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Kinetics and Mechanisms of Calcite Reactions with Saline Waters

Objectives: This project will investigate the rate limiting effects of intermediate phases on calcite precipitation and dissolution reactions in saline waters using laboratory synthesis and a suite of nanoscale characterization techniques.

Project Description: The general objective of the proposed research is to determine the kinetics and mechanisms of calcite reactions with saline waters over a wide range of saline water composition, pCO_2, and modest ranges in T and P. This will be accomplished by studying both reaction rates and solubility from changes in solution chemistry, and making nanoscale observations of calcite precipitate surface morphology and composition at the micro-to-nano-scale to provide an understanding of controlling reaction mechanisms and pathways. The specific objectives necessary to reach the general objective are: a) determination of how pCO_2, Ca^{2+}, ionic strength and “foreign” ions influence reaction rates; and b) investigate the influence of these parameters on apparent kinetic solubility from dissolution and precipitation reactions. This information will clearly be central to the construction of reliable reaction-transport models to predict reservoir and formation response to increased CO_2 in saline waters. This program was initially collaborative with John Morse at Texas A&M, however his passing shortly after the beginning of this program resulted in abbreviated research time and effort.

Summary of Results: Early studies using electron microscopy and spectroscopy indicated that carbonate precipitation from natural seawater (NSW) conditions onto aragonite substrates was mediated by a surface amorphous calcium carbonate layer. It was hypothesized that this ACC layer (observed after < 5days reaction time) was responsible for the abnormal reaction kinetics and also served as a metastable seed layer for growth of epitaxial aragonite. Further studies of the ACC formation mechanism indicated a strong dependence on the Mg concentration in solution. Subsequent studies at shorter times (10 hrs) on calcite substrates and in a wide range of supersaturation conditions did not indicate any ACC layer. Instead, an epitaxial layer by layer growth mechanism was confirmed by grazing incidence X-ray diffraction, µ-Raman spectroscopy, scanning electron microscopy, transmission electron microscopy, and electron diffraction. Extended time studies out to 45 days confirmed the epitaxial relationship of the overgrowth layer with the substrate. Under NSW conditions, overgrowths were found to have ~0.4 to 0.8 nm / hr growth rates and accommodating 4 at% Mg, resulting in a highly strained overgrowth layer. Following the initial layer by layer growth mechanism, the growth changes to Stranski-Krastanov type after a critical thickness of approximately 100 nm.

1. Research Products

1.1 Peer Reviewed Journal Articles

Morse, J.W. and Gorman B.P., "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*, submitted.

Gorman B.P., McMurray, S.G. "Epitaxial Growth of Calcite From Normal Seawater." *Marine Chemistry*, submitted.

1.2 Extended Abstracts

McMurray, S. G., and Gorman, B. P., "TEM Investigations of Amorphous Calcium Carbonate Formation in Seawater." *Microscopy and Microanalysis* (S2) 2010. Abstract received Microscopy Society of America (MSA) Presidential Scholar Award.

McMurray, S.G., Gorman, B.P., and Diercks, D., "TEM and Atom Probe Investigation of Calcium Carbonate Precipitation in Seawater." *Microscopy and Microanalysis* (S2) 2011. Abstract received Microanalysis Society (MAS) Distinguished Scholar Award.

1.3 Student Degrees

Sarah G. McMurray, "An Examination of Precipitation and Dissolution Products of Calcium Carbonate in A Marine Environment" MS, Materials Science, May 2012

2. Research Results

2.1 Growth Experiments

For the 10 hour growth experiments involving NSW, seawater was initially collected from the northern region of the Gulf of Mexico by John Morse's group at TAMU. The salinity was adjusted to around 35, which is general salinity of NSW (S= 34.6, precisely). To equilibrate the seawater with the room air, and assure the removal of nutrients, the seawater was aged for around 3 months. Gran titration was used to measure the total alkalinity of the seawater to an accuracy better than 0.1%. pH was measured to within ± 0.01 on the total H scale. The saturation state of the seawater with respect to aragonite which was around 3.6 ± 0.2, as calculated by the program SeaCarb. During the experiment, there was very little change in the saturation state, because of the low substrate area to solution volume ratio, which was less than 5 cm^2/L. All experiments took place at room temperature (~23ºC). Iceland spar calcite was cleaved into small (<1 cm) rhombs. Crystals were placed at the bottom of a 1 L beaker of seawater and the beaker was covered to prevent evaporation. At specified times (10 hr and 45 days highlighted here), crystals were removed and wicked dry, then placed in a desiccator.

Specimens relevant to this research include 4 calcite substrates, all soaked for 10 hours, at various saturation levels with respect to aragonite. The NSW solution had a saturation of 3.6 ±

0.2 with respect to aragonite, a salinity of 31.5 g/kg, Mg/Ca = 5, pH = 8.3, and [Ca] = 380 mg/L. Calcite substrates were additionally soaked in solutions with an Ω_{arag} of 2.0, 1.0 and 0.8.

2.2 Overgrowth Characterization

Following precipitation under a variety of supersaturation conditions and reaction times, samples were studied using a variety of materials characterization techniques. Specifically, by grazing incidence X-ray diffraction and μ-Raman spectroscopy were utilized to determine the crystallographic orientation and phase of the overgrowths; scanning electron microscopy was utilized to determine the morphology of the overgrowths; transmission electron microscopy, electron energy loss spectroscopy and electron diffraction were utilized to determine the atomic structure and chemistry of the overgrowths as well as their crystallographic relationships with the substrates.

Figure 1 is a high resolution TEM image of a carbonate overgrowth following 10 hours of exposure in NSW with a supersaturation (Ω_{arag}) of 2.0. As can be seen, very little overgrowth is evident (subsequent studies predicted 8 nm) and the layer by layer growth is epitaxially related to the substrate, also supported by GI-XRD and Raman spectroscopy. X-ray photoelectron spectroscopy and EELS both determined the Mg concentration as 2-4 at%, indicating that an overgrowth is indeed occurring and is below the critical thickness for Stranski-Krastanov (S-K) type growth.

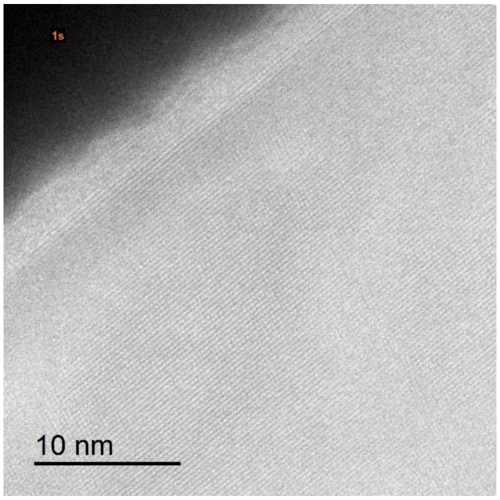
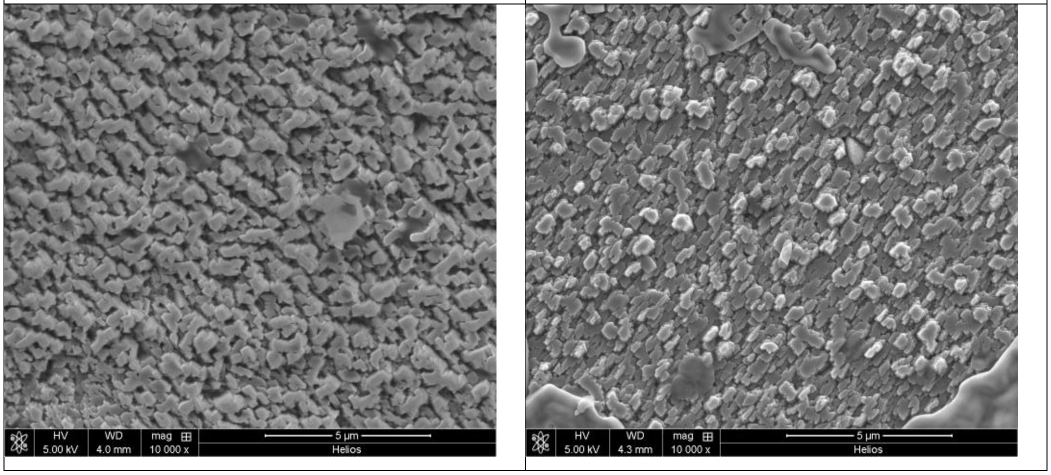


Figure 1. HRTEM image of an epitaxially oriented carbonate overgrowth on a calcite substrate after 10 hr of exposure. A small thickness is observed and pure epitaxial relationship is observed despite 2-4 at% Mg being present.

Due to the difficulty in characterizing such small thickness layers, longer reaction times (up to 45 days) were undertaken under similar conditions. Figure 2 shows a top-down view of the two overgrowths. The figure also highlights one of the more surprising findings of the SEM examination. Namely, on the specimen with slightly higher [Ca] = 420 mg/L (referred to as the Reef sample), overgrowth is clearly directionally oriented. On the NSW specimen, there is no clear orientation of the columnar growth. This observation helped to inform the FIB preparation of TEM specimens. In each condition, a specimen was prepared as oriented parallel to the substrate cleavage plane. However, on the Reef surface, an additional lift-out was made and oriented to be parallel to the overgrowth direction.



NSW surface

Reef surface, slightly Ca enriched

Figure 2. Morphological differences between two over-growths exposed to different conditions. On the surface of the Reef soaked calcite substrate, the overgrowth is clearly directionally oriented. On the NSW surface, no such dominant orientation can be pin- pointed. Both images were taken on the Helios NanoLab 600i.

EDS analysis was used to examine the composition of several common overgrowth morphologies, as seen in the secondary electron image in Figure 3. EDS spectral images confirm that the large, flat angular morphologies belong to salt, while the spindly structure is sulfur based, similar to what was seen on the 10 hour growth specimens. EDS also verified that the columnar-type overgrowth was indeed calcium carbonate. Additionally, EDS verified the presence of Mg, which appears to be present throughout the overgrowth. Following EDS quantification of regions of interest, standard focused ion beam (FIB) in-situ liftout techniques were used for TEM specimen preparation.

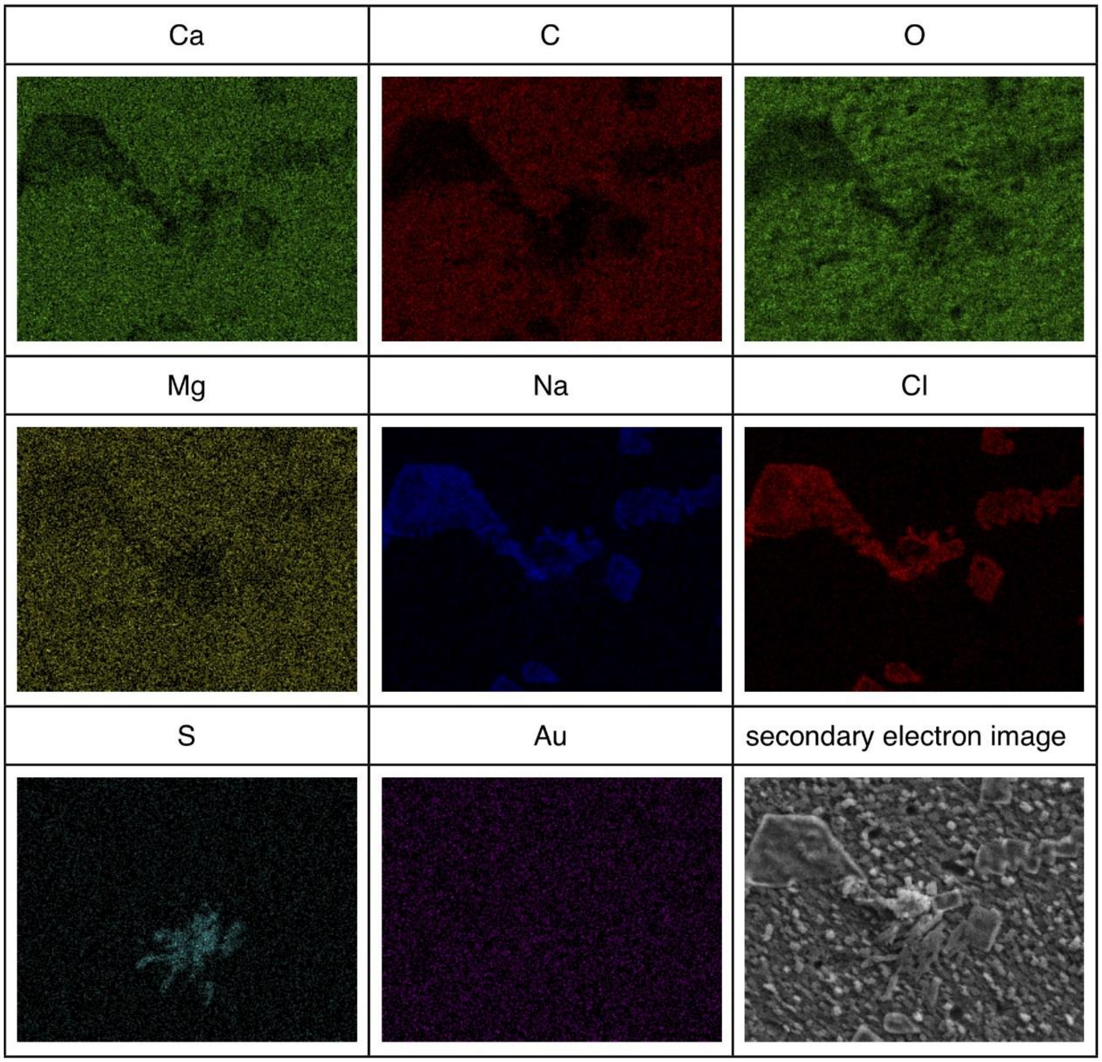


Figure 3. EDS spectral images, verifying that the continuous columnar growth on the substrate is calcium carbonate. Mg is seen throughout the carbonate overgrowths. Other formations, such as salt, and sulfur growths, which had previously been observed on the 10 hour specimens, are also visible in these specimens and are distinct from the $CaCO_3$ growth.

When viewed in the TEM, FIB prepared cross-sections clearly show faceted overgrowth over the surface of the substrate, confirming what was observed in the SEM and with EDS. Figure 4 and 5 were measured at typically low areas, and typically high areas of overgrowth, to determine the range of the height of the growth. The NSW specimen was between 400-700 nm, while the Reef specimen was 600-800 nm, approximately 100-200 nm more growth than the NSW. Overall, growth rates were quantified as being between 0.4 and 0.8 nm per hour.

Several techniques were utilized to determine the crystallographic nature of the overgrowth. The SAA was used to choose a region of the single crystal calcite substrate, then the specimen was tilted onto zone. As seen in Figure 6, SADPs were taken of the calcite substrate, the overgrowth, both the substrate and overgrowth, as well as the substrate, overgrowth and Pt coating. Comparing all of these images, one can see that regardless of what part of the specimen is selected, there is only one crystalline pattern. This would indicate that the overgrowth is of an epitaxial nature, and Reef conditions exhibited similar results. Subsequent analysis with convergent beam electron diffraction confirmed that calcite is being formed. A high amount of strain is observed in the overgrowths, most likely related to the excess Mg concentration compared with the substrate.

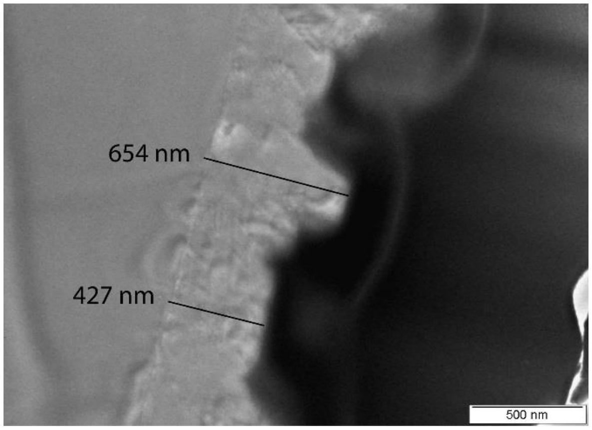


Figure 4. TEM micrograph of the cross section of the NSW specimen. Crystalline overgrowth is clearly seen on the surface of the substrate. Measuring typical low and high areas of the overgrowth yields a thickness between 400-700 nm.

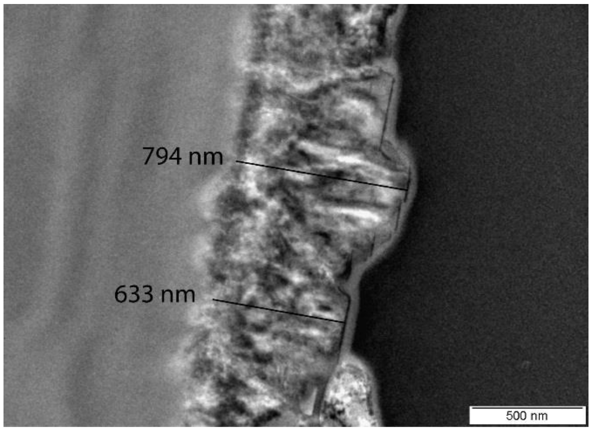


Figure 5. TEM micrograph is of the cross section of the Reef specimen. Crystalline overgrowth is again clearly seen on the surface of the substrate. Measuring the typical low and high areas of the overgrowth gave a thickness between 600-800 nm, ~100-200 nm more than the NSW specimen.

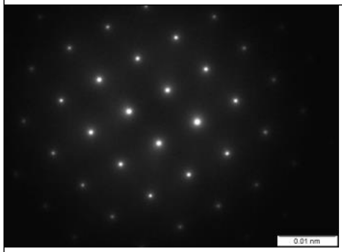
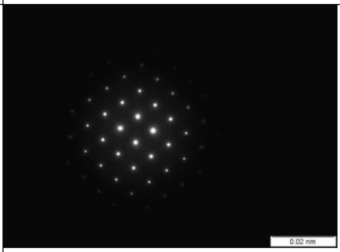
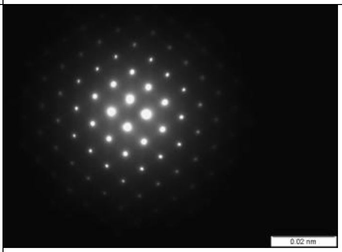
calcite substrate	overgrowth	substrate and overgrowth
		

Figure 6. Selected area diffraction patterns taken from the cross section of the NSW specimen. Though there seems to be some variance in zone axis, the DPs themselves do not change, indicating an epitaxial relationship of the entire overgrowth.

Figures 7 and 8 further verify the epitaxial nature of the overgrowth on the substrate. Figure 7 shows an HRTEM image taken at the interface between the substrate and overgrowth while in the [181] zone. Figure 8 shows an HRTEM image again taken at the interface, but while on the [481] zone. Both images show the atomic planes traveling from the overgrowth to the calcite substrate through the interface and the multiple zone axes confirm a true epitaxial relationship with the substrate.

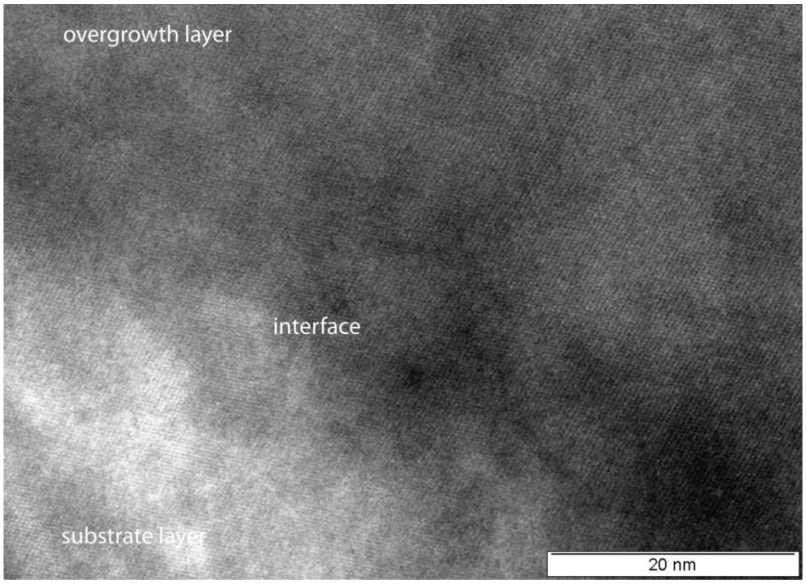


Figure 6. [181] zone axis HRTEM micrograph of the interface between the calcite substrate and the overgrowth for the Reef specimen after 45 day exposure.

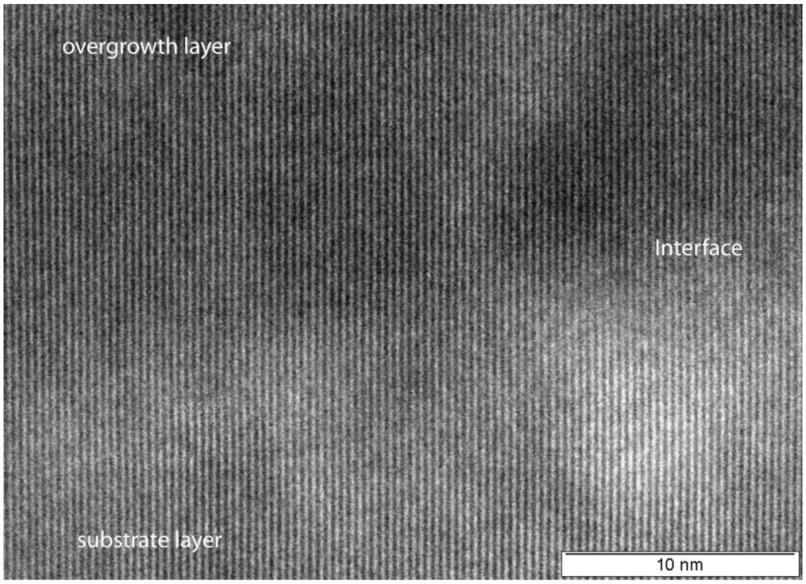


Figure 7. [481] zone axis HRTEM micrograph of the interface between the calcite substrate and the overgrowth for the Reef specimen after 45 day exposure.

4. Discussion

Characterization of the short time (10 hour) exposure NSW samples repeatedly arrived at the same three possibilities. Either there was no overgrowth, the overgrowth was too small to be resolved with the techniques, or the overgrowth was growing epitaxially and thus could not be differentiated from the substrate at such small thicknesses. After longer growth periods, there is substantial evidence that the overgrowth is indeed growing epitaxially. Assuming that growth was a somewhat linear process, and that the NSW 45 day experiment was the closest approximation to the results from the Aragonite substrates, then roughly 4-8 nm could be expected to grow in a 10 hour period. It can therefore be surmised that the early growth periods were also growing epitaxially, and were not differentiable due to the small amount of overgrowth present, and the epitaxial nature of the growth.

This early type of growth could be described as layer by layer. However, the morphology of the longer growth experiment transitions away from a layer by layer mechanism. This later growth much more resembles 3-D island growth. This switch from layer by layer to 3-D island growth would suggest that the S-K growth mechanism is occurring with a critical thickness on the order of 50 nm, or a transition time of approximately 4 days. GIXRD suggests that magnesian calcite constitutes a large portion of the overgrowth, results which are confirmed by XPS, Raman, and EDS. In the Reef sample, the Mg level is such that high magnesian calcite (HMC) is growing, whereas on the NSW sample, either low magesian calcite (LMC) is growing, or HMC is growing in smaller regions surrounded by LMC or pure calcite.

S-K growth is supported by several of the characterization techniques. GIXRD showed characteristic HMC peaks, as well as aragonite peaks in the overgrowth layer. However, no evidence of aragonite diffraction was found in the TEM specimens. This would suggest that there was no aragonite in the 20 μm field of view. Taken together, this would indicated that some small areas of the overgrowth contained aragonite, while the majority were HMC. This is not unheard of in $CaCO_3$ growth literature, though the phenomenon does not seem to be widely explored in marine environments. Paquette and Reader describe the phenomenon as intrasectoral zoning. It is known that the crystal surface itself has a large influence on crystal growth and the incorporation of trace elements. In intrasectoral zoning, the same crystal sector may contain different growth regimes, and incorporate trace elements based on surface topology, rather than by growth-sector boundary. As of yet, it remains unclear if intrasectoral zoning is occurring in this research, although it seems a strong possibility. Determining the precise reason for multiple, but not uniform phases could be the subject of interesting future work. Another possibility is a metastable transition, wherein HMC might first precipitate, and then transform to aragonite, as seen in the ACC to aragonite growth. Rather than a transformation, it could also be a result of chemistry changes over time. Further experimentation would be necessary to explain this multiphase overgrowth phenomenon.

The occurrence of multiple phases provides the necessary amount of misfit such that layer by layer growth would eventually transform to 3D island growth. Table 1 lists the dimensions of the unit cell for calcite, aragonite and HMC. The percent difference of aragonite and HMC from calcite is then calculated. Additionally, the percent difference between aragonite and HMC is also calculated. All three phases are $\leq$ 1% difference from calcite along the a axis. HMC is a fairly close fit for both a and c. Both Calcite and HMC share the space group $R\bar{3}c$, and so the close match may be expected. Aragonite, being orthorhombic, fits poorly in Table 1.

Table 1. A comparison of the dimensions of the unit cells for the three different types of calcium carbonate thought to exist in the 45 day overgrowth. The percent difference in size for HMC and aragonite were calculated in regards to the calcite substrate. Additionally, the mismatch was also calculated between aragonite and HMC.

axis	Calcite d-spacing (A)	Aragonite d-spacing (A)	% difference from calcite	HMC d-spacing (A)	% difference from calcite
a	4.99	4.96	0.7	4.94	1.0
c	17.06	5.74	66.4	16.85	1.2
b		7.97	53.3 from c		

The mismatch seen in Table 1 is what gives rise to the strain visible in TEM images of the overgrowth, such as Figures 4 and 5. The strain can be quantified from GIXRD analyses, see Table 2. In relation to the calcite substrate, the strain of the overgrowth layer is 1.3%, in agreement with Table 1. The NSW specimen, with less Mg concentration, shows less strain in the overgrowth, at 0.5%.

Table 2. Comparison of the change in strain in the overgrowth film between the two 45 day specimens with different concentrations of Mg. The positive strain would mean that the layer was in tension, while the negative strain indicates that the later was in compression.

Reef	%At Conc. Mg	$\tau\theta 20(\mu m)$	$\tau\theta 80(\mu m)$	GIXRD 2θ	strain (%)
	5	0.86	0.85	29.7	+1.3
		8.70	25.06	29.3	0
NSW	2	0.86	0.85	29.15	-0.5
		8.70	25.06	29.3	0

Though the NSW has 2 at% Mg, the overgrowth layer actually exhibits 0.5% shift in strain in the compressive direction. The reason for this unexpected strain is not understood, and would make for interesting future work.

Overall, the main goals of this study were only partially achieved, primarily due to the abbreviated timeframe and scope. Continuation of these studies using expanded growth variable space (temperature, pressure, higher supersaturations) would greatly improve our understanding of the kinetic limiting factors in carbonate precipitation. The search for ACC in calcite containing overgrowths should be continued in this parameter space.