

1. PRF#: 59178-ND2

2. Project Title: "Is there an Organo-Silica Complexing Mechanism for Carbonate Reservoir Silicification?"

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In the first year of this Petroleum Research Fund New Directions project, the research has proceeded as proposed, and important milestones laid out for the first year in the initial proposal have been accomplished. In my submitted proposal, I proposed to work together with student researchers and organic geochemistry experts at the University of Calgary to answer the fundamental question: *How do carbonate minerals become silicified during diagenesis?* To answer this question over the course of the funded project, I identified three primary objectives:

- OBJECTIVE 1:** Batch experimental determination of the stability of organo-silica complexes in amorphous silica-saturated seawater analogue solutions
- OBJECTIVE 2:** Reactive transport experimental examination of the reactivity of carbonate minerals in contact with diffusing siliceous, organic-rich pore fluids
- OBJECTIVE 3:** Pore-scale reactive transport modeling to extrapolate experimentally parameterized reaction trends over geologic time scales

Together, accomplishing these three objectives will provide new, quantitative constraints on the process of diagenetic carbonate silicification which will provide the foundation for future research applications to the rock record.

Over the first year of the project, Objective 1 was completely accomplished. The results were presented at the 2019 V.M. Goldschmidt Conference in Barcelona, Spain as both a submitted abstract and an oral presentation (Escario et al., 2019). The primary conclusions of the batch experiments performed in fulfillment of Objective 1 are shown in Figures 1 and 2. Figure 1 demonstrates two of our most important findings:

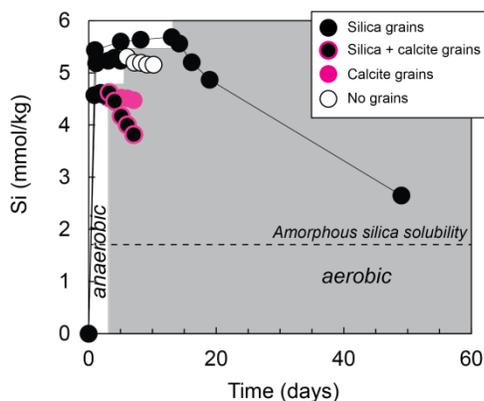


Figure 2 Demonstration of silica depletion from solution upon oxidation, and accompanying precipitation of SiO_2 . These data suggest that the thermodynamics and kinetics of silica precipitation during organic matter oxidation would only promote silica precipitation in instances where silica nucleation surfaces were already present in the reservoir.

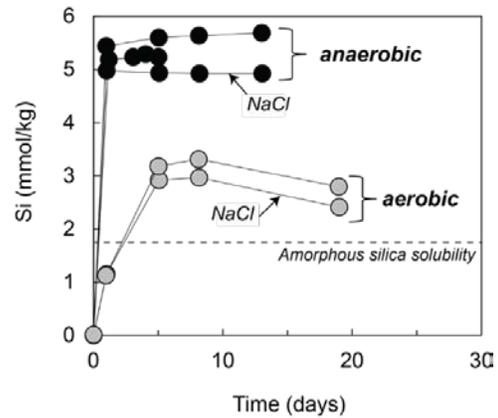


Figure 1 Experimental observations of enhanced silica solubility in the presence of catechol, and organic compound found in numerous marine organisms, such as arthropods. The experiments also demonstrate that the oxidation state (here indicated by aerobic (air-saturated) and anaerobic ($\text{pO}_2 < 1 \text{ ppm}_v$)) strongly dictates the degree to which catechol enhances SiO_2 solubility.

shown in Figures 1 and 2. Figure 1 demonstrates two of our most important findings:

1) Silica is significantly more soluble in organic (catechol, in this case) rich pore waters (lines with symbols) than it is in organic-free pore waters (dashed line).

2) The effect of the organo-silica complexes is significantly more pronounced in anaerobic solutions than it is in aerobic solutions. This represents a partial confirmation of the hypothesized organo-silica complexing mechanism for carbonate reservoir silicification, in that it shows that the oxidation of organic matter during early diagenesis can lead to decreased silica solubility and hence silica precipitation.

Building upon these initial batch experiment results, we performed an additional sequence of dynamic batch experiments specifically designed to illustrate the correlation between organic matter oxidation and silica precipitation. These experimental results are summarized in Figure 2. In these experiments, the $\text{N}_2(\text{g})$ headspace of the bottles containing silica-saturated organic-rich solutions was replaced with pure $\text{O}_2(\text{g})$ in order to examine this effect. As can be seen in the plotted experimental data points, the $\text{O}_2(\text{g})$ -induced oxidation only decreased the solubility of silica in experiments which contained solid silica. In other words, it

appears that the hypothesized mechanism for reservoir silicification is only feasible under conditions where silica minerals are initially present. These could be represented by sponge spicules or radiolarian tests, for example. A final, important result of the batch experiments performed in fulfillment of Objective 1 is illustrated in Fig. 3. This figure demonstrates that the change in silica solubility in organic-rich waters is strongly pH dependent, with the peak in the pH dependence happening at pH 6.6-8.0, depending on the concentration of organic matter and the ionic strength in the pore fluids. This result again lends support for the proposed organo-silica complexing mechanisms for carbonate reservoir silicification, since organic matter oxidation in pore fluids leads to the production of CO₂, which, in turn, will lower pore water pH. Combined with the findings detailed in Figures 1 and 2, this result indicates that the proposed mechanism for carbonate reservoir silicification is not only feasible but also very likely to represent a key mechanism for this reaction. A manuscript summarizing these findings is currently in preparation, with the expected submission date in late October.

Following the near-completion of Objective 1 in early August, work on Objectives 2 and 3 began in August 2019. We have now obtained initial x-ray computed tomography data sets at the Canadian Light Source CLS in Saskatoon, Saskatchewan for a suite of carbonate samples that will be subjected to silicification experiments over the next 3 months. A follow-up visit to CLS synchrotron facility is currently being scheduled for early 2020. Additionally, we have developed the input files and processing algorithms that will be required to run 3-dimensional reactive transport simulations on these x-ray computed tomography data sets in fulfillment of Objective 3.

Impact of the research on your career and that of participating students

This New Directions research project has had a significant impact on both my career and that of participating students. This grant has funded the salary and research expenses for a postdoc and a undergraduate in the first year, with plans to partially support a MSc student and a second undergraduate in the second year. The addition of these student and postdoctoral researchers to my lab group in the first year of this project has resulted in the transformation of my laboratory from a collection of partially-utilized equipment to a thriving facility for aqueous geochemical research. Furthermore, the acquisition of New Directions Funds, along with several other successful grant applications during the first two years of my time as an Assistant Professor at the University of Calgary has led to me being awarded the Department of Geoscience Faculty Research Excellence award. Together, the grant and this award will make a strong case for me being granted tenure in a year's time, and has already interested numerous industry representatives in funding a second stage of this project. The undergraduate who was partially funded by this project, Mr. Stephen Schroeder, has now graduated and found employment at Wolfram Research, Incorporated. The postdoc employed by this project, Dr. Sofia Escario, received an incredible level of interest in her Goldschmidt presentation. In fact, the organizers of the session in which she presented were so intrigued by her presentation that they encouraged her to switch her presentation from a poster to a talk during the conference. Since that time, she has had significant follow-up interest in her work, which will make a strong case towards her being hired in a permanent position following the conclusion of this two-year New Directions project.

Reference

Escario, S., Nightingale, M., Jaggi, A., Oldenburg, T., Larter, S., & Tutolo, B. (2019). Examining the Role of Aqueous Organo-Silica Complexes on Silicification during Carbonate Diagenesis. In *V.M. Goldschmidt Conference* (p. 923).

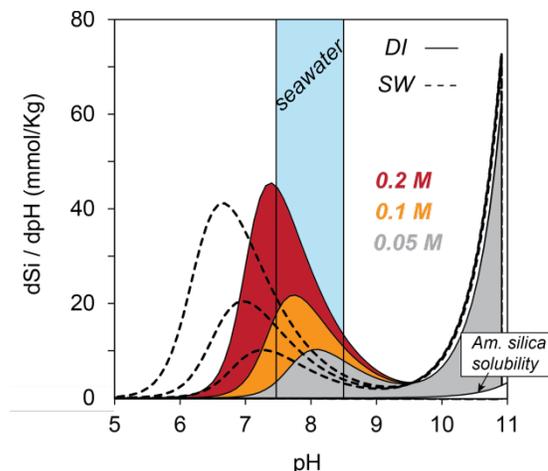


Figure 3 A plot of the change in silica solubility as a function of the change in pH for a variety of different catechol concentrations and ionic strength (DI, $I=0.01 \text{ mol.kg}^{-1}$; SW, $I=0.6 \text{ mol.kg}^{-1}$). The plotted data indicate that the organo-silica complexing mechanism for carbonate reservoir silicification will be enhanced not only by organic matter oxidation (Figures 1 and 2), but also by the resultant decrease in pH associated with CO₂ production.