

In situ X-ray diffraction apparatus and its application to hydrothermal reactions of iron sulphide growth and phase transformations

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Time resolved *in situ* X-ray diffraction is an efficient method for studying the progress of a reaction via the signature of crystalline phases present. This technique has found application in a number of hydrothermal systems including zeolite and microporous sulphide syntheses (Cahill *et al.*, 1998). The current study examines the nucleation and growth mechanism of iron-monosulphides (mackinawite and greigite) and their conversion to di-sulphides (pyrite, marcasite) at temperatures below 200°C in an attempt to verify and further examine the proposed reaction pathways (Berner 1967; Rickard, 1975, 1997; Wilkin and Barnes 1996).

Methods

The experimental set up for the time resolved, *in situ* diffraction experiments at Brookhaven National Laboratory's (BNL) National Synchrotron Light Source (NSLS) is shown in Fig. 1. Sample slurries are loaded into a 0.7 mm quartz capillary (A) and heated via an air heater. The capillary is held in place with a Swagelock[®] (B) fitting mounted on a modified goniometer head. Hydrothermal conditions are maintained with an over pressure of N₂ gas. Monochromatic synchrotron X-rays hit the sample (A) and the diffracted beams are collected on a portion (C) of the imaging plate (IP) that is defined by two steel shields (D). The IP is translated (E) to expose fresh portions of the plate and obtain diffraction data as a function of time. Time resolved diffraction patterns are then extracted from the imaging plate pixel intensities.

The Fe-S starting material was prepared *ex situ* at 25°C under highly reduced, conditions (see Benning and Barnes this issue). During the preparation special care was taken to keep the whole system free of oxygen contamination in order to avoid the reactions to proceed uncontrolled. The initial iron-monosulphide precipitate was obtained by saturating an oxygen free solution of known Fe (II) concentration with 100 % H₂S. Into the above solution, an oxygen free 1 N NaOH solution was injected promoting the immediate formation of a black precipitate. A conventional X-ray pattern verified only the presence of mackinawite. Before use in the *in situ* experiments, this suspension was stored in a polyethylene bottle in a nitrogen filled dessicator for less than one week.

Results

The initial colloid was temperature ramped to 150°C over 15 minutes and held for 60 minutes with a N₂ overpressure of 175 psi. Under these conditions, only diffraction peaks from mackinawite and a trace of greigite were observed. Compressed air was thus bubbled through an aliquot of the above suspension for approximately 50 minutes in an attempt to promote and accelerate the structural transformation through greigite to pyrite. Upon temperature ramp and hold of this oxygenated sample, the diffraction spectra show the fast disappearance of mackinawite, the persistence of greigite, the formation of pyrite and the formation of goethite and magnetite. The onset of pyrite is observed after about 10 minutes at

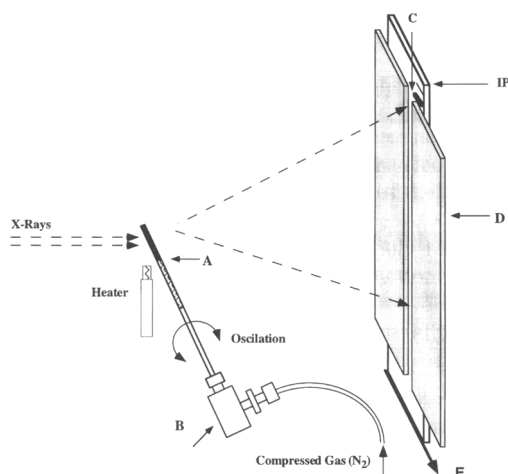


FIG. 1. Experimental set-up for time-resolved experiments at the X7B beamline at the NSLS.

150°C, while magnetite and goethite appear after approximately 40 minutes.

Additional experiments were carried out at the Advanced Photon Source (APS) located at Argonne National Laboratory (ANL). These studies utilized a steel reaction cell (Evans *et al.*, 1995), and thus required use of the higher intensity white radiation synchrotron source. For these experiments, the starting materials were prepared as above, yet rather than forming the colloid *ex situ*, the Fe/H₂S solution was loaded into the steel reaction vessel and a solution of NaOH was injected via a remotely controlled valve once the reactants reached about 100°C. The resulting suspension however, was of

insufficient density to give a satisfactory diffraction signal. The high water/solid ratio exhibited large scatter from the liquid phase and hence masked the diffraction signal from crystalline phases. When the colloid was prepared off-line and filtered to make a thicker 'paste,' the reaction proceeded as described in the capillary experiments.

Conclusion

The ability to monitor reactions under hydrothermal conditions via their X-ray diffraction signature has been demonstrated for the Fe-S-O system. More studies under more carefully controlled reaction conditions will produce kinetic and thermodynamic information. Further, the ability to extract data from the imaging plate of sufficient quality for Rietveld refinement yields the promise for in-depth study of crystal chemical mechanisms for the mackinawite → greigite → pyrite phase transitions.

References

- Berner, R.A. (1967) *Amer. J. Sci.*, **265**, 773–85.
- Cahill, C.L., Ko, Y., Hanson, J.C., Tan, K. and Parise, J.B. (1998) *Chem. Mater.*, in press, and references therein.
- Evans, J.S.O., Francis, R.J., O'Hare, D., Price, S.J., Clark, S.M., Flaherty, J., Gordon, J., Nield, A. and Tang, C.C. (1995) *Rev. Sci. Instr.*, **66**, 2442.
- Rickard, D.T. (1975) *Amer. J. Sci.*, **275**, 636–52.
- Rickard, D.T. (1997) *Geochim. Cosmochim. Acta*, **61**, 115–34.
- Wilkin, R.T. and Barnes, H.L. (1996) *Geochim. Cosmochim. Acta*, **60**, 4167–79.