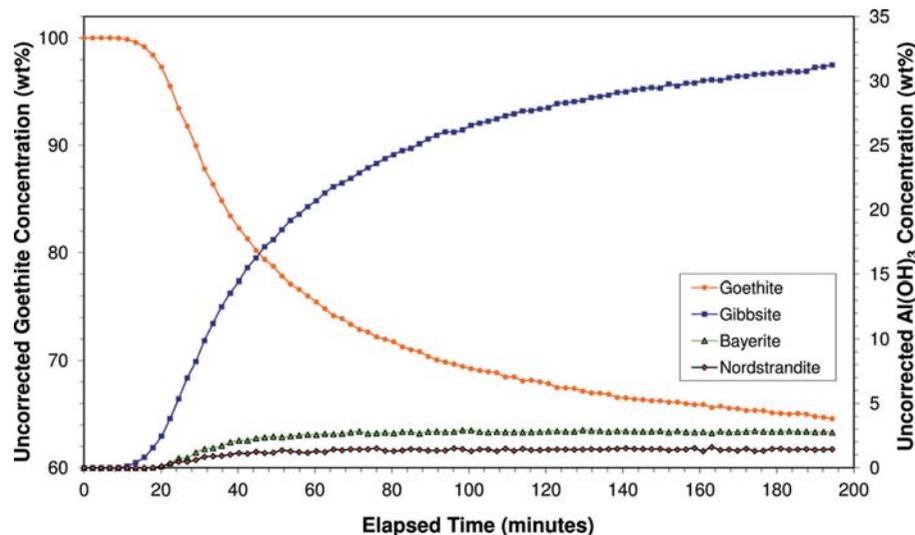3. METHODOLOGY

Figure 3.9.5

The results of QPA of the *in situ* XRD data collected during the seeding experiments of Webster *et al.* (2010). The values were derived using the Hill/Howard (Hill & Howard, 1987) relationship in equation (3.9.26). Note the decrease in apparent goethite concentration (left axis) as the polymorphs of Al(OH)$_3$ (right axis) crystallize from solution.

Figure 3.9.6

The results of QPA of the *in situ* XRD data collected during the seeding experiments of Webster *et al.* (2010).The values are absolute phase abundances derived using the internal standard relationship in equation (3.9.25).
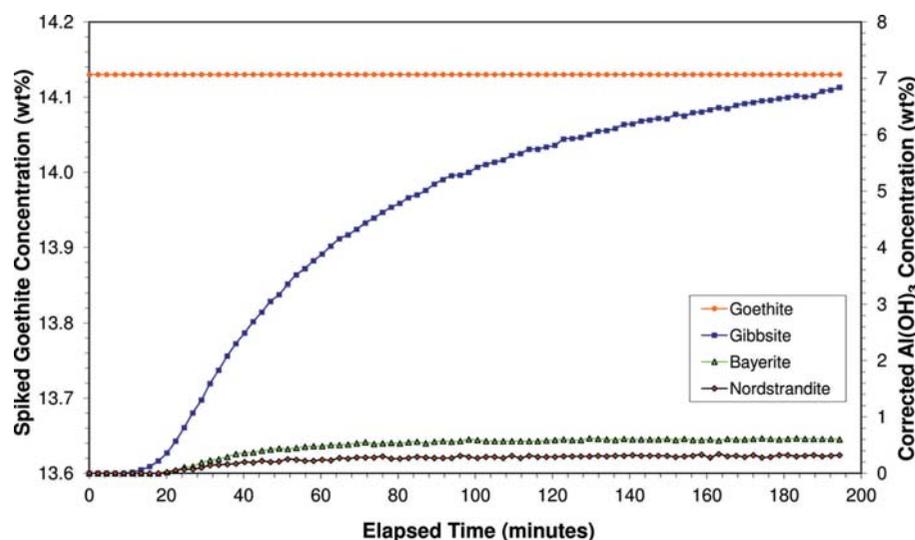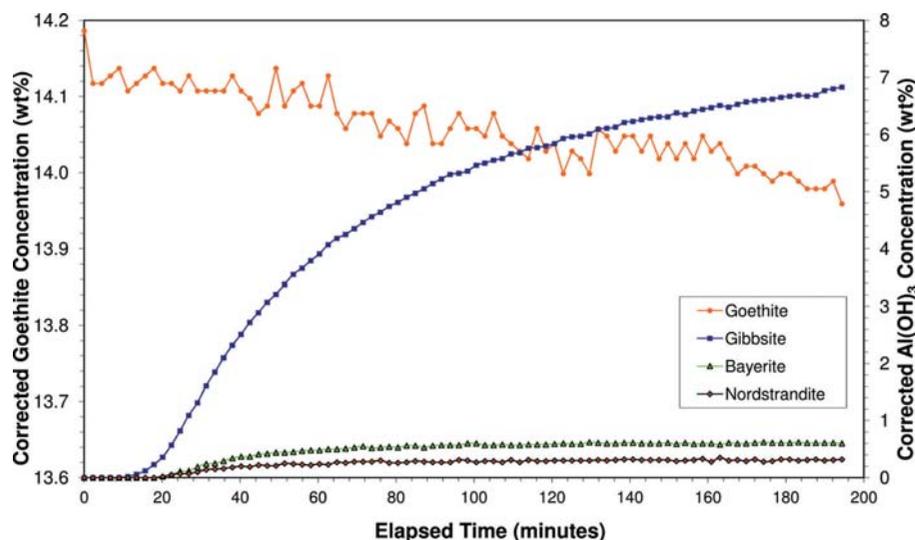

Figure 3.9.7

The results of QPA of the *in situ* XRD data collected during the seeding experiments of Webster *et al.* (2010). The values are absolute phase abundances derived using the external standard relationship in equation (3.9.22). Note the slight decrease in the goethite concentration (left axis) during the run.

for example, mineral exploration samples where a limited number of phases are present in a drill core but their abundance varies as a function of depth. In mineral processing or industrially based material manufacture, the goal is usually to control the system to minimize compositional variation in the product. The side effect of this is that the values of intensity in matrix **I** have too little variation, resulting in large errors in the derived values for *C*. In the limiting case, the system may become indeterminate with no unique solution available. To overcome this, forced or accidental changes to processing conditions may introduce sufficient compositional variation to stabilize the determination of the *C* values through equation (3.9.38). Alternatively, physical or chemical separation of selected components may be sufficient to provide the required compositional variation. Knudsen (1981) provides a detailed statistical analysis used in the determination of the errors in the phase constants.

While Zevin (Zevin & Kimmel, 1995) and Knudsen (1981) have demonstrated the application of this approach for single-peak methods, it is equally applicable if scale factors derived from whole-pattern fitting or Rietveld-based methods are used.

3.9.5.2. *Demonstration of the Zevin approach*

The sample 1 suite from the IUCr CPD round robin on QPA again provides an ideal platform for demonstrating the applicability of this method due to the wide variation of concentration of the constituent phases. A measure of intensity was derived using an hkl_phase (see Section 3.9.6) in which the peak positions were constrained to the space group and unit-cell parameters but the individual peak intensities were refined to empirical values using a pure sub-sample of each of the three phases. For the analysis of the samples, the relative peak intensities were fixed and an overall scale factor *S* for each phase in each sample (eight samples, three replicates, three phases), multiplied by the mass absorption coefficient calculated from the XRF-determined composition, was used as the measure of intensity. These $S\mu_m^*$ values then formed the intensity matrix **I** in equations (3.9.37) and (3.9.38) while all values in the vector **L** were assumed to be 1.0 (*i.e.* all samples were assumed to be fully crystalline). Microsoft Excel provides a useful platform for these calculations since it contains all of the matrix-manipulation functions required by equation (3.9.38). The determined values for *C* for the three phases are given in Table 3.9.3. The values in the C/C_{corundum} column should be compared with the values derived in Section 3.9.4.3 above.

references