

Influence of Magnetite Stoichiometry on Copper Redox Speciation: New Insights into Copper Biogeochemistry

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Copper is an essential micronutrient, when present as Cu(II), but can be toxic at elevated Cu(II) concentrations or under its reduced Cu(I) form. Therefore, the behaviour and fate of Cu in the environment is affected by naturally occurring redox active iron oxides like magnetite (Fe₃O₄).¹ Stoichiometric magnetite (with $R = \text{Fe(II)}/\text{Fe(III)} = 0.5$) may partially oxidize to non-stoichiometric one ($0 < R < 0.5$) or to maghemite ($R = 0$).² However, the effect of magnetite stoichiometry (R) on Cu redox speciation has been overlooked.

This study examines the interaction Cu with 10 nm-sized magnetite exhibiting different stoichiometries.² The effect of pH (~3 to ~10), initial [Cu(II)] (25 and 500 μM), and excess dissolved Fe(II) ions ($[\text{Fe(II)}]_{\text{aq}} \sim 1000 \mu\text{M}$) were additionally studied. The redox speciation of Cu was analyzed in solution by ion selective electrode and ICP-MS, and at the magnetite surface by soft X-ray absorption spectroscopy (XAS) and magnetic circular dichroism (XMCD) at the Cu and Fe L_{2,3}-edges.

Both solution and surface speciation revealed the co-occurrence of Cu(II) and Cu(I) at pH < 8. At pH 8 and low [Cu], where nearly 100% Cu adsorption occurred, the proportion of Cu(I) has increased by ~70% from R0.1 to R0.5. The important stabilization of Cu(I) on magnetite, unexpected from speciation calculation omitting Cu-magnetite interaction,³ suggests that magnetite affects Cu toxicity. At high [Cu], Cu(0) was detected on R0.5, which was enhanced by adding an excess of dissolved Fe(II). Cu(0) was shown to form distinct nanoparticles by transmission electron microscopy.

Quantitative analysis of electron transfer processes highlights that at low [Cu], magnetite stoichiometry is unaffected, whereas at high [Cu], significant alterations occur, unless Fe(II) recharge was ensured by an external source (or excess) of Fe(II).

This study reveals the complex interactions between Cu and magnetite nanoparticles, with significant implications for understanding Cu biogeochemistry and developing effective remediation strategies.

REFERENCES

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