Goldschmidt 2022 Abstract
https://doi.org/10.46427/gold2022.9828

Reactivity of adsorbed metals after aging with goethite: Effect of cation size and competitive adsorption

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The dynamics of trace metals at mineral surfaces influence their fate and bioavailability in the environment. For some trace metals, desorption hysteresis has been observed with iron (oxyhydr)oxides[1], suggesting that metal cations may become incorporated or irreversibly bound after aging. In this study, we selected three metals to represent a range of cation sizes (Cd, Ni, or Zn) and performed isotope exchange experiments after aging with 4 g/L goethite at pH 7 for 2 days, 1 month, 2 months, and 4 months. At each aging timepoint, a 100 mL subsample of the suspension was collected. From this subsample, 50 mL of the solution was removed to measure the dissolved metal concentration and replaced with a solution which was compositionally-identical except that the dissolved metal of interest was isotopically enriched in ^{116}Cd, ^{62}Ni, or ^{68}Zn. The evolution of the Ni, Cd, or Zn isotope ratios was then measured with time. As part of a second series of studies, competitive isotope exchange experiments are being performed in which pairs of metals (e.g., Ni-Zn) are present.

We find that the exchangeability of the adsorbed metal pool followed the order Cd > Zn > Ni, mirroring the trend in cation size. For Ni, the smallest cation with the radius closest to that of Fe(III) in goethite, there is a notable decrease in the exchangeable fraction with time, from 80% at 2 days to 52% after 4 months. This decrease may be consistent with Ni incorporation into goethite. For Zn(II), the exchangeable fraction (95%) does not change with time, however, rates of exchange slow with aging. Cd, the largest cation studied, shows nearly identical exchange rates after aging. Preliminary competitive exchange experiments reveal that Zn availability decreases in the presence of dissolved Ni, suggesting that Ni may promote Zn incorporation. These results indicate that cation size and competitive adsorption influence metal availability at iron (oxyhydr)oxide surfaces. This study also demonstrates that larger cations adsorbed to iron (oxyhydr)oxides may be predominantly bioaccessible at circumneutral pH because they are capable of rapid and near-complete desorption.

[1] Ainsworth et al. (1994) *Soil Sci. Soc. Am. J.* **58**, 1615-1623.