

Sedimentary iron cycling in waterways associated with acid sulfate soils

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Abstract

This study describes the in-situ geochemical transformations of sedimentary Fe in waterways associated with coastal lowland acid sulfate soils (CLASS) (Figure 1). The surface water was acidic (pH 3.26 – 3.54) and Fe^{III}-rich (27 – 138 μM) with low molar Cl:SO₄ ratios (0.086 – 5.73). The near-surface benthic sediments had high concentrations of oxalate-extractable Fe(III) due to schwertmannite precipitation. Subsurface sediments contained abundant pore-water HCO₃⁻ (6 – 20 mM) and were reducing (Eh < -100 mV) with pH 6.0 – 6.5. Reducing conditions caused reductive dissolution of schwertmannite (buried during sediment accretion). As a consequence, pore-water Fe^{II} concentrations were high (> 2 mM) and were constrained by precipitation-dissolution of siderite. The near-neutral, reducing conditions promoted SO₄²⁻-reduction and the formation of acid-volatile sulfide (AVS) comprising disordered mackinawite. In the presence of abundant pore-water Fe^{II}, precipitation-dissolution of disordered mackinawite maintained very low (i.e. undetectable) S^{-II} concentrations. Such low concentrations of S^{-II} caused slow rates of pyrite formation, thereby resulting in low pyrite concentrations (< 300 μmol g⁻¹ as Fe). The retarded rates of pyrite formation (i.e. conversion of disordered mackinawite to pyrite during diagenesis) allowed accumulation of relatively large concentrations of disordered mackinawite (up to 590 μmol g⁻¹ as Fe).

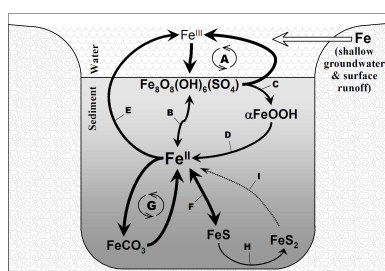


Figure 1. Conceptual model of Fe dynamics in sediments of CLASS-associated waterways. (A) precipitation-dissolution of schwertmannite (Fe₈O₈(OH)₆(SO₄)), (B) reduction-oxidation of schwertmannite, (C) schwertmannite conversion to goethite (αFeOOH), (D) reductive dissolution of goethite, (E) Fe^{II} diffusion/oxidation (F) precipitation-dissolution of disordered mackinawite (FeS), (G) precipitation-dissolution of siderite (FeCO₃), (H) formation of pyrite (FeS₂), (I) partial oxidation of pyrite.