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Inhibition of shallow carbonate sediment dissolution rates by organic coatings

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Understanding the role of calcium carbonate mineral ($CaCO_3$) dissolution in shallow coastal sediments is critical to assessing alkalinity cycling in nearshore environments. Although calcium carbonate mineral dissolution is anticipated to increase in response to increasing surface seawater carbon dioxide (CO_2) and decreasing pH and Ω_{CaCO3}, the influence of factors such as seawater carbonate chemistry, grain size distribution, mineralogy, and surface characteristics on dissolution rates of shallow carbonate sediments is not well constrained.

Here, we explore the relative influence of physical and chemical properties on bulk sediment dissolution rates by conducting free-drift dissolution experiments under different pCO_2 conditions using shallow biogenic carbonate sediments from Bermuda and Heron Island, Australia. Dissolution rates (R) for all bulk sediment samples increased with increasing seawater pCO_2, but the absolute dissolution rate and sensitivity of dissolution rate to changes in pCO_2 ($dR/dpCO_2$) were significantly different between samples. Interestingly, no relationships were found between bulk dissolution rates and grain size distribution or mineralogy. Experiments were also conducted with separated grain size fractions of bulk sediment samples and, unexpectedly, both the absolute dissolution rate and sensitivity to changes in pCO_2 were higher in larger grain size fractions. Additional experiments revealed that organic matter associated with the mineral grains may greatly influence dissolution rates and could explain these unanticipated results. Sediment samples free from organic coatings resulted in significantly higher (~2-3 times) dissolution rates compared to unaltered samples. Furthermore, bulk sediment dissolution rates at Heron Island were inversely correlated with the total organic matter content of the sediments. Isotopic evidence also suggests that organic matter coatings lowered bulk dissolution rates of the sediment samples. These results indicate that the presence of organic coatings on the surface of sediment grains may inhibit dissolution by preventing direct interaction between the surrounding seawater and mineral surface. The role of organic matter inhibition in carbonate sediment dissolution and its potential to influence sediment alkalinity production in coastal ecosystems requires further attention.