

Greigite – Now you see it now you don't: An *in situ* ED-XRD study.

STEFAN HUNGER, LIANE G. BENNING¹
AND KONSTANTIN A. TARASOV²

¹School of Earth and Environment, University of Leeds, LS2 9JT Leeds, United Kingdom,

(s.hunger@earth.leeds.ac.uk), (liane@earth.leeds.ac.uk)

²Laboratoire de Reactivite de Surface, Universite Pierre et Marie Curie, 75252 Paris, France, (tarasov@ngs.ru)

Greigite is an important, yet elusive intermediate phase on the transformation pathway of FeS to pyrite. It has been shown to exist in anaerobic sediments and has been used extensively as a paleomagnetic marker. However, the chemical conditions that control the transformation of mackinawite to greigite and prevent its further conversion to pyrite are poorly understood. We have studied the oxidation of freshly precipitated FeS by polysulfide *in-situ* at different temperatures using synchrotron-based energy-dispersive x-ray diffraction (ED-XRD) at the UK Synchrotron Radiation Source (SRS).

Our results indicate that, at equal initial polysulfide concentrations and varied temperatures, the poorly ordered mackinawite transforms to greigite within 10 to 40 minutes, followed by the growth of pyrite. The extent of the transformation to pyrite depends on the availability of polysulfide, while its kinetics are correlated to temperature.

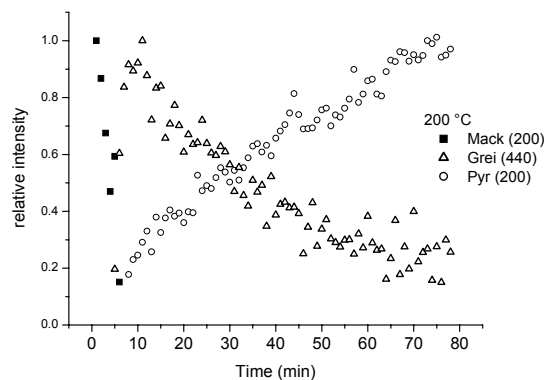


Fig. 1 Time resolved plot of the reaction progress during the isothermal transformation of mackinawite to greigite and pyrite at 200°C.

Resonant anomalous x-ray reflectivity: A new structural and spectroscopic probe of metal adsorption at mineral-water interfaces

CHANGYONG PARK¹, PAUL A. FENTER¹,
NEIL C. STURCHIO² AND JOHN R. REGALBUTO³

¹Environmental Research Division, ANL, Argonne, IL 60439, (cypark@anl.gov, fenter@anl.gov)

²Department of Earth and Environmental Sciences, UIC, Chicago, IL 60607, (sturchio@uic.edu)

³Department of Chemical Engineering, UIC, Chicago, IL 60607, (jrr@uic.edu)

Resonant anomalous x-ray reflectivity (RAXR) combines the surface specificity of conventional surface x-ray reflectivity with the spectroscopic and element-specific sensitivity of resonant anomalous x-ray scattering. RAXR measures elastic scattering intensity vs. incident photon energy near a characteristic absorption edge and at fixed momentum transfer. Here, we review the characteristics of RAXR, with particular emphasis on its ability to simultaneously probe interface-specific geometric and/or spectroscopic structures of weakly adsorbed surface metal species at the mineral-water interface. These characteristics will be illustrated by recent results.

In one example we describe the application of RAXR to the adsorption of platinum tetraammine (PTA; $\text{Pt}(\text{NH}_3)_4^{2+}$) at the quartz (100)-water interface. These results show that adsorption of electrostatically bound aqueous metal complexes at the oxide-water interface can exhibit complexities that can be understood only when both the geometric and spectroscopic sub-structures are fully resolved.

We also discuss the application of RAXR to probe the distribution of metal atoms adsorbed at the muscovite-water interface. Recent studies of cation sorption to muscovite basal planes have shown that monovalent ions appear to adsorb in direct contact with the surface (e.g., on the ditrigonal site), but that divalent metal cations have a more complex behavior (Nagy et al., 2004). Unlike the previous conventional reflectivity measurements, the RAXR results for muscovite (001) in contact with 0.01 M $\text{Sr}(\text{NO}_3)_2$ provide sensitivity to the Sr-specific distribution independent of the interfacial water profile, providing a more direct method to probe the ion distribution.

Reference

K. L. Nagy, N. C. Sturchio, M. L. Schlegel, and P. Fenter, Water-Rock Interaction, (Wanty and Seal II, Eds.) 767-769, (2004).