PRF # 59310-DNI2
Title: Microtextural Controls on Silica Diagenesis in Organic-Rich Siliceous Shales: An Experimental Approach
P.I.: Steven Chemtob, Temple University

Brief summary of research objectives: Silica-rich diatomaceous shales, including the well-studied Monterey Formation of California, are frequently identified as potential petroleum source rocks. Silica phase transitions during diagenesis, from biogenic opal-A to opal-CT and later to quartz, are known to influence secondary porosity. Organic matter and detrital minerals are known to inhibit the rate of silica phase transitions and influence the crystallinity of resultant opal-CT; however, the effects of microtextural heterogeneity of those impurities within silica-rich rocks is less well understood. The objectives of this project are 1) to design and implement experiments modeling the diagenesis of silica in the presence of organic matter in different configurations (intimately mixed, stratified, etc.); 2) to use bulk (XRD, FTIR) and high spatial resolution (imaging FTIR, Raman) techniques to characterize structural changes in silica and organic constituents with increasing diagenetic intensity; and 3) to analyze key natural diatomites from the Monterey Formation at intermediate stages of silica diagenesis to compare to experimentally produced products and textures.

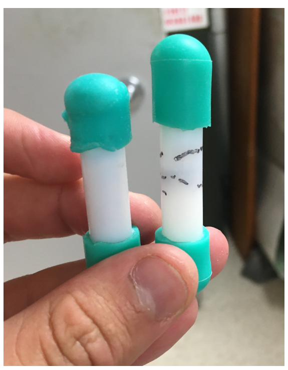

Fig. 1. *Examples of assembled experimental capsules.*

Experimental design and early results: In our experiments to date, we have employed simple constituents (Baker silica gel, humic acid) and simple configurations of silica and organic matter to test the effects of organic matter heterogeneity on early silica diagenesis. Much of our initial efforts has focused on design and testing of experimental capsules that sufficiently house these constituents and maintain their spatial integrity. In our current setup, silica gel and humic acid (10 wt%) are loaded into 2” lengths of ¼” diameter Teflon tubing in two configurations: a) well-mixed by gentle grinding with mortar and pestle; b) stratified into two layers (OM-free silica and silica-free OM) (Fig. 1). After applying a 0.22 μm filter to one end of the tubing, a syringe is applied to the other end to saturate the pore spaces with a mock seawater solution. Rubber caps were applied to each end of the tube length, then the sealed vessels were placed in Parr hydrothermal bombs and immersed in mock seawater. The vessels were heated at 200° C for up to 90 days; after heating, fluid is removed from the tubing by forcing air through with a syringe.

Analysis of pilot bulk organic-free silica diagenesis experiments by X-ray diffraction showed a reduction in the width of the opal-A amorphous hump with increasing reaction time (1-4 weeks) (Fig. 2). We have encountered some challenges in processing of the above tube-bound experiments. To prepare these experiments for microanalysis, the solids must be immobilized by epoxy, followed by cutting and polishing the tube in cross section. However, the epoxies we have employed so far have failed to permeate into the center of the silica layer. While solving this issue is a continued effort, we have developed an alternative procedure for processing the experiments involving extraction of the solids with a pipette tip at 1-2 mm intervals, providing pseudo-spatial resolution. We are analyzing these extracted powder samples by imaging FTIR microscope, although technical issues with the instrument have prevented its use in recent months. Initial bulk FTIR measurements of silica gel and a series of natural opal-A and opal-CT samples indicate that FTIR will be sensitive to diagenetic changes in both the mid-IR silicate stretching region (650-1200 cm^{-1}) and the near-IR H_2O/OH stretching region (3500-5200 cm^{-1})

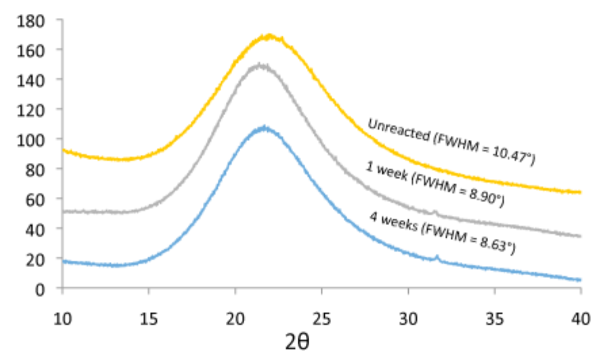

Fig 2. *XRD patterns of silica gel after 1 and 4 weeks of diagenetic treatment at 200° C. Full-width half-max (FWHM) of the broad diffraction hump decreases with increasing heating.*

Fig. 3. *Graduate students Justin Morris and Paula Araneda examining the Monterey Formation at Gaviota Beach, CA, August 2019.*

Field work at key outcrops of the Monterey Formation: Although our research objectives are primarily experimental, In August 2019, PI Chemtob led two graduate students in a five-day field trip to visit key outcrops of the Miocene Monterey Formation in the region of Santa Barbara, CA (Fig. 3). The objectives of this trip were 1) to observe the Monterey Formation across its entire depositional sequence and over a range of diagenetic conditions, and 2) to identify promising sites at intermediate diagenetic conditions near the opal-A/opal-CT boundary for later detailed study and sample collection. We followed a field trip guide by Isaacs (USGS Open-File Report 84-98, 1984). The complete Monterey sequence is available at numerous locations along the Santa Barbara coast, but apparent diagenetic temperature increases from east to west. We visited the Goleta Slough section near UCSB, where diatomaceous strata appear essentially unaltered as opal-A; Naples Beach, where both opal-A and opal-CT appear; Gaviota Beach and neighboring Gaviota Canyon, where strata are principally opal-CT; and Jalama Beach, where the upper Monterey and bounding Sisquoc Formation are opal-CT. We were unable to visit quartz-facies outcrops of the Monterey identified by Isaacs due to accessibility issues in the Hollister Ranch region. We also visited outcrops and collected pilot samples in the vicinity of the Lompoc diatomite quarry, which spans the opal-A and opal-CT diagenetic regimes.

Future efforts and research impacts: We will continue to develop methods for processing and interpreting the microtextures produced in our experiments. Raman and FTIR maps of polished thick sections from completed experiments will be produced through the fall; these maps will be used to characterize μm-scale heterogeneity in silica and organic phases after diagenesis. A new series of experiments to be commenced in Fall 2019 will employ cultured algal samples, provided by collaborator Dr. Robert Sanders (Temple), in place of bottled humic acid to test the effect of organic matter complexity on silica diagenesis. Newly collected samples from the Monterey Formation known to contain both opal-A and opal-CT will be prepared in polished section and analyzed by petrographic microscope and imaging spectroscopy to characterize the influence of organic matter, detrital matter, and other impurities on silica phase heterogeneity. Lastly, we will design and implement a set of experiments in which aliquots of unadultered Monterey Formation will be subjected to experimental diagenetic conditions.

When complete, the results of this research may have significant implications for understanding the reservoir potential of siliceous shales. These experiments may improve our ability to use remotely detected silica transition zones as a paleotemperature proxy. Studying the effects of exposing organic-bearing siliceous sediment to hydrothermal conditions may help predict the effect of thermal hydrocarbon recovery methods on reservoir properties. Planned analyses of natural sediments will have special significance of interpretation of the diagnenetic history of the Monterey Formation. This work has also impacted the education and career development of young scientists. One graduate student was supported by this grant over the past year, and a second will be supported in 2019-2020. This project has represented a new direction of research for PI Chemtob and has fostered new collaborations for him with biologists and organic geochemists at Temple and UCSB.