



Redox interactions of Fe and Cu in seawater

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ABSTRACT

The interaction between the redox chemistry of Fe and Cu at nanomolar has been studied in UV-treated seawater. The oxidation of Fe(II) was studied as a function of concentrations of Cu(II) and Cu(I) from 0 to 200 nM. The effect of added H₂O₂ (0–500 nM), pH (6.0–8.5) and NaHCO₃ (2–9 mM) on the Fe(II) rate constants was studied at Cu(II) levels (0–200 nM). To understand the competition between Fe and Cu, the reduction of Cu(II) to Cu(I) was also studied as a function of oxygen (air-saturated and anoxic seawater), Fe(II) (0–200 nM) and H₂O₂ (0–300 nM). The Fe(II) oxidation was accelerated by the presence of Cu(II) and Cu(I). This acceleration has been explained by the redox coupling between Fe and Cu, competition for different inorganic species (hydroxyl and carbonate groups studied independently) and by the formation of Fe–Cu particles (cupric or cuprous ferrite). Superoxide played a key role in the oxidation rate of Fe(II) in the presence of Cu(II). The presence of Fe(II) caused a greater reduction of Cu(II) to Cu(I). This is directly related to the levels of oxygen, Fe(II) and H₂O₂ concentrations. The presence of Fe(II) produced a rapid formation of Cu(I) in the first 2–3 min of reaction. The Cu(I) is oxidized reaching a steady-state around 20 nM levels of Cu(I). These experimental results demonstrated that the presence of Fe and Cu strongly affected the inorganic redox chemistry of both metals in UV-treated seawater.

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1. Introduction

Iron is a crucial element in the environment because it is an essential micronutrient for the growth of microorganisms. Although iron is the fourth most abundant element on Earth, it is at sub-nanomolar levels in ocean waters. Fe can be found in the ocean waters as Fe(II) and Fe(III), where Fe(III) is thermodynamically stable. The oxidation kinetics of Fe(II) in natural waters have been studied by a number of workers (Kester et al., 1975; Davison and Seed, 1983; Waite and Morel, 1984; Millero and Izaguirre, 1989; Millero and Sotolongo, 1989; Liang et al., 1993; King et al., 1995; Rose and Waite, 2002; Santana-Casiano et al., 2005, 2006; Gonzalez-Davila et al., 2006; Trapp and Millero, 2007; Gonzalez et al., 2010). In addition there are also several field work that reported Fe(II) oxidation rates (Breitbarth et al., 2009; Croot et al., 2008; Croot et al., 2001; Croot and Laan, 2002; Croot et al., 2005). Few studies have been made on the effect of other metals in the Fe(II) oxidation rates. The effect of copper on the Fe chemistry has been studied (Cher and Davidson, 1955; Huffman and Davidson, 1956; Stumm and Lee, 1961; Parker and Espenson, 1969; Sayin, 1982; Sedlak and Hoigne, 1993; Buxton et al., 1995; Matocha et al., 2005). These authors found that the redox reaction of both metals can be affected by the

redox reactions of the other. These results showed a true catalytic effect of copper on the Fe(II) oxidation in acidic solutions (Stumm and Lee, 1961). This was caused by the radical hydroperoxide, HO₂[•], which reacts with Fe(II) according to the Haber–Weiss mechanism. The same authors also reported that the effect of Cu(II) on Fe(II) kinetics is a function of the initial concentrations of both Fe and Cu. Sayin (1982) suggested that copper ions take part in an oxidation–reduction cycle of Fe(II) and act as a catalyst in the oxidation of the iron in biotite. They demonstrated that the oxidation of iron increased in the presence of Cu. Sedlak and Hoigne (1993) studied the role of copper in the redox cycling of iron in atmospheric waters and also demonstrated that the catalytic effect of copper altered the production of radicals during the oxidation. These authors also reported the reduction of inorganic Fe(III) species by Cu(I) that has been also included in modeling for atmospheric process (Ervens et al., 2003; Herrmann et al., 2005; Siefert et al., 1998). Matocha et al. (2005) showed that, under anoxic and acidic conditions, the reduction of Cu(II) to Cu(I) by dissolved Fe(II) was rapid and generally completed in the first 1–2 min and was also affected by the presence of chloride ions. The oxidation of Fe(II) by Cu(II) is thermodynamically possible by considering the speciation of these metals in solution (Matocha et al., 2005).

In addition, other authors reported the interaction between the Fe and Cu redox cycles (and also Mn) and reactive oxygen species in seawater under natural conditions (Heller and Croot, 2010, 2011, 2015; Wuttig et al., 2013a, 2013b). In fact, these authors also highlighted the key role of H₂O₂ and O₂^{•−} in the redox cycling and how the organic

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ligands reduced the reactivity of Fe and Cu. Heller and Croot (2010, 2011) demonstrated the importance of organic chelation of Fe and Cu in controlling the reactivity with superoxide, where copper seems to be the major sink for superoxide. Both Fe and Cu speciation are dominated by organic species (Campos and van den Berg, 1994; Coale and Bruland, 1988; Moffett, 1995; Gledhill and van den Berg, 1994; Rue and Bruland, 1995; Wu and Luther, 1995), mostly produced by phytoplankton or bacteria increasing the solubility of these metals. Indeed, the interaction between Fe and Cu for the humic ligands in natural waters has been reported by Abualhija et al. (2015).

The oxidation of Cu(I) by superoxide radical, $O_2^{\cdot-}$, has been considered as a competitive reaction in the kinetic models for Fe(II) oxidation in seawater (Zafiriou et al., 1998; Santana-Casiano et al., 2005, 2006) and also in field work (Heller and Croot, 2010, 2011, 2015). The composition of seawater and pH, $O_2^{\cdot-}$, H_2O_2 , and $NaHCO_3$ play a key role in the redox chemistry of both Fe and Cu. In this manuscript, we focused on the inorganic interactions between Fe and Cu in seawater, in terms of redox reactions. The oxidation rate of Fe(II) in seawater at nanomolar levels is studied in the presence of both Cu(I) and Cu(II) to levels of 200 nM. The effect of pH (6.0–8.5), bicarbonate concentrations (2–9 mM) and H_2O_2 (0–500 nM), superoxide (after superoxide dismutase treatment) in the presence of copper was also studied. The effect of chloride on the Cu(I) chemistry is minimized here due to the constant concentration of chloride in seawater. The effect of Fe on the Cu redox chemistry has been studied under similar experimental conditions, such as a function of Fe(II) concentration (0–200 nM), under air-saturated and anoxic conditions, together with the effect of H_2O_2 levels (0–300 nM). These results should improve our knowledge of the importance of these metal interactions in natural waters and improve the kinetic models for the oxidation of Fe(II) and Cu(I) in seawater.

2. Experimental

2.1. Chemicals

The Fe(II) oxidation rates were studied in seawater UV-treated and collected off the coast of Gran Canaria (Spain). The salinity, 36.968 ± 0.005 , was measured with a Portasal 8410A salinometer. The seawater samples were always filtered through a $0.1 \mu m$ filter to both remove particulate and colloidal matter and prevent the blockage of the 5-m long waveguide capillary flow cell (World Precision Instruments™).

The experiments were carried out using a Fe(II) stock solution ($4 \cdot 10^{-4}$ M) prepared using ammonium iron (II) sulfate hexahydrate (Sigma), acidified at pH 2 with Suprapure HCl (Sigma) in 0.7 M NaCl. The Fe(III) stock solutions ($4 \cdot 10^{-4}$ M) were carried out from iron (III) chloride hexahydrate (Sigma) in 0.7 M NaCl. Stock solutions of Cu(I) ($4 \cdot 10^{-4}$ M) were prepared daily using analytical grade copper (I) chloride (Aldrich) in 0.7 M NaCl. The solutions were acidified at pH 2 with Suprapure HCl and bubbled with N_2 before and after the copper was added to the reaction vessel. Stock solutions of Cu(II) ($4 \cdot 10^{-4}$ M) were prepared using copper (II) chloride (Aldrich) in 0.7 M NaCl. H_2O_2 stock solutions ($6 \cdot 10^{-4}$ M) were prepared daily and kept in the fridge under darkness conditions. The concentrations of stock H_2O_2 solutions were determined either with a Hewlett Packard 8453 UV-vis photodiode array spectrophotometer using the H_2O_2 molar absorptivity of $38.1 \pm 1.4 M^{-1} cm^{-1}$ at 240 nm (Miller and Kester, 1988) and by titration with standardized thiosulfate (0.09935 N, Panreac) to the starch-iodide end point.

All solutions were prepared with Milli-Q (18 M Ω) and the reagents used were trace analytical grade. Stock solutions of SOD (bovine erythrocytes; Sigma) were prepared daily in Milli-Q water at $3 \cdot 10^3$ kU L $^{-1}$ and stored in a fridge under darkness conditions during the experiment.

2.2. pH measurements

The pH was measured on the free hydrogen ion scale, $pH_F = -\log [H^+]$ by using an Orion pH meter combination electrode (Ross Combination, glass body). This electrode was calibrated with Tris-(hydroxymethyl) aminomethane (Tris)-artificial seawater buffers (Millero, 1986) where the effect of temperature and salinity on the pK^* of the Tris-buffers was considered.

2.3. Oxidation and reduction experiments

The kinetic studies were carried out in a covered water-jacketed glass vessel (250 mL). The temperature of the vessel was controlled at 25 ± 0.02 °C with an AG-2 bath. The samples were stirred at the same rate during all the experiments with a Teflon-coated magnetic stirrer. The oxidation kinetic studies were carried out in air-saturated conditions by bubbling the solution with pure air for 1 h, before and during the experiments. The pH was initially adjusted and controlled to ± 0.01 by bubbling with air and small additions of suprapure 0.1 M HCl using an automatic titrator system (Titrino 719S, Methrom). The addition of the Fe(II) to the sample corresponds to the zero time of reaction. Both Fe(II) and Cu(I) or Cu(II), were added simultaneously.

The effect of $O_2^{\cdot-}$ on the kinetic experiments was carried out using the method described by Garg et al. (2013), where 15 kU L $^{-1}$ of SOD was added to the solution.

2.4. Fe(II) and Cu(I) analyses

The Fe(II) and Cu(I) concentrations were determined spectrophotometrically using the ferrozine method (Violler et al., 2000; Santana-Casiano et al., 2005) and a modified version of the bathocuproine method (J. Moffett et al., 1985; J.W. Moffett et al., 1985; Gonzalez-Davila et al., 2009) respectively. The ferrozine and Fe(II) form a peak at 562 nm. Bathocuproine disulfonate salt and Cu(I) form a peak at 484 nm (J. Moffett et al., 1985; J.W. Moffett et al., 1985; Gonzalez-Davila et al., 2009; Sanchez-Rasero, 1981). Kundra et al. (1974) demonstrated the formation of Cu(I)-ferrozine at 470 nm. In order to elucidate and correct the possible interference of this peak in the Fe(II) determination we performed the calibration curves under different Fe(II) and Cu(I) concentrations (Supporting information file, Figs. SI-1 and SI-2). All our experimental data were corrected by the non-absorbing baseline at 700 nm.

The determination of Fe(II) was carried out by removing 10 mL of samples at selected times that were placed in a 25 mL glass flask containing the selected reagents: 0.01 M ferrozine (50 μ L), acetate buffer at pH 5.5 (2 mL) and $7.1 \cdot 10^{-4}$ M NaF (50 μ L). This method allows a stable absorbance reading observed for over 30 min (Gonzalez-Davila et al., 2005). In the case of Cu(I), 10 mL of sample was added to a 25 mL glass flask containing $2 \cdot 10^{-5}$ M bathocuproine (bathocuproine disulfonic acid, disodium salt hydrate) and 10^{-4} M ethylenediamine reagent following the method previously published by Gonzalez-Davila et al. (2009) and Perez-Almeida et al. (2013). It is important to remark that any chemical was used in the reaction vessel in order to be close to the inorganic conditions of natural environments.

All the experiments were carried out by triplicate and the deviation between Fe(II) concentrations was always lower than 2%. All the figures contain the error bars for the average of the Fe(II) oxidation rate.

Fe(II) and Cu(I) were measured at nanomolar levels by using a 5 m long waveguide capillary flow cell (World Precision Instruments™) connected to the UV-vis detector USB2000 (Ocean Optics™). The light used was a halogen light source (HL-2000-FHSA from Mikropack). The capillary flow cell and the UV detector were connected using a 400 μ m optical fiber. The spectra were recorded using the OOIBase32 software by Ocean Optics. The sample was introduced in the column using a peristaltic pump (EXPETEC Perimax 12) with a flux of 1 mL min $^{-1}$.

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