



Mössbauer spectroscopy provides an improved mineralogical perspective of biogeochemical iron cycling in marine sediments

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Reactive iron minerals are crucial components of global nutrient cycles: directly controlling carbon transport and storage in marine sediments. These reactive iron minerals typically exist as amorphous colloids ($<1 \mu\text{m}$ diameter) or nanoparticles ($<0.1 \mu\text{m}$ diameter) that are inherently difficult to characterise and quantify using standard geochemical techniques (e.g. XRD). Sequential chemical extraction is currently the only method for quantitatively characterising, and physically isolating, reactive iron mineral phases into separate, 'operationally-defined' groups for further (e.g. isotopic) analyses.

The Poulton and Canfield (2005) sequential extraction protocol for iron is the dominant iron mineral classification tool in geochemistry, and has been fundamental to the development of pivotal ocean and earth science hypotheses over the past decade:

- Over 20 % of the carbon sequestered in marine sediments is bound directly to reactive iron phases;
- Diagenetic reduction of iron in continental shelf margin sediments is a major deep ocean source of dissolved iron;
- Increasing the supply of bioavailable iron to high-nutrient, low-chlorophyll zones enhances deep ocean carbon transport.

Extraction protocols rely on reagent-specific mineral solubility, which is strongly affected by grain size, complexation, degree of crystallinity and organic matter content. ^{57}Fe Mössbauer spectroscopy (MBS) only probes the hyperfine interactions between next-nearest neighbouring atomic nuclei in the crystal lattice. MBS is therefore less affected by variation in grain size and crystallinity intrinsic to natural samples, and is consequently useful for the analysis of colloids and nanoparticles. MBS can also discriminate between individual iron minerals within each operationally-defined pool, and can further determine iron oxidation state. The combined use of conventional sequential chemical extraction methods and established MBS technique in a novel context therefore offers a non-destructive, more mineral specific alternative for iron mineral identification.

We have used MBS to show that not only incomplete or premature dissolution of target minerals occurs throughout most of the sequential iron extraction, but also that it varies significantly between different expressions of the same mineral. Individual minerals are effectively extracted at their target stage; however, in mineral mixtures (representative of natural samples) we tested, for example, siderite and goethite persisted well beyond their target stage, while nontronite (not targeted until the very end of the sequence) removal began during the initial stages. If the amount of residual reactive iron is underestimated, iron may have an even more crucial role in global sedimentary carbon cycling and storage (particularly in marine sediments) than was previously thought; similarly the flux of dissolved iron across the sediment-water interface of continental shelf sediments may be underrated. This work is therefore crucial for our interpretation of global biogeochemical iron, and consequently carbon, nitrogen, oxygen and sulfur cycling in coastal, continental shelf, and deep-sea sediments.