

## TEM Investigations of Amorphous Calcium Carbonate Formation in Seawater

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As  $p\text{CO}_2$  rises in the atmosphere, there is a concurrent rise of  $p\text{CO}_2$  in the upper ocean waters. This results in a decrease in carbonate ion concentration, leading to a decrease in the saturation state of seawater with respect to carbonate minerals [1]. A better understanding of  $\text{CaCO}_3$  precipitation and dissolution reaction kinetics and solubility behavior is needed. Over the last 50 years, aragonite precipitation has been observed to act unpredictably in relation to simple thermodynamics [2]. This is the case in both laboratory and natural marine environments. There is substantial indirect evidence that a phase on the surface with different solubility properties causes this unusual behavior.

SEM analysis of carbonate precipitation for different times illustrated the evolution of carbonate growth morphology on natural aragonite and calcite substrates in natural seawater ( $\Lambda_{\text{aragonite}} = 3.6$ ,  $T \sim 23^\circ\text{C}$ ,  $S = 34.6$ , Fig. 1). It was observed that aragonite growing on an aragonite substrate happens in a complex fashion that does not follow the Kossel crystal kink and step movement model [3]. Aragonite growth is observed to start with small rounded overgrowths, on a submicron scale, increasing with time until a “resting period”, where a continuous layer of small precipitates exists.

FIB was utilized to site-specifically prepare TEM cross sections of the carbonate overgrowths. Low current and low angle FIB specimen preparation combined with high accelerating voltage and low dose STEM techniques are successfully utilized to minimize beam damage. HRTEM revealed an amorphous calcium carbonate (ACC) surface layer tens of nm in thickness above an aragonite overgrowth (Fig. 2). Electron diffraction and HRTEM determined that  $\langle 111 \rangle$  aragonite planes had the highest growth rate, presumably precipitating from the ACC. STEM-EELS illustrated a large change in Ca / C ratio between the amorphous and crystalline regions. Analysis of the Plasmon edges also verified a change in bonding and structure. Mg (present as a secondary cation in the seawater) was determined to be of equal concentration in both regions, and may play a role in the precipitation of the ACC.

This and prior work indicates the possibility that as  $p\text{CO}_2$  rises, and ion concentration in the upper ocean waters decreases, carbonate precipitation may be limited by the formation of ACC. Further studies are currently ongoing to understand the thermodynamic forces behind the formation of this metastable phase. [4]

### References

- [1] S.C. Doney et al., *Annu. Rev. Marine Sci.* (2009) 169.
- [2] P.K. Weyl *Proceed. Inter. Conf. Tropical Oceanography.* (1965) 178
- [3] I. Markov. *Crystal Growth for Beginners: Fundamentals of Nucleation, Crystal Growth and Epitaxy*, Singapore (2003)
- [4] This work presented in fond memory of John W. Morse, Louis and Elizabeth Scherck Professor of Oceanography at Texas A&M University. The aid of Katherine Walton and Janie Lee at TAMU is gratefully acknowledged.

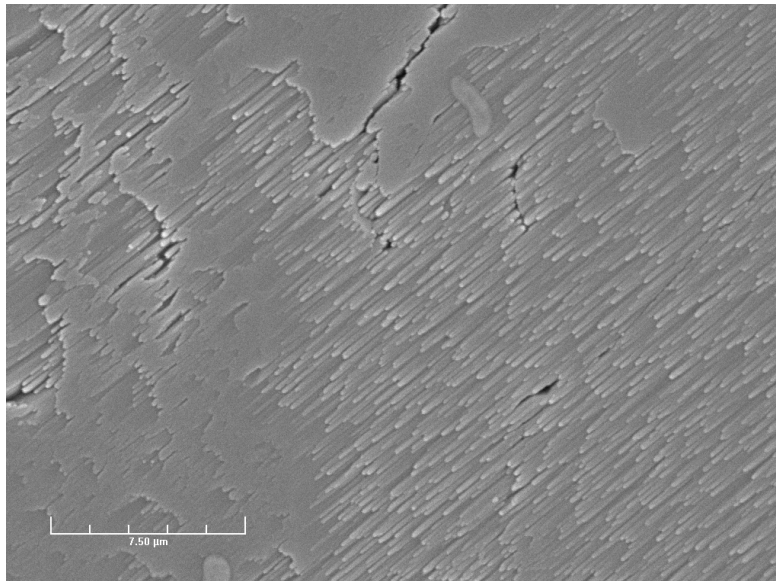


FIG. 1. SEM image of the aragonite growth surface following 50 days of growth at a supersaturation level of approximately 4.

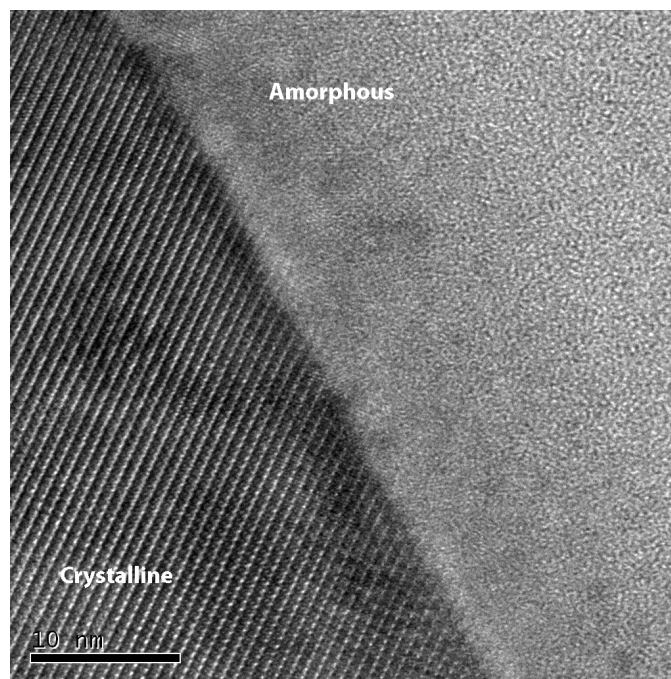


FIG. 2. HRTEM image illustrating the crystalline / amorphous calcium carbonate overgrowth interface.