

## Catalytic action of aqueous Fe(II) and S(II) on the transformation of schwertmannite to goethite

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The mineralisation of ferric oxides is of fundamental relevance to the geochemistry of marine and freshwater benthic sediments. In acidic landscapes affected by the oxidation of sulfides, schwertmannite ( $\text{Fe}_8\text{O}_8(\text{OH})_6(\text{SO}_4)$ ) is a common ferric oxide. Due to its high surface area and intrinsic reactivity, schwertmannite is an important sink for metal contaminants and nutrients. The accumulation of schwertmannite occurs often at the oxic/anoxic boundary of benthic sediments. Under acidic oxygenated conditions the schwertmannite transforms slowly (i.e. 1-2 yrs) to more crystalline iron oxides such as goethite. Near-neutral anoxic conditions are known to enhance the rate that schwertmannite transforms to goethite (i.e. 2-3 months). Here we present the results of controlled laboratory batch experiments that examine the catalytic influence on schwertmannite of two strong and often abundant reductants that occur in the porewaters of benthic sediments, aqueous  $\text{Fe}^{\text{II}}$  and  $\text{S}^{\text{II}}$ .

In the presence of  $\text{Fe}^{\text{II}}$  and at a  $\text{pH} > 5.0$ , the schwertmannite transformed rapidly (i.e. within 15 min) to goethite and lepidocrocite. At  $\text{pH} < 5$ ,  $\text{Fe}^{\text{II}}$  had no effect. The increasing tendency for  $\text{Fe}^{\text{II}}$  sorption at  $\text{pH} > 5.0$  is responsible for the catalysed transformation of schwertmannite to more crystalline phases. Increasing  $\text{pH}$  and increasing  $\text{Fe}^{\text{II}}$  concentration further enhanced this mineralisation reaction. The presence of  $\text{S}^{\text{II}}$  caused a similarly rapid transformation of schwertmannite to more crystalline iron oxides.  $\text{S}^{\text{II}}$  reacted within minutes with structural Fe(III) in the schwertmannite, producing elemental sulfur and  $\text{Fe}^{\text{II}}$ , with excess  $\text{S}^{\text{II}}$  reacting with  $\text{Fe}^{\text{II}}$  to form nano-particulate mackinawite ( $\text{FeS}$ ).

The catalytic effect of  $\text{Fe}^{\text{II}}$  and  $\text{S}^{\text{II}}$  can be attributed to electron exchange between the sorbed reductant and structural Fe(III) at the mineral surface, leading to destabilisation of the schwertmannite, its dissolution and transformation to more crystalline iron oxide phases. The catalytic influence of  $\text{Fe}^{\text{II}}$  and  $\text{S}^{\text{II}}$  on the transformation of schwertmannite to more crystalline iron oxides, and in the case of  $\text{S}^{\text{II}}$ , formation of elemental sulfur and mackinawite, have important implications for understanding the dynamics of Fe and S cycling, metal contaminant behaviour and water quality in acidic landscapes.

## Evidence for nitrogen enrichment during oceanic crust alteration

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Because N is present at only low concentration level in the Earth's mantle, subducting altered oceanic crust may have a significant contribution to the long-term evolution of the N content and isotopic composition of the mantle. To date, whether N is enriched or released during hydrothermal alteration of oceanic crust remains uncertain. Hall [1] measured N content of spilited basalts from Cornubian massif and suggested that N was enriched during alteration. However, spiliteization might not be representative of seawater-oceanic crust interactions. Nitrogen contents of oceanic basalts from several DSDP/ODP Sites support the interpretation of N enrichment but show smaller magnitude than basalts from Cornubian massif [2,3]. The analysis of altered basalts from the ODP Hole 504B contrasts with these results, and indicates a loss of N from rock to fluid [4]. These authors extracted N using a pyrolysis technique, heating samples in molybdenum crucibles. However, N was recently shown to be strongly reactive with molybdenum at high temperature [5]. The low N concentrations measured in altered basalts from Hole 504B may thus result from the incomplete recovery of N rather than a specific type of alteration. To test this hypothesis, we analyzed samples from the Hole 504B using a sealed tube combustion technique, with samples embedded in platinum foils. The results show significant N enrichment (up to 12 ppm) relative to fresh degassed MORB (~1 ppm). This confirms that oceanic crust alteration acts as a sink for N from surface reservoirs and must be considered in subduction zone budget to evaluate the efficiency of N recycling to the mantle.

### References

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