

## Combined WAXS/XAFS measurements for studying the reaction of S(-II) with lepidocrocite

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The reaction of sulfide (S(-II)) with iron oxides is an important process linking the redox cycles of iron and sulfur in many subsurface environments. Here, we studied the reductive dissolution of lepidocrocite ( $\gamma$ -FeOOH) by S(-II) in batch reactors at constant pH. A combination of wide angle X-ray scattering (WAXS) and X-ray absorption spectroscopy (XAS) at the Fe K-edge (about 7.1 keV) was used to follow on line the progress of the reaction.

Addition of Na<sub>2</sub>S solution to the lepidocrocite suspension led to a fast decrease in intensity of the characteristic lepidocrocite diffraction peaks. This change in the WAXS signal was larger than expected from the stoichiometric amount of consumed lepidocrocite and indicates that the long range order of the crystals was profoundly disturbed upon the attack of sulfide.

Principle component analysis of all collected XANES spectra revealed that the combination of two spectra is sufficient to reproduce the major features of all spectra. The two components can be attributed to the spectrum of Fe(III) in lepidocrocite and to that of Fe(II) tetrahedrally coordinated with S. The stoichiometry of the reaction regarding the consumption of H<sup>+</sup> and S(-II) per reacted Fe(III) was derived from relating the change in XANES spectra to the amount of acid, which was added during the experiment, and to the different amounts of initially added sulfide, respectively.

Analyses of EXAFS spectra demonstrated that mackinawite was not the product of the reaction, while mackinawite was shown to form when Na<sub>2</sub>S solution was added to Fe<sup>2+</sup> solution under the experimental conditions.

These observations suggest, that the reaction of lepidocrocite with S(-II) does not follow a surface controlled mechanism in which the release of Fe(II) from the surface is required for the reaction to proceed. An alternative mechanisms will be presented and the differences between observed and expected stoichiometric coefficients will be discussed.

## Lithospheric control on geochemical composition of the Louisville Seamount Chain

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Chemical changes with time in lavas erupted on long-lived seamount chains can be used to test models for the origin of intraplate magmatism and examine the effect of sub-seamount lithosphere on volcanism. Major and trace element and Sr, Nd, and Pb isotope data for lavas from 12 seamounts along the westernmost 1500 km of the Louisville Seamount Chain (LSC) in the SW Pacific show that magmatism was compositionally remarkably uniform between 80 and 40 Ma. All 56 samples analysed are alkalic or transitional; most are basalts. The youngest lavas from a given seamount tend to have the least enriched incompatible element compositions. Unlike Hawaiian volcanoes, Louisville volcanoes appear not to pass through a tholeiitic shield-building stage. The oldest Louisville seamounts formed close to the Osborn Trough fossil spreading centre, but there is no obvious effect on the composition of LSC lavas. Nor do Osborn Trough MORB contain any contribution from Louisville mantle, which suggests that spreading at the Osborn Trough ceased well before the construction of Osborn Guyot at 79 Ma. Lavas from volcanoes in the central part of the LSC are more variable and extend to more enriched compositions. These volcanoes tend to be smaller and more widely spaced, and were underlain by the oldest, thickest oceanic lithosphere. Smaller degrees of melting of heterogeneous mantle may explain the more variable compositions of these volcanoes.