

Oxyanions reactivity towards magnetite: towards defining a driving force?

LAURENT CHARLET¹, ALEJANDRO FERNANDEZ-MARTINEZ², SARA GOBERNA FERRON³, AGNIESZKA POULAIN⁴, KAIFENG WANG⁵ AND CAROLINA GUIDA⁶

¹ISTerre, CNRS

²ISTerre, Univ. Grenoble-Alpes, CNRS

³ISTerre : Institut des Sciences de la Terre

⁴ISTerre, CNRS & Univ. Grenoble Alpes

⁵ISTerre, University Grenoble Alpes

⁶Université Grenoble Alpes

Presenting Author: charlet38@gmail.com

Magnetite (Fe₃O₄) is a widely occurring mixed-valence iron oxide with important industrial and natural applications. In this talk we will compare the (nano)magnetite reactivity towards a series of oxyanions, such as perchlorate (ClO₄⁻), Nitrate (NO₃⁻), rhenate (ReO₄⁻), pertechnetate (TcO₄⁻), chromate (CrO₄²⁻), selenate (SeO₄²⁻), arsenate (AsO₄³⁻), antimonate (SbO₄³⁻) and silicate (SiO₄⁴⁻). These systems were investigated by ourselves and colleagues using wet chemistry, TEM microscopy, Mössbauer¹ and XAFS² spectroscopy, and the results interpreted at the light of magnetite surface chemistry, oxyanion symmetry and atomic size and the identity of reduced aqueous and solid species (if any).

Monovalent Cl, N, Re oxyanion reactivity with magnetite is usually very low, as their sorption is weak. The positive charge development on magnetite – and thus possible electrostatic interaction - occurs at low pH values where magnetite dissolves extensively. An exception is pertechnetate, as a complete reduction of Tc(VII) to Tc(IV) is observed, together with Tc dimerization (at high loading) or Tc substitution for Fe at low loading. This exception is questioning the often assumed “analogy” between rhenate and pertechnetate. The surface maghemite layer Fe substitution by oxyanion reduced species is also observed in the case of chromate, where Fe and Cr form nearly ideal solid solution maghemite, which may be non-conductive. On the other hand, the +III reduced product of antimonate (SbO₄³⁻) or arsenate (AsO₄³⁻) reaction with nano-magnetite is found in both cases to be a highly symmetrical tridentate surface complex formed at the position otherwise occupied by tetrahedral Fe(III)². Finally, selenate ions are reduced, via selenite surface complexes to solid nanowire-shaped solids, irrespective the co-adsorption of silicate oligomers. In conclusion, the geometrical fit of the reduced species at - or in - magnetite/maghemite and the possible surface precipitation of a distinct phase dictate altogether the extent of the reductive interactions of these oxyanions with magnetite.

[1] S. Goberna-Ferron *et al.*, «Influence of Silica Coatings on Magnetite-Catalyzed Selenium Reduction », *Env. Sci. & Tech.*, 2021 (in press)

[2] R. Kirsch *et al.*, « Reduction of antimony by nanoparticulate magnetite and mackinawite », *Mineralogical*