

## Iron isotope fractionation during goethite dissolution by oxalate

J. G. WIEDERHOLD<sup>1,2</sup>, S. M. KRAEMER<sup>1</sup>, N. TEUTSCH<sup>2</sup>,  
 A. N. HALLIDAY<sup>3</sup>, AND R. KRETZSCHMAR<sup>1</sup>

<sup>1</sup>Institute of Terrestrial Ecology, ETH Zurich, Switzerland

<sup>2</sup>Isotope Geology and Mineral Resources, ETH Zurich, CH

<sup>3</sup>Department of Earth Sciences, University of Oxford, UK  
 (wiederhold@env.ethz.ch)

Goethite ( $\alpha$ -FeOOH) is one of the dominant Fe oxide minerals in soils and sediments. Its dissolution behavior is closely connected to important biogeochemical processes (e.g., plant nutrition, weathering, pedogenesis, bacterial respiration). In the dark, oxalate dissolves goethite by a ligand-controlled process releasing Fe(III)-oxalate complexes to solution. In the presence of light, oxalate dissolves goethite by a photoreductive mechanism releasing Fe(II) to solution.

We studied Fe isotope fractionation during goethite dissolution by 0.5M HCl (proton-promoted) and by oxalate at pH 3 in dark and light conditions. Samples were taken at different time steps (5 min to 95 d), centrifuged, filtered (0.025  $\mu$ m) and measured by MC-ICPMS (Nu Plasma).

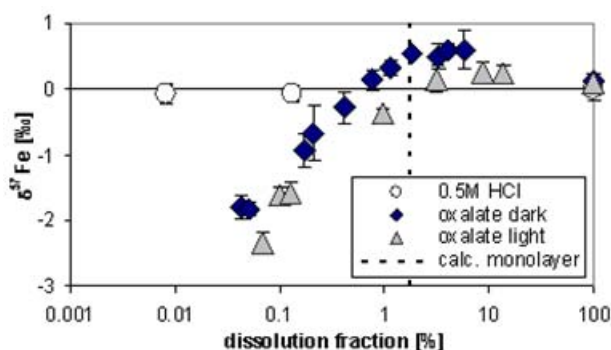


Figure 1: Fe isotopes in solution during goethite dissolution  $\delta^{57/54}\text{Fe}$  vs. bulk goethite, error bars indicate 2SD of replicate measurements (n = 3-6), 100% dissolution in 6M HCl

The 0.5M HCl experiment shows that proton-promoted dissolution does not fractionate and that our goethite is not isotopically zoned (Fig.1). In contrast, Fe isotopes are strongly fractionated during both ligand-controlled and photoreductive oxalate dissolution. The first dissolution fractions are enriched in  $^{54}\text{Fe}$ , indicating a kinetic isotope effect. However, at later dissolution fractions in the dark experiment the solution exhibits  $\delta^{57}\text{Fe}$  values  $\sim 0.5\text{‰}$  heavier than the goethite. We speculate that this is due to equilibrium isotope fractionation between Fe(III)-oxalate complexes (stronger bonding environment) and the mineral surface.