

## Caveats for assessing crystallinity in biogenic minerals

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### Assessing local and long-range order in biogenic minerals

The degree of structural order within biogenic minerals is key for understanding the temporal evolution of mineralization in biological systems.[1] Standard material characterization techniques, including Fourier transform infrared spectroscopy (FTIR) and X-ray diffraction (XRD), are widely used to assess structural differences in biogenic magnesium calcites and carbonated hydroxyapatites.[2,3] However, no single measurement tool can adequately assess both local order (as can be done with FTIR) as well as long-range periodicity (as can be done with XRD). In this work, we identify serious pitfalls that can occur when trying to extract details about the structural order in a mineral from broadened spectroscopic or diffraction peaks. We also show that these challenges can be addressed by using relatively simple analyses to track FTIR spectral changes in amorphous and poorly crystalline materials with biogenic, geogenic, or anthropogenic origins.

### Results of diffraction-limited infrared spectroscopic studies

Comparisons between FTIR transmission spectra from conventional bench-top instruments and data collected under spatially resolved, diffraction-limited conditions at the Canadian Light Source (Mid-IR beamline) highlight that there are both structural (material-specific) and measurement geometry contributions to spectral line widths. These conclusions are based on auto-correlation analyses[4] applied to spectra from a series of calcite samples with different particle size distributions. Using similar auto-correlation analyses with carbonated hydroxyapatites and other biominerals is straightforward, but the interpretation and implications of the results present new and interesting questions related to structural order at intermediate length scales. In this context, we compare our approach with other common metrics for tracking crystallinity, including the infrared splitting factor that is routinely reported for apatitic phosphate biominerals.

### Conclusions

We demonstrate that the co-existence of material-specific and measurement-specific contributions to infrared peak broadening can be beneficial for extracting information about the differences in structural order that can occur in biogenic, geogenic, and anthropogenic minerals. These effects can be decoupled in FTIR transmission measurements, obtained with standard bench-top instruments, by using a robust auto-correlation analysis of peak widths. An important implication of this result is that infrared spectroscopy has enormous potential as a quantitative tool for tracking changes in the structural order during biomineralization and biomimetic mineralization processes.

[1] Meldrum, Cölfen (2008) *Chemical Reviews* **108**, 4332-4432. [2] Poduska, Regev, Boaretto, Addadi, Weiner, Kronik, Curtarolo (2011) *Advanced Materials* **23**, 550-554. [3] Gueta, Natan, Addadi, Weiner, Refson, Kronik (2007) *Angewandte Chemie International Edition* **46**, 291-294. [4] Balan, Delattre, Roche, Segalen, Morin, Guillaumet, Blanchard, Lazzeri, Brouder, Salje (2011) *Physics and Chemistry of Minerals* **38**, 111-122.

## $\epsilon$ Nd signatures of NW North Atlantic water masses and their recording in deep corals from Orphan Knoll

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Baffin Bay seawater epsilon Nd signature was measured more than 25 years ago (Stordal and Wasserburg, 1986) at a very low value when compared to the average North Atlantic Ocean. This unradiogenic value is introduced into the North Atlantic Ocean through the Labrador current that flows on the East coast of Canada.

Seawater from all water masses from Baffin Bay and the Labrador Sea (near Orphan Knoll) were sampled during cruises of CCGS Hudson in 2008 and 2010. Using McLane™ pumping systems equipped with Mn-oxide coated cartridges, dissolved neodymium (Nd) was recovered from ~200 liters of seawater for many casts. The geographical area covered allows us to monitor the present day  $\epsilon$ Nd signatures of Baffin Bay overflow water, as well as that of all other water masses involved in the Atlantic Meridional Overturning Circulation (AMOC).

During the 2010 cruise, the Canadian remotely operated vehicle (ROPOS) was used to sample specimens of deep-water cup corals (alive and fossils) from Orphan Knoll, at a depth of approximately 1700-1800 m below surface, i.e., near the depth-limit of the Present Labrador Sea Water mass. U-Th data in modern (live-collected) specimens of *Desmophyllum dianthus* yield critical information on the efficiency of the cleaning procedure used, with respect to the removal of oxide coatings ("clean" samples must yield zero <sup>230</sup>Th-ages), and thus on the representativity of the Nd isotope data obtained. The same approach combined with <sup>14</sup>C-ages is used in fossil coral studies, as a means to document, back in time, water mass changes at Orphan Knoll, in relation with the AMOC/climate variability.

[1] Stordal and Wasserburg (1986) *Earth and Planetary Science Letters*, vol.77, 259-272.