Goldschmidt 2025 Abstract
https://doi.org/10.7185/gold2025.26360

Impact of redox conditions on the binding of redox-inert contaminants to magnetite

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Magnetite nanoparticles (MNs, $Fe^{II}Fe^{III}_2O_4$) play an important role on the behavior and fate of many contaminants and are widely used in environmental applications due to their small size, high surface area, redox and magnetic properties. Structural Fe(II) in stoichiometric MNs (R = [Fe(II)]/[Fe(III)] = 0.5) is extremely sensitive to oxidation, proton and ligand-promoted dissolution, leading to the formation of non-stoichiometric magnetite (0 < R < 0.5) or maghemite (R = 0; $Fe^{III}_2O_3$)[1]. MNs stoichiometry can then be restored with Fe(II) or chemical reductants, which makes their structure highly dynamic in fluctuating redox environments.

The effect of redox conditions (or magnetite stoichiometry) on the reduction processes of various contaminants (e.g. U(VI), Cr(VI), organics) have been studied carefully [2]. However, most of the sorption experiments with redox-inert elements were carried out in O_2 atmosphere, using NO_3^- as background electrolyte or at acidic pH. Therefore, the impact of R on the binding of redox-inert contaminants to magnetite has been overlooked, although its ability to bind ions and molecules may heavily rely on R, as evidence for silicate, humic acid and quinolone antibiotics [3].

Here the interaction of Co(II) [4], Ni(II) and Cr(III) (considered redox-inert in reduced environments) with magnetite was investigated for various stoichiometries ($0.1 \leq R \leq 0.5$). Surface speciation of metal ions (M) was probed by X-ray absorption spectroscopy (XAS) and/or X-ray magnetic circular dichroism (XMCD). Stoichiometric magnetite (R0.5) incorporates metal ions in its structure at low [M] (as MFe_2O_4-like phases), whereas surface complexes form on quasi-maghemite (R0.1). At high [M], R0.5 surface was a better template for M-hydroxide surface precipitation than R0.1. These results highlight the necessity to carefully preserve, control or monitor magnetite stoichiometry and will help to predict the effect of magnetite on metal fate and ecotoxicity in the environment.

References

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