

## **Seawater iron isotopes as a new tool to characterize the physicochemical speciation of dissolved iron: Southern East Pacific Rise case study**

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The bioavailability and scavenging fate of dissolved iron (dFe) in the ocean is dependent on its physicochemical speciation, yet there are no analytical methods that reveal the general character of marine dFe, especially basic differentiation of organically-complexed Fe from tiny nanoparticulate phases. Here, we propose that Fe isotopes can be used to derive this speciation, so long as the system meets certain assumptions.

We demonstrate how seawater dFe isotopes can reveal the physicochemical speciation of dFe using the case study of the Southern East Pacific Rise (SEPR) non-buoyant hydrothermal plume at 15°S. We objectively assign Fe isotope signatures for each of three Fe species that are present in the hydrothermal plume: background organic dFe-ligand (FeL) complexes, hydrothermal organic dFe-ligand complexes, and Fe oxyhydroxide nanoparticles. We then apply these isotope signatures to an isotope mass balance model, which also includes the soluble and colloidal Fe concentrations to reveal the complete physicochemical speciation of dFe in this plume.

We find that Fe oxyhydroxide nanoparticles are released from the SEPR in both the larger colloidal and, surprisingly, also smaller soluble size fractions. The nanoparticles are supplied in high concentration but are lost quickly from the plume. In contrast, hydrothermal FeL complexes form in the juvenile plume in the smaller soluble size fraction and aggregate into the larger colloidal size fraction down-plume. Thus, overall, the dFe in this SEPR plume does not appear to be conserved, since Fe oxyhydroxide nanoparticles are rapidly lost from both the soluble and colloidal size fractions. Assessments of bulk physicochemical speciation, such as this one, are important in order to constrain global iron biogeochemical models, especially for internal cycling rates such that are difficult to measure directly.