

Photoreductive dissolution of lepidocrocite in the presence and absence of siderophores

S.M. KRAEMER¹, P. BORER^{2,3}, B. SULZBERGER³,
S.J. HUG³ AND R. KRETZSCHMAR²

¹Department of Environmental Geosciences, University of Vienna, Austria (stephan.kraemer@univie.ac.at)

²Institute of Biogeochemistry and Pollutant Dynamics, ETH Zurich, Switzerland

³Eawag, Swiss Federal Institute of Aquatic Science and Technology, 8600 Dübendorf, Switzerland

Efficient iron acquisition is a prerequisite for survival in marine and terrestrial ecosystems that are characterized by low iron bioavailability such as marine surface waters and calcareous soils. To overcome this constraint, prokaryotic and some eukaryotic organisms use high affinity iron acquisition mechanisms involving the synthesis and exudation of iron specific ligands, the so called siderophores. Marine phytoplankton that is responsible for much of the marine primary productivity does not exude siderophores and is not efficiently taking up iron-siderophore complexes.

The generation of dissolved Fe(II) by photochemical reactions at Fe(III)(hydr)oxide surfaces may potentially increase the availability of iron to marine phytoplankton. We have shown previously that siderophores may promote such photoreductive dissolution mechanisms. Here, we report the rates of photoreductive dissolution of lepidocrocite (γ -FeOOH) in the absence and presence of siderophores at various pH ranges. Fe(II) release and hydrogen peroxide generation were observed during lepidocrocite dissolution. We interpreted the generation of hydrogenperoxide as a consequence of the light induced oxidation of coordinated hydroxyl groups at the mineral surface and formation of \cdot OH radicals. This interpretation was supported experimentally using radical scavengers and conceptually using quantitative kinetic models.

The wavelength dependence of photon flux normalized photodissolution rates were also observed. Increasing dissolution rates below 515 nm in the absence of siderophores are consistent with photolysis of surface Fe(III)-hydroxo groups. In the presence of the siderophore DFOB, maximum photodissolution rates were observed in a spectral window between 395-435 nm that corresponds to the absorbance maximum of the soluble Fe-DFOB complex, suggesting that adsorbed DFOB is directly involved in the reduction of surface Fe(III) by a light-induced ligand-to-metal charge-transfer reaction within the surface Fe(III)-DFOB complex.

Lessons from failed experiments on the U-Pb dating of fossils

JAN D. KRAMERS^{1*}, LEE R. BERGER²,
BRUCE S. RUBIDGE² AND JUERGEN TITSCHACK³

¹Institut für Geologie, Universität Bern, Switzerland
(*correspondence: kramers@geo.unibe.ch)

²School of Geosciences, University of the Witwatersrand, Johannesburg, South Africa

³GeoZentrum Nordbayern, Universität Erlangen, Germany

We present results of U-Pb dating attempts on coldwater coral and tooth enamel samples. In all cases, several small subsamples 5-50 mg were taken from single fragments, to minimize the effect of common Pb isotope heterogeneity.

(1) 4 borehole samples of cold-and deep water coral from the Challenger Mound in the North Atlantic Ocean (1317E 2H-2, 4H-4, 7H-3 and 16H-5) range in age from 0.5 to over 3 Ma (determined by Sr isotope stratigraphy). U contents decrease from 3.4 – 4.2 ppm for the youngest, to 2.1-2.3 for the oldest sample. Pb concentrations vary between 15 and 120 ppb. The youngest sample yielded a U-Pb date of 507 ± 170 ka and a consistent ($^{234}\text{U}/^{238}\text{U}$) age of 511 ± 30 Ma. In the three older samples, both U-Pb and ($^{234}\text{U}/^{238}\text{U}$) dates first increased and then decreased with true age. Apparently ^{234}U was re-introduced into the samples in diagenesis, and at the same time Pb was partially rehomogenized within samples.

(2) A c. 700 ka old antelope tooth enamel sample (Gladysvale cave, Cradle of Humankind site, Gauteng, South Africa) has U contents between 1.3 and 25 ppm, Pb between 0.17 and 2.4 ppm (high U correlates with high Pb) and ($^{234}\text{U}/^{238}\text{U}$) ratios between 1.17 and 1.27, anticorrelated with U content, and much higher than ($^{234}\text{U}/^{238}\text{U}$) of associated flowstone (1.09), pointing to post-deposition uptake of U.

(3) Enamel from a *lystrosaur* tusk from the Permian-Triassic boundary in the Karoo, South Africa, has 300 ppm U and between 86 and 115 ppm Pb. Isochron and concordia dates yield 300-320 Ma, which is 50-70 Ma older than the stratigraphic age. These data clearly indicate uptake of U as well as radiogenic Pb from the surrounding rock.

These combined observations show exchange in the course of diagenesis, in the oceanic sedimentary environment as well as in shallow water sediments and soils, with onset after several 100 ka at the latest, and continuing for millions of years. The unpredictable uptake of radiogenic Pb makes tooth enamel unsuitable for U-Pb dating, even if U uptake could be quantified via modeling. For ESR dating, the data imply that, at least for the pleistocene age range, the linear U uptake model is more appropriate than early uptake.