

## Citrate impairs the diffusion of phosphate into goethite

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### Objective and Methodologies

Root excreted citrate has been shown to mobilise phosphate ( $\text{PO}_4$ ) in the rhizosphere by competition for sorption sites of Fe- and Al (oxy)hydroxides. We hypothesize that citrate additionally impairs the diffusion of  $\text{PO}_4$  into micropores ( $<2$  nm) of goethite in the rhizosphere.

We studied the  $\text{PO}_4$  sorption kinetics of a synthetic goethite and, to be closer to soil conditions, a goethite that was coated with dissolved organic matter (DOM). Sorption kinetics were determined in batch systems (three weeks, pH5). We varied the order of addition of citrate and  $\text{PO}_4$  at equimolar concentrations (500  $\mu\text{M}$ ). In addition, we studied the  $\text{PO}_4$  sorption kinetics in the absence of citrate. We analyzed our samples for specific surface area, porosity and  $\zeta$ -potential prior and after  $\text{PO}_4$  and citrate sorption.

### Results and Discussion

Both,  $\text{PO}_4$  and citrate diffused into micropores of pure and DOM-coated goethite, causing a partial clogging of these pores. While the clogging of micropores by  $\text{PO}_4$  has recently been observed (Makris et al., 2004), no evidence for citrate-induced micropore clogging exists in literature yet.

The diffusion of  $\text{PO}_4$  into the micropores of pure and DOM-coated goethite during three weeks of sorption was impaired in the presence of citrate by up to 100%. The competition of  $\text{PO}_4$  with citrate for micropore diffusion depends on the order of addition of both ions. A greater diffusion limitation of  $\text{PO}_4$  occurred when citrate was added before  $\text{PO}_4$ .

### Conclusion

Our results indicate that  $\text{PO}_4$  and citrate not only compete for sorption sites but also for diffusion into goethite particles. This mechanism might reduce the  $\text{PO}_4$  fixation in micropores of Fe (oxy)hydroxides in the rhizosphere and thus enhance the availability of  $\text{PO}_4$  to plants following the exudation of low molecular weight organic acids.

### Reference

Makris, K.C. et al., (2004), *Environ. Sci. Technol.* **38**, 6590-6596.

## Nucleation and growth of manganese oxide films

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Manganese oxide in surface and ground waters dissolves and precipitates in response to natural and anthropogenic cycling of aqueous pE and pH conditions. When precipitating, the manganese oxides form thin coatings on mineral surfaces. Although the thin coatings affect the overall rates of manganese dissolution and precipitation, the current understanding of the active mechanisms is limited.

In the current work, we use atomic force microscopy to investigate how surface morphology, manganese concentration, and substrate chemistry affect the manganese oxide film's characteristics such as orientation, height, and shape. The  $(10\bar{1}4)$  surfaces of  $\text{MnCO}_3$ ,  $\text{MgCO}_3$ , and  $\text{CaCO}_3$  are used as substrates. Aqueous  $\text{Mn}^{2+}$ , which serves as the source material for the manganese oxide film, derives in some experiments from  $\text{MnCO}_3$  dissolution and in others from external addition of  $\text{Mn}^{2+}(\text{aq})$ .

We find that the growth of manganese oxide films depends on substrate morphology, i.e., terraces versus highly stepped surfaces. Rhombohedral two-dimensional manganese oxide islands grow on terraces of  $\text{MnCO}_3$ . The islands are rotated  $90^\circ$  relative to the crystallographic axis of the underlying carbonate. Island heights self-limit between 2 and 3 nm depending on reaction conditions. In comparison to island height, the lateral dimensions observed begin at 60 nm and grow steadily to several microns before the islands begin to collide and coalesce. The two-dimensional islands do not grow over substrate steps. In contrast to terraces, highly stepped surfaces result in the growth of manganese oxide film along steps. The areal growth rate in regions of highly stepped surfaces is three times faster than that on terraces.

Comparison studies done with  $\text{MgCO}_3$  and  $\text{CaCO}_3$  show that the former also promotes heteroepitaxial growth whereas the latter does not. This difference is explained by the relative bond length mismatch between the structures of the carbonate substrates and the atomic structure of the Mn oxide film. A free energy model is also presented to explain why the heights of the Mn oxide islands self-limit.

These results provide an improved basis both for the development of predictive models of contaminant fate and transport and for the modelling of hydraulic flow through carbonate aquifers.