

**EVIDENCE FOR PHOSPHATE UPTAKE IN AQUIFER MIXING WATERS OF
FLORIDA'S KEY LARGO LIMESTONE.**

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ABSTRACT

Phosphate behaves non-conservatively during aquifer mixing with seawater in Key Largo Limestone (KLL). This uptake appears to be driven by absorption of phosphate to carbonate mineral surfaces and subsequent precipitation as an octacalcium phosphate precursor. Using first order removal kinetics, about 95% of phosphate delivered to saline groundwaters (~37 psu) by low salinity, phosphate- and organic-rich injected sewage waste (~0.5 psu) is taken up in the porous bedrock (i.e., within 10 to 15 feet of the injection site). Aquifer transmissivity in this limestone is about 1,400 m/day and groundwater flow is driven primarily by Atlantic Ocean tides along the Florida Keys' archipelago. The coastal limestone aquifer waters are supersaturated with carbonate fluorapatite [CFA, $\text{Ca}_{10}(\text{PO}_4)_{6-x}(\text{CO}_3)_x(\text{F},\text{OH})_{2+x}$]; thus, formation of CFA is at least thermodynamically feasible though kinetics are slow. Phosphate removal from solution in this aquifer-mixing zone is likely via rapid adsorption onto charged sites with low activation energies where phosphate rapidly undergoes nucleation to a non-apatitic, precursor calcium phosphate phase. Scanning electron microscopy and energy dispersive x-ray spectrometry analyses of KLL well cuttings further support deposition of phosphorus-bearing precipitants on void space rims. Phosphorus-bearing streaks are identified in pore spaces in several locations of the thin section. These SEM results make a convincing argument that a cryptocrystalline calcium phosphate is removing phosphate from solution and precipitating along mineral surfaces of KLL. Perhaps ground water is not always the "nutrient delivery truck" it appears to be in coastal waters. Potential deleterious effects of sewage waste on coastal waters may be decreased if phosphate is sequestered in limestone as a calcium phosphate.

Keywords: ground water, tides, phosphate, apatite, limestone, coastal aquifer

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