



Phosphate retention by Fe(III)- and Ca-phases formed upon oxygenation of anoxic groundwater

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Introduction. Exfiltration of anoxic nutrient-rich groundwater into surface waters leads to the formation of Fe(III)-precipitates that can retain phosphate (P). Over time, fresh Fe(III)-precipitates may transform into crystalline solids and P released again^{1,2}. The concomitant CO_2 outgassing and pH increase promote formation of Ca-phosphate or -carbonate that can also sequester P³.

Objective. Study the complex interdependent effects of key solutes (Ca, Mg, P, silicate-Si) on the structure of fresh Fe(III)-precipitates, their transformation over time, the formation of Ca-phases, and consequences for P removal and retention in environmental systems.

METHODS

Aging experiments were performed with fresh P-containing Fe(III)-precipitates to study their transformation, Ca-precipitate formation and P retention over 100 d in synthetic "natural" waters. The fresh precipitates were formed by oxidation of 0.5 mM Fe(II) in 8 mM bicarbonate-buffered solutions at pH 7.0, with 0.15 mM or 0.025 mM P (P/Fe 0.30 or 0.05), with 8 mM Na, 4 mM Ca, or 4 mM Mg as electrolyte cation, and without or with 0.5 mM Si. They consisted of mixtures of amorphous (Ca)Fe-phosphate ((Ca)FeP), ferrihydrite (Fh), and lepidocrocite (Lp).

Dissolved P fractions over time in Na, Mg, Ca, Na+Si, Mg+Si, and Ca+Si electrolyte at P/Fe 0.30 and 0.05 in. Released P fractions decreased along 3 sequences (i) Na > Mg > Ca, (ii) no Si > with Si, and (iii) P/Fe 0.3 > P/Fe 0.05. In the Ca electrolytes, dissolved P decreased again after ~50 days at P/Fe 0.30 due to Ca-phosphate precipitation and after ~3 days at P/Fe 0.05 due to Ca-carbonate formation.



After synthesis of the precipitates, the suspension pH was raised to 7.9 by purging with air to outgas CO₂, and the suspensions were aged for 100 d in the dark at 25°C, with regular solid and solution sampling. Solutions were analyzed by inductively coupled plasma-mass spectrometry (ICP-MS). Solids were characterized using Fe K-edge extended X-ray absorption fine structure (EXAFS) spectroscopy, X-ray diffraction (XRD), and transmission electron microscopy with energy dispersive X-ray spectroscopy (TEM-EDX).



CONCLUSIONS

Ca (and to lesser extent Mg) stabilizes Fe(III)-phosphate against transforming into ferrihydrite or lepidocrocite.

Si inhibits the initial formation of lepidocrocite and stabilizes Fe(III)phosphate/ferrihydrite mixtures against transformation over time. Na Mg Ca NaSi MgSi CaSi

Fe K-edge EXAFS results for precipitates at P/Fe 0.30, indicating the fractions of Fe in lepidocrocite (Lp), ferrihydrite, (Fh), and amorphous (Ca-)Fe(III)-phosphate ((Ca)FeP). In the Mg and Ca electrolytes, transformation of (Ca-)FeP into Fh and Lp is slowed down relative to Na electrolyte. With Si, initial precipitates consist only of (Ca)FeP and Fh and transformation of (Ca-)FeP is inhibited.

XRD results for precipitates in Ca and Na electrolytes at P/Fe 0.30 (Calc: calcite, ACP: am. Ca-phosphate). Lp crystallinity increased more in Na than Ca electrolyte. ACP was identified in Ca electrolyte after 100 d.





Ca-phosphate can sequester P released from Fe(III)-precipitates at high Ca and P concentrations, and Ca-carbonate can co-precipitate released P at high Ca and low P concentrations.

This study documents the complex interdependent effects of Ca, Mg, P and Si on Fe(III)- and Ca-precipitate formation and transformation in natural waters and consequences for P retention, and highlights the important roles of Ca and Si in limiting P release into solution over time.

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TEM-EDX images of fresh (F) and 100-d aged (A) precipitates in Na, Ca, and Ca+Si electrolytes at P/Fe 0.30. Fresh precipitates consist of spherical (Ca)FeP cores surrounded by a shell of Fh (Ca+Si) or by Lp platelets (Na, Ca). In Na and Ca suspensions, aging led to (Ca)FeP transformation into Lp and (in Ca electrolyte) ACP formation. In Ca+Si electrolyte, aging did not induce detectable changes .

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