



MSc Departmental Seminar

Brian Espinosa Acosta

Department of Chemistry | Supervisor: Dr. Kristin Poduska

Thursday, May 16, 2024 at 1:00 p.m. (Room: CSF-1302)

Title: Study and detection of the dissolution-recrystallization phase conversion of biogenic carbonates

Abstract:

Aragonite and calcite, the most common CaCO_3 polymorphs, are among the most abundant minerals in the ocean. Both are insoluble, yet aragonite dissolves slightly more than calcite. Therefore, an aragonitic suspension will be supersaturated with respect to calcite, which, consequently, should precipitate. Thus, an aqueous co-suspension of aragonite and calcite powders should transform into a calcite suspension. Since most CaCO_3 in the ocean are of biogenic origin, using them to study this transformation has applicability to understanding the carbonate marine minerals cycle. This work focuses on several biogenic sources of aragonite (butter clam shells and blue mussels) and one of calcite (oyster). We examined whether biogenic carbonate mixtures alone trigger conversion or if composition differences from lab-synthesized carbonates affect dissolution-recrystallization behaviour.

We first explored different parameters and configurations, such as mechanically removed organics, preheated samples, different shell parts, and shell composition. Our results show that butter clams are aragonitic shells with less than a few percent calcite, and blue mussels are biological mixtures of calcite and aragonite. Elemental content showed less than 0.5 wt% impurities in clams. Heating reduced its organic carbon by 60% and 75% nitrogen. Then, we prepared ultrapure water suspensions of either single aragonitic material or mixtures of polymorphs and monitored the phase conversion before and after suspension. None of the starting biogenic carbonate with or without organics and, regardless of the spot, showed reconversion after one week of stirred water suspension, whereas our synthetic aragonite does. Small amounts of biogenic calcite in the biogenic aragonite structure or the mechanic addition of biogenic calcite does not accelerate the transformation in these timeframes. However, adding pure reagent-grade calcite triggers detectable aragonite dissolution and recrystallization as calcite in every case. We used Attenuated Total Reflectance-Fourier Transformed Infrared spectroscopy to track polymorph changes before and after water treatment. Powder X-ray diffraction is complementary to assigning crystal structure differences. Inductively coupled plasma-optical emission spectrometry gives insight into the elemental composition of selected samples. Total organic carbon helps us to assess the organic content before and after heating treatments.

These results indicate that there are variabilities across biogenic carbonates that will make them undergo aragonite-to-calcite transformation at different paces and, in many cases, at a slower conversion rate when compared to lab-synthesized carbonates. Removing organic material (by heating or scraping) does not qualitatively change the polymorphic phase transformation within our monitored time frames. These experiments suggest that solubility differences are insufficient when explaining biogenic polymorphs' dissolution-recrystallization. Future oceanic carbonate minerals studies could evaluate if biogenic carbonate-dependent conversion rates are more suitable than those for lab-synthesized carbonates.