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Oxidation of Cu(I) in Seawater at Low Oxygen Concentrations

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S *Supporting Information*

ABSTRACT: The oxidation of nanomolar copper(I) at low oxygen (6 μM) concentrations was studied as a function of pH (6.7−8.2), ionic strength (0.1−0.76 M), total inorganic carbon concentration (0.65−6.69 mM), and the added concentration of hydrogen peroxide, H_2O_2 (100−500 nM) over the initial 150 nM H_2O_2 concentration in the coastal seawater. The competitive effect between H_2O_2 and O_2 at low O_2 concentrations has been described. Both the oxidation of Cu(I) by oxygen and by H_2O_2 had a reaction order of one. The reduction of Cu(II) back to Cu(I) in the studied seawater by H_2O_2 and other reactive oxygen intermediates took place at both high and low O_2 concentrations. The effect of the pH on oxidation was more important at low oxygen concentrations, where $\delta\log k/\delta$pH was 0.85, related to the presence of H_2O_2 in the initial seawater and its role in the redox chemistry of Cu species, than at oxygen saturation, where the value was 0.6. A kinetic model that considered the Cu speciation, major ion interactions, and the rate constants for the oxidation and reduction of Cu(I) and Cu(II) species, respectively, was applied. When the oxygen concentration was lower than 22 μM and under the presence of 150 nM H_2O_2, the model showed that the oxidation of Cu(I) was controlled by its reaction with H_2O_2. The effect of the pH on the oxidation rate of Cu(I) was explained by its influence on the oxidation of Cu(I) with O_2 and H_2O_2, making the model valid for any low oxygen environment.
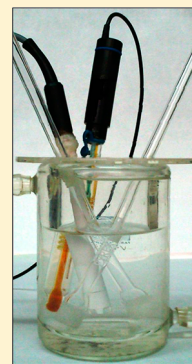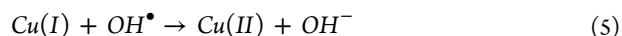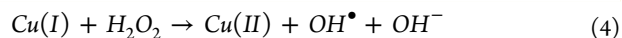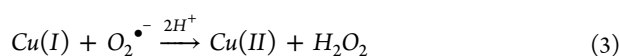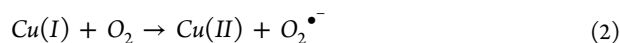
■ INTRODUCTION

Copper is an essential trace metal required by aquatic microorganisms for their growth,[1−3] but is toxic at high concentrations, as it affects the permeability of membranes together with several other metabolic processes.[4] In response to its toxicity, microorganisms excrete dissolved organic ligands in order to complex copper[5−8] that, thereafter, acts as a protective barrier.[9] The biogeochemical cycle of copper is complex due to its presence in seawater as Cu(I) and Cu(II). The most stable form in seawater is Cu(II)[10] but Cu(I) has also been detected in surface oceanic waters.[11] The ratio Cu(II)/Cu(I) in seawater is affected by the different physicochemical properties of the environment.[12]

Most of the oceanic waters are oxic and the redox chemistry of trace metals is controlled by the O_2/H_2O_2 system. While surface waters have oxygen concentrations in the range of 200−220 μM at 25 °C,[13] concentrations can reach 71 μM in brine or less in coastal waters, anoxic trenches, and fjords.[14,15] In coastal waters which are rich in organic matter and nutrient concentrations, the oxygen concentrations can reach hypoxic or even anoxic levels.[16]

The overall reaction for oxidation of Cu(I) in the presence of oxygen (eq 1)

$$Cu(I) + O_2 \rightarrow products \tag{1}$$

is described via the Haber−Weiss mechanism (eqs 2−5).

$$Cu(I) + O_2 \rightarrow Cu(II) + O_2^{\bullet-} \tag{2}$$

$$Cu(I) + O_2^{\bullet-} \xrightarrow{2H^+} Cu(II) + H_2O_2 \tag{3}$$

$$Cu(I) + H_2O_2 \rightarrow Cu(II) + OH^\bullet + OH^- \tag{4}$$

$$Cu(I) + OH^\bullet \rightarrow Cu(II) + OH^- \tag{5}$$

At nanomolar levels of Cu(I), the reduction of both inorganic and organic Cu(II) complexes by the superoxide radical (eq 6)[17,18] should be considered, despite its apparent strong complexation with organic ligands.

$$Cu(II) + O_2^{\bullet-} \rightarrow Cu(I) + O_2 \tag{6}$$
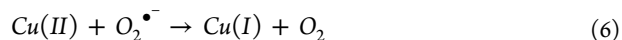
Moreover, in seawater, other oxidants besides oxygen are present, such as hydrogen peroxide, which plays a special role in the redox chemistry of copper.[19,20] Hydrogen peroxide is an intermediate in the reduction of oxygen to water but it is also photochemically generated by the photo-oxidation of dissolved organic matter in seawater.[21−23] H_2O_2 can also be produced by biological processes in the ocean.[24] H_2O_2 concentrations range from 10 to 150 nM in oligotrophic waters, to concentrations of over 500 nM in coastal waters.[22,23,25−27] Reactions with metal species such as Fe(II) and Cu(I) via reaction 4 can lead to the decay of H_2O_2. The reduction of Cu(II) by hydrogen peroxide (eq 7)[28] is one of the processes that explains the formation of Cu(I) in surface oceanic waters.
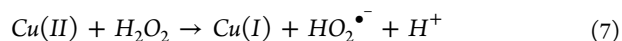
$$Cu(II) + H_2O_2 \rightarrow Cu(I) + HO_2^{\bullet-} + H^+ \tag{7}$$

In addition, the direct photoreduction of Cu organic complexes is the most likely process to generate Cu(I) in surface waters, as suggested by field studies[29] and laboratory work.[30] When Cu(I) is produced, its half-life will be controlled by the presence and concentration of the different oxidants, namely O_2, $O_2^{\bullet-}$, and H_2O_2. Several studies have now demonstrated the high reactivity of both the inorganic complexes of Cu (also applicable for Fe)[17,31] and of some of their organic complexes[18,32−34] with $O_2^{\bullet-}$. These reactions act as a major sink for superoxide in the ocean water.

Most of the studies that analyzed oxidation of Cu(I) have been carried out in conditions of oxygen saturation or in the presence of H_2O_2 without oxygen.[35−38] Recently, the oxidation of Cu(I) was also investigated in NaCl solutions for a wide pH range at oxygen saturation.[39] There is a need to study the oxidation of copper where there are low oxygen concentrations because other oxidants may compete with oxygen for Cu(I). These are the typical conditions found in coastal waters and in anoxic and suboxic waters.

The oxidation rate of Cu(I) in both oxic and anoxic conditions with added H_2O_2[19,36−38] at micromolar and nanomolar concentrations[35,39] is mostly controlled by chloride ion concentration and the relative proportions of Cu^+, $CuClOH^-$, and $CuCO_3$. It is also controlled to a lesser extent by major ion interactions in seawater and interactions with intermediates generated during its oxidation. To consider the different effects of H_2O_2 and of other intermediates on the Cu(I) and Cu(II) redox chemistry at nanomolar concentrations in a natural environment, both the oxidation of Cu(I) and the reduction of Cu(II) were considered simultaneously.[35] This paper presents the effect of oxygen concentration on the oxidation kinetics of nanomolar Cu(I) and the effects of pH (6.8−8.2), ionic strength (0.1−0.76 M), total inorganic carbon concentration (0.65−6.69 mM), and hydrogen peroxide concentration (100−500 nM) under low oxygen concentrations (6 μM). A kinetic model that took all of these effects and processes into account was applied.

■ EXPERIMENTAL SECTION

Chemicals. Stock solutions of Cu(I) (10^{-3} M) were prepared on a daily basis using analytical grade copper(I) chloride (Aldrich) in NaCl 0.7 M. The solutions were acidified to pH 2 with Suprapur HCl and bubbled with N_2 before and after adding the copper. The initial concentration of Cu(I) was maintained at 200 nM in the reaction cell. Stock solutions of Cu(II) (10^{-3} M) were prepared using copper(II) chloride (Aldrich), and the initial concentration in the reaction cell was 200 nM.

The experiments with sodium chloride were carried out using 0.7 M NaCl and 2 mM NaHCO$_3$. The seawater used in this study was collected 200 m off the northeast coast of Gran Canaria (The Canary Islands) at an 8-m depth not far from a fish farm. This seawater was filtered with 0.45-μm and then 0.1-μm filters and used as natural seawater without UV-treatment. The salinity, determined via salinometer (Portasal, 8410A), was 36.691. For the salinity studies, dilutions were produced using Milli-Q ion exchange water (18 MΩ) with the bicarbonate concentration always kept constant at 2.1 mM. All of the chemicals used for the copper determination were trace analytical grade.

Hydrogen Peroxide Measurements. The hydrogen peroxide concentration was measured experimentally by a chemiluminiscence method using the acridinium ester reagent.[40] By the filtration of the seawater with a 0.1-μm filter which causes a dramatic reduction in the decay rate of H_2O_2,[41] very stable ($\pm$5 nM) concentrations of H_2O_2 were obtained during the 2 months that the study lasted. Due to the origin of the seawater used in this study, the H_2O_2 concentration was of 150 $\pm$ 3 nM, a typical concentration of hydrogen peroxide of surface seawater of mid to low latitudes.[22]

The hydrogen peroxide stock solution (2×10^{-4} M) for standard addition experiments was prepared daily from 30% H_2O_2 (Sigma) which was kept under dark conditions in the refrigerator and the exact concentration of which was determined iodometrically.[42]

pH Measurements. Tris-(hydroximethyl)aminomethane (Tris)-artificial 0.005 mol·kg^{-1} seawater buffers[43] were used to calibrate the electrode on the free hydrogen ion scale, pH$_F$ = $-\log[H^+]$. The pH was measured using an Orion pH-meter with a combination electrode (Ross Combination, glass body). The effect of temperature and salinity on the pK^* of the Tris-buffers was considered in this study.[43] The pH was adjusted to the desired value ($\pm$0.01 pH units) during the experiments with small additions of supra-pure HCl 0.1 M using an automatic titrate system (Titrino 719S, Methrom).

Oxygen Determination. The concentration of oxygen at suboxic conditions was controlled to 6 $\pm$ 0.4 μM, except when the oxidation kinetics of Cu(I) was studied at different oxygen concentrations in the range between 1.0 and 218 μM. The level of dissolved oxygen in each study was controlled by independently bubbling both pure N_2 and pure air (Carburos Metálicos S.A.) into the reaction vessel. The dissolved oxygen concentration was determined in each case via an oxygen sensor (Aqua Lytic OX 22) with a detection limit of 0.25 μM. The sensor was calibrated on a daily basis with the value determined by the Winkler method as modified by Hansen.[44] At oxygen concentrations below 70 μM, and due to the need for sampling the seawater in a bottle for the Winkler method that introduced traces of atmospheric oxygen, the linearity between the sensor and the Winkler was lost. Thus, the reading from the sensor was used in all of the studies at high and low oxygen concentrations.

Total Carbonate Concentration. The effect of the total dissolved inorganic carbon (C_T) on the oxidation kinetics was studied in the range of 0.6−6.7 mM by adding NaHCO$_3$ to the reaction vessel. The concentration of C_T was determined coulometrically according to the method described in DOE 1994.[45]

Oxidation Experiments. The oxidation and reduction kinetic experiments of copper were studied in a 250-mL glass thermostat reaction cell controlled to 25 $\pm$ 0.02 °C in a refrigerated bath RB-5A (Techne). The solution was bubbled with N_2 and pure air until the oxygen sensor signal was stable at the desired value. When the oxygen concentration remained constant for 10 min, the system was considered to be ready for use. In each experiment, the concentration varied at most by $\pm$0.4 μmol L^{-1}. The addition of the Cu(I) stock solution to the samples corresponded to the zero time of reaction.

Copper Analysis. The concentration of Cu(I) was determined spectrophotometrically using a modified version of the bathocuproine method[46] as described by González-Dávila et al.[35] The copper concentration was measured with a UV−vis USB2000 (Ocean Optics) connected to a 5-m path-length capillary column (World Precision Instruments) and a UV+Vis A1S Min-DT lamp (Analytical Instrument Systems,
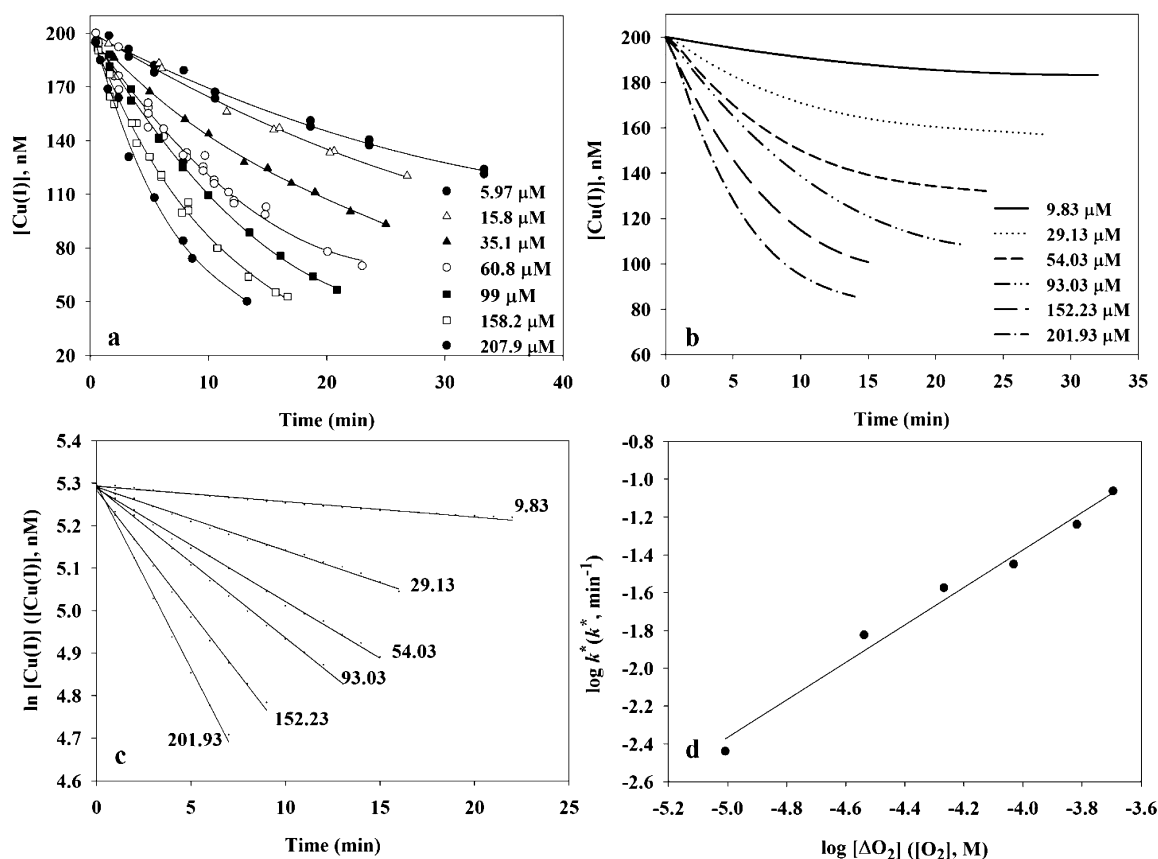
Figure 1. Experimental data for the oxidation of Cu(I) at different oxygen concentrations at $pH_F = 8.0$, 25 °C, and with 150 nM H_2O_2 initially present in the solution. (A) Experimental data and cubic polynomial fitting curves. (B) [Cu(I)] at each oxygen concentration determined as difference of each fitting values with respect to those at 6 μM. The oxygen concentrations are presented as differences. (C) Pseudo-first-order plot for data in (B). (D) Logarithm of the pseudo-first-order rate constants from (C) as a function of the difference in dissolved oxygen concentrations determined as $[O_2]_i - [O_2]_{6\ \mu M}$.

Inc.). Under these conditions, a linear relationship ($R^2 = 0.999$) was found for the Cu (I) range of 0–280 nM[46] (eq 8).

$$Absorbance_{(484nm)} = -3(\pm 4)10^{-4} + 582(\pm 4)10^{-5}[Cu(I)] \tag{8}$$

Numerical Model. The Gepasi program version 3.21[47] was used to design the kinetic model and to determine the best set of constants to describe experimental dependences between the concentrations observed plotted against time and the parameters provided by the model.

■ RESULTS AND DISCUSSION

Cu(I) Oxidation Rate Constant. The rate of oxidation of Cu(I) under oxygen saturation[37] is given by eq 9.

$$\frac{d[Cu(I)]}{dt} = -k[Cu(I)][O_2] \tag{9}$$

where k is the oxidation rate constant for the oxidation of Cu(I). The reaction was described in terms of a pseudo-first-order oxidation rate at nanomolar Cu(I) concentrations.[35,39] At low oxygen concentrations and in the presence of other natural oxidants, the oxidation of Cu(I) should be described by eq 10

$$\frac{d[Cu(I)]}{dt} = -(k_{O_2}[O_2]^{n1} + k_{H_2O_2}[H_2O_2]^{n2}$$

$$+ \sum_j k_{other}[oxidant]_j)[Cu(I)]$$

$$+ k_{red}[H_2O_2][Cu(II)] \tag{10}$$

where k_{other} is the rate constant for Cu(I) oxidation by other intermediates which are naturally present in the solution. Due to their decay rates, and under the experimental conditions for the seawater which was used in our studies, the initial concentration of $O_2^{•-}$ and $OH^•$ radicals was assumed to be zero.[29,34] k_{red} is the rate constant for the positive contribution to the Cu(I) oxidation process due to the reduction of the Cu(II) species with the initially present H_2O_2.[35] To compute the reaction orders for oxygen, n_1, and for hydrogen peroxide, n_2, the experimental Cu(I) concentrations as a function of time at different oxygen (Figure 1a) and H_2O_2 concentrations were analyzed.

The effect of oxygen on the oxidation kinetics of Cu(I), in the presence of other natural oxidants (the initial H_2O_2 concentration was 150 nM), was computed by determining the difference between the concentration of Cu(I) in the solution at any oxygen concentration, and that under 6 μM of oxygen, which was the lowest value considered in this study, ΔO_2 (Figure 1b). Pseudo-first-order oxidation kinetics were

observed at times close to the half-life time (Figure 1), under which conditions eq 10 reduces to

$$\left(\frac{d[Cu(I)]}{dt}\right)_{O_2effect} = -k_{O_2}[\Delta O_2]^{n1}[Cu(I)] = k_{O_2}^*[Cu(I)]$$

(11)

where $k_{O_2}^*$ is computed from the linearization of eq 11.

At $pH_F = 8.0$, $T = 25$ °C, and at constant oxygen concentration, the log $k_{O_2}^*$ (k^* in min^{-1}) and the log $[\Delta O_2]$ ($[O_2]$ in M) were fitted to eq 12 (Figure 1) where $R^2 = 0.987$ and the estimated error was 0.07 for log $k_{O_2}^*$, confirming a reaction order of one for oxygenation of Cu(I).

$$\log k_{O_2}^* = 2.59(\pm 0.27) + 0.99(\pm 0.06)\log[O_2]$$

(12)

The overall oxidation rate constant for Cu(I) by oxygen alone in the anoxic to oxic range is log k_{O_2} (in M^{-1} min^{-1}) = 2.59 ± 0.27, in good agreement with those measured in oxygen saturated solutions in both NaCl with bicarbonate and in seawater at nanomolar concentration.[35,39]

The effect of H_2O_2 on the oxidation kinetics can be computed by determining the difference between the Cu(I) concentrations in the experiments carried out with seawater spiked with H_2O_2 and those without H_2O_2 added, ΔH_2O_2 (Figure S1 in Supporting Information (SI)). Under such conditions, eq 10 can be expressed as eq 13 at low oxygen concentrations

$$\left(\frac{d[Cu(I)]}{dt}\right)_{H_2O_2effect}$$

$$= -k_{H_2O_2}[\Delta H_2O_2]^{n2}[Cu(I)]$$

$$= k_{H_2O_2}^*[Cu(I)]$$

(13)

where $k_{H_2O_2}^*$ can be used to compute the reaction order with respect to hydrogen peroxide.

A set of studies was carried out where the H_2O_2 concentration added to the natural seawater varied over a range between 100 and 500 nM at $pH_F = 8.0$, $T = 25$ °C, and keeping the oxygen concentration constant at 5.1 ± 0.4 μM. The log$k_{H_2O_2}^*$ (k^* in min^{-1}) and the log $[H_2O_2]$ ($[H_2O_2]$ in M) were fitted to eq 14 where $R^2 = 0.999$ and with an estimated error of 0.01 for log$k_{H_2O_2}^*$.

$$\log k_{H_2O_2}^* = 4.1(\pm 0.1) + 1.04(\pm 0.01)\log[H_2O_2]$$

(14)

The slope of eq 14 shows that the oxidation of Cu(I) by H_2O_2 has a reaction order of one for H_2O_2. The overall oxidation rate constant for Cu(I) by only hydrogen peroxide in natural seawater is log $k_{H_2O_2}$ (in M^{-1} min^{-1}) = 4.07 ± 0.04, confirming the previously determined value at micromolar concentration.[19,48]

Reduction of Cu(II) with H_2O_2 at Low O_2 Concentration. The reduction of 200 nM Cu(II) at low dissolved oxygen (5.2 ± 0.2 μM) was studied at a fixed pH_F of 8.0 and 25 °C (Figure S2, SI). Without added H_2O_2 and considering the initial 150 nM H_2O_2 that was naturally present in the seawater used in this work, the amount of Cu(I) produced initially increased and reached a constant value after 40 min. The amount of Cu(I) obtained was 21%, that is 43 nM of Cu(I) regenerated from Cu(II). When an additional 500 nM of H_2O_2 was added, the amount of Cu(I) reached 69 nM, that is 34% of

the initial Cu(II). A fast increase in the Cu(I) (Figure S2, SI) was produced when 500 nM of H_2O_2 was added to the seawater in the first 20 min, at a rate of 1.76 nM Cu(I) min^{-1}. With no added H_2O_2, the rate of Cu(I) production was of 0.87 nM Cu(I) min^{-1},which is valid for the first 40 min. At the total of 650 nM H_2O_2, the Cu(II) reduction dominated over the oxidation of Cu(I) resulting in higher Cu(I) production and, as a result, a decrease in the oxidation rate. Both at low and at saturated oxygen conditions[35] in the presence of 150 nM H_2O_2, the reduction of Cu(II) to Cu(I) by H_2O_2 and $O_2^{\bullet-}$, as shown in eqs 6 and 7, took place (Figure S2, SI). At oxygen saturation, the reactions of Cu(I) with O_2 and $O_2^{\bullet-}$, eqs 2 and 3, counterbalanced the reduction process, resulting in reduction of 9% of the initial Cu(II) added (18 nM of Cu(I)) at steady-state. At low oxygen concentrations, reactions 2 and 3 contributed to a lesser extent to the observed rate, and the steady-state was controlled via the oxidation of Cu(I) by H_2O_2 and the intermediates present in the solution, eqs 4 and 5.

These results show that the reduction of Cu(II) to Cu(I) in seawater took place both at high and low O_2 concentrations when H_2O_2 was in solution, at least at 150 nM. There were no studies done at lower initial H_2O_2. The amount and the lifetime of Cu(I) present in the media was controlled by the amount of O_2 and H_2O_2 found in the solution and by the initial Cu(II) concentration.

Cu(I) Oxidation Rate Constant As a Function of pH at Low Oxygen. The oxidation of Cu(I) as a function of pH_F was studied at the pH range of 6.6−8.2 in seawater at 25 °C and with an oxygen concentration of 5.8 ± 0.8 μM and 150 nM H_2O_2 (Figure 2). Due to the presence of both oxidants in the
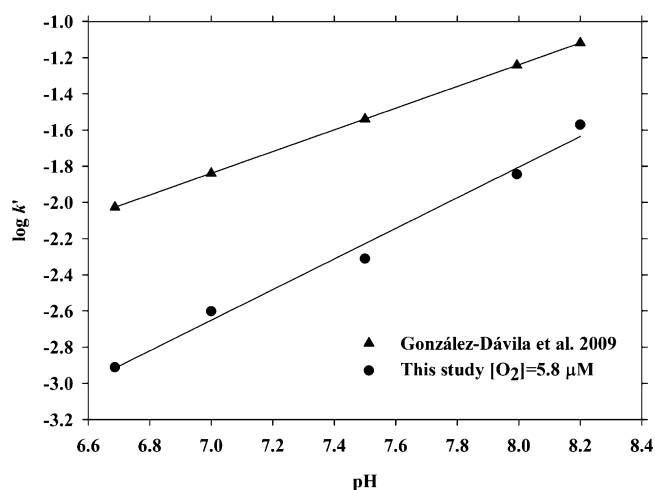

Figure 2. Effect of pH on the oxidation rate constant of Cu(I) (k' in min^{-1}). The initial experimental conditions were $[Cu(I)]_0 = 200$ nM; $[H_2O_2]_0 = 150$ nM; $[O_2] = 5.8 \pm 0.8$ μM; $T = 25$ °C; $S = 36.691$. Data from González-Dávila et al.[35] have been included for comparative purposes.

initial solution, oxidation rates are presented as pseudo-first-order values. Values of log k' for Cu(I) oxidation increased linearly with the pH (Figure 2). Log k' changed from −2.91 min^{-1} at pH_F 6.7 to −1.57 at pH_F 8.2, that is k' increased by 2.6 × 10^{-2} min^{-1}. This behavior (eq 15) was previously observed under oxygen saturation conditions both at micromolar and nanomolar Cu(I) concentrations.[35−38]

$$\log k' = -8.6(\pm 0.2) + 0.85(\pm 0.05)pH_F$$

(15)

Table 1. Rate Constants Used in the Kinetic Model

no.	reaction	log k (M^{-1} s^{-1})	ref
1	$Cu(I) + O_2 \rightarrow Cu^{2+} + O_2^{\bullet-}$	0.929	b
2	$Cu(I) + O_2^{\bullet-} + 2H^+ \rightarrow Cu^{2+} + H_2O_2$	9.30	17
3	$Cu(I) + H_2O_2 \rightarrow Cu^{2+} + OH^\bullet + OH^-$	3.021	b
4	$Cu(I) + OH^\bullet \rightarrow Cu^{2+} + OH^-$	7.9	b
5	$H_2O_2 + OH^\bullet \rightarrow HO_2^\bullet + H_2O$	8.74	b
6	$HO_2^\bullet + O_2^{\bullet-} + H^+ \rightarrow H_2O_2 + O_2$	4.5	17
7	$O_2^{\bullet-} + OH^\bullet \rightarrow OH^- + O_2$	10	57
8	$O_2^{\bullet-} + H_2O_2 \rightarrow OH^\bullet + OH^- + O_2$	0.57	58
9	$Cu^{2+} + O_2^{\bullet-} \rightarrow Cu(I) + O_2$	9.025^a	17
10	$CuHCO_3^+ + O_2^{\bullet-} \rightarrow Cu(I) + HCO_3^- + O_2$	8.792	17
11	$CuCO_3 + O_2^{\bullet-} \rightarrow Cu(I) + CO_3^{2-} + O_2$	8.792	17
12	$Cu(CO_3)_2^{2-} + O_2^{\bullet-} \rightarrow Cu(I) + 2CO_3^{2-} + O_2$	8.792	17
13	$Cu^{2+} + H_2O_2 \rightarrow Cu(I) + HO_2^\bullet + H^+$	3.5^a	b
14	$CuHCO_3^+ + H_2O_2 \rightarrow Cu(I) + HO_2^\bullet + HCO_3^- + H^+$	3.8	b
15	$CuCO_3 + H_2O_2 \rightarrow Cu(I) + HO_2^\bullet + CO_3^{2-} + H^+$	2.6	b
16	$Cu(CO_3)_2^{2-} + H_2O_2 \rightarrow Cu(I) + HO_2^\bullet + 2CO_3^{2-} + H^+$	3.5	b
17	$CO_2 + H_2O + O_2^{\bullet-} \rightarrow HO_2^- + CO_3^\bullet + H^+$	5.0^c	59
18	$HCO_3^- + O_2^{\bullet-} \rightarrow HO_2^- + CO_3^\bullet$	6.0^c	59
19	$CO_3^{2-} + O_2^{\bullet-} \rightarrow HO_2^- + CO_3^\bullet$	5.0^c	59
20	$CO_3^\bullet + O_2^{\bullet-} \rightarrow CO_3^{2-} + O_2$	8.0	60
21	$Fe^{2+} + O_2^{\bullet-} + 2H^+ \rightarrow Fe^{3+} + H_2O_2$	7.0	61
22	$Fe^{3+} + O_2^{\bullet-} \rightarrow Fe^{2+} + O_2$	8.18	61

^{a}Cu^{2+} refers to copper(II) free and hydroxyl species. ^{b}This study. ^{c}Log k for reactions 17, 18, and 19 are close to $(1-2)\bullet10^6$ M^{-1} s^{-1} proposed in ref 59.

where $R^2 = 0.988$ and the standard estimated error for log k' was 0.07.

The effect of the pH was more important at low oxygen concentrations where the slope of log k versus pH was 0.85 than at oxygen saturation[35] where the slope was 0.6 (Figure 2). A slope of log k versus pH of ~0.2 was observed[39] in NaCl solutions without bicarbonate. The presence of bicarbonate has been shown to increase the Cu(I) oxidation rate through both changes in Cu(I) speciation and in the rate contribution.[35,39] If the Yuan et al.[39] set of rate constants is applied to seawater, a value of 0.51 is determined in the pH range of 7−8.25. Moreover, Cu(II) speciation is also affected. At high oxygen concentrations, oxidation of Cu(I) is dominated by its reactions with oxygen and the superoxide radical (eqs 2 and 3). The effect of pH on the speciation of Cu(II), as inorganic Cu^{2+}, CuOH$^+$, Cu(OH)$_2$, and carbonate−Cu(II) complexes, affects its contribution to the apparent rate, especially due to the superoxide radical, with rate constants as high as log k = 9.025 and 8.792, respectively[17] (Table 1). At low oxygen concentrations, and considering that the oxidation of Cu(I) with the H$_2$O$_2$ which was initially present (eqs 4 and 5) is not strongly affected by pH,[19] the experimental data suggested that the acid and basic species of Cu(II) control the log of the rate constant for reduction to Cu(I) by H$_2$O$_2$. Indeed, the reduction of

Cu(II) has been shown to present a pH dependence of 1.28 in seawater,[49] with Cu(OH)$_2$ being the most reactive species. The presence of low oxygen concentrations together with H$_2$O$_2$ in our studies contributed to a decrease in the pH dependence of log k to 0.85, while at oxygen saturation in seawater the slope was reduced to 0.6.

Effect of Ionic Strength on the Oxidation of Cu(I) at Low Oxygen Levels. The effect of the ionic strength on the oxidation of Cu(I) was studied over the range between 0.20 and 0.76 M at pH$_F$ of 8.0 and 25 °C, with the oxygen concentration kept constant at 6.0 ± 0.6 μM. The oxidation rate decreased as ionic strength increased, moving from log k' = −1.20 min^{-1} at I = 0.20 M to log k' = −1.85 at I = 0.76 M. The results (Figure S3, SI) were fitted to a linear equation, eq 16, with an estimated standard error of 0.03 for log k' and R^2 = 0.994. Similar dependences were observed for the oxidation of Cu(I) at micromolar levels[36−38,50] and for nanomolar Cu(I).[35]

$$\log k' = -0.96(\pm0.03) - 1.14(\pm0.06))I \qquad (16)$$

At high ionic strengths when total carbonate concentration was kept constant (2.1 mM), the lowest rates are attributed to the inertness of the higher order CuCl$_2^-$ and CuCl$_3^{2-}$ species.[38] Moreover, the concentrations of major cations in seawater are reduced by dilution, while the total carbonate is kept constant,

and the amount of carbonate available for copper complexation is increased as ionic strength is decreased. The results of this study at low oxygen levels, where the initial H_2O_2 concentration can be more relevant, as compared with those at saturated oxygen,[35] indicated that the ionic strength effect is more significant at low oxygen levels where the slope of log k versus I is 1.14 (eq 16) compared to that of 0.65 at oxygen saturation. This dependence on ionic strength indicates that free Cu^+ and CuCl species are more reactive with H_2O_2 than with oxygen. The values of log k = 8.22 for the oxidation of Cu^+ by H_2O_2 provided by Sharma and Millero[19] at ionic strength of 1 and 9.2, when extrapolated to 0.7, is 3 units higher than that for Cu^+ oxidation by O_2 calculated by Yuan et al,[39] and 4 units higher than that calculated by González-Dávila et al.[35]

Effect of Total Dissolved Inorganic Carbon in the Oxidation of Cu(I) at Low Oxygen Levels. The oxidation of Cu(I) was studied in NaCl 0.7 M and $[O_2]$ = 6.1 ± 1.6 μM at different carbonate concentrations over the range of 0.49 to 9 mM at pH_F = 8.0 at 25 °C (Figure S4, SI). To decrease the oxygen concentration, the solution was bubbled with N_2 which also removed CO_2. The relationship between the total carbonate concentration, C_T, before and after bubbling was defined by eq 17, where R^2 = 0.992 with a standard calculated error of 0.3 mM and C_T in mM.

$$[C_T]_{real} = 0.3(\pm0.2) + 0.71(\pm0.05)[C_T]_{theoretical} \quad (17)$$

Equation 17 showed that C_T in the postbubbled solution ranged from 0.65 to 6.69 mM. The oxidation rate increased with C_T. The data was fitted to a second order polynomic function where R^2 = 0.969 and the estimated standard error was of 0.085 for log k'. C_T is given in mM and k' in min^{-1}, eq 18.

$$\log k' = -2.5(\pm0.1) + 0.21(\pm0.08)[C_T]$$
$$- 0.01(\pm0.01)[C_T]^2 \quad (18)$$

From C_T values of 0.65 to 3.8 mM, log k' increased by 0.46 units, whereas from 3.8 to 6.7 log k' increased by 0.08 units. The larger increase at lower inorganic carbon concentrations is related to the increase in Cu(I)−carbonate complexes that are oxidized at a faster rate than Cu(I)−chloride complexes.[39] At the same time, when the C_T concentration increased, Cu(II)−carbonate complexes were more rapidly reduced to Cu(I), resulting in a decrease in the net oxidation rate of Cu(I).

Kinetic Model. A kinetic model that considered the Cu speciation in seawater and major ion interactions (Table S1, SI) together with rate constants for the oxidation and reduction of Cu(I) and Cu(II) species, respectively (Table 1), was applied to the results obtained under the various different experimental conditions described above. The initial H_2O_2 concentration was included for all of the studies at the experimental value of 150 nM. For completeness, the model also included Fe redox chemistry due to its competition for the oxidation intermediates,[51,52] however at the experimentally determined Fe(III) concentration[53] of 5 nM, its effect was found to be minor in the range of 1−5 nM. To reduce the number of unknown variables, the model considered the Cu(I) species as a whole while Cu(II) species were split into carbonate and noncarbonate species (including free, hydroxyl-, and chloride-complexes, and organic complexes). The model output described the experimental values of Cu(I) as a function of time at the different oxygen concentrations considered in this work, at pH_F = 8 and 25 °C (Figure S5, SI).

The experimental results and model output for the oxidation of 200 nM of Cu(I) and the reduction of 200 nM of Cu(II) with H_2O_2 at 5.2 ± 0.2 μM oxygen (pH_F = 8.0 and 25 °C) were used to compute the best fit for the rate constants for reactions 3, 4, and 9−12 when the carbonate effect was also included (Figure S6, SI). The values for the effect of carbonate on the oxidation of Cu(I) by oxygen (reaction 1) which were determined by applying the rate constants provided by Yuan et al.[39] and based on the speciation of Cu(I) in seawater, indicated that the apparent rate constant was only affected when carbonate was over 5 mM, where log $k_{app} = \sum \alpha_i k_i$[39] only changed from 1.0 to 1.6. Due to the high ionic strength and major ions in seawater, carbonate complexes are a minor fraction in the Cu(I) speciation. However in this study the effect of carbonate concentration was included due to its influence on Cu(II) carbonate species.

Table 1 shows reactions 2, 6, and 21 produce H_2O_2. These same reactions are controlled by superoxide radical concentration and consequently depend on the oxygen concentration, as in reaction 1. H_2O_2 is consumed in reactions 3, 5, 8, and 13−16; reaction 8 depends on the superoxide radical concentration and therefore on reaction 1. The concentration of H_2O_2 at any reaction time, t, $[H_2O_2]_t$, is given by eq 19, where $[H_2O_2]_0$ = 150 nM. The term in brackets in eq 19 may be positive or negative depending on the oxygen and H_2O_2 concentrations throughout the reaction process, indicating which reaction was dominant in the oxidation of Cu(I). Equation 20 thus allowed the relative importance of each set of equations to be evaluated.

$$[H_2O_2]_t = [H_2O_2]_0$$
$$+ \left(\sum [H_2O_2]_{reac.2,6,21} - \sum [H_2O_2]_{reac.3,5,8,13-16} \right)_t \quad (19)$$

$$\Delta[H_2O_2]_t = [H_2O_2]_0 - [H_2O_2]_t$$
$$= \left(-\sum [H_2O_2]_{reac.2,6,21} + \sum [H_2O_2]_{reac.3,5,8,13-16} \right)_t \quad (20)$$

Equation 20 was applied to the model output under the different experimental conditions considered in this work and plotted in Figure 3, where the $\Delta[H_2O_2]_t$ was computed for the different oxygen concentrations considered in this study. Figure 3 also shows the concentration of oxygen that yielded $\Delta[H_2O_2]_t \approx 0$. When the oxygen concentration was under 22 (±2) μM and the initial H_2O_2 was 150 nM, the reaction of Cu(I) was controlled by reactions where H_2O_2 acted as a reagent (reactions 3, 5, 8, and 13−16). In this case, H_2O_2 was consumed and produced hydroxyl and superhydroxyl radicals. When the oxygen concentration was over 22 (±2) μM, the oxidation of Cu(I) was controlled by oxygen (reactions 1, 2, 6, and 21), where hydrogen peroxide and the superoxide radical were produced. When $[H_2O_2]_0$ changes, the critical oxygen concentration also does, being 5 μM when the hydrogen peroxide in solution was 40 nM.

The model value for reaction 3 is close to that provided by Sharma and Millero[19] at micromolar Cu(I). The reaction of Cu(I) with OH-radicals (reaction 4) can probably occur via a secondary radical intermediate, such as carbonate or bromide radicals in seawater.[17,54] In our model, a log k value of 7.9 was used.[54,55] The values of log k for the reduction of Cu(II) by H_2O_2 (reactions 13−16) are in accordance with those determined by Millero et al.[20]
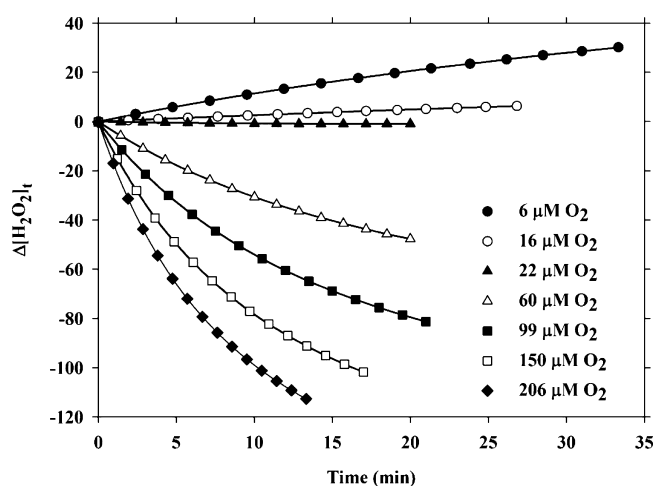
Figure 3. Predictive model outputs for the competitive effect between oxygen and hydrogen peroxide on the Cu(I) oxidation kinetics. $\Delta[H_2O_2]_t > 0$ indicated H_2O_2 dominated the oxidation. $\Delta[H_2O_2]_t < 0$ indicated O_2 dominated the oxidation. The initial experimental conditions were $[Cu(I)]_0 = 200$ nM; $pH_F = 8.0$; $T = 25$ °C; $S = 36.691$.
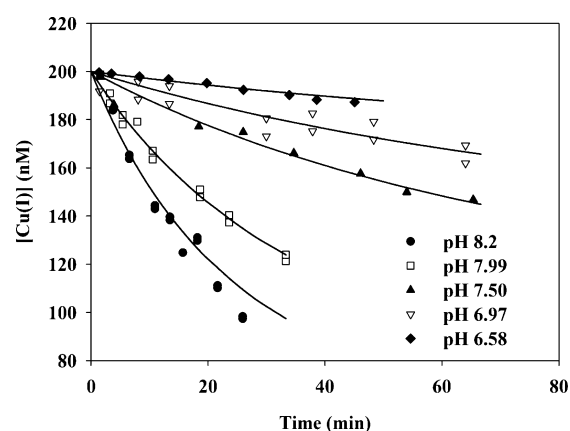

Figure 4. The evolution of the experimental Cu(I) concentrations over time at different pH_F values (symbols) and model outputs (lines). The initial experimental conditions were $[Cu(I)]_0 = 200$ nM; $[H_2O_2]_0 = 150$ nM; $T = 25$ °C; $S = 36.691$.

The model values in Table 1 were perturbated by up to 1 order of magnitude to evaluate the contribution of each reaction to the accuracy of the model. The most critical balance in the oxidation of Cu(I) at low oxygen concentrations is the competition between H_2O_2 and O_2, where the oxidation rate by H_2O_2 (reaction 3) is the most sensitive. When the rate constants were increased by 1 order of magnitude with an initial $[H_2O_2] = 150$ nM and $[Cu(I)] = 200$ nM, the Cu(I) concentration decreased by 80 nM after the first 10 min for reaction 3 and by 50 nM for reaction 1. Overall, the process was less sensitive to the reduction of Cu(II) by H_2O_2 in the presence of carbonate, increasing the Cu(I) concentration by 20 nM when the rates for carbonate species (reactions 14–16) were increased. Among the carbonate species, the most sensitive was the $Cu(CO_3)_2^{2-}$, which also contributed to a greater extent to the regeneration of Cu(I) at pH 8 at low oxygen and 150 nM H_2O_2. The reactions 13–15 resulted in very little change to the process; however the reactions were included to account for the carbonate effect at lower pH. For a low oxygen water (6 μM), and according to our model, if the H_2O_2 concentration in the initial sample is decreased to 40 nM (a value determined for surface waters in the tropical Atlantic[34]) the half-time, $t_{1/2}$, of Cu(I) will increase from 50 to 94 min, showing the important competitive effect between oxygen and H_2O_2 in anoxic and suboxic waters. However, in oxic waters, the presence of 40 nM instead of 150 nM of H_2O_2 will not affect the $t_{1/2}$ appreciably.

The oxidation of Cu(I) was studied as a function of pH at low oxygen (Figure 4). To account for the pH effect, the reaction of Cu(I) with O_2 was fitted to eq 21, where the rate constants provided by Yuan et al.[39] in NaCl solution and the inorganic speciation of Cu(I) in seawater[39] were considered (Figure S7a, SI). Ionic interactions among the major ions in seawater, which affect carbonate speciation, were also considered in calculations. The pH dependence given by Yuan et al.[39] when applied to seawater solution with 2.1 mM total dissolved inorganic carbon in the pH range of 8.25 to 7, was 0.5, close to the value of 0.6 experimentally determined under oxygen saturated conditions.[35] Under the experimental

conditions of our study with concentrations of oxygen below 22 μM and H_2O_2 of 150 nM, the pH effect on the oxidation rate by oxygen alone did not explain the observed dependence (Figure S7a, SI). Reaction of Cu(I) with superoxide was assumed to be pH independent following Zafiriou et al.[17] The unexplained pH dependence was described by considering the influence of pH both on the reaction of Cu(I) with hydrogen peroxide (reaction 3), eq 22 (Figure S7b, SI), and on the reaction of the noncarbonated Cu(II) species with H_2O_2 (reaction 13), eq 23 (Figure S7c, SI). According to the fitting procedure, the effect of pH on oxidation of Cu(I) at low oxygen concentrations for the pH range of 6.6–8.2 was also affected by the effect of pH on Cu(I) oxidation by hydrogen peroxide, which indicated that Cu^+, $CuClOH^-$, and $CuCO_3^-$ are the most kinetically reactive species. The effect of decreasing the pH on the reduction of the noncarbonate Cu(II) species affected the pH dependence for the oxidation of Cu(I) at low pH values, related to the decrease in the concentration of the species $CuOH^+$ and $Cu(OH)_2$. The species $Cu(OH)_2$ has been described as the most reactive[49] in the reduction of Cu(II) by H_2O_2.

$$\log k_1 = -3.03(\pm0.20) + 0.50(\pm0.03)pH \qquad (21)$$

$$\log k_3 = -2.61(\pm0.30) + 0.71(\pm0.04)pH \qquad (22)$$

$$\log k_{13} = 1.59(\pm0.10) + 0.23(\pm0.01)pH \qquad (23)$$

Implication of Findings. The oxidation of Cu(I) at different oxygen concentrations in natural seawater has a reaction order of one for both oxygen and hydrogen peroxide. This study provided information about the competitive effect that natural oxidants, dissolved oxygen and H_2O_2, exert on the Cu(I) and Cu(II) concentrations in natural and low oxygenated seawaters. H_2O_2 contributes significantly to the oxidation of Cu(I) when its concentration is 150 nM and the concentration of oxygen is below 22 μM, an oxygen concentration found in hypoxic and anoxic environments and when pH is below 8. In coastal areas with high organic matter production, low values of oxygen and high H_2O_2 concentrations can be observed. Moreover, in these same environments, the superoxide radical is a major product of the photo-oxidation of the colored dissolved organic matter. Any form of Cu and Fe present in the solution can react rapidly with the superoxide producing more

H_2O_2 and oxygen. This makes the rate constants for the oxidation of reduced species by the different reactive oxygen species of particular importance. The model developed in this work includes the state of the art of Cu redox processes for seawater media. The model confirmed the roles played by O_2, H_2O_2, and superoxide on Cu redox transformations and combined all of them in order to provide a full description of the processes which act in oxygen minimum zones and coastal waters. To make the model applicable to any chemical conditions in seawater, the effect of pH on copper speciation and on the oxidation rates by oxygen and H_2O_2 were considered. A sensitivity analysis indicated that at pH 8 when H_2O_2 concentration varied from 150 to 40 nM and the oxygen concentration was below 22 and 5 μM respectively, the primary reactions determining the oxidation rate are those involving H_2O_2, which become more important when the pH is lower than 8.0. These are conditions observed in coastal waters and in oceanic oxygen minimum zones of the Atlantic and Pacific at 300−500 m depths, where pH can reach values below 7.6.[56] In the eastern Pacific, they become suboxic with dissolved oxygen concentrations of less than 1 $\mu mol\ kg^{-1}$ while in the eastern South Atlantic values are about 17 $\mu mol\ kg^{-1}$.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

A list of equilibrium constants used in the kinetic model and figures showing significant results obtained in this study. This information is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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