

Oxidative disintegration of greigite (Fe_3S_4): New insights from SAXS and XAS

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Greigite (Fe_3S_4) is a ferrimagnetic iron sulfide mineral, containing both Fe(II) and Fe(III) centres. It is typically found in lacustrine sediments, acid sulfate soils and hydrothermal veins. There is ongoing debate over the role of greigite in sedimentary settings: the partially oxidised nature of greigite has traditionally been seen as indicative of a metastable intermediate in low temperature sulfide mineralisation (e.g. [1]) however others have found greigite to be a distinct end-member that forms under partially oxic (or oscillating redox) conditions [2]. From a thermodynamic perspective it should have limited stability with respect to pH and dissolved sulfur activity, yet it has been identified in natural sediments of up to a few million years old ([3] and references within).

The iron sulfides are an important sink and potential source for metals in contaminated environments. Understanding the oxidative transformation of greigite in terms of particle size, nanostructure and growth mechanism of metastable and long-lived phases is vital for understanding contaminant release and sequestration.

We present a study into the oxidation of greigite under aqueous conditions. The effects of temperature, pH, chloride and sulfate concentration are examined with respect to transformation kinetics, mineralogy of the oxidation products, and the relationship between Fe and S oxidation (using X-ray absorption spectroscopy), as well as particle size, shape and nanostructure (using small angle X-ray scattering). The results of this study provide new insights into the role and longevity of greigite in natural sediments and will underpin new remediation strategies for acid sulfate soils, while also adding to our understanding of the geochemical cycling of Fe and S.

[1] Hunger and Benning (2007) *Geochem. Trans.* **8**, 1. [2] Burton et al. (2011) *Geochim. Cosmochim. Acta* **75**, 3434-3451. [3] Dekkers et al. (2000) *Geophys J. Int.* **141**, 809-19