

Fast ligand controlled goethite dissolution kinetics under non-steady state conditions in the presence of siderophores and oxalate

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Ligand controlled dissolution of goethite

Non-steady state weathering processes are commonly observed in natural systems. Iron stressed plants, for instance, mobilize iron from poorly soluble iron (hydr)oxides by diurnal pulse-release of siderophores into the rhizosphere.

This study investigates the mechanism of non-steady state dissolution of goethite (α -FeOOH) in the presence of oxalate and pulsed additions of the microbial siderophore desferrioxamine B (DFO-B). All experiments for this study were carried out in batch reactors at pH 6 with a constant oxalate concentration of 100 μ M. In a series of batch experiments, spikes of 40 μ M DFO-B were added to the oxalate-goethite system after defined initial pre-equilibration times, whereby in each batch the addition times of the spike were different. In another experiment, multiple spikes of DFO-B were successively added to one single batch. The additions of the siderophore spikes led to very fast dissolution reactions with subsequent steady state dissolution. It was observed that the magnitude of the fast dissolution reaction was a function of the pre-equilibration time of the oxalate-goethite system. The experiment involving multiple spikes of DFO-B revealed that the fast dissolution reaction occurred reproducibly with every added DFO-B spike.

In analogous experiments, oxalate was replaced by malonate and citrate, respectively. Similar results were observed, verifying that this effect is not exclusive to oxalate.

Discussion and conclusion

Due to the low solubility of goethite at pH 6 little dissolution of iron is observed in the oxalate-goethite system. However, the addition of DFO-B causes a disequilibrium in the system that leads to fast dissolution of iron. Since the magnitude of the fast dissolution reaction is a function of the pre-equilibration time, it seems likely that the adsorbed oxalate destabilizes the surface sites of the goethite in a slow reaction that leads to the accumulation of labile iron centers at the mineral surface. Thus, the observed fast dissolution corresponds to the release of labile iron which is triggered by the disequilibrium caused by the addition of DFO-B.

Identifiability Analysis of a Diagenetic Model

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Introduction

Due to the large base of scientific knowledge, the description of environmental systems is often based on complex simulation models, which contain parameterizations of a large number of processes. The parameters of such models are typically not identifiable from a data set available for a specific system. In such situations, identifiability analysis techniques are useful in order to find identifiable subsets of parameters and to gain insight into the degree of non-identifiability (Brun et al., 2001). Such techniques have not been applied to diagenetic models so far.

Results

Based on such techniques, it has been shown that for a diagenetic model of Lake Zug, Switzerland (Dittrich et al., 2002), an exceptionally large number of parameters (more than 20) can be identified from the available data. This is due to the availability of a comprehensive data set consisting of measured sediment profiles of 9 dissolved (pH, HCO₃⁻, NH₄⁺, HPO₄²⁻, SO₄²⁻, Mn²⁺, Fe²⁺, CH₄, Ca²⁺) and 6 particulate (POC, PON, MnO₂, FeOOH, CaCO₃, FeS) substances. Major uncertainties remain with respect to time-dependent boundary conditions at the water-sediment interface (due to the lack of measurements over the 200 year simulation period), to oxic and denitrifying mineralization rates (due to the lack of oxygen and nitrate at the sediment water interface during the past 50 years), to the precipitation rates of vivianite and manganese carbonate (due to the absence of measurements of these compounds), and to joint determination of maximum degradation rates and half-saturation concentrations (due to the small spatial variability of important substrates).

Conclusions

It is shown that identifiability analysis techniques are very useful in order to determine the lack of uniqueness of the values of model parameters and the conditional dependence of fitted parameters of the values of parameters that were kept constant during the fit. The determination of effective mineralization rates of different mineralization processes can be a first step towards a more universal mineralization model that considers the density of the bacteria responsible for mineralization.

References

- Brun, R., Reichert, P. and Künsch, H.R. (2001), *Water Resources Research* 37(4), 1015-1030.
Dittrich, M., Reichert, P. and Wehrli, B., this conference.