In situ synchrotron studies of mineral crystallization and dehydration reactions

C. M. B. Henderson
S. Shaw
S. M. Clark

Department of Earth Sciences, University of Manchester, M13 9PL, UK and Daresbury Laboratory, CCLRC, Warrington WA4 4AD, UK

Background

In recent years the unique properties of synchrotron radiation (e.g. intensity, tunable white radiation, low divergence) have been exploited increasingly by Earth and environmental scientists. Techniques are available for studying solid and/or liquid samples at controlled temperatures and pressures with the ability to study systems dynamically on the time scale of the reactions taking place. Of particular interest are novel techniques which allow reactions to be followed *in situ* by using combined powder wide-angle X-ray diffraction (XRD; WAXS) and small-angle X-ray scattering (SAXS), or combined XRD and element-specific X-ray absorption spectroscopy (XAS). Thus long-range order (XRD), short-range order (XAS), and sample heterogeneity (electron density contrast; SAXS) can be simultaneously probed as a function of temperature (or pressure), in real time depending on the inherent kinetics of the reactions being studied. Information can be obtained on the natures of reacting and growing crystal phases by XRD while SAXS and XAS provide structural information even for amorphous phases. In addition, white-beam, energy dispersive XRD (EDXRD) techniques allow the dynamical study of hydrothermal crystallization reactions occurring between amorphous starting materials and fluid reactants heated to about 300°C.

We have been using some of these techniques for studying the hydrothermal crystallization of hydrated calcium silicate minerals, and the conditions under which they dehydrate and recrystallize. The results provide new insights into the mechanisms and kinetics of the reactions observed.

Hydrated calcium silicates in the CSH system

Hydrated calcium silicates occur naturally in hydrous, high pH environments and are also important in the context of possible cement-rock reactions occurring in concrete-encapsulated toxic and nuclear waste sites. We are investigating reaction mechanisms, thermodynamics and kinetics of tobermorite [$Ca_5Si_6O_{16}(OH)_2{\cdot}4H_2O$], gyrolite [$Ca_{16}Si_{24}O_{60}(OH)_8{\cdot}(14+x)H_2O$], xonotlite [$Ca_6Si_6O_{17}{\cdot}(OH)_2$], and hillebrandite [$Ca_2SiO_3(OH)_2$] both 'off-line' in the laboratory (combined TGA/DSC) and *in situ* at the Daresbury SRS. Two types of *in situ* experiments have been carried out so far: (i) isothermal hydrothermal synthesis from amorphous starting materials at 150–250°C (40 bar s.v.p.) monitored by EDXRD using the white beam station 16.4; and (ii) dehydration and breakdown of crystalline starting materials with temperature ramped to 900°C, monitored by SAXS/WAXS at the monochromatic station 8.2. In both types of experiments diffraction data were collected at 1 minute intervals.

(i) In the EDXRD hydrothermal studies of a gyrolite composition gel between 200 and 220°C the first crystalline material was detected after about 10 minutes with peaks forming at 3.1 and 1.8 Å which are characteristic of a C-S-H 'gel'. Subsequently a peak at 15.3 Å due to an intermediate reaction product (Z-phase) appeared. After about 1 hour this peak decreased in intensity and was replaced by gyrolite peaks at about 22 Å (001) and 11 Å (002) (Fig. 1). Interestingly, the (001) peak of the Z-phase

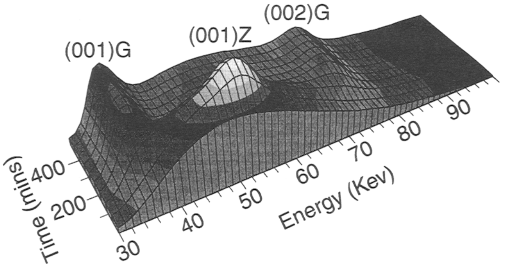

FIG. 1. EDXRD of hydrothermal crystallization of gyrolite gel at 205°C versus time.

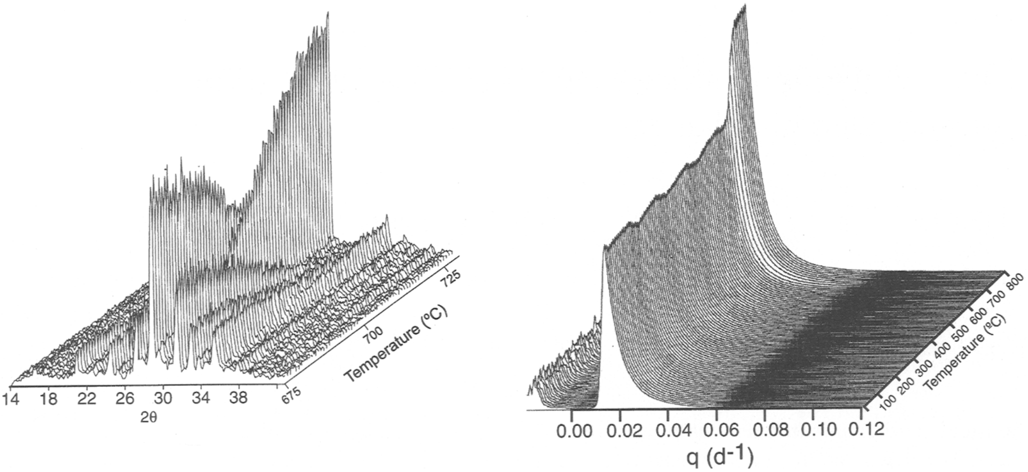

FIG. 2. (a) XRD of xonotlite from 675 to 750°C. (b) SAXS of xonotlite from 25 to 900°C.

seems to move round progressively to the position of the (001) peak for gyrolite suggesting a continuous transformation mechanism.

(ii) SAXS/WAXS experiments were carried out on natural minerals mainly from the Natural History Museum, London. Integration of these data with TGA/DSC results allows reaction mechanisms to be deduced.

Xonotlite lost some water over the T range 200–500°C and recrystallized directly to α-wollastonite ($CaSiO_3$) with two-phase assemblages occurring between about 700 and 750°C (Fig. 2a), and with substantial decrease in weight due to loss of (OH); in addition, the SAXS invariant increased in intensity (Fig. 2b) during the early stages of breakdown of xonotlite to α-wollastonite. A high intensity invariant points to the presence of a heterogeneous sample with substantial density differences occurring between component phases, while a low intensity invariant indicates that the sample is comparatively homogeneous. Thus the increase in invariant intensity above about 700°C is consistent with the presence of mixed xonotlite/ wollastonite assemblages.

The main water loss from tobermorite occurred from 100 to 250°C accompanied by decreases in diffraction peak intensities. Further weight loss occurred to 550°C with no significant change in the XRD peak intensities. At about 750 to 780°C, the tobermorite peaks disappeared to be replaced by those for α-wollastonite; at this stage the SAXS invariant showed a large decrease in intensity consistent with the formation of a comparatively homogeneous product. Gyrolite underwent a large weight loss between 100 and 150°C followed by further steady losses to about 650–700°C where the sample became amorphous. During the collapse of the structure to a more homogeneous amorphous product the invariant decreases in intensity. At about 750°C, recrystallization to β-wollastonite as the main product was initiated accompanied by a slight increase in the intensity of the SAXS invariant reflecting the presence of mixtures of the amorphous intermediate and β-wollastonite. Hillebrandite shows little change in X-ray peak intensities up to about 600°C at which temperature it rapidly collapses to be replaced by an amorphous phase. Peaks for a crystalline intermediate phase appear briefly before larnite (Ca_2SiO_4) forms as the final product. The SAXS invariant shows complex intensity variations reflecting the density contrasts accompanying the 3-stage reaction process.

Data reduction is underway to extract quantitative information on reaction kinetics and activation energies and SAXS/WAXS experiments are being planned to follow the early stages of hydrothermal crystallization of amorphous starting materials.