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Prediction of the impact of the environmental conditions on the stoichiometry (Fe(II)/Fe(III)) of magnetite nanoparticles

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Magnetite nanoparticles (MNs, Fe_3O_4) are fascinating nanoparticulate minerals due to their electronic, magnetic and chemical properties. Ubiquitous in the environment, they play an important role on the behavior and fate of many contaminants. They are also among the most used ferromagnetic nanomaterials in environmental, industrial and biomedical applications (e.g. environmental remediation, catalysis, energy storage, MRI, medicine therapy) due to their unique physicochemical properties (e.g. redox, magnetic, high surface areas, optic, semiconductor). Their intriguing structural and reactivity features arise both from the “nano-effect” and the co-occurrence of Fe^{2+} and Fe^{3+} ions in their structure.

However, if stoichiometric MNs (R = [Fe(II)]/[Fe(III)] = 0.5) are extremely sensitive to oxidation, leading to the formation of non-stoichiometric magnetites ($0 < R < 0.5$) or maghemite (R = 0; Fe_2O_3), the impact of environmental factors on its transformation has not been fully understood and cannot be predicted numerically. To fill this gap of knowledge, we performed wet chemistry experiments, X-ray absorption spectroscopy (XAS) and magnetic circular dichroism (XMCD) to determine the stoichiometry of 10 nm-sized MNs [1], with initial R values ranging from 0.1 to 0.5, under various environmentally relevant conditions (pH, redox, presence of dissolved Fe(II) or organic ligands).

The results confirmed previous findings that oxidation-recharge cycles of magnetite using H_2O_2 or O_2 and Fe^{2+} were reversible. In the absence of O_2, an H^+-promoted dissolution process is responsible for the preferential release of Fe(II) into solution. This process was particularly important and implied that stoichiometric MNs cannot exist at pH < 7 despite a high magnetite concentration and an excess of dissolved Fe(II). Instead, non-stoichiometric magnetite co-existed with dissolved Fe^{2+}. We developed a thermodynamic model for the magnetite-maghemite solid solution able to predict the stoichiometry of MNs [2], that might be used to unravel the complex behavior and reactivity of these nanomaterials in many environmental settings as well as for broad range of applications involving MNs in aqueous solutions.

References

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