

The effect of Cu on the Fe redox cycle: The role of reactive oxygen species

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The interaction between the redox chemistry of Fe and Cu at nanomolar has been studied in UV-treated seawater, both in the presence of Cu(I) and Cu(II) (0-200 nM) and considering the effect of H₂O₂ (0 – 500 nM), pH (6.0 – 8.5) and NaHCO₃ (2 – 9 mM). 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).

This study demonstrates that Cu accelerate the Fe(II) oxidation rate in seawater where O₂^{•-} is playing a key role during the interaction of Fe(II) and Cu(II). The increase in the Fe(II) oxidation rate can be due to the added Cu, and to the competition of Fe and Cu interaction with hydroxyl, H₂O₂, O₂^{•-} and carbonate groups. However, the overall results are not fully explained by the reactions with the reactive oxygen species (ROS), and the formation of Fe-Cu particles (cupric and cuprous ferrite) should be considered.

On the other hand, Cu(II) was rapidly reduced to Cu(I) in the presence of Fe(II) in seawater under air-saturated and anoxic conditions. The concentration of Cu(I) formed was affected by the concentrations of both Fe(II) and H₂O₂ in seawater.

These results demonstrate that the full understanding of the Fe and Cu redox cycles can only be explained by considering the interaction between these two essential metals that will also have impact on the marine biogeochemical cycles.