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Mineral Distribution and Weathering in the Greater Everglades: Implications for Restoration

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The Greater Everglades encompasses two regions of mineralogical contrast—the Lake Okeechobee Basin (LOB) and the region south of the lake that includes the Everglades and Florida Bay. Lake Okeechobee is a transition zone with mineralogical similarities to both regions. Weathering in the LOB is mainly unidirectional and flow driven, whereas in the Everglades it tends to be cyclical and driven by diurnal and seasonal biogeochemical gradients. LOB soils formed in quartz-dominated marine sediments of various ages under diverse landscape, hydrology, vegetation, and weathering intensities. Calcite and quartz are dominant south of the lake, with quartz diminishing southward. Secondary calcite forms via algal photosynthesis to become a major constituent of marl soils and periphyton. Phosphorus immobilized via periphyton formation is mainly in microbial biomass, but calcite is essential to the process. Minerals of lesser abundance can have disproportionate ecological influence. These include phyllosilicates, oxides, sulfates, sulfides, and phosphates, which have roles in turbidity and biogeochemical processes affecting the fate of P, Hg, and possibly As. Mineral-related perturbations of ecological impact include inhibited precipitation of calcite in periphyton mats, enhanced Hg methylation via sulfide formation from agricultural sulfate, and entrainment of readily-suspended minerals via construction of canals. The nature and rate of Ca-P interactions bear on the rate of ecological recovery. Understanding the dynamics of mineral redistributions is critical for effective restoration.

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INTRODUCTION

The area called the Greater Everglades is a southward-trending flow path of matter and energy extending from the upper reaches of the Lake Okeechobee Basin (LOB) to the outer reaches of Florida Bay. Its soils and rocks are diverse and collectively contain many minerals, some of which get caught in the flow and are redistributed. These displaced minerals have potential to degrade water quality, particularly if their entrainment is exacerbated by anthropogenic activity such as the building and operation of canal systems. Other minerals respond to biogeochemical gradients, forming and dissolving diurnally and seasonally with changes in respiration and photosynthesis. These ephemeral minerals participate in ecologically significant processes and have potential to serve as indicators of degradation or restoration. In this paper we review mineral distribution and reactions that are pertinent to understanding and restoring the interconnected ecosystems of the Greater Everglades. Statements regarding general abundance of minerals are based on the Florida Soil Characterization Database (FCDB; 2010) unless otherwise indicated.

GEOGRAPHIC WEATHERING DISTINCTIONS

The Greater Everglades consists of contrasting areas from the perspective of mineral distribution—the LOB, the lake itself, and the region south of the lake (Everglades and Florida Bay). Soils north of the lake (LOB) formed under a wider range of parent materials, hydrologic conditions, and weathering intensities than soils south of the lake. Soils and other geologic material of the LOB mainly conform to a weathering model familiar to most soil mineralogists, but weathering in the Everglades is of a different character (Figure 1). Consequently, the relative abundance of minerals differs markedly between the two regions (Table 1). Lake Okeechobee is a transition zone with mineralogical similarities to both regions.

Soils of the LOB, which formed mainly in clastic marine sediments, have undergone weathering since their terrestrial emergence. The humid subtropical climate promotes intense weathering. High soil temperatures favor fast reaction rates. High rainfall enables prolific biological activity and accompanying acidification as well as thorough flushing of reaction products except in the case of some very poorly drained soils. Hence, weatherable minerals of the marine deposits are subject to irreversible dissolution or transformation during soil formation (Figure 1). The irreversibility is attributable to the
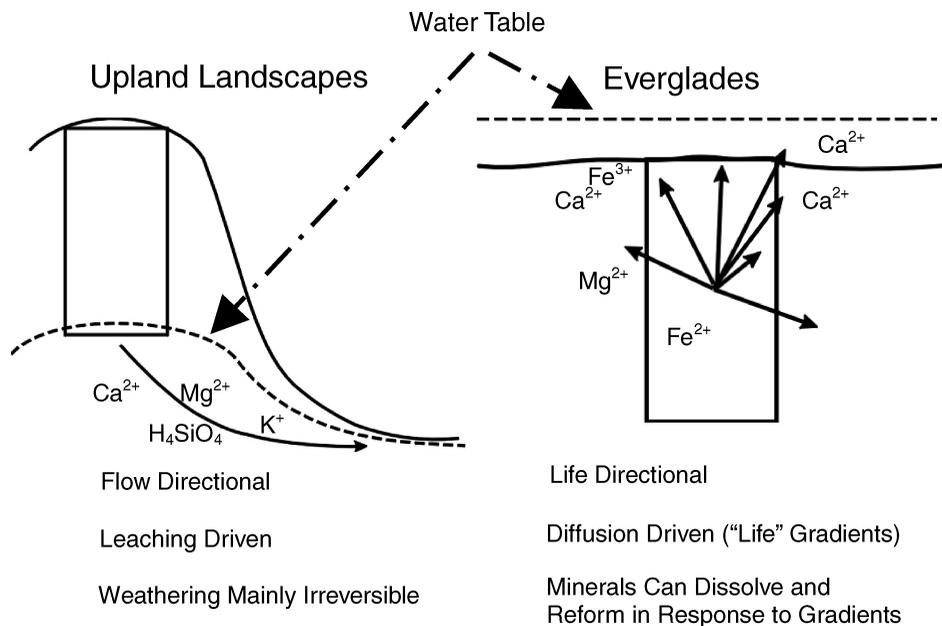
FIGURE 1. Water flows through soils of upland landscapes in the LOB, carrying with it the products of weathering that are not replenished except by fertilizer. Gravity-driven gradients and unidirectional flow characterize this upland scenario but biogeochemical gradients (e.g., organic matter influence on redox-driven Fe redistribution) can still be important. The Everglades also have hydrologic gradients, but of low enough magnitude that diffusion gradients established by biogeochemical processes profoundly influence mineral distributions. Gradients in oxidation-reduction potential and CO_2 concentrations affect stability of Fe and carbonate minerals on a seasonal and even diurnal basis. These minerals can hence be ephemeral and serve as biogeochemical indicators.

geochemistry of the minerals undergoing weathering—most formed at pressures and temperatures that markedly differ from their present environment. In contrast, the minerals that form secondarily from the products of weathering are thermodynamically stable in the soil environment. Examples of weatherable minerals are mica and feldspar, which would be precursors to resistant secondary minerals such as hydroxyl-interlayered vermiculite (HIV; Cabrera-Martinez et al., 1989; Harris et al., 1987a, 1987b; Harris et al., 1992) or kaolinite.

Sediments of Lake Okeechobee and soils of the Everglades undergo less irreversible weathering than do soils north of the lake (Figure 1). Mineral transformations are driven to a greater extent by biogeochemical gradients. Such gradients are established by microbe-mitigated chemical reduction–oxidation (redox) of Fe and S, photosynthetic or respiratory effects on partial pressure of CO_2, or local release of organic acids. They are manifested at different scales and their rates vary seasonally and diurnally. Alkaline conditions and minimum leaching of reaction products in the lake

TABLE 1. Geographic- and particle-size occurrences of minerals found in the Greater Everglades

Mineral	Mineral class	Geographic occurrence	Abundance		Areas of greatest abundance or (in case of rare) where it has been found
			In < 50 μm fraction	Whole-soil or whole-sediment abundance	
Quartz	Silicate	widespread	high	high	Okeechobee Basin
Smectite	Silicate	widespread	high	low	Okeechobee Basin, Lake Okeechobee
Kaolinite	Silicate	widespread	high	low	Okeechobee Basin
HIV[a]	Silicate	widespread	high	low	Okeechobee Basin
Sepiolite	Silicate	occasional	high	high	Lake Okeechobee; muck soils S and E of the lake
Palygorskite	Silicate	occasional	medium	medium	Lake Okeechobee; muck soils S and E of the lake; Everglades canals
Illite	Silicate	occasional	low	low	Okeechobee Basin to Florida Bay
Chlorite	Silicate	rare	very low	very low	Florida Bay
Gibbsite	Oxide[b]	occasional	low	very low	Okeechobee Basin
Goethite	Oxide	occasional	low	very low	Okeechobee Basin
Lepidocrocite	Oxide	rare	low	very low	Okeechobee Basin; possibly Everglades
Hematite	Oxide	rare	low	very low	Okeechobee Basin
Calcite	Carbonate	widespread	high	high	Lake Okeechobee; Everglades; Florida Bay
Dolomite	Carbonate	occasional	medium	medium	Lake Okeechobee; muck soils S and E of the lake; Everglades canals
Aragonite	Carbonate	occasional	medium	medium	Lake Okeechobee; muck soils S & E of the lake; Everglades canals
Apatite	Phosphate	rare	low	low	Okeechobee Basin (dairy ditch); Everglades HID
Vivianite	Phosphate	rare	low	very low	Okeechobee Basin (dairy ditch)
Pyrite	Sulfide	occasional	low	very low	Lake Okeechobee; muck soils S and E of the lake; Everglades canals
Gypsum	Sulfate	rare	low	low	Okeechobee Basin
Weddellite	Ca oxalate	rare	Low	low	Everglades organic soils

Note. Table entries are judgments based on the author's experience, scientific literature cited in this chapter, and the Florida Soil Characterization Data Base (FCDB, 2010) generated during the Florida Cooperative Soil Survey Program (http://flsoils.ifas.ufl.edu/).
[a]HIV = hydroxyl-interlayered vermiculite. [b]Oxides include metal hydroxides and oxyhydroxides; noncrystalline analogues are common.

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and Everglades tend to preserve minerals unless they are susceptible to thermodynamic destabilization by these biological processes. Carbonates and redox-sensitive minerals are among those that can disappear or re-emerge temporally and spatially. That is because carbonate-, Fe-, and S-bearing minerals (unlike primary minerals that crystallize from cooling magma) can rapidly precipitate or dissolve under ambient conditions of temperature and pressure as thermodynamically dictated. Hence these ephemeral minerals can serve as indicators of ecological perturbations. Their reactions in some cases influence the fate of nutrients and contaminants.

The previous regional distinctions regarding the nature of gradients are not absolute. For example, there are important biogeochemical gradients in the LOB (e.g., formation of redoximorphic features) as well as significant hydrologic gradients in the Everglades.

IMPORTANT MINERAL REACTIONS AND DISTRIBUTIONS

Silicates

Silicate minerals comprise a diverse and overwhelmingly dominant mineral class in the LOB. They are less abundant south of Lake Okeechobee but are still ecologically significant in the Everglades, particularly toward the west in the area of Big Cypress as land elevation rises slightly. Their reactivity relates to crystal structure and particle size. Distribution of silicates within the soil matrix reflects weathering and other pedological processes.

Quartz, a tectosilicate, has relatively low reactivity because of its thermodynamic stability and its lack of structural internal surface area that defines expansible phyllosilicates. However, quartz sand grains comprise the bulk of most soils in the LOB and serve as the girders for the matrix within which biogeochemical processes occur. It is a common misconception that soils with sand textures are inert. Sandy soils undergo processes such as podzolization and redox-driven redistributions that are profoundly biogeochemical in nature. Biogeochemical processes aren't restricted to wetlands or organic soils. Coatings on quartz sand grains are the primary zones of reactivity in sandy upland soils of the region.

Sand grain coatings in Florida soils consist of silt- and clay-sized particles of comparable proportions that together total about 20–80 g kg^{-1} of the soil by weight. The silt in the coatings is mainly quartz. The coating clay fraction commonly contains quartz, HIV, and kaolinite (Harris et al., 1987b) with lesser amounts of metal oxides that serve as binding agents holding the coatings to the sand grains (Harris et al., 1987b, 1995). Organic C in the form of organometal complexes is also a prevalent grain-coating component in Bh horizons of Spodosols.

There is evidence that the HIV in Florida soils is derived from mica weathering (Harris et al., 1988; Harris et al., 1989; Harris et al., 1992).

Specifically, HIV grains are mica-like in crystal habit and contain nonexchangeable K in the form of small occluded domains of mica. The K associated with HIV is a potential source to plants (Comerford et al., 1990). Selectivity for K^+ and NH_4^+ has been reported for HIV (Rich, 1968), which has implications for their bioavailability.

The transformation of mica to HIV could explain a consistent depth-distributional trend across sandy–loamy boundaries in Florida soils north of Lake Okeechobee. The trend is that HIV comprises a large proportion of the small amount of clay (restricted mainly to sand-grain coatings) in the upper sandy horizons, but its abundance decreases relative to kaolinite in the clay fraction of the subjacent loamy horizon (Harris et al., 1987b; Harris et al., 1989). A sand-sized mica precursor in the original marine parent material would likely have weathered in place during the period when colloidal components such as kaolinite eluviated to deeper zones to form the loamy layer. Thus the transformation product (HIV) would comprise a significant proportion of the $< 50\ \mu$m fraction persisting in sandy eluvial horizons.

Minerals of the smectite group are prevalent in the clay fraction of alkaline, very poorly drained soils (Mollisols and Alfisols) on riverine landscapes of the LOB. These minimally leached environments tend to have higher activities of silica and bases that favor smectite stability. Smectite is commonly replaced by kaolinite in highly leached, acidic soils (Karathanasis and Hajek, 1983).

The mud sediment in Lake Okeechobee (Kirby et al., 1994) as well as in canals and storm water treatment areas extending south of the lake contains a significant mass fraction of the Mg silicate minerals sepiolite and palygorskite (Harris et al., 2007). Their small particle size, fibrous crystal habit (Figure 2), and low-density favor sustained resuspension. They have been found in the water column of the lake at multiple locations (Harris et al., 2007) and are therefore an abiotic source of turbidity, a water quality problem on the lake in recent years (Hanlon et al. 1998, James et al., 1997; Maceina and Soballe, 1991). Havens (1995) has inferred that light attenuation in the pelagic region of the lake is mainly due to abiotic particles, not phytoplankton as is common in many lakes. Risk of turbidity arising from sediment resuspension in Lake Okeechobee is compounded by its long fetch and shallow depth.

The provenance of sepiolite and palygorskite and of the mud sediment in which they are entrained is pertinent to restoration but has not been established. Is the mud being transported to the lake via stream flow from Miocene and Pliocene phosphatic sediments that occur upstream and that also contain dolomite, calcite, and Ca phosphates (Compton, 1997)? If so, did channelization of the Kissimmee River initiate or accelerate the delivery of Mg-rich minerals to the lake? A significant accretion of the mud occurred in the 20th century (and subsequent to Kissimmee canal construction) according to a study by Brezonyk and Engstrom (1998). An alternative origin for these minerals is precipitation within the lake environment itself.
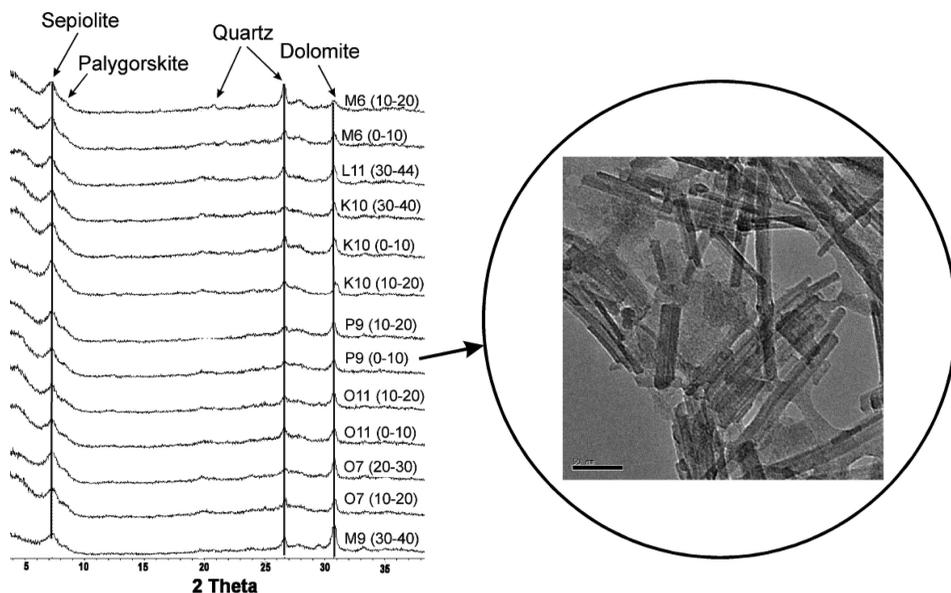
FIGURE 2. X-ray diffraction patterns (left) documenting extreme clay mineralogical unifor-mity among mud sediment samples collected at various stations and depths (cm) in Lake Okeechobee. A high-resolution transmission electron microscope image (right) documents fibrous habit and very small particle size (scale bar = 50 nm) of sepiolite in mud sediment (0–10 cm depth increment) at station P9.

Their stabilities are favored by the alkaline conditions of Lake Okeechobee (Table 2) and some areas of the Everglades (e.g., Farve et al., 2004; Olila et al., 1994). Sepiolite has been reported to form in lacustrine (Mayayo et al., 1998; Singer et al., 1998) as well as marine (Isphording, 1973) environments. The

TABLE 2. Saturation indices for Lake Okeechobee pore water as modeled from data reported by Reddy et al. (2002) using Visual MINTEQ (Gustafsson, 1997)

Station	Depth (cm)	Sepiolite E	Aragonite E	Calcite EM	Dolomite E	Apatite EM	Whitlockite M	Brushite
K8	10–20	1.51	1.22	1.36	1.97	12.41	2.81	−1.31
K10	0–10	1.59	1.41	1.56	2.37	13.51	3.48	−1.08
K10	30–40	1.93	1.17	1.32	1.83	13.27	3.40	−0.99
L11	30–44	1.31	0.87	1.01	1.27	13.11	3.39	−0.84
M6	10–20	1.87	1.49	1.63	2.48	12.83	3.00	−1.34
M9	30–40	0.88	0.83	0.98	1.25	11.28	2.18	−1.43
O7	0–10	2.07	1.69	1.83	2.92	13.15	3.15	−1.37
O7	20–30	2.28	1.36	1.51	2.31	11.95	2.46	−1.55
O11	0–10	2.10	1.57	1.71	2.68	13.53	3.44	−1.16
O11	10–20	1.12	0.76	0.9	1.09	12.55	3.06	−0.95
P9	0–10	2.28	1.66	1.80	2.87	13.66	3.50	−1.18
P9	10–20	2.93	1.72	1.86	3.03	13.68	3.49	−1.22

Note. A positive value indicates supersaturation (stability) of the mineral in the pore water. All samples were alkaline, with pH ranging from 8.5 to 9.0. E = minerals found in the Everglades; M = minerals found in manure.
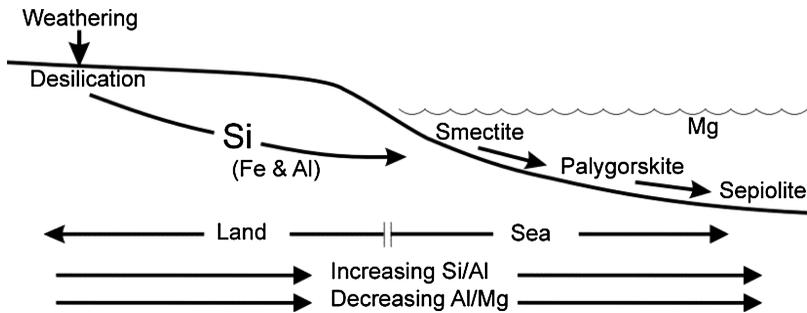
FIGURE 3. Conceptual representation of how terrestrial desilication at ocean margins can geochemically favor the formation of progressively more Mg enrichment of silicates with distance from the shore as the Al/Mg ratio declines (redrawn after Zelazny and Calhoun, 1977).

Mg silicates in Florida phosphatic sediments presumably originated in a shallow sea as terrestrial sources of Si and oceanic Mg converged (Isphording, 1973; Figure 3).

Silicates associated with carbonates of the Everglades and Florida Bay are also of uncertain origin. Manker and Griffin (1971) invoked eastern and western currents at the southern peninsula tip to explain distributions of smectite, chlorite, and illite. Aerosolic dust from Africa has also been named as a source of mineral input in south Florida (Glaccum and Prospero, 1980; Holmes and Miller, 2004; Muhs et al., 2007; Prospero, 1999; Prospero and Nees, 1987; Prospero et al., 2001). It is unlikely that HIV and kaolinite, minerals normally associated with intense acid-enhanced weathering, would have formed in situ in these young alkaline environments. Therefore, they are likely either detrital in origin or inherited from soils formed in climate of greater weathering intensity.

Biogenic forms of silica such as sponge spicules, plant phytoliths, and diatoms are ecologically significant components of aquatic systems (Struyf and Conley, 2008). They are commonly noncrystalline but can be diagenetically crystallized (e.g., to cristobalite, an SiO_2 polymorph of quartz). They serve as indicators of paleoecology and water quality changes. Sponge spicules are ubiquitous in wet soils and sediments. They occur in the mud sediment of Lake Okeechobee (Harris et al., 2007). Diatoms are conspicuous in sediment and suspended water-column particulates within the water conservation areas of the northern Everglades (Figure 4; Cooper et al., 1999; Farve et al., 2004). They occur in periphyton, an ecological indicator in shallow freshwater bodies (Dodd, 2003; McCormick and Stevenson, 1998), and have been studied in relation to nutrient gradients in Water Conservation Area 2A (Cooper et al., 1999). The abundant quantity of diatoms in Everglades suspended particulates, based on qualitative scanning electron microscopic observations (Farve et al., 2004), confirm that in their planktonic form they
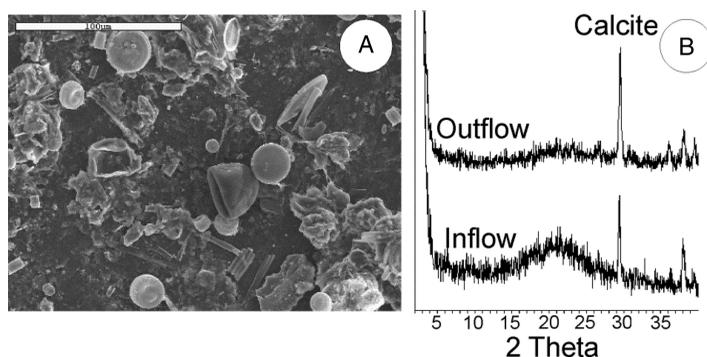
FIGURE 4. (A) Scanning electron image of pinnate and centric diatom frustules filtered from the water collected at the inflow region of an Everglades Nutrient Removal Project Storm Water Treatment Cell (Cell 4; Farve et al., 2004). Microscopic observation indicated a decline in relative abundance of frustules between inflow and outflow corresponding to a parallel decline in suspended solids concentrations. These amorphous forms of silica are more soluble than other silicates (e.g., quartz, smectite, sepiolite, palygorskite) and hence may help to preserve them via maintaining high Si activity. (B) X-ray diffraction patterns of suspended solids from Cell 4 inflow and outflow which show calcite peaks and a broad peak centered at approximately 21° 2 θ that likely arises mainly from poorly crystalline silica ($SiO_2 \cdot nH_2O$). The broad peak feature was more prominent for samples from Cell 4 inflow than outflow regions, which is consistent with the greater abundance of diatom frustules seen in the inflow particulates.

contribute to particulate P in the water column. Hence, anthropogenic and ecological factors affecting their occurrence in planktonic versus attached (i.e., benthic or periphytic) form also affect total P concentrations in the water column (Farve et al., 2004).

Oxides

Oxides have a much greater influence on soils of the Greater Everglades than their low concentrations would suggest. Sorption isotherms and selective dissolution assessments show that they significantly influence dynamics of phosphate in the LOB (Reddy et al., 1995; Reddy et al., 1998) and even in the lake itself (Moore and Reddy, 1994; Olila and Reddy, 1997). Redox sensitivity of Fe oxides can result in their redistribution in response to spatial and temporal shifts between aerobic and anaerobic conditions. These redistributions result in contrasting zones of Fe concentrations (high-chroma colors) and depletions (low-chroma colors) that are morphological indicators (redoximorphic features) of seasonal water saturation. Oxidized Fe at the sediment/water interface in lakes or flooded soils can serve as a barrier to P flux from sediment to water column that can release P as conditions become more reducing (Moore and Reddy, 1994).

Redox is not the only means by which metal oxides can be destabilized and redistributed. They have a key role in podzolization, the process by which soils of the major soil order of the LOB—Spodosols—are formed (Harris, 2001). They serve as the cementing agent of sand-grain coatings described previously. Their dissolution via organometal complexation either destabilizes grain coatings or prevents their formation, resulting in thorough eluviation of fine-textured or dissolved components. Left behind are clean quartz grains, which impart a white to light gray color when viewed macroscopically. This process produces the strongly expressed E horizons of Florida Spodosols (Harris and Hollien, 1999, 2000; Harris et al., 1995; Tan et al., 1999), which have minimal P retention capacity (Harris et al., 1996). The organometal complexes precipitate below the E horizon, within the matrix of other transported material, to form dark Spodic (Bh) horizons. Spodic horizons have a high P retention capacity despite sandy texture due to the affinity of P for organically associated Al; Fe has been largely depleted from these soils, presumably due to their occurrence on poorly drained uplands. This weathering–pedogenic process has produced an E–Bh motif of highly contrasting P retention capacities within which water tables fluctuate and lateral water movement is prevalent. Hence water table depth in relation to Bh-horizon depth affects potential of P loss from the flatwoods landscapes on which these soils predominate.

Carbonates

Calcite and aragonite ($CaCO_3$ polymorphs) weather (dissolve) and precipitate rapidly in response to biogeochemical dynamics in the Everglades. Calcite is by far the most abundant carbonate in soils and rocks of the region. It is less soluble at ambient temperatures than aragonite. Aragonite formation is associated with (but not restricted to) shell biomineralization in mollusks (Falini et al., 1996). Calcite is also a common shell component. Control of which polymorph is precipitated in shell generation has been linked to macromolecules produced by the organism (Falini et al., 1996).

Calcite of Everglades limestone is subject to dissolution from biological sources of acidity such as organic acids and CO_2 from respiration (Figure 5). Photosynthetic uptake of CO_2 by algae in the shallow water column induces the reprecipitation of the limestone-derived Ca, again as $CaCO_3$ (Gleason et al., 1974), especially noticeable in periphyton mats. This solar-driven process could maintain diffusion gradients of Ca from limestone (where exposed on the lake bottom) to photic zones thereby transforming calcite from hard rock to gelatinous masses of periphyton (subject to gas entrapment and flotation) or epiphytic encrustations. Periphyton mats house suites of microorganism whose biological responses to environmental conditions potentially foster the precipitation or dissolution of calcite—and hence the growth or disintegration of the mat. Relatively thick layers of fine secondary
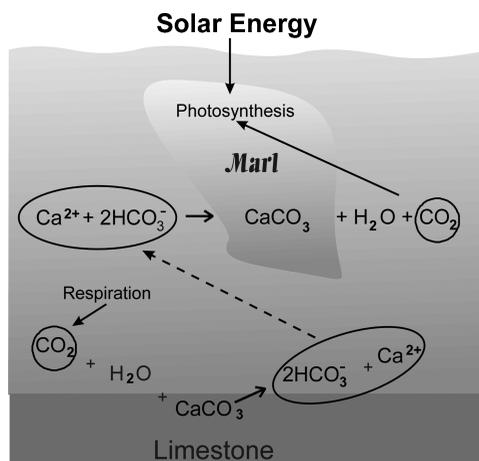
FIGURE 5. Schematic representation of marl formation in the Everglades.

calcite (marl) have accumulated in the Everglades where vegetation such as sawgrass is not well established, particularly areas that experience periodic unflooded surfaces (Davis et al., 2005).

The role of periphyton in P dynamics has received considerable attention in the Everglades and elsewhere (e.g., Dodd, 2003; Gaiser, 2008; McCormick and O'Dell, 1996; McCormick et al., 2000; McCormick et al., 1996; McCormick et al., 2001; McCormick et al., 2006; Scinto, 1997). Periphyton is prevalent in the least impacted areas of the Everglades but its abundance apparently decreases with increasing degree of P impact (Browder et al., 1994; Gaiser et al., 2005). A mesocosm study showed a decline in epiphytic biomass and floating mat coverage in response to high P loading (McCormick et al., 2001). This P-induced perturbation apparently entails an ecological response in which biogeochemical dissolution of calcite could be a factor.

Formation of periphyton mats amounts to at least temporary immobilization of P via the agglomeration of microbes, which in planktonic form would contribute to particulate P in the water column (Farve et al., 2004). Sorption of P onto the periphytic calcite has also been invoked as a P immobilization mechanism (Dodd, 2003). However, P sorption on marl soils and limestone of the southern Everglades was shown to be more strongly controlled by silicate clay than by carbonates (Zhou and Li, 2001). Also, particulate P was strongly associated with organic matter but not with calcite in an Everglades Nutrient Removal Project storm water treatment cell (Farve et al., 2004). Coprecipitation of phosphate and carbonate is a commonly inferred mechanism based on their simultaneous disappearance from solution when pH is artificially elevated (e.g., Dodd, 2003; Otsuki and Wetzel, 1972).

Unequivocal documentation of that mechanism requires solid-state evidence of Ca phosphate within the matrix of periphyton.

The aggregate of data and observations suggest that most P associated with periphyton abides in organisms—not surprising in a highly P-limited system. For example, Scinto and Reddy (2003) found the > 83% of P incorporated in periphyton after 12-hr incubation was in biotic form. Nevertheless, calcite precipitation to form the inorganic matrix is still an ecologically important process that indirectly affects P movement in the Everglades. Aquatic humic substances can inhibit calcite crystal growth rate via mechanisms reviewed by Reddy and Hoch (2000). Inhibitory effects have been experimentally documented using actual humic substances collected in the Everglades (Hoch et al., 2000). Possibly, effects of elevated inorganic P concentrations could influence calcite precipitation and periphyton stability via its effect on microbial ecology and the resultant production and speciation of humic substances.

A marl-like carbonatic sediment (aka lime mud) occurs extensively in Florida Bay (Stockman et al., 1967). Macroalgae (e.g., *Penicillus*, *Hallimeda*) have been implicated as a source for this sediment (Lodge, 2005). These algae precipitate $CaCO_3$ in a bio-mineralization process (Wefer, 1980) whereby the carbonate provides them with stalk-like rigidity and plant-like appearance. The carbonate minerals accumulate as sediment when the algae die.

Relatively high levels of As, sometimes exceeding 50 mg kg^{-1}, have been found in Everglades carbonatic materials (Chen et al., 2000, 2002; Ma et al., 1997). These materials include marl soils as well as limestone that has undergone rock plowing for vegetable production. The forms and origin of this As are uncertain but evidence suggests that it is from natural sources. Possibly the As levels are the result of bioaccumulation in the marine environments where the limestone originated (Chen et al., 2002; Cullen and Reimer, 1989). Arsenic may also be associated with Fe sulfides, as evidence from the upper Florida aquifer has strongly suggested (Price and Pichler, 2002). Ecological effects of this carbonate-associated As are not an issue if it is a natural and immutable part of the system. However, the high concentrations warrant attention with respect to potential human toxicological effects. Oxidative mobilization of As in limestone during aquifer water storage and recovery is an additional concern (Arthur et al., 2002, 2005; Price and Pichler, 2002, 2006).

The origin of dolomite [$CaMg(CO_3)_2$] in the Greater Everglades is far less obvious than that of calcite. It occurs abundantly and ubiquitously along with other Mg-rich minerals (sepiolite and palygorskite) in the mud sediment and suspended particulates of Lake Okeechobee and water conveyances of the northern Everglades (Harris et al., 2007). There is no evidence that it forms secondarily in periphyton, though its microbially mediated precipitation has been confirmed in the laboratory (Vasconcelos et al., 1995) and in lacustrine settings (del Cura et al., 2001; Wright, 1999). Dolomite is common in some
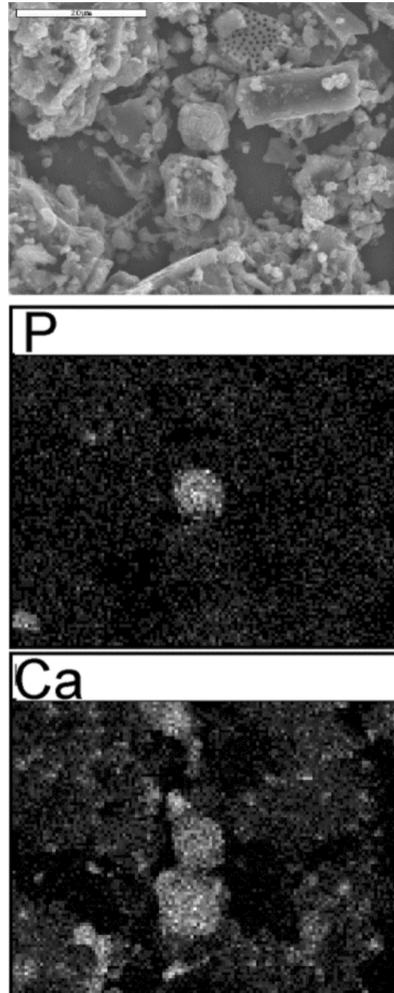
FIGURE 6. Secondary electron image (top) of silt from Lake Okeechobee mud sediment (scale bar = 20 μm; Reddy et al., 2002). Below this image are elemental dot maps showing zones of elevated P (middle) and Ca concentrations based on Kα characteristic X-ray emissions. Two zones of elevated P concentrations are evident, both corresponding to Ca enrichment. However, P is not associated in a diffuse way with Ca, but only as localized concentrations. Similar Ca-P associations were confirmed for five other silt fractions of Lake Okeechobee mud samples that were analyzed (Harris et al., 2007).

Florida carbonate rocks (Randazzo, 1997) as well as the Florida phosphoritic deposits on the western fringe of the Greater Everglades, which also contain sepiolite and palygorskite. The dolomite–sepiolite–palygorskite association in Greater Everglades mud, along with common occurrence of discrete Ca-P particles in the mud (Harris et al., 2007; Figure 6), amounts to circumstantial evidence that these minerals could be detrital derivatives of the phosphoritic deposits.

Phosphates

Reports of phosphate-mineral detection are rare in Greater Everglades soils and sediments despite the environmental impacts of P (e.g., Steinman et al., 1999). Documented formation of stable P minerals would have favorable implications for ecological restoration. It could mean a decline in dissolved inorganic P concentrations once anthropogenic inputs are reduced to sustainable levels. Failure of phosphate to stabilize, on the other hand, portends a more dismal trajectory in the absence of drastic remediation efforts.

Phosphate minerals identified via crystallographic techniques in the Greater Everglades (Table 1) generally reflect the environment in which they were found. Organic-matter-rich sediment, influenced by dairy barn drainage in the LOB, contained the minerals vivianite (ferrous phosphate) and apatite (Ca phosphate; Harris et al., 1994). The presence of vivianite confirmed both a highly reduced chemical state of the sediment and a P influx from the dairy barn. The apatite was also likely related to dairy operations. Hence both minerals are indicators of ecological perturbation.

Another site of apatite occurrence is historically-farmed carbonatic soils of the Everglades Hole-in-the-Donut (HID) region (Zhang et al., 2001). The fertilizer applied in the region has been implicated as at least one explanation for the Brazilian pepper infestation (Li and Norland, 2001). The HID apatite indicates that P stability can be achieved or maintained (if the fertilizer happened to be rock phosphate) over a few decades. Apatite precipitation can be nucleated by $CaCO_3$ mineral surfaces, as evidenced by a dark patina found on oyster shells in ancient shell mounds that once served as prehistoric refuse piles in coastal Florida (Harris, 2002). The phosphate presumably came from food wastes such as fish bones.

Phosphate minerals were not detected in Lake Okeechobee mud sediment by X-ray diffraction, likely because of insufficient concentrations (Harris et al., 2007). However, Ca-P particles were commonly observed using scanning electron microscopy in conjunction with energy dispersive X-ray fluorescence elemental microanalysis (EDX) (Figure 6) leaving open the possibility that apatite is present. All EDX observations of silt-sized particles from the mud showed that P was not associated with Ca in a diffuse way but only as isolated discrete particles or zones. These observations show that P is not significantly associated with carbonates in the mud but rather that it exists as an independent Ca-P phase. It is possibly an allochthonous or autochthonous detrital component. Provenance of this Ca-P phase is pertinent to Lake Okeechobee restoration. Is it a product of agricultural P or is it reworked geologic P transported to the lake via stream entrainment?

Crystallization of calcium phosphate minerals can be inhibited by dissolved organic C (Amjad and Reddy, 1998; Brown, 1981; Cao and Harris, 2008; Cao et al., 2007; Inskeep and Silvertooth, 1988) and inorganic ions such as Mg^{2+} and CO_3^{2-} (Cao and Harris, 2008; Ferguson and McCarty,

1971; Salimi et al., 1985). Effects include reduced rate of precipitation and elevated solubility relative to the crystalline analogue. Organic acids apparently suppress Ca phosphate crystallization by adsorbing onto the newly formed nuclei. Magnesium inhibition is due to substitution for Ca, thereby preventing long-range order development and crystal stability. Its presence in solution can also result in the precipitation of Mg-substituted whitlockite (Cao and Harris, 2008). Carbonate interferes with crystallization by substituting for PO_4^{3-} or by preemptive precipitation as $CaCO_3$. The joint presence of Mg^{2+} and CO_3^{2+} at high pH (> 8.5) can enable Ca phosphate precipitation due to the formation of the highly stable neutral species $MgCO_3$ (aq; Cao and Harris, 2008).

Sulfides and Sulfates

Sulfides and sulfates reflect the redox condition of the parent material in which they form. They commonly occur at low concentrations but are occasionally detected in the Greater Everglades or vicinity (e.g., Harris et al., 2007; Syslo et al., 1988; Figure 7). The chemistry and mineralogy of sulfur is driven by the drastic changes in its ionic radius (r) over the wide range of oxidation states that it assumes (S^{6+} with r = 0.035 nm; S^{2-} with r = 0.185 nm). The crystallographic result is that in the oxidized state it is a cation in the structure coordinated by O atoms whereas in the reduced state it is the anion that coordinates a metal (commonly Fe^{2+}).

Oxidation of sulfides and elemental S to sulfates produces sulfuric acid. Draining sediments that contain high sulfide concentrations can lead to extreme acidification (e.g., acid mine drainage; Fanning et al., 2002) unless a neutralizing component such as $CaCO_3$ is present. Acid-hydrolytic weathering associated with the extreme acidity is termed *acid sulfate weathering*. The chemical collision between acid sulfate weathering and subjacent $CaCO_3$ produces gypsum ($CaSO_4 \cdot 2H_2O$; Fanning et al., 2002; Syslo et al., 1988). Dominance of fresh water wetlands (low natural S inputs) and ubiquitous $CaCO_3$ have spared the Everglades from experiencing an oxidation-related acid-sulfate-weathering problem.

Sulfur minerals are involved in the dynamics of Hg. A link has been established between Hg methylation and chemical reduction of sulfate from fertilizers originating from the Everglades agricultural area (Bates et al., 2002). Sulfate-reducing bacteria can mediate the production and ultimate bioaccumulation of toxic methylmercury (CH_3Hg^+) (Khan and Tansel, 2000; Rumbold et al., 2008). Factors promoting or inhibiting Hg^{2+} methylation have been elucidated in a number of studies (e.g., Aiken et al., 2001; Ravichandran et al., 1998, 1999; Reddy and Aiken, 2001; Reddy et al., 1996). Details of the biogeomchemistry underlying the linkages of S, dissolved and particulate organic C, and Hg methylation, along with ecological implications, are given in other sections of this review.
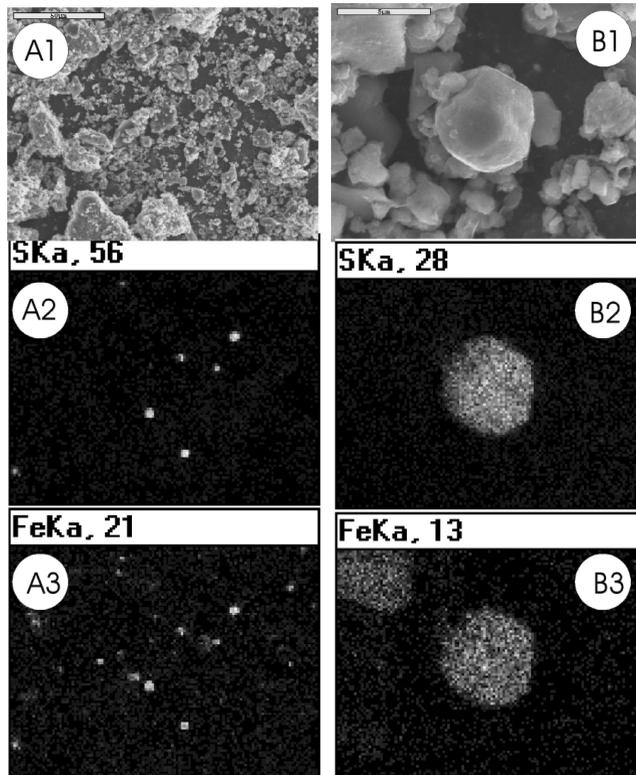
FIGURE 7. Secondary electron images (A1 and B1) and elemental dot maps (A2, A3, B2, B3) of silt from sample of Okeechobee mud sediment core (Station 7 = 20–30 cm; Reddy et al., 2002). The A sequence (scale bar = 50 μm) shows widespread correspondence between S (A2) and Fe (A3), consistent with the presence of FeS_2 minerals (e.g., pyrite) that were indicated by XRD data. The B sequence (scale bar = 5 μm) shows what appears to be a subhedral pyrite crystal, with S (B2) and Fe (B3) concentrations verified by the dot maps.

The fate of As in the Everglades may also be linked to sulfides if this element exists in Everglades carbonates in association with trace amounts of Fe sulfides, as has been documented in aquifer limestone (e.g., Jones and Pichler, 2007; Price and Pichler, 2002). Arsenic associated with sulfides would tend to be released upon oxidation.

Oxalates

The calcium-oxalate minerals whewellite and weddellite have been reported to occur in soils (e.g., Graustine et al., 1977), though rarely, and generally in barely detectable quantity. Weddellite has been detected in Everglades muck soils (Griffin et al., 1984; Sawyer et al., 1988). Oxalic acid is a microbial metabolic product that can promote mineral weathering and react with Ca to form these stable carbon-bearing minerals.

RESTORATION IMPLICATIONS

Minerals of the Greater Everglades are redistributed at various scales via biogeochemical and hydrodynamic processes. Biogeochemical redistribution is generally cyclic in response to diurnal and seasonal effects. Hydrodynamic redistribution tends to be unidirectional. Perturbations that disrupt or accelerate either mode of redistribution have the potential to alter ecological communities and degrade water quality. Such perturbations include inhibited precipitation of calcite in periphyton mats, sulfide formation from agricultural sulfate with concomitant Hg methylation, and accelerated entrainment of readily suspended minerals via construction of canals. Hence, knowledge of mineral distributions and dynamics of redistributions directly bear upon the efficacy of restoration strategies for Lake Okeechobee and the Everglades.

Direct abiotic linkage between P and calcite should not be overestimated. In the battle for P between life and calcite, life usually wins in a P-limited environment. However, calcite that is precipitated via algal photosynthesis indirectly fosters P accumulation within microbial residents of periphyton and epiphytic encrustations. Phosphorus incorporated in these agglomerated (nonplanktonic) organisms is at least temporarily removed from the water column and rendered less mobile. Mechanisms responsible for the formation or loss of periphyton are a core aspect of Everglades ecology. Calcite solubility in relation to microbial responses to environmental perturbations may be a component of those mechanisms.

The nature and rate of Ca-P interactions bear on the rate of ecological recovery in the Greater Everglades once P incursions are reduced to sustainable levels. Formation of stable Ca phosphates would have favorable implications if the P associated with them proved to be minimally bioavailable. The presence of apatite in heavily fertilized HID fields confirms that it can persist in the Everglades. An important unresolved question is whether the HID apatite or the Ca-P of Lake Okeechobee mud formed in place or were introduced as fertilizer (rock phosphate) or sediment (e.g., from the Kissimmee River), respectively. Recent research has shown that P concentrations are significantly higher in tree islands than in surrounding marsh, possibly due to bird rookeries (Wetzel et al., 2009). These islands would be a promising place to search for evidence of Ca-phosphate formation using selective dissolution in conjunction with solid-state assessments.

The consistent association of Mg-bearing silicates and carbonates in Lake Okeechobee and the northern Everglades suggest that they originated from the same source. These minerals are prevalent in the mud sediments of the lake and are suspended in the water column as an abiotic source of turbidity. Mineralogy of the mud sediment is similar to that of geologic phosphate deposits on the western fringe of the LOB. These deposits are a possible source of the mud. Mitigation efforts focused exclusively on

P-induced biogeochemical processes do not address the origin or effects of these minerals. Ecological management issues such as turbidity control and suitability of dredging are related to mud-sediment provenance and rate of accumulation.

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