Fate and role of arsenic during green rust formation via reductive dissolution of ferrihydrite

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Green rust (GR) minerals, also known as anionic clays, consist of Fe^{II}-Fe^{III} hydroxide sheets with interlayer anions and water. They form nanometer-sized particles that have a zero point of charge around pH 8, making them excellent adsorbents for oxyanions in natural environments. However, the interactions with and behaviour of toxic oxyanions, like arsenic, in the presence of GR phases are not well understood. We recently showed that under reducing conditions, up to 160 mg of As(III) and 105 mg of As(V) could be sorbed by 1 g of freshly-synthesized GR sulfate (GR_{SO4}).[1] These adsorption capacities are among the highest for any iron (oxyhydr)oxide phases found in subsurface environments.

In non-sulfidic reduced waters and soils, GR often forms via interactions between Fe^{2+}_{aq} and soild Fe^{III} (oxyhydr)oxides such as ferrihydrite (Fh).[2-3] While the mechanisms for such Fh-GR inter-transformations are fairly well-known, the fate of mineral-associated As during this process (i.e. whether As desorbs, remains adsorbed or becomes associated with GR) is still poorly understood, although such information is critically needed to model As cycling in such environments.

To fill this gap, we quantified the fate of As(III) and As(V) species (100 μM) during Fe(II)-induced transformation of Fh at environmentally-relevant groundwater conditions (pH 8, IS = 0.1 M, As/Fe = 0.008). Our results show that, compared to the pure system, the presence of As delayed the Fh transformation to GR_{SO4} and that As(III) had a stronger inhibitory effect than As(V). While the dissolution of Fh led to an intial release of As into the aqueous phase, it was removed by the newly-formed GR_{SO4} particles. Overall, these results highlight the importance of GR_{SO4} minerals in As cycling in pristine and contaminated soils and groundwaters, and potentially also in ancient settings (e.g. Precambrian oceans).[4]

References: [1] Perez, et al., 2018 (in review). [2] Sumoondur, et al., *Mineral. Mag.*, 2008, **72**, 201-204. [3] Wang, et al., *Environ. Sci. Technol.*, 2014, **48**, 14282-14290. [4] Halevy et al., *Nat. Geosci.*, 2017, **10**, 135-139.