

Weathering in modern carbonate terrains: Biological controls on redox conditions, dissolution and atmospheric CO₂ fluxes

JONATHAN B. MARTIN¹, AMY BROWN¹, JOHN EZELL¹,
ANDREA PAIN¹ AND CAITLIN YOUNG¹

¹Department of Geological Sciences, University of Florida,
Gainesville, Florida, USA 32611 jbmartin@ufl.edu

Carbonate minerals dissolve in modern carbonate depositional settings by naturally produced carbonic and sulfuric acids. Sulfuric acid forms through coupling of microbial oxidation of organic carbon and sulfate reduction to sulfide followed by reoxidation of sulfide by atmospheric oxygen and oxygen produced photosynthetically in the local environment. Microbial oxidation of organic carbon also forms CO₂, which along with CO₂ dissolved from Earth's atmosphere, hydrates to carbonic acid. Although carbonate mineral dissolution is often congruent, a common early diagenetic reaction is the dissolution of biogenically produced aragonite and subsequent co-precipitation of thermodynamically more stable calcite. Precipitation of solid carbonate minerals from bicarbonate produced from hydrated atmospheric CO₂ releases CO₂ back to the atmosphere; therefore, these coupled reactions do not affect atmospheric CO₂ concentrations. In contrast, CO₂ released during dissolution of solid carbonate minerals via sulfuric acid results in a net contribution of CO₂ to the atmosphere. The magnitudes of these two types of reactions depend on the hydrologic dynamics of the systems. Water filled sinkholes (called blue holes in The Bahamas and cenotes in the Yucatán) are fairly static and organic carbon oxidation occurs at the pycnocline where organic matter is trapped at the density interface. Dissolution occurs as diffusion and tidal pumping bring low pH water into contact with carbonate minerals of sinkhole walls. In regions with large fresh-water lenses such as the Yucatán, fresh water discharges dynamically from offshore springs. Backflooding of these springs during times of elevated sea surface drives dissolution through mixing oxic and sulfide-rich water. Both organic carbon oxidation and carbonate mineral dissolution affect P cycling in these system through release of organic- and carbonate-bound P, thereby providing a feedback to the microbial and benthic communities. Although dissolution in carbonate systems can be congruent, and thus not form regolith, weathering, early diagenesis, and atmospheric fluxes critically depend on the relationship between biotic processes, oxidation of carbon fixed by primary productivity, and dissolution reactions.