Experiment title: SAXS/WAXS study of the crystallization processes in the Fe-OH and Fe-Ssystems, and its application to mobility of toxic contaminants in the natural environment		Experiment number: CH-1071
Beamline: BM 26	**Date of experiment**: from: Aug 29th 2001 to: Sept. 1st 2001	**Date of report**: 29 Aug. 2002
Shifts: 9	**Local contact(s)**: Wim Bras	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

Dr Sam Shaw University of Oxford, UK

Dr. Liane G. BENNING University of Leeds, UK

Dr. Nicholas TERRILL Daresbury Laboratory, UK

Report:

Iron oxyhydroxide and sulphide phases are the most widespread iron bearing minerals in all geologic environments, and are important in controlling the global iron flux. In the natural environments these phases occur as ultra-fine particles (2-200 nm) suspended in anoxic and oxic groundwater or as coatings on mineral grains. Their high specific areas and reactive surfaces make them vital in controlling the mobility of toxic trace species (e.g., As, Cd, PO_4^{3-}). However, the factors governing their crystallisation from poorly-ordered gels are still equivocal despite their vital importance in a large variety of natural and industrial processes.

The Small and Wide angle Scattering (SAXS/WAXS) experiments performed on BM26 were aimed at developing the understanding of the mechanisms and kinetics of iron (oxy)hydroxide e.g. goethite (FeOOH) and iron sulphides e.g. mackenawite (FeS) formation from poorly-order Fe^{3+}-oxide and Fe^{2+}-sulphide gels. Analysis of the data has allowed a detailed description of the nucleation and growth processes during the crystallization reactions. Figure 1 a and b show time-resolved SAXS/WAXS data for the crystallisation of goethite from phosphate doped 2-line ferrihydrite (poorly-ordered iron oxide). Note that initially the SAXS scattering intensity increases slowly followed by a stage of more rapid increase before leveling off after approximately 85 minutes.

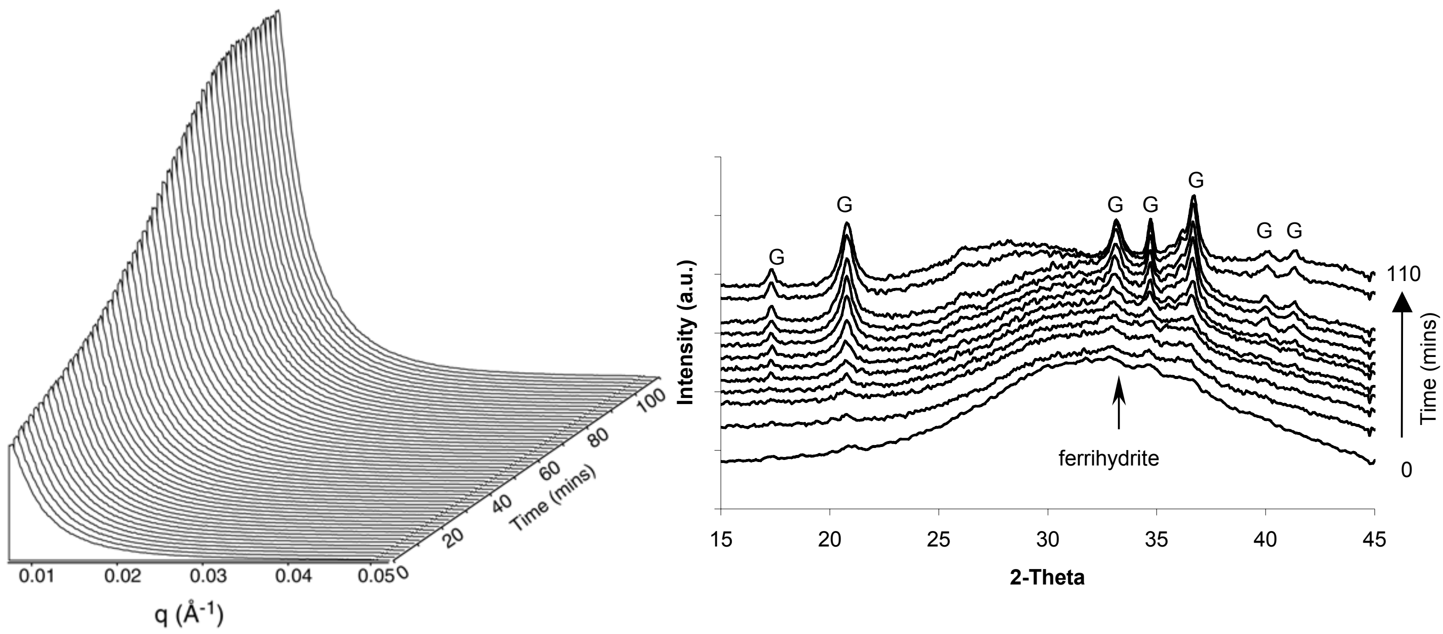

Figure 1. Time-resolved (a) SAXS (b) WAXS plots for the crytallisation of goethite from phosphate doped ferrihydrite. Note the broad ferrihydrite peak in the WAXS data at T=0. This rapidly decreases with time as peaks for goethite (G) grow.

Figure 2a and b show the Rg, Invariant and goethite (110) Bragg peak intensity as a function of time. From these data it can be seen that the reaction can be divide into 4 distinct stages. Avrami analysis of the change in goethite Bragg peak intensity with time is shown in figure 3. From the Avrami exponent (n) it can be determined that during stage 1 of the reaction 1D particle growth (n= 0.8) predominates whereas during stages 2 and 3 2D growth (n= 2.7) predominates.

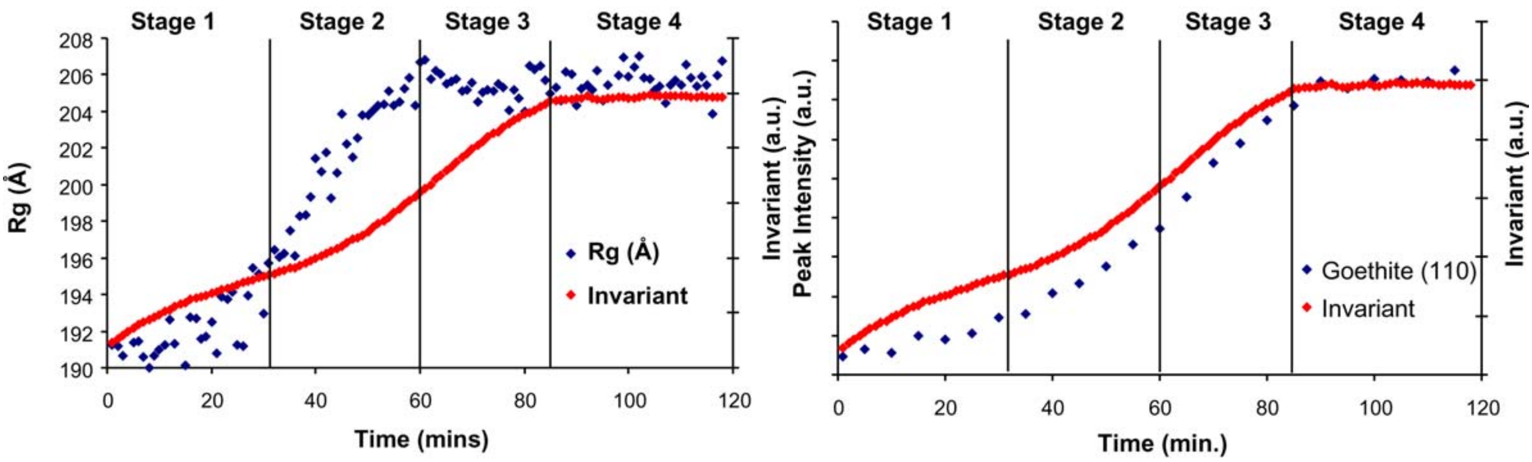

Figure 2 (a) Rg and SAXS invariant and (b) goethite (110) Bragg peak intensity and SAXS invariant as a function of time for the crystallisation of goethite from phosphate doped ferrihydrite. Note that the crytallisation process can be divided into 4 stages.

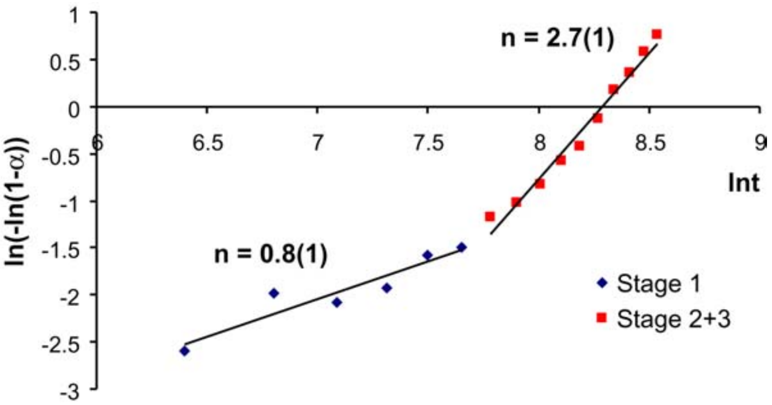

Figure 3. Avrami plot of the geothite (110) Bragg peak intensity. Avarmi exponent for stage 1 and stages 2+3 are marked.

These data indicate the potential of in situ time-resolved SAXS/WAXS for the study of crystallisation and transformation reactions of environmentally important nanoparticulate phases.

Published work on the data:

Shaw, S, Warner, J.A. , Benning, L.G. and Brown Jr., G.E. (2002) SAXS/WAXS studies of the precipitation and crystallisation of iron and aluminium (oxy)hydroxides. Geochimica et Cosmochimica Acta, **66(S1)**, A704. (Abstract from Goldschmidt conference 2002).