Iron oxides are strong sorbents of arsenic, thereby regulating its fate and transport. As a consequence, reductive iron transformations can have pronounced influences on arsenic partitioning. In fact, the primary process by which arsenic is displaced from solids appears to be a shift from aerobic to anaerobic conditions. Nevertheless, it is presently unclear whether arsenic mobilization under anaerobic conditions results from a transformation from $\text{As(V)}$ to $\text{As(III)}$ or from mineralogical changes as a consequence of iron and manganese reduction. Furthermore, the specific conditions that may lead to arsenic release within anaerobic environments have yet to be fully resolved.

Here we examine desorption behaviour of arsenic from ferrihydrite-, goethite- and hematite-coated sand within aerobic and anaerobic systems under hydrodynamic conditions. It is widely believed that reductive transformation, inclusive of dissolution and recrystallization, invokes a displacement of $\text{As(III)}$ and $\text{As(V)}$. However, desorption and transport of $\text{As(V)}$ is transitory whereas $\text{As(III)}$ undergoes prolonged and pronounced desorption. Furthermore, we observe that ferrihydrite transformation limits (rather than promotes) desorption of $\text{As(III)}$ under conditions of intense $\text{Fe(III)}$ reduction, potentially through precipitation of a secondary arsenic-bearing ferrous-iron phase. Formation of reduced iron oxide phases through the generation of high $\text{Fe(II)}$ concentrations (>0.8 mM) severely retards $\text{As(III)}$ desorption. Conversely, at lower $\text{Fe(II)}$ concentrations (<0.8 mM), ferrihydrite transformation does not appear to retard arsenite desorption—although it does not promote it either. Interestingly, we observe the greatest arsenite mobilization in the absence of $\text{Fe(II)}$, and concomitant resulting mineralogical transformations of ferrihydrite.

In contrast to ferrihydrite, desorption of $\text{As(III)}$ from both goethite- and hematite-coated sands is not impacted by aqueous $\text{Fe(II)}$. Thus, long-term respiration on $\text{Fe(III)}$ within goethite or hematite would result in arsenic release once the surface sites are sufficiently depressed to induce desorption. While $\text{As(III)}$ desorption from hematite and goethite appears to fit the current paradigm of arsenic release under anaerobic conditions, (bio)transformation of ferrihydrite (or lepidocrocite) may in fact stabilize $\text{As(III)}$, limiting its mobility within soils and sediments.