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Influence of co-existing phosphate on the speciation and partitioning of arsenate in Fe(II)-bearing minerals

JEFFREY PAULO H. PEREZ[1], ALICIA LI HAN CHAN[1], J. FREDERICK W. MOSSELMANS[2] AND LIANE G. BENNING[1,3]

[1]GFZ German Research Centre for Geosciences
[2]Diamond Light Source
[3]German Research Centre for Geosciences, GFZ
Presenting Author: jpperez@gfz-potsdam.de

Groundwater contamination by geogenic arsenic remains a global environmental and public health concern, especially in South and Southeast Asia.[1] Arsenic toxicity and mobility in contaminated aquifers are controlled by the interaction of arsenic with reactive mineral phases, particularly iron-bearing minerals. However, the immobilization of As in such Fe-bearing minerals can be destabilized by co-existing ions in groundwater, which can lead to As remobilization. Among these ions, dissolved phosphate has a strong inhibitory effect on As sorption onto iron minerals,[2] especially for inorganic arsenate [As(V)]. This arises from the chemical and structural similarity of aqueous arsenate and phosphate at near-neutral pH conditions. Competitive sorption between arsenate and phosphate to Fe(III)-bearing minerals has been extensively studied, but their fate in reduced aquifers is largely unknown. Under reducing conditions, Fe(III) minerals can transform to redox-active Fe(II)-bearing phases (e.g., green rust (GR), magnetite, vivianite), and could potentially induce changes in speciation and partitioning of arsenate and phosphate.

Here, we followed the Fe^{2+}-induced transformation of arsenate- and phosphate-bearing ferrihydrite (FHY) under anoxic and near-neutral pH conditions in the presence of varying ratios of phosphate and arsenate ([As(V) = 100 µM, P:As(V) = 1–20). We document that the immobilization of both phosphate and arsenate in the mineral transformation products, as well as their phase composition, was largely controlled by the initial P:As(V) ratio. Low P:As(V) ratios led to GR_{SO4} formation, which ultimately transformed to magnetite after 180 d. Meanwhile, high P:As(V) ratios resulted in a mixture of GR sulfate and vivianite, with magnetite as a minor fraction. In turn, the speciation and partitioning of As(V) were also affected by the P:As(V) ratio. Higher P:As(V) ratio led to faster partial reduction of mineral-bound As(V) to As(III). Ultimately, As(V) was structurally incorporated into magnetite[3] (low P:As(V) ratio), or vivianite (high P:As(V) ratio). Overall, these results highlight influence of co-existing phosphate in controlling the toxicity and mobility in anoxic, Fe^{2+}-rich subsurface settings such as contaminated aquifers.

References

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