

3. METHODOLOGY

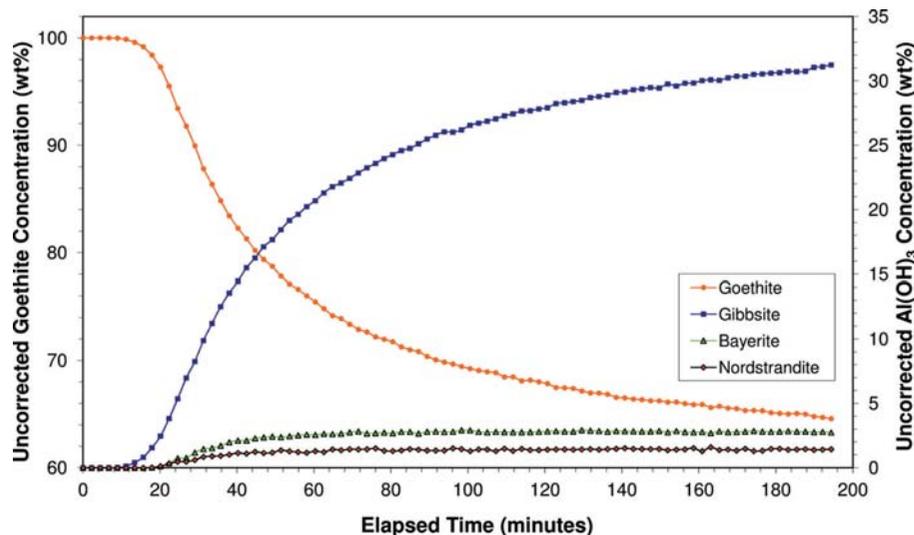


Figure 3.9.5

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 $\text{Al}(\text{OH})_3$ (right axis) crystallize from solution.

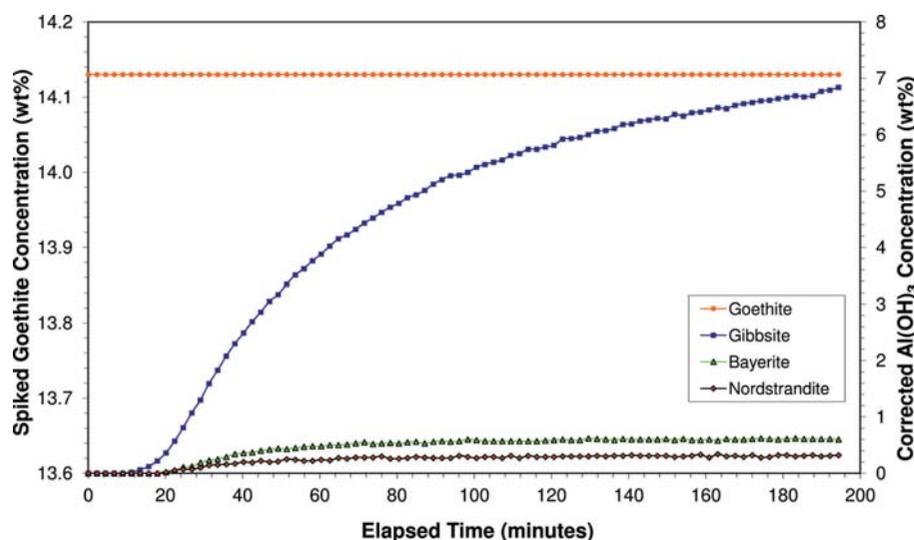


Figure 3.9.6

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).

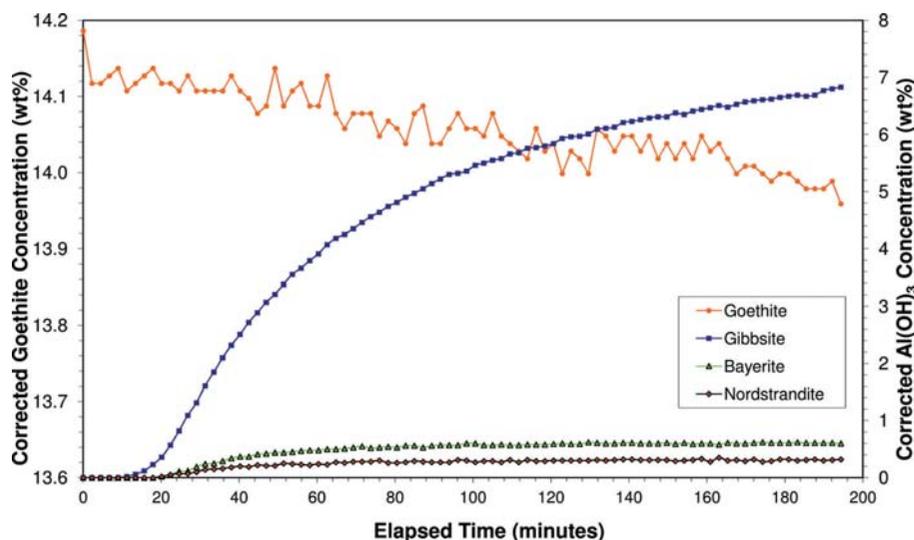


Figure 3.9.7

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.

3.9. QUANTITATIVE PHASE ANALYSIS

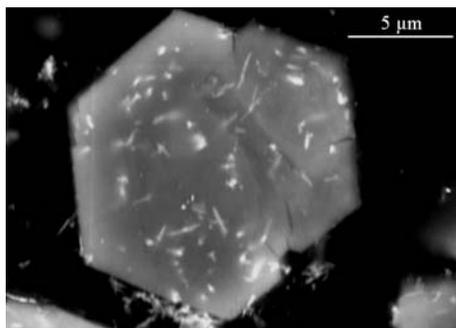


Figure 3.9.8
SEM image of $\text{Al}(\text{OH})_3$ (grey hexagon) which has crystallized on goethite seed (light grey needles) (Webster *et al.*, 2010).

Application of these C values to the analysis of all samples *via* equation (3.9.34) yields the results given in Fig. 3.9.9. The results, displayed as bias from the known values, show that at all concentration ranges the analyses are within about $\pm 1\%$ of the weighed values. The important point to note here is that there has been *no prior calibration* conducted to obtain this result; the system is self-calibrating and has only relied on having a wide range of concentrations of the three phases in the sample suite. The only prior knowledge used in the analysis is (i) a measure of peak intensity embodied in the empirical phase scale factor and (ii) an estimate of μ_m^* for each sample calculated from the elemental composition.

3.9.5.3. Experiment constant – a whole-sample approach

Earlier discussion has noted that the experiment constant K used in equation (3.9.21) can be determined using (i) a standard pure phase or mixture measured separately from the measurement of the actual unknown mixture being analysed, or (ii) using a phase that is present in the sample in a known amount. However, in some cases, these approaches are not always effective in producing reliable values of K because the methodology assumes that the mass of sample contributing to the diffraction process is constant. While this condition is true for infinitely thick samples in Bragg–Brentano geometry, it is unlikely to be true for capillary or flat-plate samples in transmission geometry. In these cases, the sample thickness and packing density will have a significant influence on the amount of sample contributing to the diffraction process and hence on the observed intensity and the derived values of K . Therefore, a K value determined from one capillary sample is unlikely to be applicable to another capillary even though all other instrumental conditions remain the same. However, for *in situ* studies, a K value determined at the start of an experiment should remain valid as the analysis proceeds.

K can also be determined using the whole sample, rather than an individual phase. Since the determined value of K then applies equally to all phases in the sample, equation (3.9.21) can be summed over all analysed components thus:

$$\sum_{i=1}^n W_i = (\mu_m^*/K) \sum_{i=1}^n S_i(\text{ZMV})_i. \quad (3.9.39)$$

If the crystallinity of the sample is known (or can safely be assumed), then individual phase abundances are not required and K can be calculated from

$$K = \frac{\mu_m^* \sum_{i=1}^n S_i(\text{ZMV})_i}{\sum_{i=1}^n W_i}, \quad (3.9.40)$$

where $\sum W_i$ is the assumed crystallinity of the entire sample.

Table 3.9.3

Phase calibration constants for corundum, fluorite and zincite determined using the Zevin (Zevin & Kimmel, 1995) and Knudsen (Knudsen, 1981) method

The RIR values were derived earlier in this chapter.

Phase	C	C/C_{corundum}	RIR
Corundum	240.91	1.0	1.0
Fluorite	874.27	3.629	3.617
Zincite	1190.81	4.943	4.856

For a sample that is 100% crystalline and all components included in the analysis, then the denominator is unity and K is simply the sum of the product of the scale factors and their respective ZMV 's multiplied by the mass absorption coefficient of the entire sample.

For *in situ* studies where a reaction or process is examined dynamically, sealed capillary sample geometry is frequently used. In this environment, the *chemical* composition of the capillary contents will not change during the course of the reaction even though individual phases may be undergoing transformation. Equation (3.9.40) can be further simplified since the overall sample mass absorption coefficient remains constant throughout the reaction and can therefore be deleted and its effect incorporated into K .

This whole-sample approach to the determination of K is also useful in systems where there are residual errors that may not be evident when equation (3.9.21) is used with the concentration of a single phase. By way of demonstration, the sample 1 suite from the IUCr CPD round robin on QPA has been used to calculate K in two distinct ways:

- (1) *Phase specific*: Three replicate measurements of the eight mixtures were analysed using a Rietveld-based surface-analysis approach (Stinton & Evans, 2007). This approach refines a single model to all data sets in the suite simultaneously allowing parameters that are common to all samples to be determined with a greater degree of certainty. Since the sample suite contains corundum, fluorite and zincite in a wide range of concentrations, application of a rearranged equation (3.9.21) using the refined scale factors results in 72 separate determinations of K . The value of μ_m^* for each sample was derived from XRF-determined compositions using equation (3.9.5), while the values for W_i were taken from the known weight additions.
- (2) *Whole sample*: Equation (3.9.40) was applied to each of the 24 data sets (*i.e.* three replicates each of the eight samples) assuming (i) that all phases were known and fully crystalline, *i.e.* $\sum W_i = 1$; and (ii) μ_m^* for each sample was derived in the manner described above.

Fig. 3.9.10 shows the 72 individual determinations of K from the phase-specific method as a function of known phase concentration. At high concentrations, the values for K derived from each of the three phases are similar indicating that, for effectively pure phase samples, the approach embodied in equation (3.9.21) is valid. However, if K is determined using the known concentration of a single phase at a lower concentration in a multiphase sample, then residual errors in the measurement of pattern intensity serve to reduce its accuracy. At lower concentrations of corundum, there is a systematic increase in the determined value of K resulting from a small microabsorption effect present in these samples. Since corundum has the lowest mass absorption coefficient of the three phases in this system its intensity, and hence Rietveld scale factor, is slightly