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Phase Identification of Phosphorus Uptake onto Carbonate Minerals in Coastal Wastewater Injection Zones

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The nearshore, oligotrophic waters of the Florida Keys National Marine Sanctuary (FKNMS) are sensitive to fluctuations of phosphate, a limiting nutrient in the Florida Bay. Shallow, 27-meter injection wells are the primary method for disposing treated wastewater effluent in the FKNMS. This remediation method relies on the rapid adsorption of phosphate onto the carbonate mineral surfaces of the Key Largo Limestone (KLL) before the effluent emerges into nearshore waters. However, laboratory studies have demonstrated there are potential drawbacks to this mode of remediation, including limits to phosphate adsorption in the bedrock or desorption from seawater incursions.

We assessed the uptake capacity and permanence of wastewater-derived phosphate onto KLL (1) in the field at the Area 3 Wastewater Facility in Marathon, Florida, (2) with geochemical modeling, and (3) in a laboratory flow-through experiment. In Marathon, we tracked the migration and chemical evolution of the effluent plume following injection by analyzing concentrations of total and soluble reactive phosphate and sucralose, a conservative pharmaceutical tracer found in wastewater, over two years. Geochemical data (i.e. pH, salinity, [DIC], [PO4], alkalinity, etc.) collected from nested monitoring wells were used in PHREEQC (USGS) to model the thermodynamic feasibility of mineralization of phosphorus-containing carbonate minerals forming in the wastewater pathway. Finally, we tested the behavior, reaction kinetics, and mineralogy of phosphate uptake via flow-through experiments on KLL cores using wastewater standards and phosphate-spiked seawater.

Phosphate phases in experimental cores and cores recovered from Marathon were investigated via X-ray Absorption Near Edge structure spectroscopy, X-ray Fluorescence, and Raman spectroscopy to determine the mode of phosphorus incorporation into carbonate minerals. These spectroscopic studies will be essential for understanding carbonate's role in coastal wastewater remediation in addition to determining the phases that preserve phosphate-carbonate interactions in the rock record. This modern study will inform the development of carbonate-associated phosphorus as a proxy for phosphorus bioavailability in Earth History.