

Quantifying nitrogen fixation in the North Atlantic using paired analyses of Cd and N stable isotopes.

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For Cd and fixed N in the ocean, there are important similarities in the depth profiles of both dissolved concentration and stable isotopic composition ($\delta^{114}\text{Cd}$, and $\delta^{15}\text{N-NO}_3^-$). Both elements are biologically assimilated in surface waters and regenerated from sinking organic matter in the ocean interior. Preferential uptake of the lighter isotopes during biological assimilation typically leads to an increase in both $\delta^{114}\text{Cd}$ and $\delta^{15}\text{N-NO}_3^-$ in surface waters, and the isotopic signal of nutrient uptake in high latitude waters is subducted into water masses (such as Subantarctic Mode Water) that ventilate the mid-depths at low latitudes. Against this background of similar behaviour due assimilation and regeneration, differences between $\delta^{114}\text{Cd}$ and $\delta^{15}\text{N-NO}_3^-$ are expected in regions of active nitrogen fixation and denitrification, as these processes lower and raise the $\delta^{15}\text{N-NO}_3^-$, respectively, while they should not directly affect $\delta^{114}\text{Cd}$. Paired analyses of dissolved $\delta^{114}\text{Cd}$ and $\delta^{15}\text{N-NO}_3^-$ from the US GEOTRACES North Atlantic transect appear to show the expected distinction due to nitrogen fixation. Dissolved $\delta^{114}\text{Cd}$ increases from deep water into the permanent thermocline and then more sharply into the surface, due to biological assimilation, while $\delta^{15}\text{N-NO}_3^-$ decreases from deep water into the permanent thermocline, which has been interpreted as resulting from the remineralization of low $\delta^{15}\text{N}$ material from nitrogen fixation in low latitude surface waters.

Here, we use the difference between $\delta^{114}\text{Cd}$ and $\delta^{15}\text{N-NO}_3^-$ profiles in the North Atlantic to quantify the amount of low- $\delta^{15}\text{N-NO}_3^-$ 'newly fixed' nitrogen in the water column. $\delta^{114}\text{Cd}$ is used to calculate the $\delta^{15}\text{N-NO}_3^-$ profiles expected in the absence of nitrogen fixation, and the differences between this and the observed $\delta^{15}\text{N-NO}_3^-$ profiles are used to calculate the fraction and concentration of newly fixed N that has been oxidized to NO_3^- in the Atlantic interior.

Structure and fate of Zn-bearing green rust nanominerals in slightly acidic mine drainage crossing a steep redox boundary

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The fate and transport of inorganic contaminants in mine drainage systems are strongly dependent on pH and redox conditions. As drainage water crosses geochemical gradients, changes to the transporting particle and/or the contaminant speciation will dictate how the contaminant continues to be transported and how bioavailable it is. In order to gain insights into these processes, we examined water and sediments directly taken from a mine drainage outflow environment. Our field site is a former uranium mine near Ronneburg, Germany, where water outflow from the underground mine at pH 6 crosses a steep redox boundary. Contact with oxygen causes dramatic changes in the mineralogy of suspended particles that interact with metal(loid)s in the water and sediments. After careful sample preparation, we use analytical transmission electron microscopy to characterize the nanoscale structure and elemental composition and compare with measurements from standard bulk techniques.

The suspended particles in the anoxic mine outflow consist primarily of nanometer-thin pseudo-hexagonal Zn-bearing green rust platelets ($(\text{Fe}^{2+})_6\text{Fe}^{3+}_2(\text{OH})_{18}\cdot 4\text{H}_2\text{O}$) co-precipitated with amorphous silica. Green rusts have been found previously in groundwater systems, but are difficult to track due to rapid oxidation in aerated water. Zinc is the contaminant of second-highest concentration in the outflow. Once these particles cross the redox boundary, they undergo oxidative dissolution and rapidly co-precipitate with silica to form aggregates of spheroidal iron oxide nanoparticles. Some aggregates settle to the streambed where they get larger and grow needles, many of which are nanocrystalline goethite.

In this ongoing study, we show why knowledge of the formation, transformation, reactivity, and dissolution of nano-components are important in understanding the behavior and evolution of environmental systems.