of the Organic-Silica Interfaces: the Case of Diatom Frustules and Marine Siliceous Sponge Spicules. *Magnetism and Magnetic Resonance: Magnetic Resonance, Understanding, Measurements and Modeling*, Jun 2019, Strasbourg, France. . <hal-02156116>

HAL Id: hal-02156116

<https://hal.sorbonne-universite.fr/hal-02156116v1>

Submitted on 18 Jun 2019

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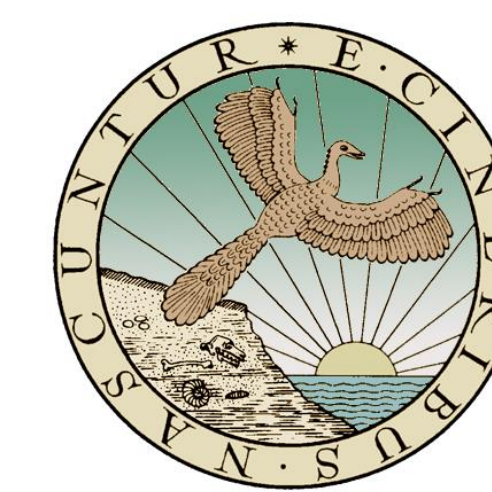
New Expectation from DNP-Enhanced SS-NMR to figure out the Role of the Organic-Silica Interfaces: the Case of Diatom Frustules and Marine Siliceous Sponge Spicules



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Microalgal culture at ISOMER- in collaboration with Dr Véronique Martin-Jézéquel and Dr Benoit Tesson Faculté des Sciences et Techniques, Nantes, France



NMR Facility-Sorbonne Université Campus P. et M. Curie -T 32-33 SB

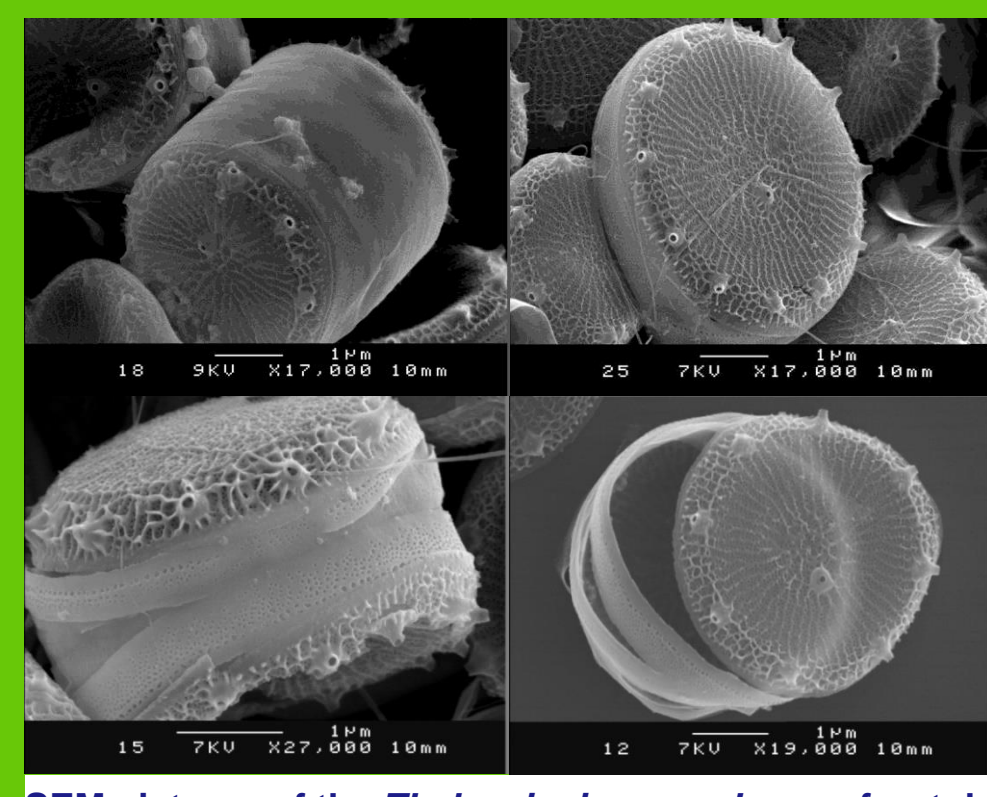


Living sponge collection: Pr A. PISERA on board of the IRD ship for an expedition in New Caledonia (Financially supported by National Science Centre, Grant No. 2016/21/B/ST10/02332)

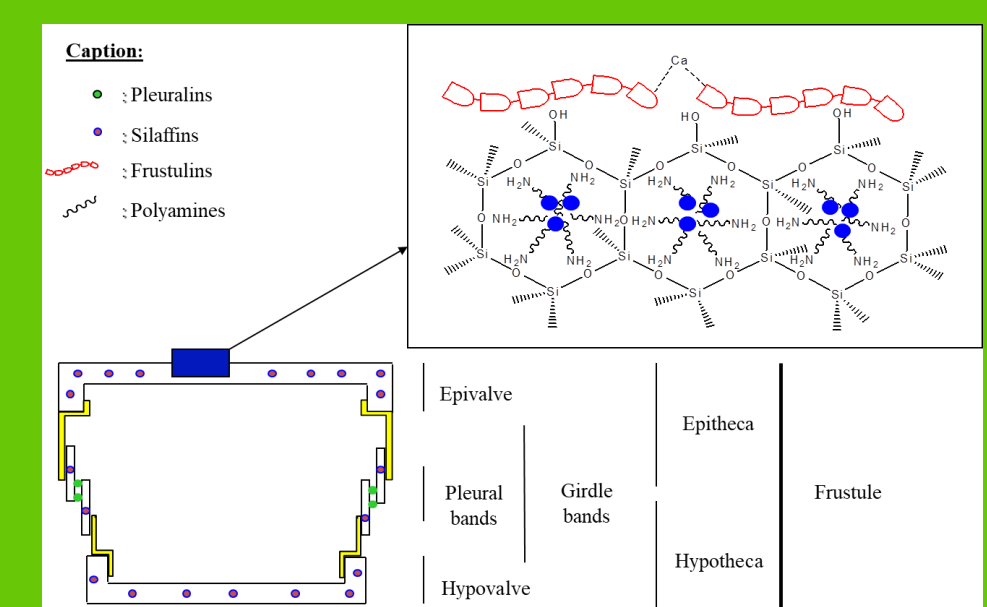
Diatoms

Living Materials producing Biogenic Silica

Marine Sponges

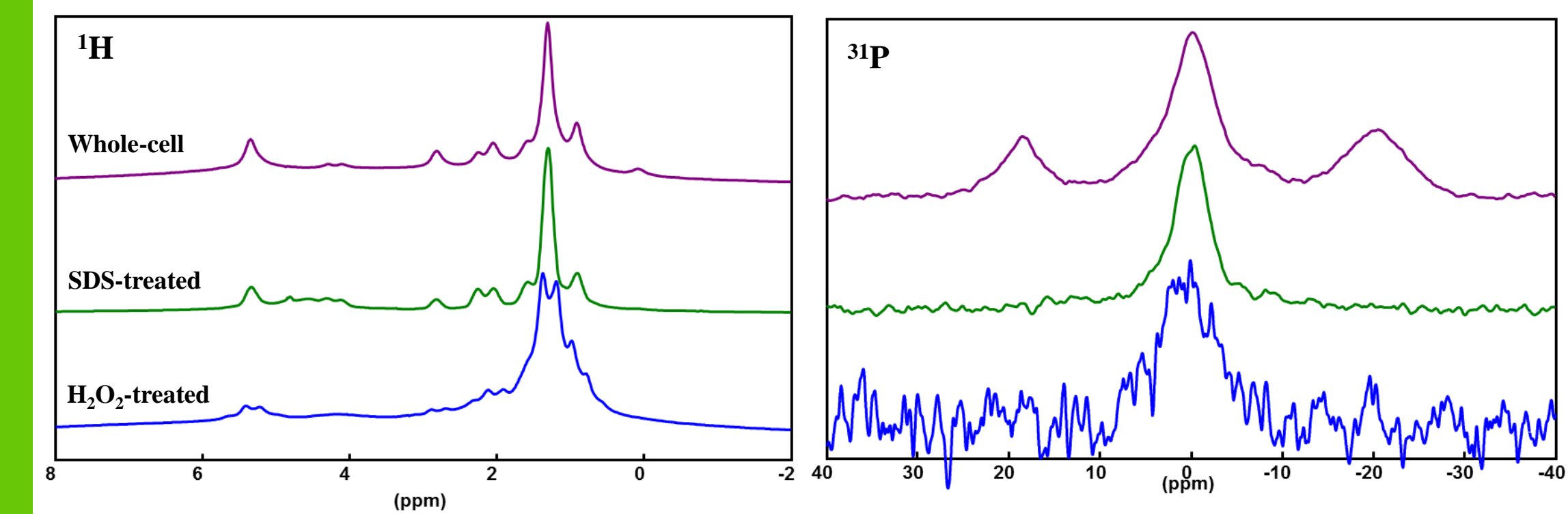
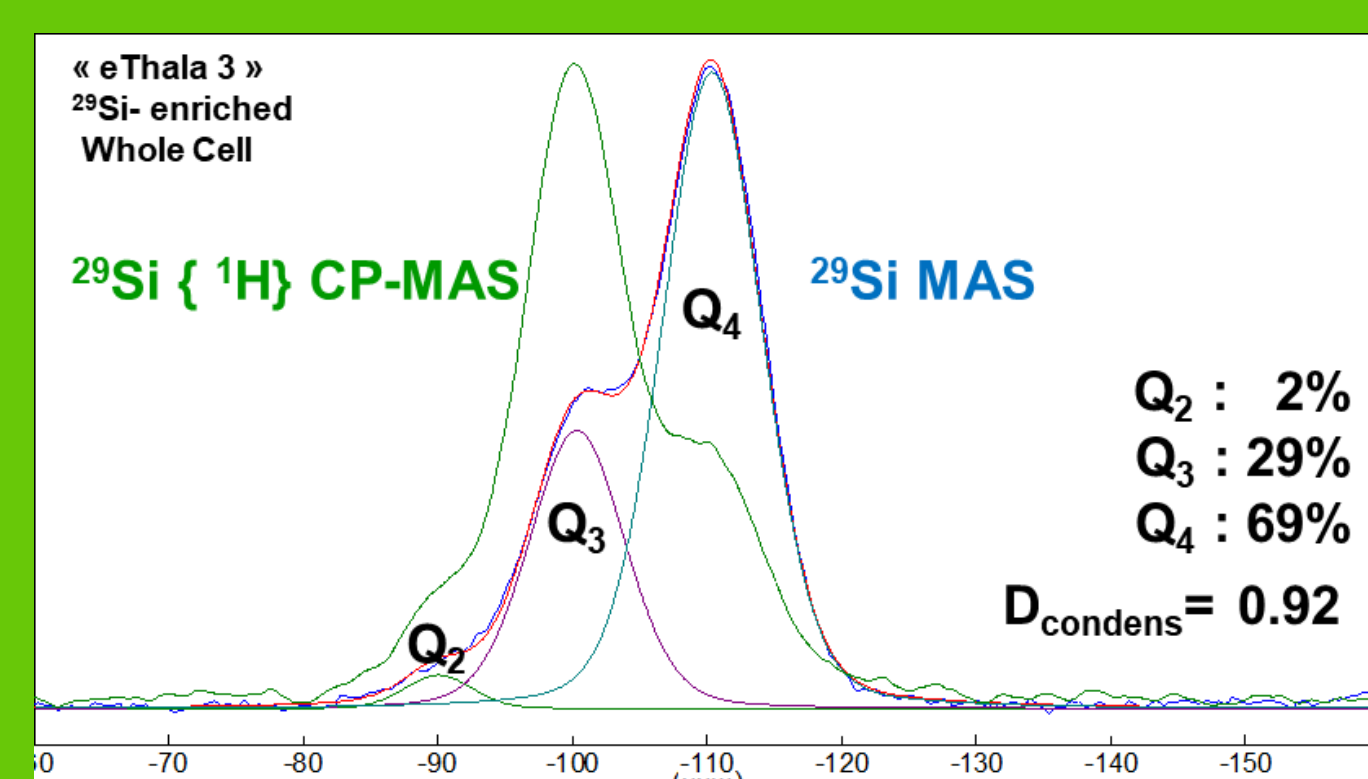


SEM pictures of the *Thalassiosira pseudonana* frustule

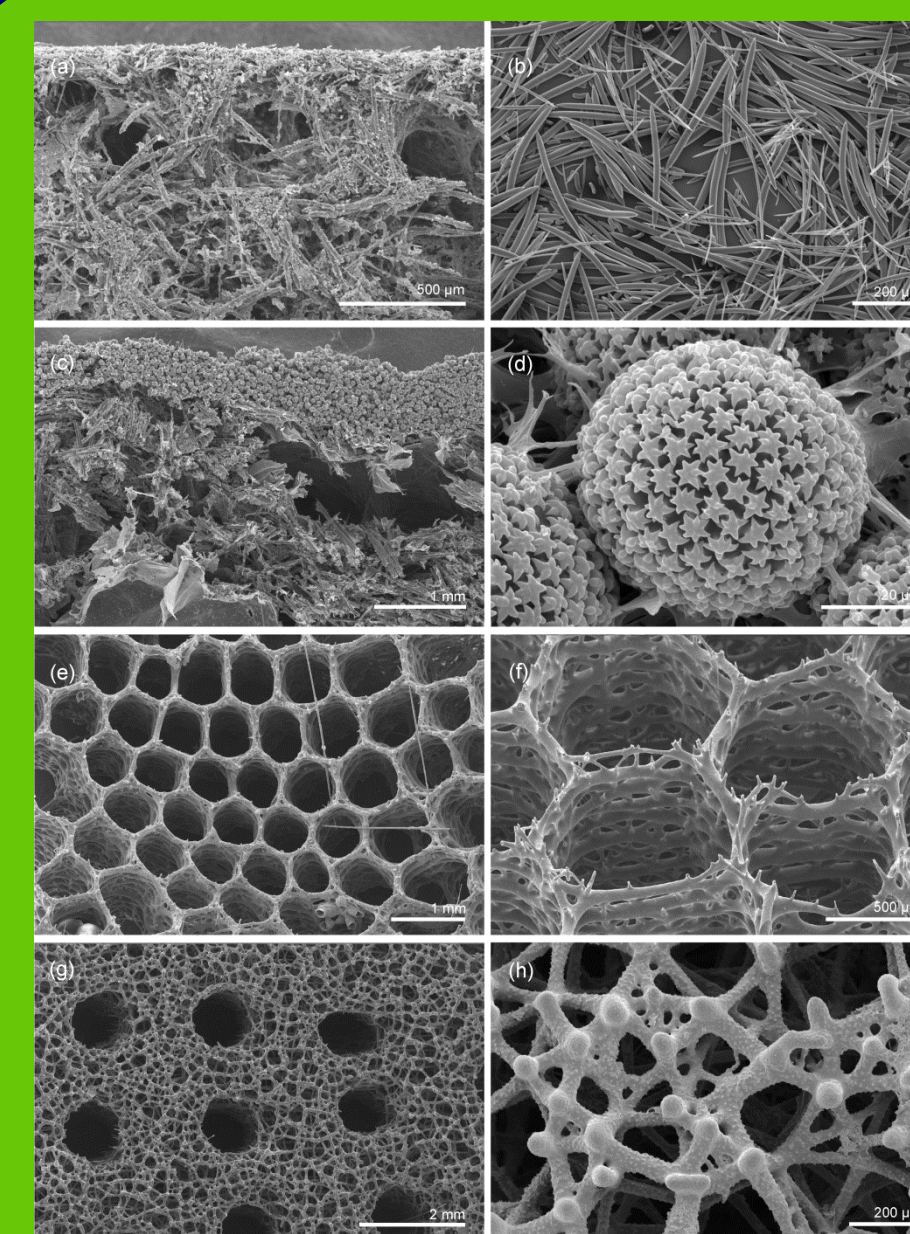


Frustule and associated organic matter, from Hatte *et al.*, Mar. Chem, 2008

The two-valves silica cell wall (« Frustule ») of diatoms: the silaffin-mediated formation of a silica shell embedded with organic matter.

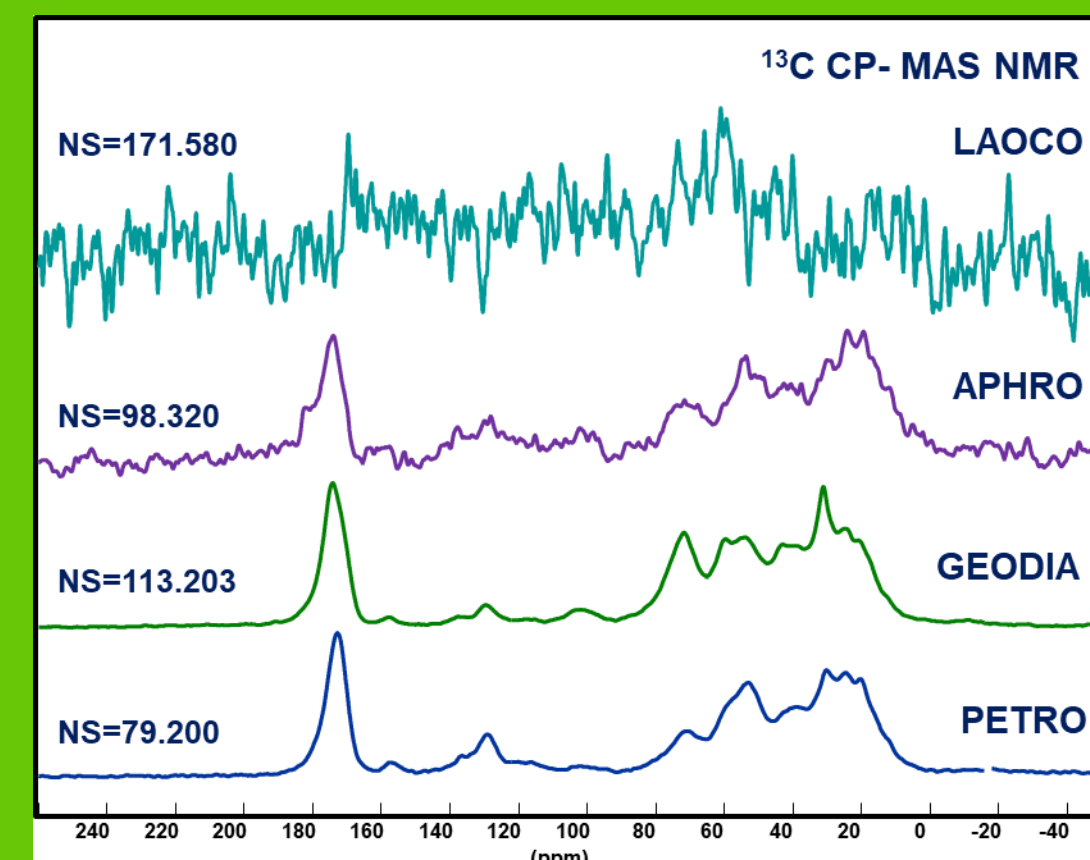


¹H MAS and ³¹P HPDEC-MAS NMR spectra of the Whole-cell, SDS-treated and H₂O₂-treated diatom frustule samples isotopically enriched in ²⁹Si, ¹³C/²⁹Si/¹⁵N and ¹³C/¹⁵N, resp. (Ref.1). A signal broadening and a loss in intensity are observed after chemical treatment. While SDS/EDTA is used first to clean the frustule, further H₂O₂ treatment seems to be much more aggressive, probably leading to partial dissolution-recrystallization

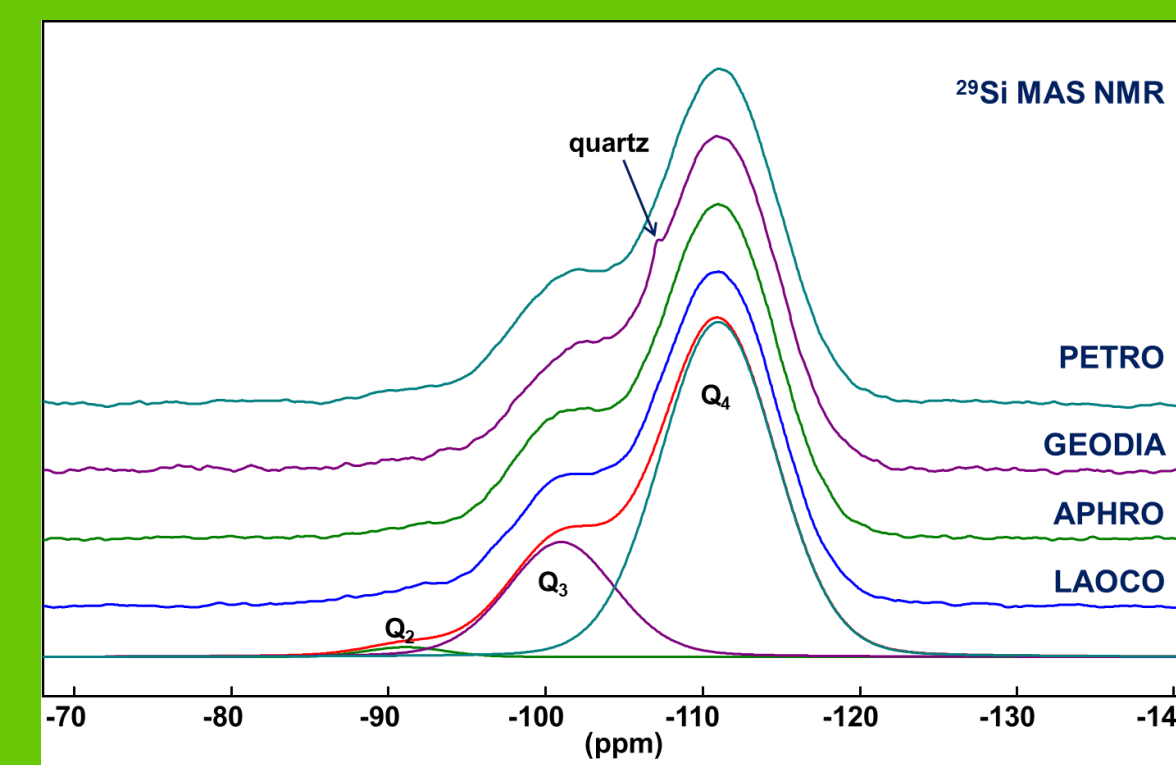


SEM pictures of a series of sponge spicules

(a,b) Petrosid demosponge PETRO: (a) untreated, scale bar = 500 mm; (b) after organics removal, scale bar = 200 mm; (c,d) *Geodia* sp. demosponge GEODIA: (c) untreated, scale bar = 1 mm; (d) untreated, scale bar = 20 mm; (e,f) *Aphrocallistes* sp. hexactinellid sponge APHRO: (e) untreated, scale bar = 1 mm; (f) after organics removal, scale bar = 500 mm; (g,h) *Laocoetis perion* hexactinellid LAOCO: (g) after organics removal, scale bar = 2 mm; (h) after organics removal, scale bar = 200 mm.



The silica skeleton of sponges: the silicatein-mediated formation of a silica shell around an axial filament, mainly composed of proteins.

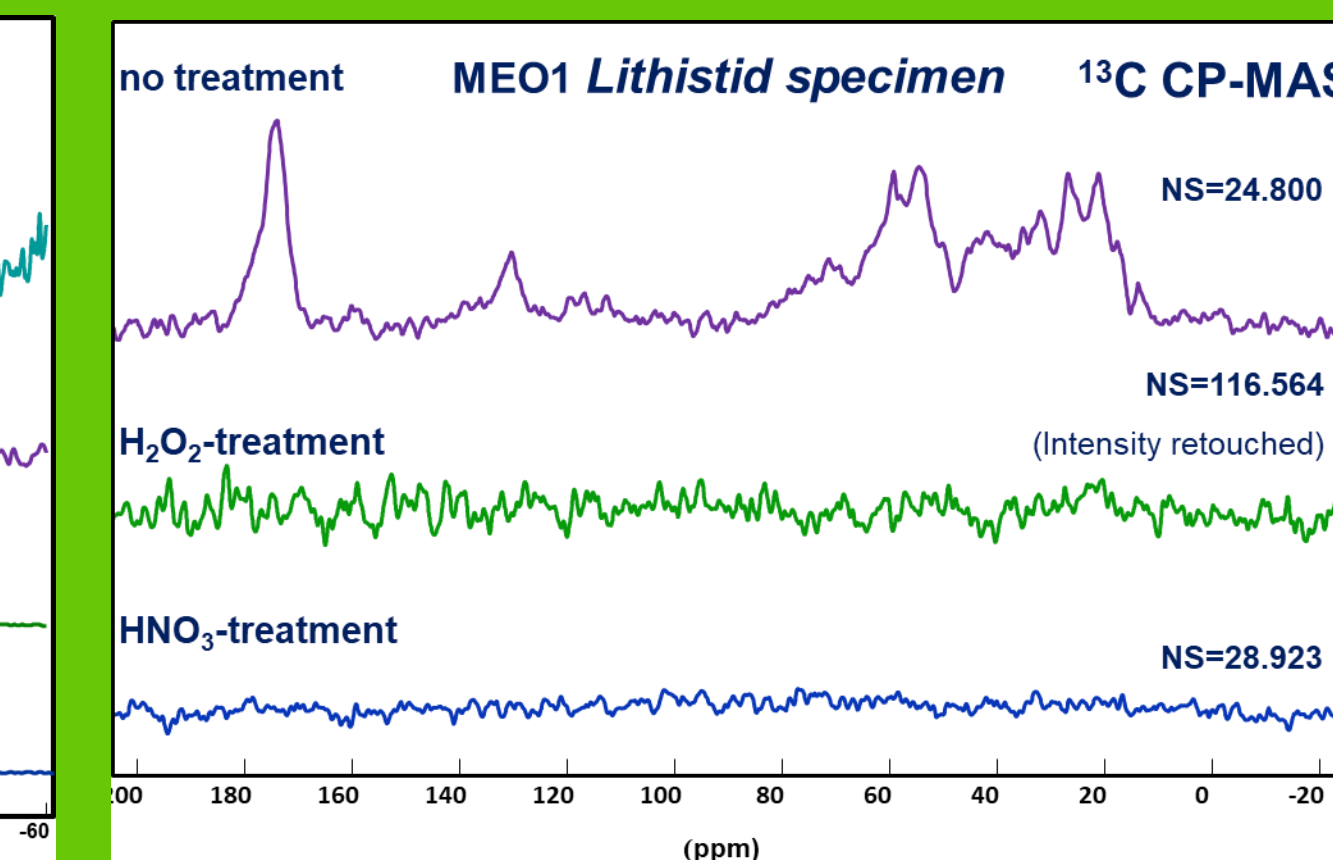


Aphrocallistes (e): raw specimen

Chemical treatment

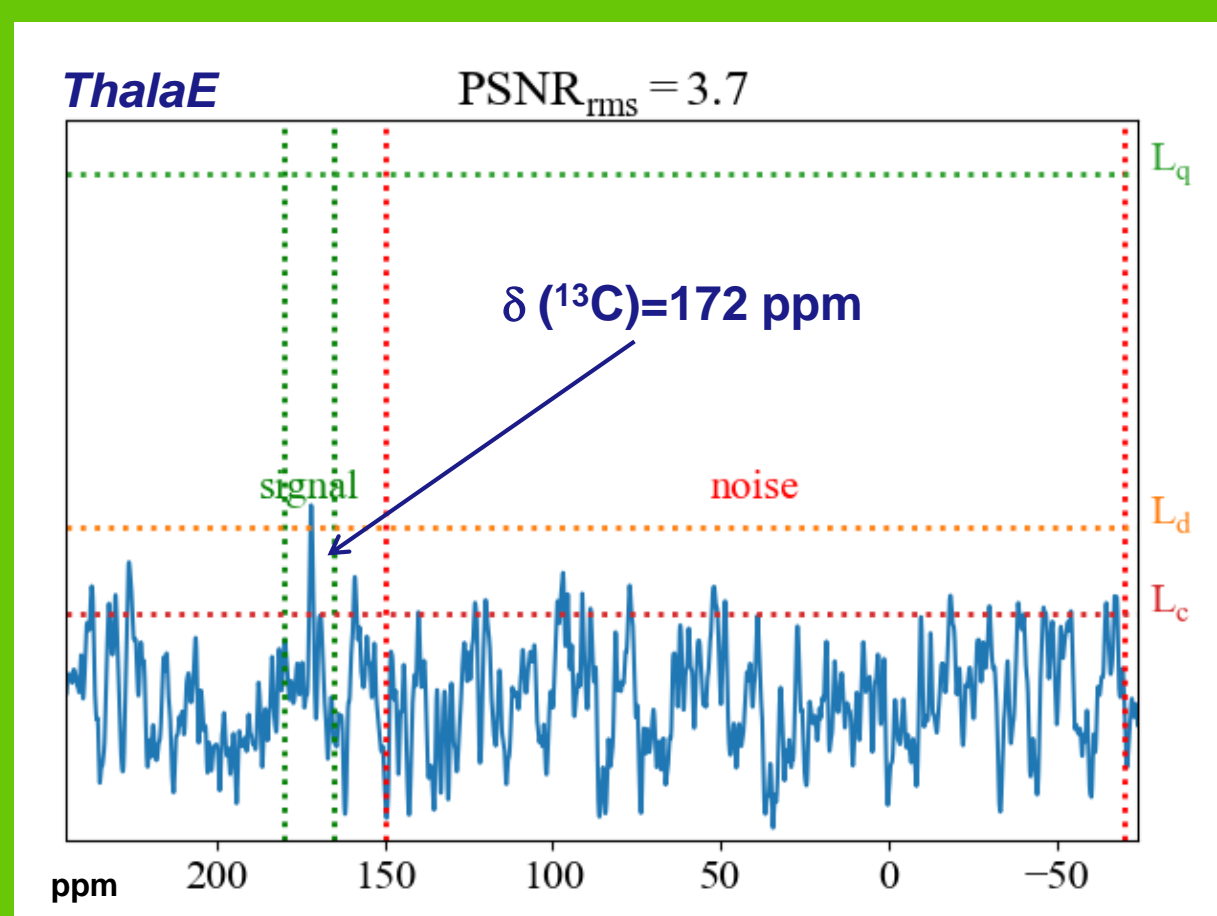


Aphrocallistes (f): HNO₃/H₂O₂-treated specimen (Please note the color change)



Variability in ¹³C CP-MAS NMR response depending on species and history: nature of the taxon, aging, conservation, chemical treatment... (Ref.2).

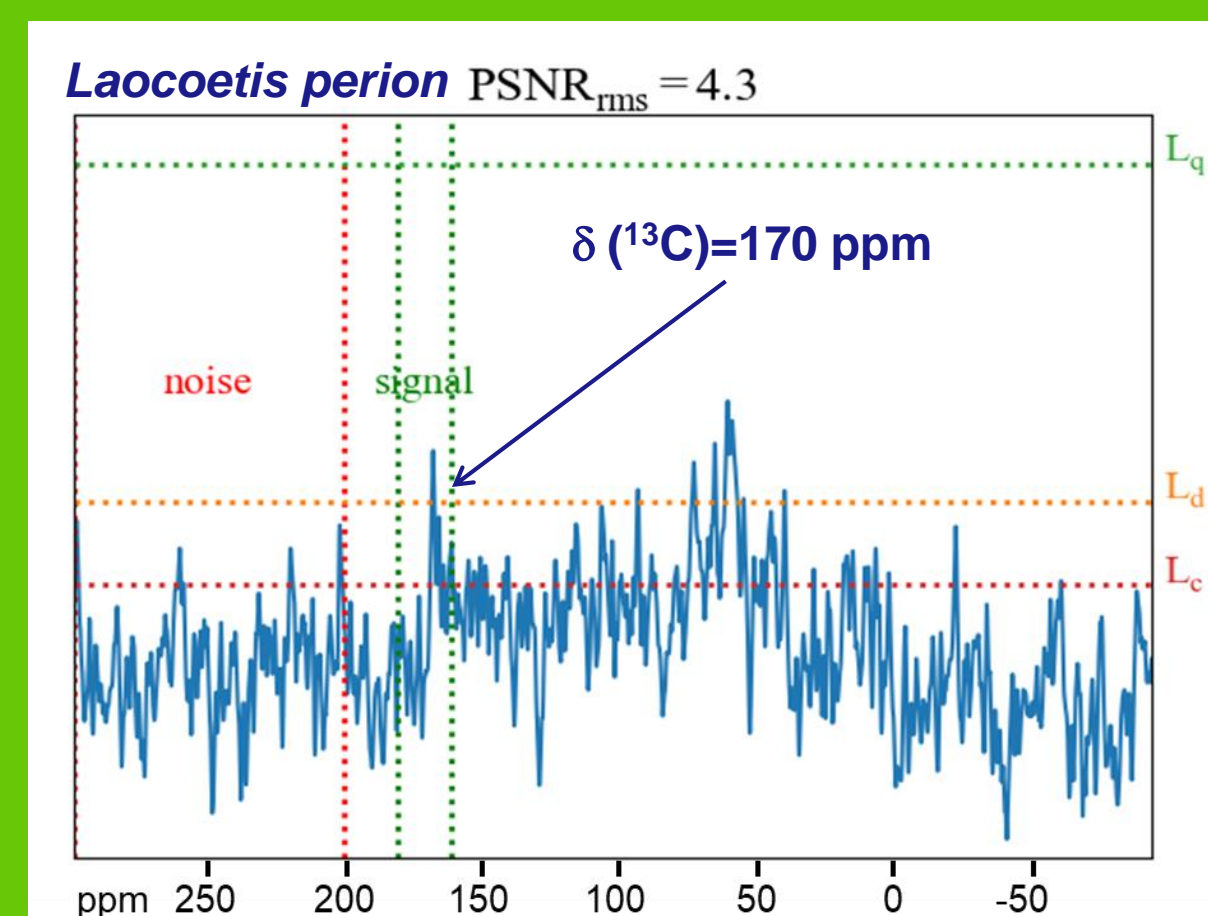
Sensitivity limit



Peak Signal-to-Noise Ratio (PSNR) and Root Mean Square (rms) for the ¹³C CP-MAS SS-NMR spectrum of the *ThalaE* (diatom frustule) and *Laocoetis Perion* (sponge spicule) samples. Signal and noise regions are highlighted with dotted vertical red and green lines, resp.; critical (L_c), detection (L_d) and quantitative (L_q) limits with dotted horizontal red, orange and green lines, resp. (according to ref. 3). In both cases, signal is detected but must be amplified.

{¹H}-²⁹Si-¹³C double-CP MAS NMR spectrum at 9.4T (AV400) of a triply-enriched (¹³C,²⁹Si,¹⁵N) *Thalassiosira Pseudonana* frustule sample (d1=3s, tcp1=3ms, tcp2=40ms, NS=9.600, ro=5kHz and LB=100Hz).

{¹H}-¹³C CP MAS NMR spectrum at 9.4T (AV400) of a *Laocoetis Perion* Hexactinellid sponge spicule sample from Madagascar (d1=2s, tcp=1ms, NS=171.580, ro=14kHz and LB=100Hz).



Conclusion

While a lot of work is needed to figure out the organic-silica interfaces in natural materials such as diatom frustules or marine siliceous sponge spicules, Solid-State NMR appears to be a powerful toolbox with several nuclei and methods to carry out. Nevertheless, natural abundance in ¹³C as well as a too poor C-content in the cleaned specimen do not allow nor 2D correlations neither well-resolved 1D spectra, that are necessary to go further on species proximity and connectivity assessment. Conjugating DNP to SS-NMR appears to be a promising solution to enhance the signal.

References

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