Goldschmidt 2023 Abstract
https://doi.org/10.7185/gold2023.19014

Nanoparticulate iron oxyhydroxides aggregated in carbon matrices dominate iron speciation in hydrothermal plumes over the 1-100 km distance from vent source

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Iron (Fe), a limiting nutrient for phytoplankton productivity, connects hydrothermal vents to surface waters. Supply by sediments and dust deposition are typically considered the main sources of iron to the oceans, but recent work suggests hydrothermal vents could also be an important source of iron to the surface ocean via upwelling at high latitudes. Dissolved iron concentrations in hydrothermal fluids are a million times those of surrounding ocean water. Considerable amounts of iron (>90%) precipitate close to vent sources, but in a major breakthrough, the international GEOTRACES program revealed signatures of hydrothermally-derived iron transported across deep ocean basins worldwide. Models show that through density-controlled upwelling, this iron could support up to 10% of primary production in the North Pacific Ocean and up to 30% in the Southern Ocean. It remains unclear how some iron persists in dissolved form in the water column rather than being sequestered into sinking particles. The fate of iron likely depends on speciation and aggregate size, with organic ligand-bound iron, pyrite, and iron oxyhydroxide nanoparticles all having different lifetimes in hydrothermal plumes. Critical processes constraining export of iron from vent sources to open ocean waters occur within the first ~100 km of plume evolution.

We worked with hydrothermal plume particle samples from the Rainbow vent system (Mid Atlantic Ridge) to show that aggregates of morphologically uniform iron oxyhydroxide nanoparticles dominate iron speciation within the first 70 km of dispersing plume evolution. In this low-sulfur system, iron oxyhydroxides dominate despite ubiquity of pyrite in hydrothermal plumes on a global scale. Here, aggregates consist of iron oxyhydroxide nanoparticles held in a carbon matrix composed of organic and inorganic carbon. We will compare speciation of >0.2 μm to <0.2 μm particles to reveal how speciation varies with particle size, asking if pyrite might be present in smaller size fractions. We use synchrotron-based methods (bulk extended X-ray absorption fine structure spectroscopy, X-ray fluorescence spectromicroscopy, and scanning transmission X-ray microscopy) and electron microscopy. These results increase our understanding of export mechanisms delivering iron to open ocean and surface waters.