Project Title:	**Kinetics and Mechanisms of Calcite reactions with Saline Waters**
Proposal Number:	**DE-FG02-06ER15816**
Principal Investigator:	Dr. John Morse (deceased) Dr. Piers Chapman Department of Oceanography Texas A&M University
Submitted:	15 November 2010

1. Objective

The general objective of this research was to determine the kinetics and mechanisms of calcite reactions with saline waters over a wide range of saline water composition, carbon dioxide partial pressure (pCO$_2$), and modest ranges of T and P. This would be done by studying both reaction rates and solubility from changes in solution chemistry. Also, nanoscale observations of calcite surface morphology and composition would be made to provide an understanding of rate controlling mechanisms.

2. Project Report

I am greatly saddened to report that Dr. John Morse, the original PI for this project, died suddenly in November 2009 following complications resulting from lung cancer and subsequent surgery. As a result, this report is being written by Dr. Piers Chapman, Head of the Department of Oceanography at Texas A&M University. It is undoubtedly less comprehensive than Dr. Morse's own report would have been. Sections 2.1-2.3 consist of the "Results of prior studies" portion of Dr. Morse's renewal proposal; we received the letter announcing it would be funded the week after he died. Section 3 describes very briefly what was accomplished during the final few months of his life.

2.1 General Considerations and Products

The research conducted under this funding can be divided into three major areas based on the size range of the processes being considered:

1) macro-scale batch reactor studies of calcite dissolution and precipitation in high I solutions over a range of I, pCO$_2$, and T at 1 atmosphere;
2) micro-scale (SEM level) studies of the morphology of overgrowths and nucleated precipitates from a variety of solutions that involved CaCO$_3$ polymorphs in addition to calcite: and
3) nano-scale (TEM level) studies of the mechanism of CaCO$_3$ precipitation on substrates.

Results are discussed specifically in the following subsections. Table 1 presents a summary of research products to date (this has been amended to take account of changes since May 2009; I am not certain of the status of some of the talks).

Table 1. Research products (peer, reviewed papers, abstracts, talks outside of meetings) of current project at the time of this renewal application. Copies of the five published papers and the Gordon Conference talk are included as appendices.

Peer Reviewed Papers

Morse, J.W., R.S. Arvidson and A. Lüttge, 2007, Calcium carbonate formation and dissolution. Chemical Reviews **107**, 342-381.

Finneran, D.W. and J.W. Morse, 2009. Calcite dissolution kinetics in saline waters. Chemical Geology **268**, 137-146..

Lee, J. and J.W. Morse, 2010, Influences of alkalinity and pCO_2 on $CaCO_3$ nucleation from estimated Cretaceous composition seawater representative of "calcite seas". Geology, **38**, 115-118; doi: 10.1130/G30537.1.

Finneran, D.W. and J.W. Morse, 2010 Calcite precipitation kinetics in saline waters. Chemical Geology, accepted and in press.

Morse, J.W. and Gorman B.P., submitted. Epitaxial growth of aragonite from normal seawater via an amorphous $CaCO_3$ surface layer: A possible explanation for the peculiar solubility behavior of aragonite in seawater. Marine Chemistry (undergoing final revision).

Morse J.W. and K. Walton, submitted, Vaterite formation and transformation to calcite in aqueous solutions with widely varying ionic strength. Geochimica et Cosmochimica Acta. (rejected).

Abstracts from Scientific Meetings

Morse, J.W., 2007, Reaction kinetics of shallow water marine carbonates: successes and failures in bringing laboratory experiments and the ocean together. R.V. Goldschmidt Conference, Cologne, Germany, invited talk.

Finneran D.W., and Morse, J.W., 2007, Calcite dissolution in saline waters. Annual AGU Meeting, San Francisco.

Morse, J.W., Finneran, D.W., Walton, K. and Arvidson, R.S., 2008, Calcite nucleation and epitaxial growth from high ionic strength NaCl solutions. R.V. Goldschmidt Conference, Vancouver, Canada.

Lee, J. and Morse, J.W., 2008, Influence of variable Phanerozoic seawater chemistry on the form and rate of $CaCO_3$ nucleation. R.V. Goldschmidt Conference, Vancouver, Canada.

Morse, J.W., Gorman, B.P., Walton, K. and Lee, J., 2008, Nanoscale insights into the mechanisms responsible for the strange kinetic and solubility behavior of aragonite in seawater. GSA Annual Meeting Abstracts. **Ingerson Lecture** (invited).

Lee, J. and Morse, J.W., 2008, Influences of alkalinity and pCO_2 on $CaCO_3$ nucleation from seawater of estimated Cretaceous Period composition. GSA Annual Meeting Abstracts.

Morse, J.W., 2009. Calcium carbonate formation from saline waters: from astronauts to atoms. Gordon Conference Lecture (invited).

Morse, J.W., in press. The importance of magnesium to understanding the behavior of marine carbonates. ACS Annual Spring Meeting Abstracts (invited keynote address).

Morse, J.W., in press. Adventures in marine carbonate chemistry with Frank J. Millero. ACS Annual Spring Meeting Abstracts (invited keynote address).

Additional Talks and Seminars

Invited seminar Yale University September, 2008
Invited seminar Woods Hole Oceanographic Institution, September, 2008

Student Degrees

Janie Lee, awarded MS in December 2008
David Finneran, awarded PhD in August 2010

2.2. Macro-Scale Studies of Calcite Dissolution and Precipitation in Saline Waters

2.2.1. Dissolution

In this study, the observation of Gledhill and Morse (2006b) of the importance of ionic strength on the first order reaction constant for calcite dissolution was further investigated in a series of free-drift pH experiments that were conducted in magnesium-free, phosphate-free, low calcium (~0.01 molal) simple electrolyte solutions in order to further elucidate the specific effect that I has on the dissolution kinetics of calcite. Both KCl and NaCl solutions were investigated because KCl is not believed to strongly interact with carbonic acid system components (Davis and Oliver, 1972; Frantz, 1998; Oliver and Davis, 1973). The details of the experimental method used are given in Gledhill and Morse (2006b). However, the experimental system was entirely rebuilt and refined (Fig. 1) and new LabView computer software was written to give more precise results.

The experimental rate data were modeled using the general rate equation over the range of $0.4 \leq \Omega \leq 0.8$. The upper limit of Ω was chosen as the small voltage change with respect to time and the analytical uncertainty of the final solution chemistry may lead to erratic rate measurements at higher Ω as demonstrated by Gledhill and Morse (2004). Three experimental solutions, KCl 2.0 (I ≈ 2.2), NaCl 2.0 (I ≈ 2.2) and NaCl 5.0 (I ≈ 5.5) were repeated (individual batches of solution) under the same initial conditions ($pCO_2 = 1$ atm, T = 25 °C, $m_{Ca^{2+}} \approx 0.01$ molal). This Ca^{2+} concentration was chosen as it is approximately equivalent to that found in modern seawater with salinity of 35. Additionally, this low Ca^{2+} concentration does not result in erroneously high calculated saturation states using EQPITZER (He and Morse, 1993) that calcium rich brines do (Gledhill and Morse, 2006b). The first two sets of solutions (KCl 2.0 and NaCl 2.0 with I ≈ 2.2) yielded dissolution rate constants with a precision (RSD) of better than 6%. The NaCl 5.0 (I ≈ 5.5) had a much lower precision of 25%. Additionally, five replicates of the same batch of solution (I ~ 2.5) were reacted (though no analyses of the solution conditions were performed) yielding a precision (RSD) better than 7%. Therefore, 7% precision (RSD) has been assumed for solutions of I ≤ 2.2, whereas for solutions with I > 2.2, precision was assumed to vary linearly from 7 – 25% as a function of I from 2.2 to 5.5.

It was found that the calcite dissolution rates can be described using first-order kinetics by the general rate equation: $R = k(1 - \Omega)^n$, where n = 1 (first-order) and k is a function of temperature, partial pressure of CO_2, I, or perhaps more appropriately, a_{H_2O}. Additionally, the identity of the cation of the supporting electrolyte appears to play a minor role as rates were found to be faster in KCl than NaCl solutions under the same experimental conditions (Fig. 2).
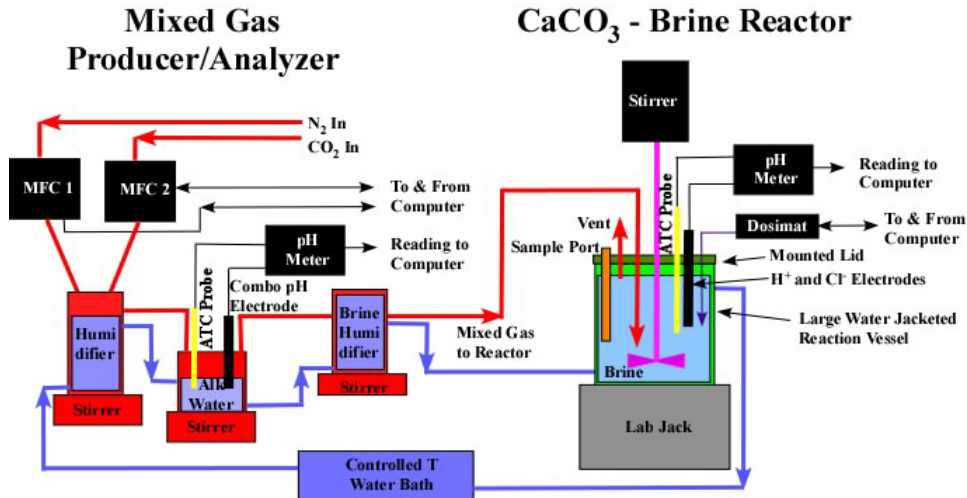
Figure 1. Schematic diagram of the experimental pH free drift reactor system used in this study.
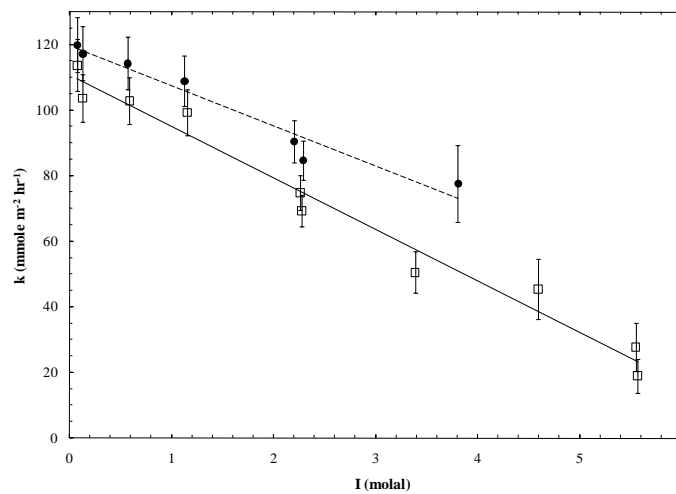

Figure 2. k (mmole m^{-2} hr^{-1}) as a function of I (molal scale) for KCl (●) and NaCl (□). As I increases, k decreases for both solutions.

The influence of I on the dissolution kinetics of calcite becomes more dominant (compared with pCO$_2$ and T), as I is increased. This does not appear to be simply due to a_{H_2O} but may in some complex and ion specific way involve hydration mechanisms on the calcite mineral surface. The most significant finding was X$_{"free"\,H_2O}$ has been postulated to play a significant role in the dissolution kinetics of calcite as water becomes limiting regardless of the temperature (25-55 °C) or the pCO$_2$ (0.1-1 atm) examined in this study. In addition, it was calculated that approximately 45-50% X$_{"free"H_2O}$ represents a critical threshold below which dissolution will not occur (or occur very slowly) in undersaturated solutions, which may be related to the transition from a two-dimensional to three-dimensional water layer adsorbed on the calcite surface. Finally, the MR model presented by Gledhill and Morse (2006a) has been modified slightly:

$$k_{prec} = \beta_0 + \beta_1 T + \beta_2 pCO_2 + \beta_3 X_{"free"\,H_2O} \quad (3)$$

where $X_{"free"\,H_2O}$ has been found to have the largest influence on k. Results are shown in Figure 3.
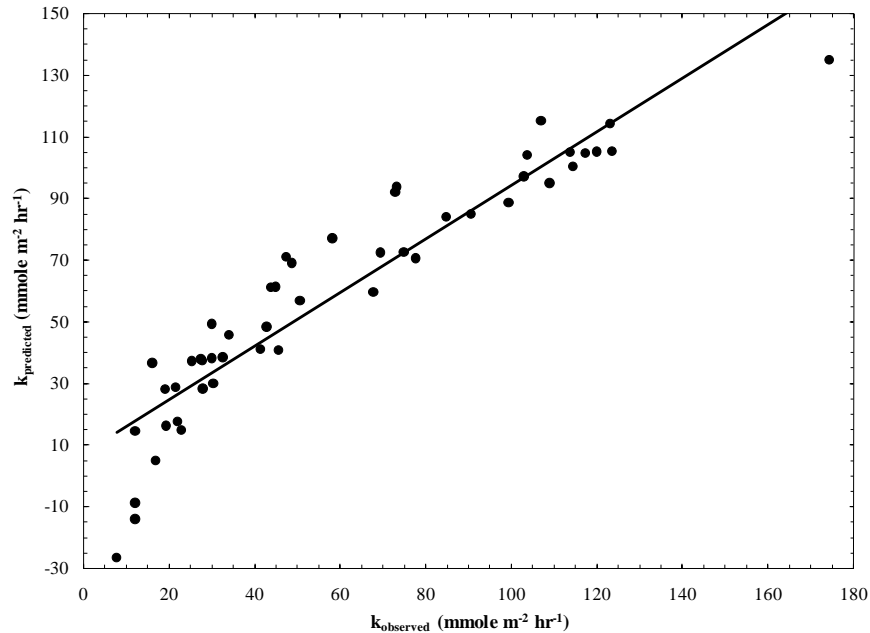

Figure 3. The predictive capability of the MR model (equation 12) with an adjusted $R^2 = 0.862$.

2.2.2. Precipitation

The effect of ionic strength (I), pCO_2, and temperature on the precipitation rate of calcite was investigated in magnesium-free, phosphate-free, low calcium ($m_{Ca}2+ \approx 0.02$ molal) simple KCl and NaCl solutions in a series of classical free drift experiments that largely reproduced the experimental matrix used in the dissolution studies. Rates were modeled using the general rate equation and reaction orders were found to typically range between 0.8 and 2.5, regardless of the electrolyte. For both solutions, rate constants were found to range between $10^{0.8}$ and $10^{1.7}$ mmole m^{-2} hr^{-1}. Under the experimental conditions employed and the resultant precision (~20-25%), I and pCO_2 do not have a significant influence on the precipitation rate of calcite. Precipitation rates increased with temperature although Arrhenius plots yield a broad range of activation energies ($E_a \approx 15 - 28$ kJ mol^{-1}, $R^2 = 0.7232$). The relatively low calculated activation energies coupled with the precision of the results suggest the possibility of surface nucleation in the present results. The observation that I does not have nearly as large an influence on precipitation kinetics as it does on dissolution kinetics is consistent with the hypothesis that the availability of free water to hydrolyze calcium in dissolution exerts a major control on dissolution whereas this is not a primary factor in precipitation where water of hydration is shed during calcium carbonate formation.

2.2.3. Current Efforts

Current efforts in studying $CaCO_3$ dissolution and precipitation using the *batch reactor* approach are divided between those using the previously described system in a chemostat rather than free drift mode and a system capable of working at elevated pCO_2, T and P conditions. A schematic diagram of this system is shown in Figure 4 and a photo of the titanium brine-CO_2 reactor components is shown in Figure 5. This reactor is now complete and undergoing testing and technique development. We anticipate starting serious experimental work with this system during the remainder of the current grant and future planned activities for the proposed renewal are discussed in the proposed research section.
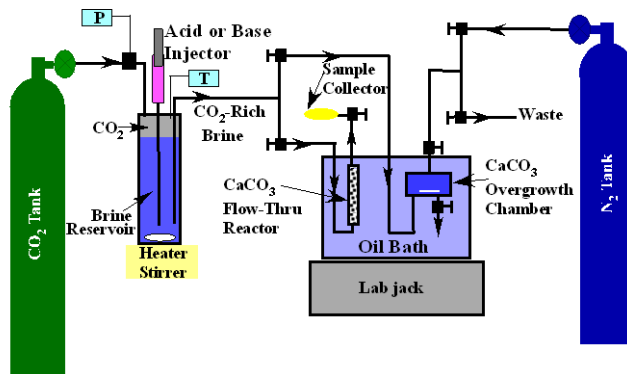

Figure 4. Schematic diagram of flow through system for elevated pCO_2, T and P reaction kinetic studies.

Figure 5. Photograph of titanium brine-CO_2 reactor.

2.3. Microscale Studies of CaCO$_3$ Formation

2.3.1. Nucleation of CaCO$_3$ from NaCl Solutions and Variable Composition Seawater

It is the nature of basic research that unforeseen results are often encountered that open new avenues of investigation. In trying to prepare high ionic strength solution for precipitation, it was found that in supersaturated solutions, nucleation of a precipitate occurred that had a spherical morphology and by XRD analysis was determined to be the CaCO$_3$ polymorph vaterite. It was also found that the vaterite was converted to calcite in hours to days at room temperature. This led us to study the formation, morphology, and rate of transformation of vaterite that formed from NaCl-dominated solutions with low (~10 mM) Ca^{2+} concentrations.

Results indicate the nucleation was possible at low (~1.5 to 4) values of $\Omega_{vaterite}$ and decreased with increasing I. Up to an I of ~1 the $\Omega_{vaterite}$ of nucleation showed major dependence on I, decreasing with increasing I, and was not very reproducible. At II the $\Omega_{vaterite}$ was close to constant and quite reproducible (Fig. 6). The rate of transformation of vaterite to calcite decreased with increasing I and there was evidence of an increasing importance of aragonite as an intermediate metastable CaCO$_3$ polymorph at low I demonstrating the Ostwald step rule.
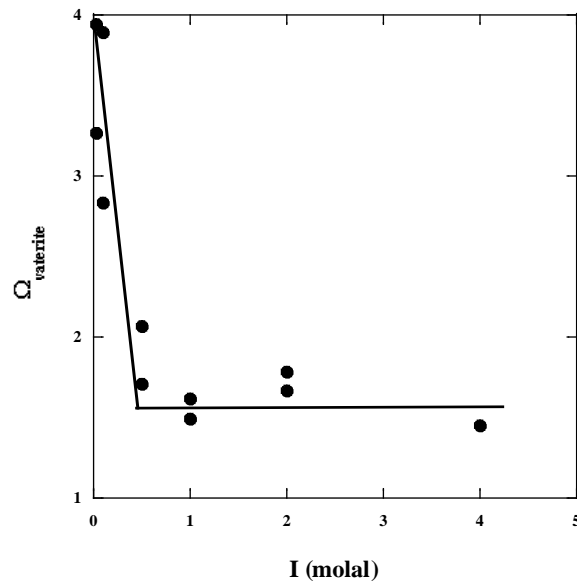

Figure 6. The relationship between I and $\Omega_{vaterite}$ at nucleation. The two lines represent the regions where $\Omega_{vaterite}$ is and is not sensitive to I.

The morphology of the vaterite also was dependent on I, with framboidal spheres being more common at high I, whereas "flower petals" and interleaved plates were common at low I (Fig. 7). Very regular and SEM apparently smooth calcite crystals (and occasionally aragonite) were produced, often in apparent contact with the precursor vaterite during transformation (Fig. 8). This calcite morphology was not produced on overgrowths on Iceland spar calcite (Fig. 9), indicating the possible different crystal growth mechanisms of mononuclear versus polynuclear surface growth.

These findings indicate that vaterite may play a more important role in $CaCO_3$ formation in natural waters and biomineralization than is generally appreciated due to vaterite's ephemeral nature in most natural systems.
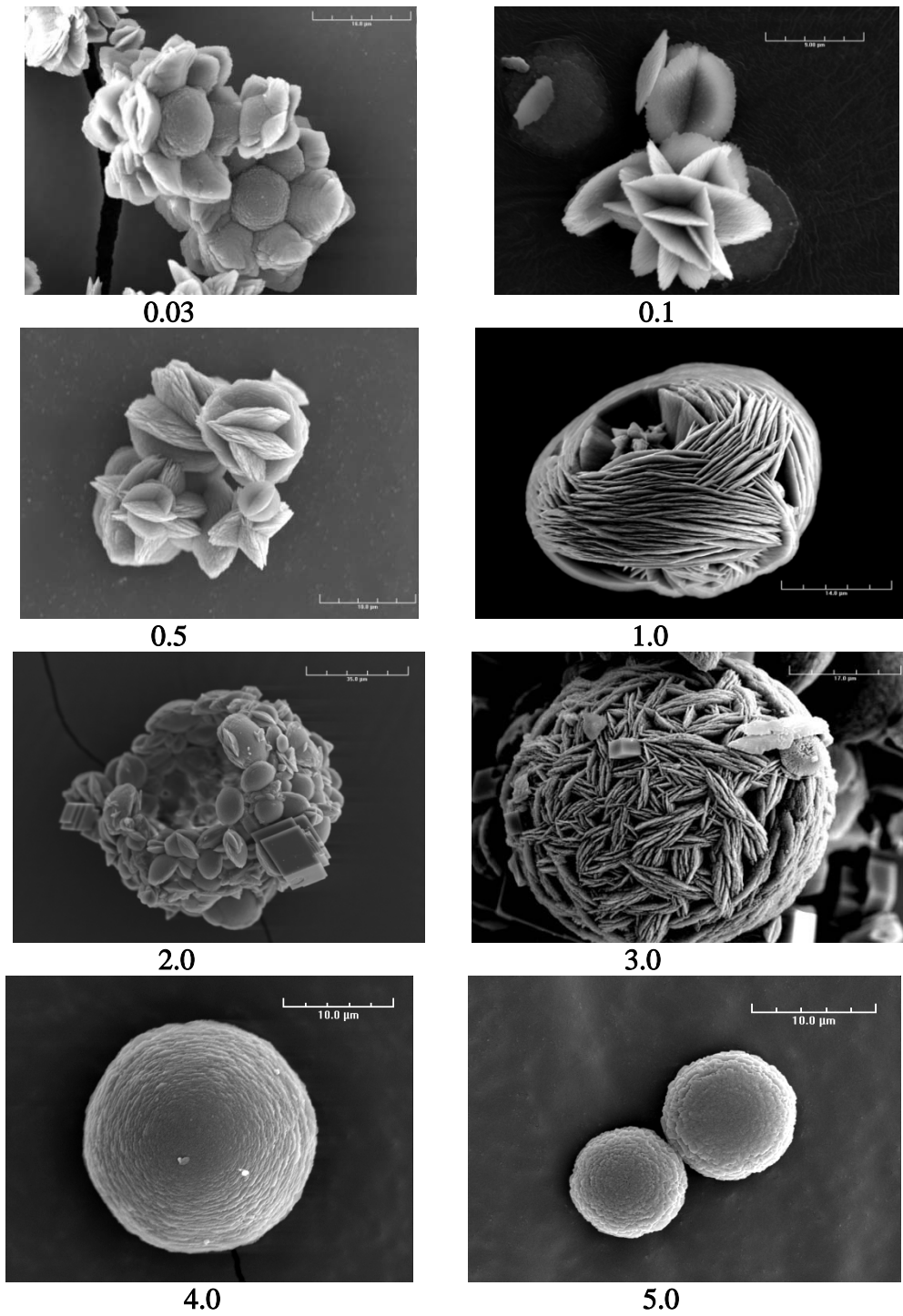

Figure 7. SEM photomicrographs of vaterite precipitated from differing I solutions. I (m) is given below each photomicrograph.
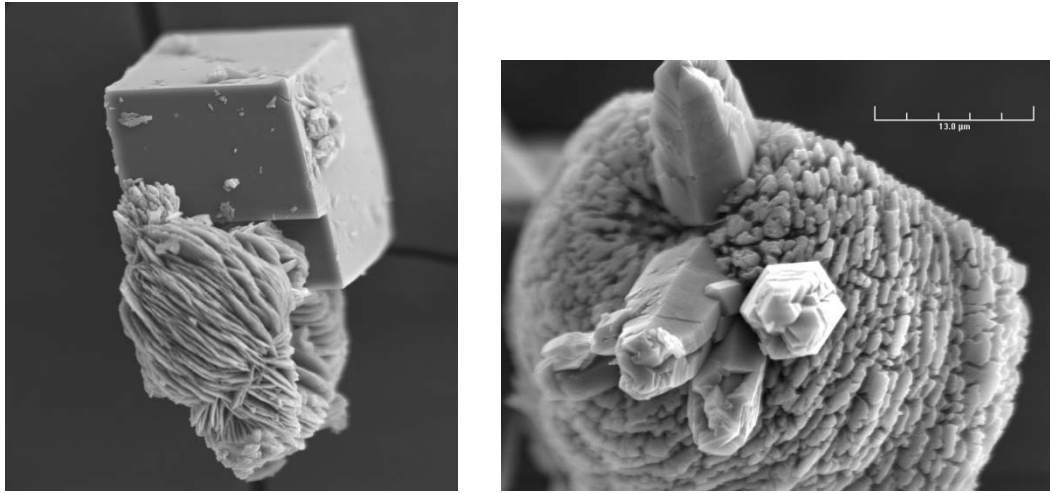
Figure 8. SEM photomicrograph showing a close physical connection between dissolving vaterite and precipitating calcite (left; ~ 30 μm on an edge) and aragonite (protruding needle-like grains).
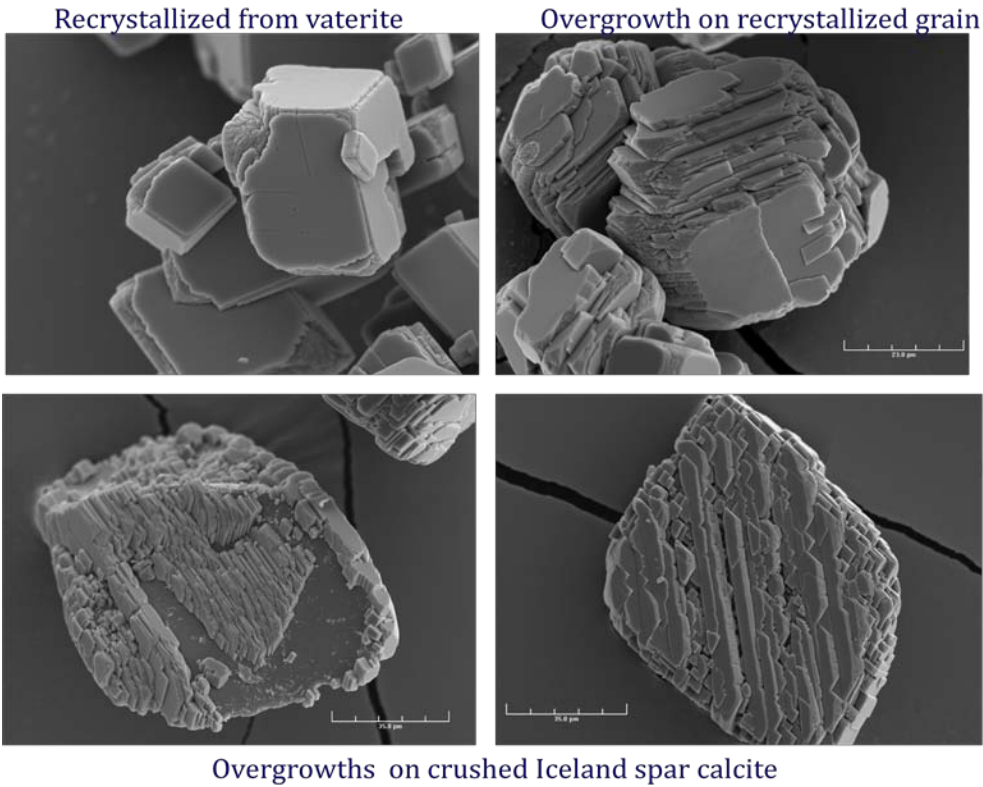

Figure 9. SEM photomicrographs of calcite formed from the transformation of vaterite (upper left), over growths formed on this calcite (upper right) and overgrowths on Iceland spar calcite.

Further nucleation experiments were conducted in synthetic seawater a lowered Mg/Ca ration of about 1-2 believed to be typical of ancient sweater during various times such as the Cretaceous. The pH was continually monitored throughout the experiments and it was used, in combination with the initial alkalinity, to calculate the pCO$_2$ and saturation state of aragonite and calcite at the time of nucleation. The morphology and mineralogy of the precipitates were determined using SEM and XRD analyses.

It was observed that the initial alkalinity greatly affected the nucleation-pCO$_2$ and the CaCO$_3$ polymorph that was precipitated. In seawater with Mg^{2+}/Ca^{2+}=1.2, ~10 mM alkalinity, and a pCO$_2$ below 2,500 µatm, calcite was the initial polymorph nucleated, while aragonite nucleated when the pCO$_2$ was above 2,500 µatm. Seawater with Mg^{2+}/Ca^{2+}=1.2 and a wide range of initial alkalinities (5-50 mM) produced variable results. Seawater with Mg^{2+}/Ca^{2+}=1.7 produced only aragonite at lower alkalinities (<~11 mM), but calcite was nucleated when the alkalinity was above ~18 mM. These results demonstrate the need to also consider the effects of alkalinity and pCO$_2$ in the "critical" Mg^{2+}/Ca^{2+} region of about 1 to 2 for "calcite seas" and "aragonite seas" at various times throughout the Phanerozoic Eon and to use *reasonable* estimated values in experimental studies.

2.3.2. Epitaxial Growth Studies

Experiments were conducted in a variety of saline solutions and seawater in which a CaCO$_3$ substrate was used consisting of either Iceland spar calcite cleaved thin rhombs or aragonite crystals cut perpendicular the c-axis and polished. In these experiments both initial saturation state and time of reaction were followed by SEM examination of the crystal surfaces. A striking feature of these experiments was that both calcite and aragonite growth appeared to occur primarily through the spread of layers of sub- to a few-micron crystals constituting stacked layers of overgrowths. For calcite it was often observed that most growth appeared on one crystal surface and for aragonite the morphology of the overgrowths varied with time. The initial morphology of aragonite surface precipitates more closely resembled those of amorphous calcium carbonate (ACC) or vaterite, but changed on a time scale of months to more commonly fibrous and bladed shapes typical of aragonite. These observations raised a number of questions about growth mechanisms that will be further pursued as part of the proposed research. Saturation state was observed to alter the morphology of the epitaxial precipitates.

2.4. Nanoscale Studies of CaCO$_3$ Formation

Based on the observations made in the microscale studies and in consultation with experts, such our collaborator Dr. Schweikert, it was decided that the best initial nanoscale studies of the precipitates should be conducted using TEM and related techniques. This lead to a collaborative effort with Dr. Brian Gorman of the Colorado School of Mines, who is submitting a "companion" proposal to continue and expand our collaborative studies of nanoscale processes. The initial effort focused on epitaxial CaCO$_3$ overgrowths on an aragonite substrate exposed to normal seawater.

HRTEM observations found an amorphous calcium carbonate (ACC) surface layer a few tens of nm in thickness from which nanocrystalline aragonite was forming epitaxially on a host aragonite substrate (Fig. 10). The ACC and newly formed aragonite crystal contained minor amounts of Mg, which was absent from the aragonite substrate. The epitaxial growth of aragonite on the surface of an aragonite crystal substrate appears to take place by a complex mechanism that does not follow the classic Kossel crystal kink and step movement model for crystal growth. The presence of an ACC layer from which crystal growth occurs may explain the large (about a factor of 2) difference between predicted thermodynamic solubility and "kinetic" solubility of newly formed aragonite.
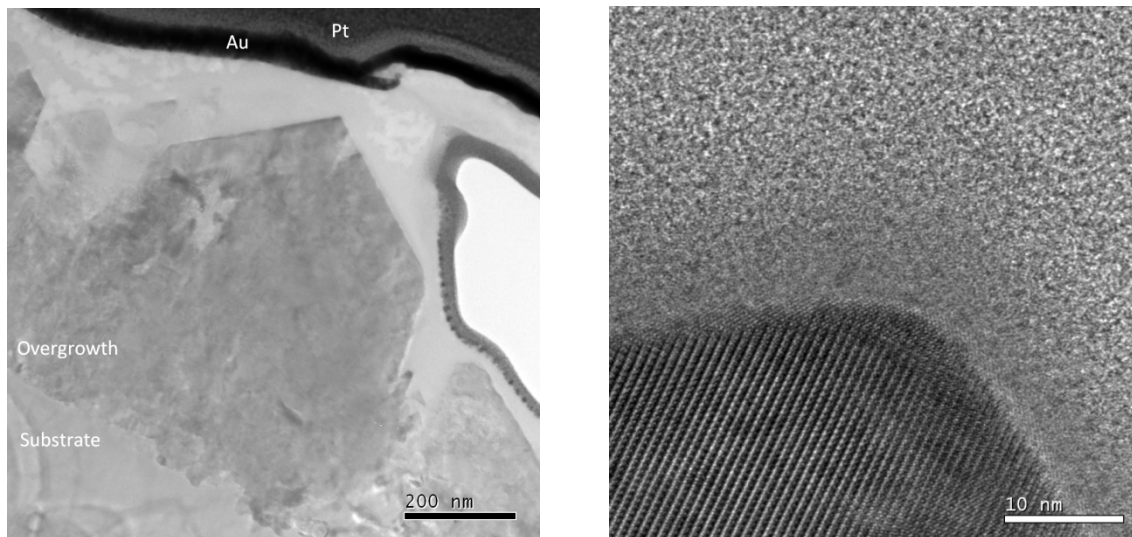
Figure 10. Left: Bright field TEM image illustrating the overall structure of the substrate and carbonate overgrowth, along with the Au and Pt coatings used to preserve the structure during FIB specimen preparation. ACC occurs between the overgrowth and coating. Right: High resolution TEM image of the crystalline and amorphous calcium carbonate overgrowths at a higher magnification image showing the interface between the crystalline and amorphous phases.

3. Work since May 2009
• The main work completed during this period was the assembly and testing of the high-pressure system discussed above. Ms. Luz Romero, the technician employed on the project, resigned at the end of February 2010 and accepted a position in another department of the university. No experiments were therefore carried out with the instrumentation.

• Some preliminary experiments on nucleation were run by adding 1 molal $NaHCO_3$ to 0.01 molal Ca in 1 molal NaCl solution in the presence of carbon dioxide gas. The aim of these experiments was to determine some basic parameters relating changes in pH and mineral composition of the nucleated solids (calcite and aragonite) to carbon dioxide exposure times. It is not possible to draw any conclusions from the small amount of work done.

• Dr. Morse became ill in June 2009. He was never really able to concentrate on laboratory work after this time, because of the various operations he had to undergo.

References

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Frantz, J.D. (1998). Raman spectra of potassium carbonate and bicarbonate aqueous fluids at elevated temperatures and pressures: comparison with theoretical simulations. *Chemical Geology* 152, 211–225.
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