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Application of iron L3 edge XANES spectroscopy to colloid speciation

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L-edge XANES spectroscopy has been used to identify the speciation of iron (Fe) in natural samples. The majority of previous analyses are limited to the identification of Fe(II) versus Fe(III) speciation in complex natural samples however, these spectra are rarely used to identify different mineral phases in soils and sediments. Using the fine spectral variations between different crystalline and amorphous Fe phases, we developed a technique to evaluate the local coordination environment of Fe in in natural samples. The technique makes use of splitting of the main electronic transitions in the L3 edge region, and the ratio of their peak intensities. These spectral parameters are sensitive to the valence state, electronegativity of the coordinated ligands and the degree of distortion of the polyhedra of Fe.

Based on our findings of the Fe L3-edge spectral responses to variations in Fe mineralogy, we have applied this spectroscopic tool to colloids and nanoparticles suspended in the Southern Ocean. Here, Fe is known to be limiting to phytoplankton primary productivity, and Fe speciation and thus bioavailability, impacts global biologically-mediated air-sea carbon dioxide exchange. Our findings classify five broad categories of suspended Fe rich particles including ferric oxides, magnetite, other mixed valence species and at least two ferrous species. The distribution of these phases in the Southern Ocean is discussed in terms of primary productivity and in terms of their association with organic carbon.

Summary

Critical evaluation of the chemical information contained in the Fe L3 edge.
Novel spectroscopic tool developed for evaluating Fe mineralogy (down to 12 nm sized particles).
Application of this technique to investigate natural particles interacting in complex global biogeochemical systems.

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