

Journey of calcium in seawater: from dissolved ion complexes to mineralization

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Calcium carbonate (CaCO_3) polymorphs are crucial minerals in marine biogeochemistry, as numerous organisms choose CaCO_3 as the building material of their hard tissues, and this biomineralization process has made CaCO_3 one of the most abundant fossils in the ocean. The trace elements incorporated into the lattice during CaCO_3 formation (e.g., Sr, Mg, U) have been used as proxies to reconstruct paleoclimate, therefore understanding the formation mechanism of CaCO_3 is critical to accurately interpreting carbonate records.

The formation of CaCO_3 in the ocean is controlled by both the supersaturation of CaCO_3 and the kinetics of the transformation of amorphous calcium carbonate (ACC), which is a precursor phase of crystalline CaCO_3 used by organisms like coral for growing skeleton. However, both two factors remain poorly understood: the supersaturation of CaCO_3 in surface seawater is coupled with the speciation of dissolved Ca, which is under debate; trace elements incorporated into ACC would alter its solubility and metastability; furthermore, how dissolved Ca species initiate the nucleation of solid phase is still unclear.

To address these knowledge gaps, we investigated the speciation of Ca in surface seawater as well as the nucleation and transformation of ACC in aqueous solutions using a suite of experimental and computational techniques. While researchers have long believed that the majority of dissolved Ca is free, our molecular dynamics simulations and X-ray scattering measurements of seawater samples show that half of the dissolved Ca forms outer-sphere complexes with Cl^- and SO_4^{2-} , therefore the supersaturation of CaCO_3 in surface seawater could have been overestimated. These aqueous Ca complexes have different reactivity compared with free Ca ions, as reflected through the residence time of water molecules coordinated to Ca. To connect dissolved Ca species with CaCO_3 formation, we characterized the nucleation of ACC in simulated seawater with in-situ X-ray and infrared spectroscopy and monitored the transformation of the solid phase. The presence of seawater ions was found to greatly affect the residence time of structural water and the metastability of ACC. Molecular dynamics simulations of the nucleation of CaCO_3 polymorphs from solution and the energy landscape of nucleation pathways will also be presented.