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Changes in speciation and spatial distribution of iron and zinc during mineral transformation of Zn–bearing ferrihydrite in sediments

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In soils and sediments, ferrihydrite plays a major role in the cycling of many elements, including toxic or nutrient trace metals. Although the impact of metals incorporated into ferrihydrite has been well described in model experiments with mixed mineral suspensions, the applicability of these results to natural environments is still to be confirmed.

Here, we focus on the impact of the Fe(II)-catalyzed transformation of ferrihydrite (Fh) on the mobility of zinc, as an example of divalent trace metals. We performed laboratory mesocosm experiments to compare the rates and products of transformation of Fh with coprecipitated Zn (Fh-Zn), in conditions that mimic natural environments. Natural intertidal sediments were flooded with artificial seawater until reducing conditions were established (Eh < –200 mV, dissolved Fe(II) at ~ 0.8 mM). Fh-Zn labelled with ^{57}Fe was mixed with sediment [1] and placed in porous meshbags that were inserted into the anoxic sediments. Fh-Zn samples were thereby incubated in the presence of dissolved Fe(II) for more than three months, and we tracked the kinetics and products of the Fh-Zn transformation by ^{57}Fe Mössbauer spectroscopy. We show that Fh-Zn transformed under the established reducing conditions to a poorly crystalline mixed-valence Fe(II)-Fe(III) phase similar to green rust, without formation of new Fe(III) minerals such as goethite. Overall, the observed Fh-Zn transformation rates are much slower than in comparable mixed-suspension experiments. Higher Zn concentrations do not drastically slow down the Fh-Zn transformation rate compared to Zn-free Fh, as expected from the literature on mixed-suspension experiments.

Micro-X-ray fluorescence and bulk- and micro-X-ray absorption spectroscopy at the Zn *K*–edge show that Fe and Zn become spatially separated during the transformation and that a large fraction of Zn is scavenged by locally produced sulfide with precipitation of ZnS. This decoupling of the fate of Fe and Zn, combined with removal of released Zn, may explain the apparently small effect of Zn on Fe mineral transformation.

These results underline the need to carefully evaluate the applicability to natural systems of results (transformation rates and products) from laboratory model experiments.

[1] Notini *et al*, 2023, *Environ. Sci. Technol.* 57, 10008–10018.