Mechanisms of tetrahedral iron formation in ferrihydrite observed via soft x-ray spectroscopy

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Introduction

Ferrihydrite is a poorly crystalline ferric hydroxide nanomineral. It rapidly transforms to more stable crystalline minerals such as goethite (FeOOH) in the lab, but it is metastable in natural systems and found as persistant coatings as well as discrete particles. Its high reactivity and widespread occurrence make its structure important for geochemists, life scientists (as ferritin), and environmental engineers. However, disagreement among researchers remains as the structure of this enigmatic material. The central question in the structural debate is whether iron in ferrihydrite is purely octahedral, or if tetrahedral ferric iron is present. Recent studies proposing tetrahedral iron in this phase have proposed that it may form via condensation of keggin-type aqueous polymers similar to aluminum, but these have never been directly observed for iron.

Accordingly, the objective of our study was to monitor the precipitation of ferrihydrite from forced hydrolysis of ferric chloride *in situ* using high resolution Fe L-edge XANES spectroscopy of solutions in a flow through liquid cell. Spectra were collected using both Fe partial yield and the newly developed IPFY approach for self absorption-free bulk XAS measurements. The precipitation process was followed from pH 1 to 7.5, and results from these aqueous measurements were compared to air dried samples prepared at the same pH. STXM measurements of wet and dried ferrihydrite were also collected for comparison.

Our results demonstrate clearly that L-edge XANES are extremely sensitive to shifts in ligand field that accompany hydrolysis of metals and coordination changes. There is clear evidence that tetrahedral iron is present in air-dried samples, but that the *in situ* measurements are consistent with only octahedral iron. This suggests that the dominant mechanism for tetrahedral iron in ferrihydrite may be physical dehydration rather than a chemical reaction. This has enormous implications for natural systems, where wetting and drying cycles are expected to strongly influence mineralogy

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Novel insights on a traditional proxy: Combining the stable and radiogenic Sr isotope systems to characterise continental weathering

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The radiogenic strontium isotope system (^{87}Sr/^{86}Sr) is one of the most established methods for tracing continental weathering, as subtle, but resolvable, differences in ^{87}Sr/^{86}Sr ratios enable the Sr content of water, vegetation and humans to be linked to specific locations and lithologies[1]. On a global scale, shifts in weathering processes control the composition of the oceans, with differences in the relative flux of silicate and carbonate material over geological timescales reflected in the ^{87}Sr/^{86}Sr ratio of marine carbonates[2]. Unlike the radiogenic system, variations in stable Sr isotopes ($\delta^{88/86}$Sr) are controlled by mass dependent processes, with the main driver of fractionation thought to be incorporation into carbonates[3]. The combined application of the ^{87}Sr/^{86}Sr and $\delta^{88/86}$Sr systems therefore has the potential to differentiate source variations from other weathering processes, providing a valuable method for assessing strontium transport through the critical zone.

This study presents isotopic data from both Sr systems at various points in the hydrological cycle; ^{87}Sr/^{86}Sr and $\delta^{88/86}$Sr values from glacial ice, precipitation, river water, dust and bedrock are used to constrain the sources and cycling of Sr on the continents. Samples dominated by atmospheric Sr transport typically display lower $\delta^{88/86}$Sr compositions than equivalent surface waters, and are thought to be influenced by anthropogenic contamination effects. River water samples dominated by surface run-off have ^{87}Sr/^{86}Sr and $\delta^{88/86}$Sr values that depend on the underlying lithology: Continental silicate terrains typically have $\delta^{88/86}$Sr values within 0.10 ‰ of the global riverine mean (0.34 ‰), whereas rivers draining carbonate and basaltic terrains (i.e. those with ^{87}Sr/^{86}Sr ratios <0.7100) show considerably greater $\delta^{88/86}$Sr variation, ranging from 0.10 ‰ to 0.86 ‰. Differences are also observed within individual drainage basins and between wet and dry flow regimes, confirming the sensitivity of the stable Sr system to fractionation processes during weathering and transport. The findings of this study are compared to other isotopic weathering proxies, and the implications for the future application of the Sr weathering proxy are discussed.

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