Multimodal and multiscale microscopies to study biomineralization and crystallization processes

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For years, imaging and spectroscopic methods have been intensively used to obtain information on properties of minerals present on Earth and the processes involved in their formation. Recently, dramatic improvements have been made in terms of spatial and spectral resolutions. For instance, a resolution better than 0.1 nm may now be achieved on crystalline compounds using Z-contrast on STEM-HAADF imaging mode. It is also possible to combine both high spectral (0.1 eV) and spatial resolutions (20 nm for STXM, better than 1 nm for EELS). Moreover, owing to the FIB sample preparation method, these highly local techniques can be associated with complementary large scale analytical methods allowing a multi-scale approach.

Here, we shall present recent studies focused on the nm-scale processes involved in the formations of (i) aragonite in corals, (ii) intra-cellular magnetite in magnetotactic bacteria and (iii) crystal nucleation in glasses. For coral biomineralization, combined nano-diffraction studies, HRTEM and polarization-dependent synchrotron-based STXM imaging, have evidenced the biological control exerted by the organism leading to a hierarchically structured solid material [1]. Concerning the intracellular magnetites, we focused on asymmetric crystals formed by bacteria belonging to the *Nitrospira* phylum [2]. Atomic scale processes and crystal shape control involved during crytal growth will be discussed on the basis of ultra-high resolution observations performed on an aberration corrected STEM. In addition, we will present some results related to nanoscaled heterogeneities in glasses leading to the crystal nucleation [3]. The ability to identify directly the crystallized phase from the image will be also addressed.

[1] Benzerara *et al*. (2011) *Ultramicroscopy,* **111**, 1268 - 1275. [2] Li *et al*. (in prep) [3] Dargaud *et al*. (2012) *J. of Non-Cryst. Solids*, **358**, 1257–1262

Application of a novel microfluorination technique to quantify biogenic opal $\delta^{18}O$

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$\delta^{18}O$ data from organisms that precipitate biogenic silica, such as diatoms or grass phytoliths, are relatively rare in the literature. The paucity of opal $\delta^{18}O$ data is due to the difficulty in isolating, purifying, and analyzing the covalently bound oxygen for geochemical analysis, which typically involves dangerous fluorination reagents and/or IR laser systems. We have developed a new microfluorination technique for opal and quartz analysis that utilizes polytetrafluoroethylene powder (PTFE, C_2F_4, Teflon) as a fluorine source. Cleaned and purified samples are dehydrated-dehydroxylated at 1060ºC in vacuum prior to analysis and 0.4 mg of sample is then mixed with PTFE and graphite in silver foil capsules. Samples are analyzed at 1450ºC with a vario PYRO cube TC/EA and IRMS in continuous flow mode. All data are calibrated to VSMOW using NBS-28 quartz. Acceptable data were obtained when sample yields exceeded 88% (>80% of >300 samples analyzed), yielding replicate precision better than ± 0.4‰ (1σ).

Utilizing this method we analyzed a suite of diatom samples from a sediment trap time series collected in the Gulf of California, Guaymas Basin. Samples were collected in the late fall/early winter during three different years (1993, '94, '96). Diatom $\delta^{18}O$ ranged between 35 and 36.2‰ (VSMOW) (n=7). Five samples span a single fall through early winter period and when converted to temperature using the Labeyrie (1974) relationship, record surface water temperatures between 25-27ºC that are in good agreement with temperatures during the peak fall opal flux. These data suggest sinking diatom frustules remain suspended in the deep pycnocline through early winter and data from sediment cores are likely to be seasonally biased.

[1]Labeyrie (1974), *Nature* 248, 40-42.

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