

Competing immobilization pathways for arsenate and phosphate in Fe(II)-bearing minerals: Adsorption versus structural incorporation

JEFFREY PAULO H. PEREZ¹, ALICIA LI HAN CHAN¹, MARHARYTA OKHRYMENKO¹, ROBERTS BLUKIS¹, J. FREDERICK W. MOSSELMANS², SATHISH MAYANA^{1,3}, VLADIMIR RODDATIS¹ AND LIANE G. BENNING^{1,4}

¹GFZ German Research Centre for Geosciences

²Diamond Light Source

³Carl Zeiss Microscopy GmbH

⁴Freie Universität Berlin

Presenting Author: jpperez@gfz-potsdam.de

Arsenic (As) contamination in soil and groundwater affects more than 150 million people worldwide [1], mostly in South and Southeast Asia. Contaminated groundwater in these regions are usually oxygen-poor and Fe²⁺-rich [2] where green rust (GR) phases could form. GR is a highly reactive Fe^{II}-Fe^{III}-bearing mineral phase [3] that often forms via transformation of metastable Fe^{III} (oxyhydr)oxides (e.g., ferrihydrite, FHY) in the presence of dissolved Fe²⁺ [4]. We have shown the high As adsorption capacity of synthetic GR sulfate (GR_{SO4}) [5,6], making it a potentially important substrate for As immobilization. We, however, lack knowledge on how GR phases form in the presence of As, or what influence of common competing ions (e.g., phosphate, PO₄³⁻) have on the ultimate fate of As-bearing GR phases.

To fill this knowledge gap, we monitored the Fe²⁺-induced transformation of As(V)-bearing FHY ([As]_{initial} = 100 μM) to GR_{SO4} (As/Fe = 0.008) in the presence of varying concentrations of dissolved PO₄³⁻ (0.1-2 mM, P/As = 1-20) at relevant groundwater conditions (pH 8, ionic strength = 0.1 M). Our results showed that at all P/As ratios, both As and P were quickly sequestered by the mineral products. However, the mineralogical composition was dependent on the P/As ratio. GR_{SO4} was the dominant phase at low P/As ratios, while high P/As ratios led to a mixture of FHY, GR_{SO4} and vivianite (Fe^{II}₃(PO₄)₂·8H₂O). In GR-dominated samples (i.e., low P/As ratio), As(V) was adsorbed onto GR_{SO4}, while at high P/As ratio, As(V) was structurally incorporated into vivianite (~53%) with the remaining As fraction adsorbed onto FHY and GR_{SO4}. Structural incorporation of As^VO₄³⁻ into vivianite was possible through the substitution of PO₄³⁻ in its crystal structure. Overall, these results highlight the importance of GR in controlling As toxicity and mobility in anoxic, Fe²⁺ and P-rich subsurface environments.

References:

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