

Isotope exchange and Fe(II)-catalyzed ligand-controlled dissolution of iron(hydr)oxides in the carbonate system

JAGANNATH BISWAKARMA^{1,2*}, KYOUNGLIM KANG³, WALTER D. C. SCHENKEVELD⁴, STEPHAN M. KRAEMER³, JANET G. HERING^{1,2,5} AND STEPHAN J. HUG¹

¹Eawag, Swiss Federal Institute of Aquatic Science and Technology, Switzerland

²ETH, Swiss Federal Institute of Technology Zurich, Switzerland

³Dept. of Environmental Geosciences, University of Vienna, Austria

⁴Faculty of Geosciences, Utrecht University, the Netherlands

⁵EPFL, Swiss Federal Institute of Technology Lausanne, Switzerland

(*correspondence: jagannath.biswakarma@eawag.ch)

Iron acquisition through ligands (e.g. siderophores) is a key process for plants and micro-organisms in Fe-limiting conditions. Recently, we demonstrated that submicromolar concentrations of Fe(II), in anoxic conditions at circumneutral pH, led to accelerated ligand-controlled dissolution of iron(III)(oxyhydr)oxides. The catalytic effect of Fe(II) was ascribed to electron transfer (ET) to surface Fe(III) and accelerated detachment of surface Fe(III)-ligand complexes. However, the role and extent of ET on the mineral surface before and during accelerated dissolution remained unclear. Here we addressed these questions by performing experiments under anoxic conditions with lepidocrocite and goethite and varying concentrations of Fe(II), ⁵⁷Fe(II), and bacterial siderophore desferrioxamine (DFO-B). Most experiments were performed at pH 7.0 in bicarbonate-CO₂-buffered suspensions.

Our results show that addition of DFOB after ⁵⁷Fe(II) led to accelerated detachment of ⁵⁶Fe(III) from lepidocrocite and release of already adsorbed/exchanged ⁵⁷Fe into the solution. A kinetic model considering exchange of charge between ⁵⁷Fe(II) and ⁵⁶Fe(III) on the surface can explain our experimentally observed kinetics of the formation of dissolved ⁵⁷Fe and ⁵⁶Fe in solution.

Interfacial Fe(II)/Fe(III) ET plays a crucial role in many natural processes, for example, in Fe cycling and bioavailability, and in incorporation and release of trace metals. This study contributes to the quantification of ET from added Fe(II) to the surface of iron (hydr)oxides and of the acceleration of overall non-reductive dissolution by traces of Fe(II) in anoxic environments.