Bull. Environ. Contam. Toxicol. (2006) 77:60–66

DOI: 10.1007/s00128-006-1032-9

# Influence of Light on the Adsorption of Copper from Seawater onto Goethite and Birnessite

M. A. Huerta-Diaz

Institute of Oceanographical Research, Autonomous University of Baja California,
PMB-133, Post Office Box 189003, Coronado, CA 92178-9003, USA

Received: 4 March 2006/Accepted: 25 May 2006

Undersaturation of seawater with respect to many trace metals in the world's oceans has been attributed to adsorption or scavenging by particles, particularly on iron and manganese oxides and oxyhydroxides, because of their large adsorption and cation-exchange capacities and their importance as traps for trace metals (*e.g.*, Holmström and Öhlander, 2001; Pretorius and Linder, 2001). Oxyhydroxides of manganese and iron are frequently observed in sediments, either as discrete particles or as coatings on the surfaces of other particles (Feely *et al.*, 1983). Furthermore, these two oxides are among the most important components influencing the availability of metals to benthic fauna. According to Jenne (1977) and Loganathan and Burau (1973) the iron and manganese oxides most frequently observed in sediments are goethite and birnessite. Different factors affect the adsorption of trace metals onto oxyhydroxides, such as the Eh, pH, dissolved concentration of the metal of interest, concentration of competing metals, concentration of other ions capable of forming inorganic complexes, and organic chelates. However, there has been little investigation on the effect of light on the adsorption of metals by oxyhydroxides. Photochemical processes are particularly important because they may influence the distribution of transition metals through changes in their redox states. This work presents results of the influences of surface photochemical reactions on Cu adsorption from seawater onto goethite and birnessite. Copper was selected because of its importance as an essential element in biological systems (e.g., Morel and Price, 2003) as well as for its well known toxicity towards some organisms (e.g., Mann et al., 2002). Therefore, this study will provide an assessment as to whether photoreactive trace metals (e.g., Cu) adsorbed on Fe and Mn oxyhydroxides are likely to be mobilized or immobilized during Fe(III) and Mn(IV) oxide photoreduction, thereby providing important insights into the bioavailability/toxicity and biogeochemical cycling of trace metals within the photic zone of natural waters. It is hypothesized that photochemically induced reduction of Cu(II) to Cu(I) may be important in contamination studies, especially considering the semiconductor properties of Fe(III)- and Mn(III,IV)-hydroxides.

## MATERIALS AND METHODS

Goethite was synthetically prepared according to the procedure of Atkinson *et al.* (1967), whereas synthetic birnessite was prepared by the oxidation of manganous ion by permanganate (Murray, 1974); the mineral composition of the prepared oxides was confirmed by X-ray diffraction (Keeney-Kennicutt and Morse, 1984). Surface areas of 45.5 ± 0.4 and 348 ± 8 $m^2$ $g^{-1}$ for goethite and birnessite, respectively, were determined by the Kr-BET method. These two values are in good agreement with the surface areas measured by Appelo and Postma (1999) and Pretorius and Linder (2001) for similar preparations. The oxides were kept in dilute aqueous solutions for approximately two years prior to their use in this study. While the possibility exists that there was a change in crystallinity or specific surface area of the synthetic goethite and birnessite after the two years of storage, they can be used as guides for the comparison of sorptive capacities.

Experiments were conducted in a photochemical reactor which consisted of a custom-made metallic dark box containing a quartz photochemical immersion well (Ace Glass) in combination with a 250-mL capacity photochemical reaction vessel (Ace Glass). For each experiment, approximately 250 mL of natural near-surface Gulf Stream seawater, weight-diluted to a salinity of 35, was used. A predetermined volume of a dissolved copper standard was added to the reaction vessel, and the solution was then stirred overnight to allow the metal to equilibrate with the solution and with the glass and quartz surfaces. It was assumed that all Cu in the standard was in the form of Cu(II) since under dark conditions and in the presence of oxygen the concentration of Cu(I) has been found to be exceedingly small (Moffett and Zika, 1987). After equilibration, a 1-mL sample was withdrawn to determine the copper concentration, which was found to be 6.7 ± 0.2 μM for the birnessite experiment, and 3.6 ± 0.2 μM for the goethite experiment. The metal oxide was then added to the solution (165 and 156 $m^2$ $kg^{-1}$ of seawater for birnessite and goethite, respectively) which was stirred continuously until the end of the experiments (78 and 76 hr for the birnessite and goethite experiments, respectively). At varying intervals, an aliquot of solution was removed, filtered through a polycarbonate Nucleopore® filter of 0.4 μm nominal pore size and acidified to 0.1% $HNO_3$ (J.T. Baker, Ultrex®) for the analysis of total dissolved Cu.

The experiments were carried out in the absence and presence of light. A 450-watt photochemical immersion lamp (Canrad-Hanovia) was used as the light source. Of the total energy radiated by the lamp, 40 to 48% was in the ultraviolet portion of the spectrum, 40 to 43% in the visible, and the balance in the infrared. Cu concentrations were determined by flameless atomic absorption spectrophotometry (Hitachi model 170-70 with Zeeman background correction) using the method of standard addition. Although the light intensity and copper concentrations used in these experiments are much greater than observed in the surface ocean, the results are, nonetheless, applicable to the understanding of Cu adsorption processes in nature.

## RESULTS AND DISCUSSION

Equilibration of copper with goethite took approximately four to five days (Figure 1), which compares well with the one or two days found by Loganathan and Burau (1973), and five days found by Lion *et al.* (1982). Copper adsorbed rapidly onto the birnessite at the beginning of the experiment (0-10 hr) and continued to adsorb at a significantly lower rate over the entire experimental period (76 hr). As shown in Figure 1, a significant larger fraction of Cu adsorbs to birnessite than to goethite. After the equilibration time, Cu on birnessite was slowly adsorbed under dark conditions. Under light, however, there was a significant difference in the Cu adsorption behavior onto the two mineral phases (Figure 1). Adsorption of Cu by birnessite increased substantially, from 37% to a maximum of 62% (i.e., Δ adsorption = 25%) during the first light period, and from 66% to a maximum of 90% (i.e., Δ adsorption = 24%) during the second light period (Figure 1a). After reaching the maximum in adsorption during both light periods, there were small gradual desorptions of Cu (Δ desorption = 5 – 6%). Hence, both light periods were characterized by essentially equal changes in adsorption and desorption with time (Figure 1a). For goethite, the adsorption of Cu remained essentially constant with time during the first dark period (Figure 1b), but during the initial part of the light stage there was a substantial desorption of the metal (from 30% to 13%), followed by a rapid, almost linear increase in adsorption until a maximum was reached (39%), after which the adsorption values returned to the levels observed during the preceding dark conditions. During the second dark stage, the values of adsorption increased gradually until, by the end of the experiment, levels similar to the maximum observed during the light period were reached (36% to 40%). Three basic questions remain: (1) Why does Cu continue to adsorb onto birnessite over a 50-hour dark period, when Cu equilibrates very rapidly with goethite? (2) Why does a period of desorption occur at the beginning of a lighted cycle for goethite and not for birnessite? (3) Why is there a period of desorption following adsorption under lighted condition for both minerals?

Goethite (Wells and Mayer, 1991; Waite and Morel, 1984) and birnessite (Sherman, 2005) are photoreduced in natural waters, especially if a chromophore (e.g., humic acids) is present. Hence, light could have interacted with humic acids naturally present in the Gulf Stream seawater to photoreduce the goethite and birnessite, enhancing in the process the adsorption of Cu through the creation of new, fresh surface attachment sites produced by the photodissolution of the oxides. Keeney-Kennicutt and Morse (1986), who studied the influence of light on plutonium adsorption on a number of mineral surfaces, found that oxidation-reduction reactions were important on goethite and birnessite surfaces and could be significantly catalyzed by light. Similar conclusions were also reached by McCubbin and Leonard (1996) with $^{239+240}$Pu sorbed on marine sediments.

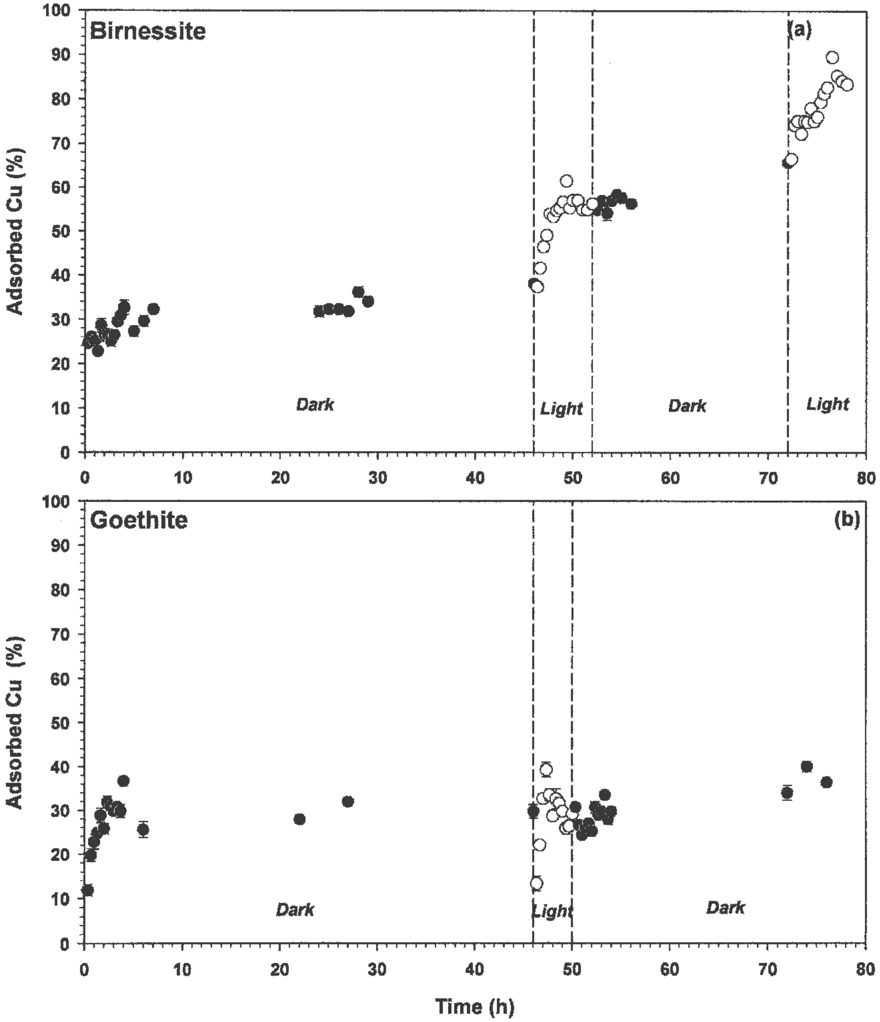

**Figure 1**. Adsorption of copper on (a) birnessite and (b) goethite as a function of time and contrasting light conditions. Birnessite concentration was 0.165 $m^2$ $kg^{-1}$ of seawater and the Cu initial concentration was 6.7 ± 0.2 μM. Goethite concentration was 0.156 $m^2$ $kg^{-1}$ of seawater and the Cu initial concentration was 3.6 ± 0.2 μM. Filled and open symbols represent dark and light conditions, respectively. Uncertainty was determined by propagation of analytical error and is reported at the 1σ level.

It has been reported that sunlight leads to an increase in Cu(II), probably as a result of the photo-destruction of ligands and/or Cu complexes (Moffett and Zika, 1983). Sunlight is also capable of reducing Cu(II) to Cu(I) in the surface layers of the oceans (Moffett and Zika, 1988). Apparently, these Cu(I) concentrations are a consequence of the photolytic reduction of Cu(II) complexes and the reduction of Cu(II) by photochemically formed reactive oxygen species, with superoxide and hydrogen peroxide among the main Cu(II) reductants (Buerge-Weirich and Sulzberger, 2004). Significant steady-state levels of Cu(I) in seawater (~15% of total Cu in surface seawater; Moffett and Zika, 1983) can, in turn, be maintained by chloride complexation (Moffett and Zika, 1983) and by the low complexation capacity of Cu(II) by organic ligands (Buerge-Weirich and Sulzberger, 2004). Hence, if Cu(I) was photochemically produced during the light periods of the experiments, it was kept in solution by chloride complexation and part of it could be adsorbed on oxide surface sites that were not taken by the Cu(II) during the preceding dark period. The fact that a number of oxide mineral surfaces are redox active and that this activity can be enhanced by light means that changes in the oxidation state of copper between Cu(I) and Cu(II) may occur on the oxide surfaces. For example, oxidation on the surface of synthetic birnessite of Co(II) to Co(III) and of Cr(III) to Cr(IV), Cr(V) and Cr(VI) have been previously reported (Crowther et al., 1983; Banerjee and Nesbitt, 1999). Changes in redox state are probably rapid, since laboratory studies have indicated that oxidation of Cu(I), at least in seawater, has a half life of 4-6 minutes (Moffett and Zika, 1983) with redox reactions capable of achieving redox state changes in less than a minute (Leal and van den Berg, 1998). The oxidation-reduction mechanisms at the mineral-water interface, with subsequent desorption of Cu, may be related to the semiconductor properties of Fe(III)- and Mn(III,IV)-hydroxides (Waite, 1990). Upon absorption of light with energy equal to, or greater than, the band-gap energy of the semiconductor, an electron is promoted from the valence band into the conduction band (McCubbin and Leonard, 1996). Since the photo-generated holes and photoelectrons are generally characterized by strong oxidizing and reducing potentials, respectively (Waite, 1990), it is possible that part of the adsorbed Cu(II) may have been directly reduced to Cu(I) by interaction with valence band holes. Hence, once adsorbed, a portion of the Cu(II) can be directly reduced to Cu(I), followed by desorption of the metal from the oxide surface. Since goethite (and maybe birnessite as well) is regarded as "hard" (Evans, 1980), it is possible that "borderline" metal cations like Cu(II) have more affinity for Fe and Mn oxides than "soft" metal cations like Cu(I).

The adsorption of Cu from seawater onto goethite and birnessite surfaces is a highly dynamic process in which the adsorption of this metal can be photochemically enhanced, especially on birnessite. The process was found to be repeatable, at least for the birnessite experiment, by alternating light and dark conditions, and, therefore, may be important in the photic zone of Cu contaminated natural waters showing sediment resuspension or with moderate loads of particulates. Further research is needed to elucidate the mechanisms by which this process occurs.

## REFERENCES

Appelo CAJ., Postma D (1999) A consistent model for surface complexation on birnessite ($\delta$-$MnO_2$) and its application to a column experiment. Geochim Cosmochim Acta 6:3039-3048

Atkinson RJ, Posner AM, Quirk JP (1967) Adsorption of potential-determining ions at the ferric oxide-aqueous electrolyte interface. J Phys Chem 71:550-558

Banerjee D, Nesbitt HW (1999) Oxidation of aqueous Cr(III) at birnessite surfaces: Constraints on reaction mechanism. Geochim Cosmochim Acta 63:1671-1687

Buerge-Weirich D, Sulzberger B (2004) Formation of Cu(I) in estuarine and marine waters: Application of a new solid-phase extraction method to measure Cu(I). Environ Sci Technol 38:1843-1848

Crowther DL, Dillard JG, Murray JW (1983) The mechanism of Co(II) oxidation on synthetic birnessite. Geochim Cosmochim Acta 47:1399-1403

Evans TD (1980) The interfacial electrochemistry of goethite ($\alpha$-FeOOH). Part II. Ion adsorption and HSAB: mercury is "soft' but goethite is "hard". J Electroanal Chem 111:257-252

Feely RA, Massoth GJ, Paulson AJ, Gendron JF (1983) Possible evidence for enrichment of trace elements in the hydrous manganese oxide phase of suspended matter from urbanized embayment. Est Coast Shelf Sci 17:693-708

Holmström H, Öhlander B (2001) Layers rich in Fe- and Mn-oxyhydroxides formed at the tailings-pond water interface, a possible trap for trace metals in flooded mine tailings. J Geochem Explorat 74:189-203

Jenne EA (1977) Trace element sorption by sediments and soils. Sites and processes. In: Chappell WR, Petersen KK (eds) Molybdenum in the Environment, vol 2. Marcel Dekker, New York, p 425

Keeney-Kennicutt WL, Morse JW (1984) The interaction of Np(V) with common mineral surfaces in dilute aqueous solutions and seawater. Mar Chem 15:133-150

Keeney-Kennicutt WL, Morse JW (1986) The redox chemistry of $Pu(V)O_2^+$ interaction with the surfaces of common mineral surfaces in dilute solutions and seawater. Geochim Cosmochim Acta 49:2577-2588

Leal MFC, Van Den Berg CMG (1998) Evidence for strong copper(I) complexation by organic ligands in seawater. Aquatic Geochem 4:49-75

Lion LW, Altmann RS, Leckie JO (1982) Trace-metal adsorption characteristics of estuarine particulate matter: Evaluation of contributions of Fe/Mn oxide and organic surface coatings. Environ Sci Technol 16:660-666

Loganathan P, Burau RG (1973) Sorption of heavy metals by hydrous manganese oxide. Geochim Cosmochim Acta 37:1277-1293

Mann EL, Ahlgren N, Moffett JW, Chisholm SW (2002) Copper toxicity and cyanobacteria ecology in the Sargasso Sea. Limnol Oceanogr 47:976-988

McCubbin D, Leonard KS (1996) Photochemical dissolution of radionuclides from marine sediment. Mar Chem 55:399-408

Moffett JW, Zika RG (1983) Oxidation kinetics of Cu(I) in seawater: implications for its existence in the marine environment. Mar Chem 13:239-251

Moffett JW, Zika RG (1987) Photochemistry of copper complexes in sea water. In: Zika RG and Cooper WJ (eds.) Photochemistry of Environmental Aquatic Systems. ACS Symposium Series:Washington D.C., p 116

Moffett JW, Zika RG (1988) Measurement of copper(I) in surface waters of the subtropical Atlantic and Gulf of Mexico. Geochim Cosmochim Acta 52:1849-1857

Morel FMM, Price NM (2003) The biogeochemical cycles of trace metals in the oceans. Science 300:944-947

Murray JW (1974) The surface chemistry of hydrous manganese dioxide. J Colloid Interface Sci 46:357-371

Pretorius PJ, Linder PW (2001) The adsorption characteristics of δ-manganese dioxide: A collection of diffuse double layer constants for the adsorption of $H^+$, $Cu^{2+}$, $Ni^{2+}$, $Zn^{2+}$, $Cd^{2+}$ and $Pb^{2+}$. Appl Geochem 16:1067-1082

Sherman DM (2005) Electronic structures of iron(III) and manganese(IV) (hydr)oxide minerals: Thermodynamics of photochemical reductive dissolution in aquatic environments. Geochim Cosmochim Acta 69, 3249-3255

Waite TD (1990) Photo-redox processes at the mineral-water interface. In: Hochella MF., White AF (eds.) Mineral-Water Interface Geochemistry. Reviews in Mineralogy, vol. 23. Mineralogical Society of America, p 559

Waite TD, Morel FMM (1984) Photoreductive dissolution of colloidal iron oxides in natural waters. Environ Sci Technol 18:860-868

Wells ML, Mayer LM (1991) The photoconversion of colloidal iron hydroxides in seawater. Deep-Sea Res 38:1379-1395