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Effect of siderophores on the light-induced dissolution of colloidal iron(III) (hydr)oxides

Paul M. Borer[a], Barbara Sulzberger[a], Petra Reichard[b], Stephan M. Kraemer[b,*]

[a]*Swiss Federal Institute for Environmental Science and Technology (EAWAG), Überlandstrasse 133, 8600 Dübendorf, Switzerland*
[b]*Institute of Terrestrial Ecology, Swiss Federal Institute of Technology, Zürich, Grabenstrasse 3, 8952 Schlieren, Switzerland*

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Abstract

Siderophores play an important role in biological iron acquisition in iron-limited aquatic systems. While it is widely accepted that the solubilization of iron-bearing mineral phases is a key function of siderophores, the mechanism of siderophore-promoted mineral dissolution in aquatic systems is largely unknown. In this study, we investigated the effect of siderophores (desferrioxamine B (DFOB) and aerobactin) on light-induced dissolution of goethite and lepidocrocite in the presence or absence of oxalate in aerated and deaerated suspensions at pH 6. For the irradiated two-ligand system (oxalate/siderophore), the experimental results suggest that oxalate acts as the electron donor for the formation of surface Fe(II), and the siderophore acts as an efficient shuttle for the transfer of surface Fe(II) into solution. Furthermore, even in the absence of an electron donor such as oxalate, both DFOB and aerobactin accelerated the light-induced dissolution of lepidocrocite as compared to the thermal dissolution. Experiments with dissolved Fe(III)–DFOB and Fe(III)–aerobactin complexes suggest that this enhancing effect is not due to photolysis of corresponding surface complexes but to efficient transfer of reduced surface Fe(II) into solution, where surface Fe(II) may be formed, e.g., through photolysis of surface Fe(III)–hydroxo groups. Based on this study, we conclude that the interplay of light and siderophores may play a key role in the dissolution of colloidal iron(III) (hydr)oxides in marine systems, particularly in the presence of efficient electron donors.

Keywords: Photodissolution; Iron oxides; Siderophore; Desferrioxamine B (DFOB); Aerobactin; Oxalate; Marine iron limitation

1. Introduction

Iron bioavailability has been shown to limit or colimit primary productivity in several oceanic waters, particularly in 'High Nutrient, Low Chlorophyll' (HNLC) regions (Martin and Fitzwater, 1988; Martin et al., 1994). A significant external iron source to these and other oceanographic regimes is atmospheric input (Martin and Fitzwater, 1988; Martin et al., 1994). For example, it has been estimated that atmospheric deposition of aeolian iron-containing mineral dust accounts for 84–93% of the external iron input to the

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* Corresponding author. Tel.: +41 1 633 6077; fax: +41 1 633 1118.

E-mail address: kraemer@env.ethz.ch (S.M. Kraemer).

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subarctic Pacific, which lies in the path of an extended aerosol plume that originates in China (Martin et al., 1989). At the relatively low pH values (3–6) of atmospheric waters, solid iron phases (e.g., crystalline iron oxides and iron aluminium silicates) in the aerosols are subject to photoreductive dissolution (Faust and Hoffmann, 1986; Pehkonen et al., 1993; Zhu et al., 1993; Siefert et al., 1994; Sulzberger and Laubscher, 1995a,b; Johansen et al., 2000). Besides crystalline iron oxides (this term will be used for the various Fe(III) oxides, Fe(III) oxohydroxides, and Fe(III) hydroxides), photoproduced Fe(II) also enters open ocean surface waters by wet deposition. However, without significant stabilization of Fe(II) by some organic ligands, Fe(II) undergoes fast oxidative precipitation in seawater (Millero et al., 1987).

The extent to which iron limits primary production in open ocean waters depends on both the abundance of iron and its bioavailability. Particulate and colloidal iron is believed to be unavailable to phytoplankton (Wells et al., 1983; Finden et al., 1984; Rich and Morel, 1990), and the solubility of iron in open ocean waters is extremely low, log [Fe(III)]<-9 (Liu and Millero, 2002). Regarding dissolved iron, it has been proposed that eukaryotic phytoplankton species utilize only inorganic iron species (Anderson and Morel, 1982). However, more recent studies have shown that some eukaryotic algae are able to utilize iron bound to (strong) organic chelators via a cell surface reductase mechanism (Jones et al., 1987; Soria-Dengg and Horstmann, 1995; Hutchins et al., 1999; Maldonado and Price, 1999, 2001; Weger, 1999).

Unlike eukaryotic algae, marine bacteria acquire iron through a siderophore-mediated uptake system (Winkelmann, 1991). Siderophores are low-molecular-weight organic ligands (0.5–1.5 kDa) with a high affinity and specificity for iron. Under iron-limiting conditions, siderophores are excreted by cyano- and heterotrophic bacteria (Gonye and Carpenter, 1974; Reid and Butler, 1991; Haygood et al., 1993; Wilhelm and Trick, 1994; Tortell et al., 1999). The stability constants of Fe(III)–siderophore complexes are in the range of log K=25–50 (Albrecht-Gary and Crumbliss, 1998). Besides increasing the solubility of iron, siderophores also accelerate iron oxide dissolution (Hersman et al., 1995; Yoshida et al., 2002; Cheah et al., 2003; Kraemer, 2004). Iron-binding groups of bacterial siderophores typically include hydroxamate, catecholate, α-hydroxycarboxylate, and, less often, carboxylate groups (Winkelmann, 1991).

Hitherto, there is no clear picture of the roles of siderophores for iron acquisition by the phytoplankton community. The acquisition of iron from iron–siderophore complexes by eukaryotic phytoplankton (e.g., diatoms) is obscure and controversially discussed in literature. Although eukaryotic phytoplankton generally do not produce siderophores, it has been shown that some species may utilize siderophore-bound iron under iron-limiting conditions by a cell surface reductase mechanism (Soria-Dengg and Horstmann, 1995; Maldonado and Price, 2001). Other studies, however, have pointed out, that strong iron–siderophore complexes are not available to eukaryotic phytoplankton in iron-replete waters (Wells et al., 1994; Wells, 1999). For an in-depth discussion of these contrasting results, we refer to Maldonado and Price (2001).

It has been reported, that most (>99%) dissolved ferric iron in the HNLC upper ocean water is complexed by strong organic ligands having conditional stability constants in seawater similar to siderophores (Van den Berg, 1995; Wu and Luther, 1995; Rue and Bruland, 1997; Witter et al., 2000; Powell and Donat, 2001). The nature of these ligands has been partly elucidated by Macrellis et al. (2001). They have determined size classes as well as conditional Fe-binding affinities of iron binding compounds collected in the central California coastal upwelling system. The size class and conditional stability constants of these ligands were similar to known siderophores. Moreover, hydroxamate as well as catecholate Fe(III)-binding groups were found in all compounds for which strong iron binding was detected.

1.1. Roles of siderophores in the light-induced redox cycling of dissolved iron

The effect of siderophores on the redox chemistry of dissolved iron is dominated by two processes: (i) stabilization of the trivalent state of iron due to the much higher affinity of siderophores for Fe(III) compared to Fe(II), and (ii) photolysis of certain Fe(III)–siderophore complexes resulting in the formation of Fe(II). It has been demonstrated that Fe(III)