

## CONCLUSIONS AND FUTURE WORK

The work set forth in this thesis greatly advances the field of seawater calcite dissolution kinetics. In Chapter 1, we found that the complex relationship between dissolution rate and  $\Omega$  was due to the activation of different surface processes upon crossing “critical”  $\Omega$  thresholds. We went on in Chapter 2 to show that these same transitions occurred in the natural environment and, when combined with variations in dissolved organic carbon (DOC) concentrations, explained previously contradictory measurements of *in-situ* dissolution rates. We noted that the energetic parameters in our surface model were likely affected by the chemical speciation of the solution, so in Chapter 3 we proceeded to test this hypothesis. We measured dissolution rates in artificial seawater and found that sulfate enhanced dissolution rates near equilibrium, but inhibited them far from equilibrium. The latest speciation models were then used to fit our rate data with a mechanistic equation of ion attack at the calcite surface. This model successfully explained all of our near equilibrium rate data, regardless of solution. Finally, during the testing of carbon capture reactors, we demonstrated that an enzyme shown to catalyze calcite dissolution rates, carbonic anhydrase, most likely does so via direct proton transfer, rather than increasing the effective concentration of carbonic acid. This result matched predictions from the mechanistic equation in Chapter 3.

The advances discussed above also highlight several remaining questions to be explored in future research. For example, although the rate law in Chapter 2 reconciles disparities amongst previous *in-situ* water-column measurements, a flux analysis reveals that the overall magnitude of inorganic dissolution is insignificant in the North Pacific. One of the goals of CDisK-IV was to quantify the contribution of inorganic dissolution to “Alk\*,” the amount of alkalinity above and beyond the amount expected from purely transport processes (Feely et al., 2002). In a box model combining an aragonite dissolution rate law with measured *in-situ* particle counts and  $\Omega$ s, Dong et al. (2019) showed that inorganic aragonite dissolution could only explain ~0.2% of the Alk\* signal in the N. Pacific. We reach the same conclusion

when modeling the inorganic dissolution rate for calcite, even when imposing unrealistically low sinking rates to the highest productivity, most undersaturated waters of the cruise (Fig 5.1). Inorganic water-column dissolution can explain  $\sim 8\%$  of the  $\text{Alk}^*$  signal at a sinking rate of  $1 \text{ m day}^{-1}$ , but only  $\sim 0.1\%$  at the more commonly cited  $100 \text{ m day}^{-1}$  (Noji et al., 1997; Timothy et al., 2013). It is clear that more work needs to be done quantifying  $\text{Alk}^*$  signals from respiration driven fluxes (Dong et al., 2019; Jansen et al., 2002) and fluxes out of the sediments (Chen, 2002).

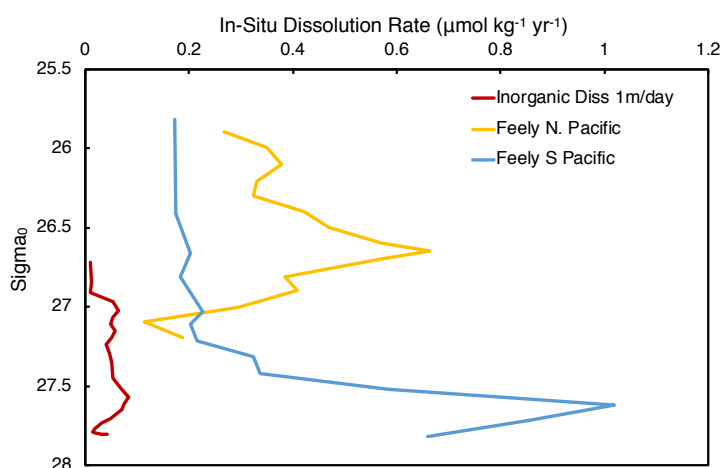


Figure 5.1: Comparison of dissolution rates inferred by  $\text{Alk}^*$  measurements from Feely et al. (2002) with box model results for inorganic calcite dissolution at CDisK-IV Station 5 using the rate law from Chapter 2, a sinking rate of  $1 \text{ m day}^{-1}$ , and particle flux of  $0.69 \text{ mmol m}^{-2} \text{ day}^{-1}$  (upper limit calcite flux from Dong et al. 2019).

On the mechanistic front, more advanced seawater dissolution models will need to be developed and evaluated. The mechanistic model proposed in Chapter 3 is powerful, but can only be applied to a narrow  $\Omega$  range where dissolution proceeds by defect-assisted etch pit formation. The model cannot account for dissolution rates resulting from homogenous etch pit formation from  $0 < \Omega < 0.75$ . While it is possible that dissolution kinetics in this regime are driven solely by surface processes (Bibi et al., 2018; Fischer et al., 2014, 2012; Fischer and Lüttge, 2018; Lüttge et al., 2013), there are a variety of alternative models coupling the surface and solution that should be tested. A more rigorous treatment of the calcite crystal

structure (Zhang and Nancollas, 1998, 1990) and/or the electrical double layer (Wolthers et al., 2008) could provide additional explanatory power.

In addition to different surface processes, these new models will need to take into account changes due to solution chemistry. An issue that has been lurking throughout this dissertation is how our results were potentially affected by a change in the sourcing of Dickson seawater. The labeled  $^{13}\text{C}$  material used by our group has remained constant for the last 6 years, but the dissolution measurements published by Subhas et al. (2015) and Dong et al. (2018) are an order of magnitude slower than those published by Naviaux et al. (2019). The results are plotted together in Fig. 5.2. Note that the  $\Omega$ s reported by Subhas et al. (2015) were calculated using a temperature of  $25^\circ\text{C}$ , when the actual temperature was closer to  $21^\circ\text{C}$ . The temperature has been corrected in Fig. 5.2, such that the data are therefore shifted  $\sim 0.04 \Omega$  units farther from equilibrium, increasing the disparity between Subhas et al. (2015), Dong et al. (2018), and Naviaux et al. (2019). All experiments published in Dong et al. and Subhas et al. were conducted in Dickson seawater batches collected prior to July 25, 2014 (B142). According to personal communications with Dr. Dickson, his seawater sourcing transitioned from offshore cruises to seawater pumped up from the Scripps pier over the period of May 2013 to July 2015. Although the change in sourcing does not exactly match the change in rates (Subhas et al. measured slow rates in B135 and B138, both of which were collected from the pier), it is clear from Fig. 5.2 that experiments conducted after the transition was completed yielded faster rates. These fast experiments include an independent test by Dr. Subhas, as well as an inter-comparison test conducted by me, Dr. Subhas, and Dr. Dong where we each used the same seawater and calcite material. The results strongly suggest that a change in the seawater composition was responsible for the increase in rates. We hypothesize that the DOC content could have decreased after the sourcing change, as DOC was shown to slow dissolution rates in Chapter 2. However, DOC was not measured by Dr. Dickson, and there is no seawater remaining from the original offshore cruises that may be retested.

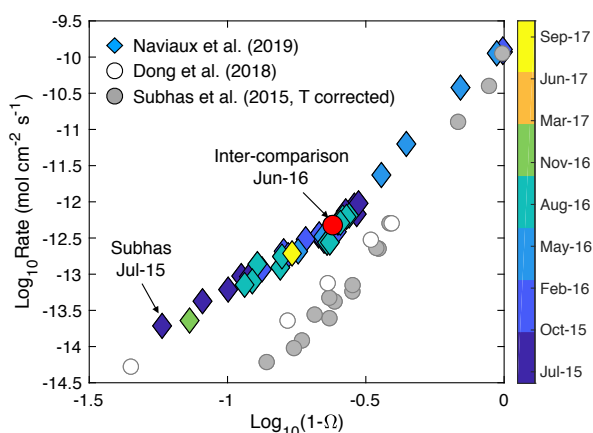


Figure 5.2: Comparison of calcite dissolution rates ( $\text{mol cm}^{-2} \text{s}^{-1}$ ) versus  $\text{Log}_{10}(1-\Omega)$  at  $21^\circ\text{C}$  published by our group. The Subhas et al. (2015)  $\Omega$  values have been corrected from 25 to  $21^\circ\text{C}$ . All dissolution rates measured from July 2015-2017 have been faster than those measured prior to July 2015. These fast measurements were replicated independently by Dr. Subhas (July 2015) as well as during an inter-comparison study by each member in our group. They also include multiple different size fractions (20-53 and 70-100  $\mu\text{m}$ ) from different powder batches, as well as homegrown calcite (300-500  $\mu\text{m}$ ).

There are many other chemical factors known to affect calcite dissolution rates that have yet to be evaluated in seawater. Of particular interest are the impacts of changing the magnesium concentration, as well as the calcium to carbonate ion ratio. These have each been shown profoundly affect calcite growth and dissolution rates in simple solutions (Compton and Brown, 1994; Klasa et al., 2013; Lin and Singer, 2009; Nielsen et al., 2013; Ruiz-Agudo et al., 2010; Sand et al., 2016; Wolthers et al., 2012a). The concentrations of  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  have also changed significantly over the last 120 million years (Hain et al., 2015), making it important to incorporate their effects on calcite dissolution rates into our understanding of past climates. Additional experiments in various ionic compositions will also allow for rigorous tests of coupled solution-surface speciation models, especially if combined with atomic force microscopy experiments

The field of calcite dissolution kinetics remains exciting and open to large developments. It has been a pleasure to work on such a complex and interesting problem with such great implications for the global climate system.