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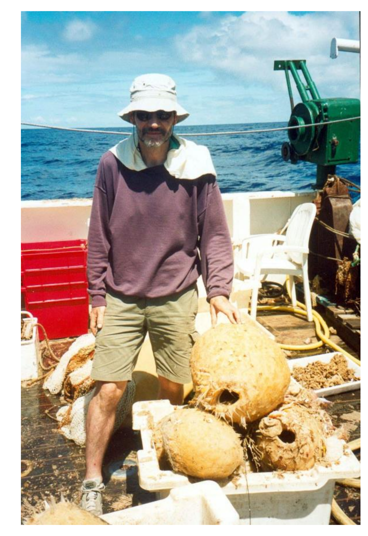
<u>Microalgal culture at ISOMER- in collaboration with</u> Dr Véronique Martin-Jézéquel and Dr Benoit Tesson Faculté des Sciences et Techniques, Nantes, France

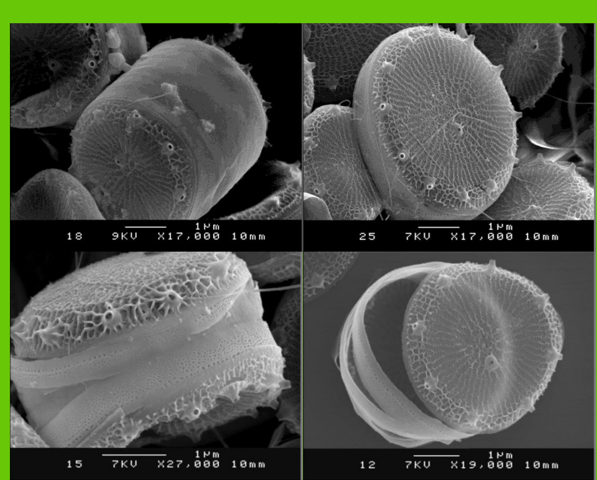
NMR Facility-Sorbonne Université Campus P. et M. Curie -T 32-33 SB



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)

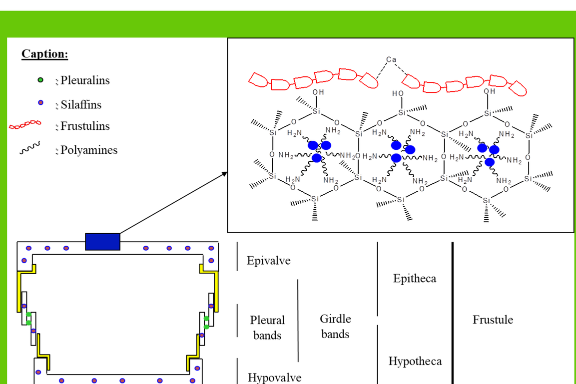
Living Materials producing Biogenic Silica

Diatoms

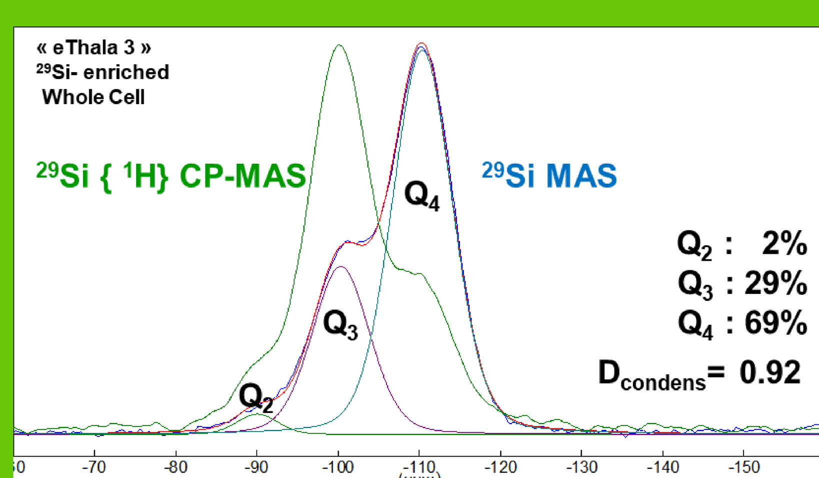


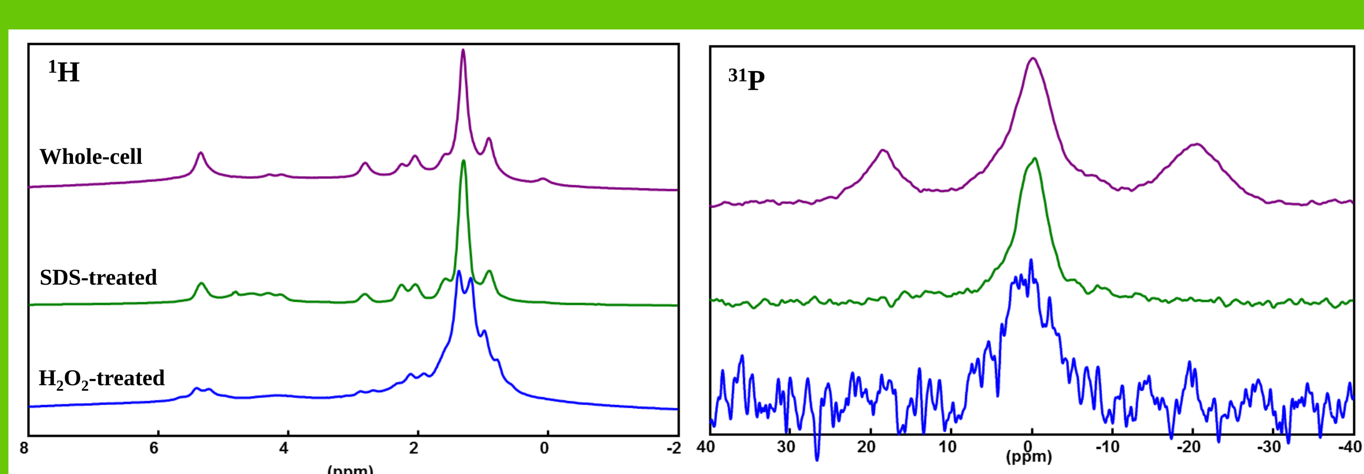
<u>SEM pictures of the *Thalassiosira pseudonana* frustule</u>

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



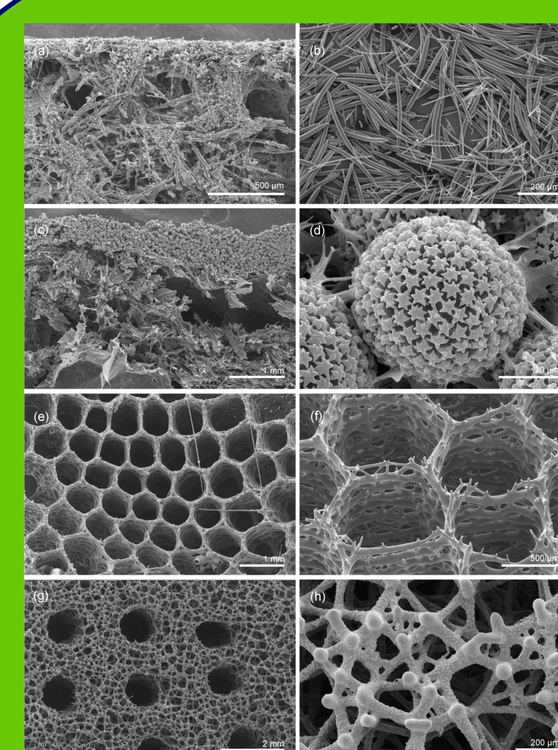
Frustule and associated organic matter, from Hatte *et al*, Mar. Chem, 2008





^1H MAS and ^{31}P HPDEC-MAS NMR spectra of the Whole-cell, SDS-treated and H_2O_2-treated diatom frustule samples isotopically enriched in ^{29}Si, $^{13}C/^{29}Si/^{15}N$ and $^{13}C/^{15}N$, 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 H_2O_2 treatment seems to be much more aggressive, probably leading to partial dissolution-recrystallization

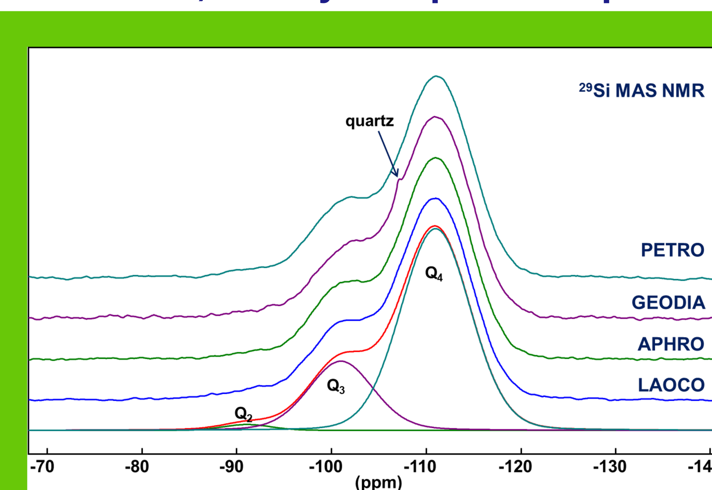
Marine Sponges



<u>SEM pictures of a series of sponge spicules</u>

(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 = 1mm, (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.

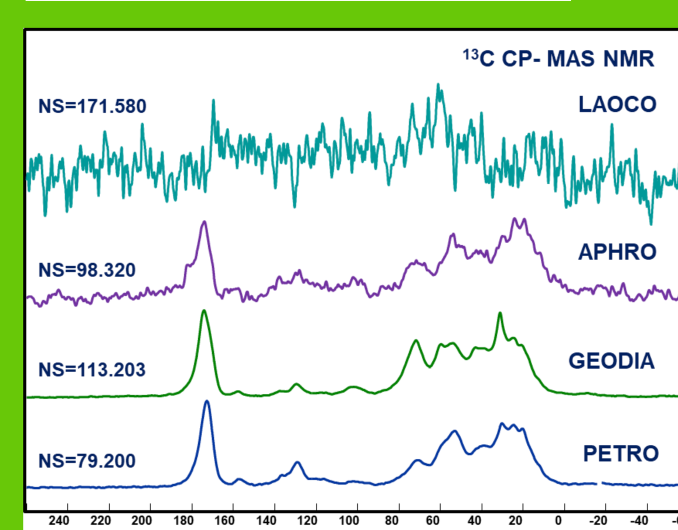
The silica skeleton of sponges: the silicatein-mediated formation of a silica shell around an axial filament, mainly composed of proteins.

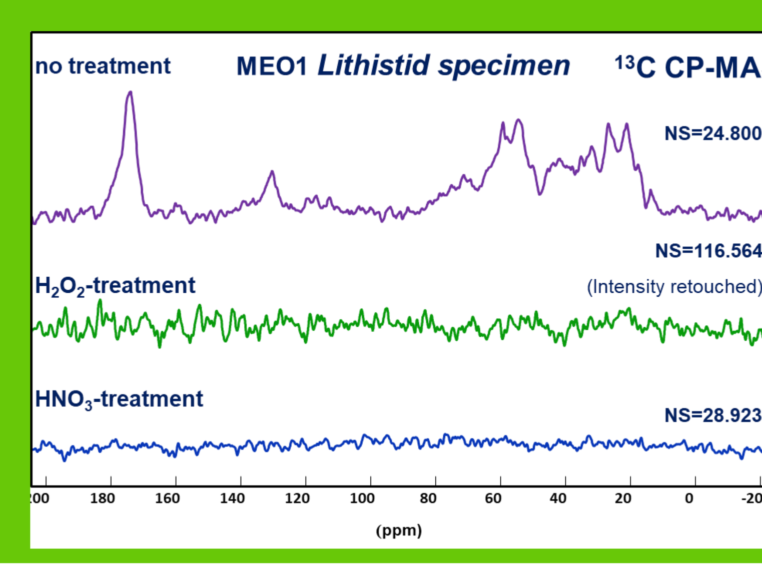


Aphrocallistes (e): raw specimen

Chemical treatment

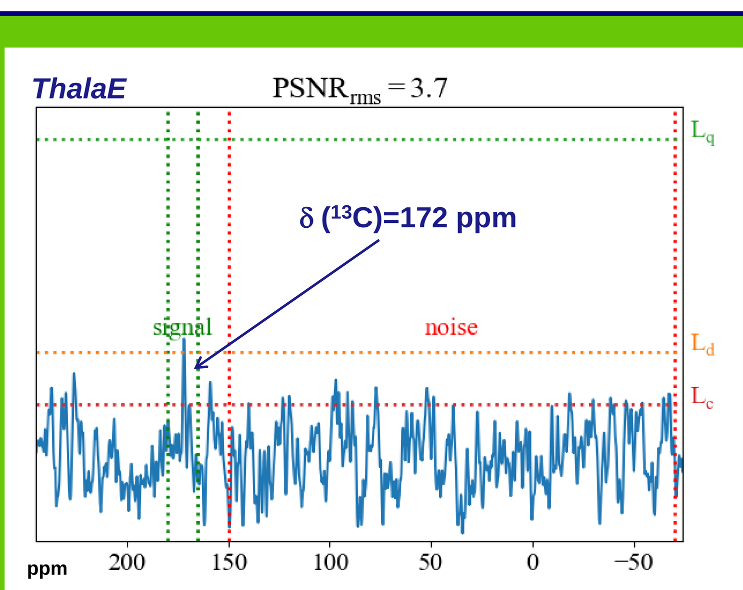
Aphrocallistes (f): HNO_3/H_2O_2-treated specimen (Please note the color change)





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

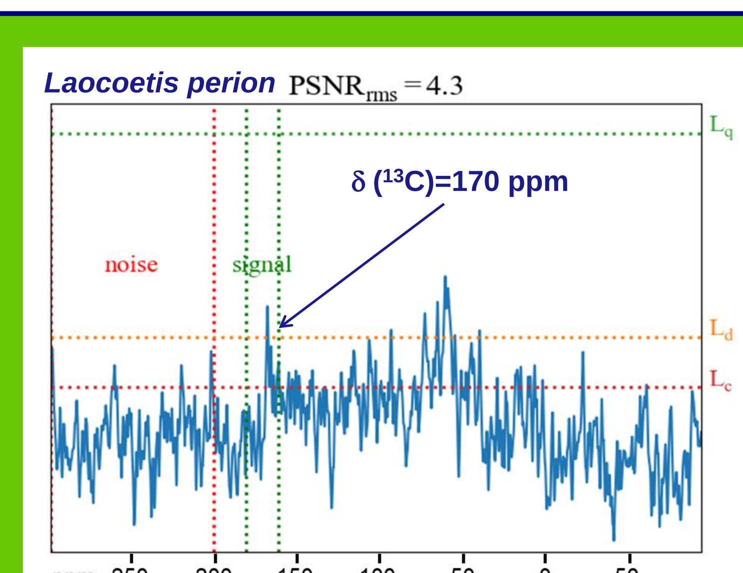
Sensitivity limit



Peak Signal-to-Noise Ratio (PSNR) and Root Mean Square (rms) for the ^{13}C 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 (Lc), detection (Ld) and quantitative (Lq) 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}-^{29}Si-^{13}C double-CP MAS NMR spectrum at 9.4T (AV400) of a triply-enriched (^{13}C,^{29}Si,^{15}N) *Thalassiosira Pseudonana* frustule sample (d1=3s, tcp1=3ms, tcp2=40ms, NS=9.600, ro= 5kHz and LB=100Hz).

{^1H}-^{13}C 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 ^{13}C 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

1. Tesson B., Masse S., Laurent G., Maquet J., Livage J., Martin-Jézéquel V. and Coradin T. « Contribution of multi-nuclear solid state NMR to the characterization of the *Thalassiosira pseudonana* diatom cell wall », *Anal Bioanal Chem*, 390, 1889–1898 (2008), doi 10.1007/s00216-008-1908-0
2. Masse S., Pisera A., Laurent G., Coradin T. « A Solid-State NMR Investigation of Recent Marine Siliceous Sponge Spicules », *Minerals*, 6, 21-30 (2016), doi: 10.3390/min6010021
3. Laurent G., Woelffel W., Barret-Vivin V., Gouillart E., Bonhomme C. « Denoising applied to spectroscopies – part I : concept and limits », Appl. Spectrosc. Rev., doi: 10.1080/05704928.2018.1523183

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