Goldschmidt 2023 Abstract
https://doi.org/10.7185/gold2023.15773

Heterogeneous Fenton-like reactions in natural soils and sediments at neutral pH with O_2 as oxidant

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Heterogeneous Fenton-like processes using O_2 as oxidant and iron(II) minerals as substrate is a rapidly growing research field with important implications especially for in-situ organic pollutant degradation in natural media. These reactions can be conducted at neutral pH and several minerals are considered such as iron oxides [1], sulfides and clays. Autochthonous soil minerals have been also proposed as putative substrates for such heterogeneous Fenton-like reactions. However, the identity and efficiency of the reactive species produced upon air-oxidation reactions is still debated and may also depend on the mineral involved as well as on physicochemical conditions.

We will present new spectroscopic results focusing on the identity and origin of reactive species produced upon oxygenation of a variety of natural soils and sediments at neutral pH. The air-oxidation protocol was performed on samples collected under anoxic conditions to preserve the reactivity of Fe(II) phases and X-ray absorption spectroscopy was used to monitor the changes in Fe speciation during the oxidation. Electron Paramagnetic Resonance (EPR) spin-trapping was used to investigate the identity and quantity of radicals yielded by these natural samples in the same air-oxidation experiments. Although hydroxyl radical was identified, our results yield strong evidences for the implication of another reactive species able to produce alkyl radicals in the presence of alcohols. Based on its significant dependence on the presence of Fe(II)-complexing ligands, this species is interpreted as the high-valent iron species Fe(IV) [2].

[1] Ardo *et al.* Oxidative Degradation of Nalidixic Acid by Nano-Magnetite via Fe^{2+}/O_2-Mediated Reactions (2015), *Environ. Sci. Technol. 49* (7), 4506–4514.

[2] Morin *et al.* Phosphate boosts non-hydroxyl radical species production upon air-oxidation of magnetite and iron-sulfides at neutral pH. Submitted to *The Journal of Physical Chemistry C*