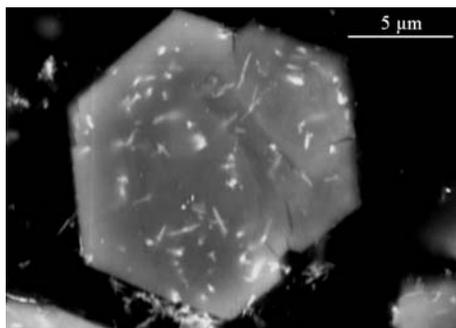


3.9. QUANTITATIVE PHASE ANALYSIS

**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:

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

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

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

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

3. METHODOLOGY

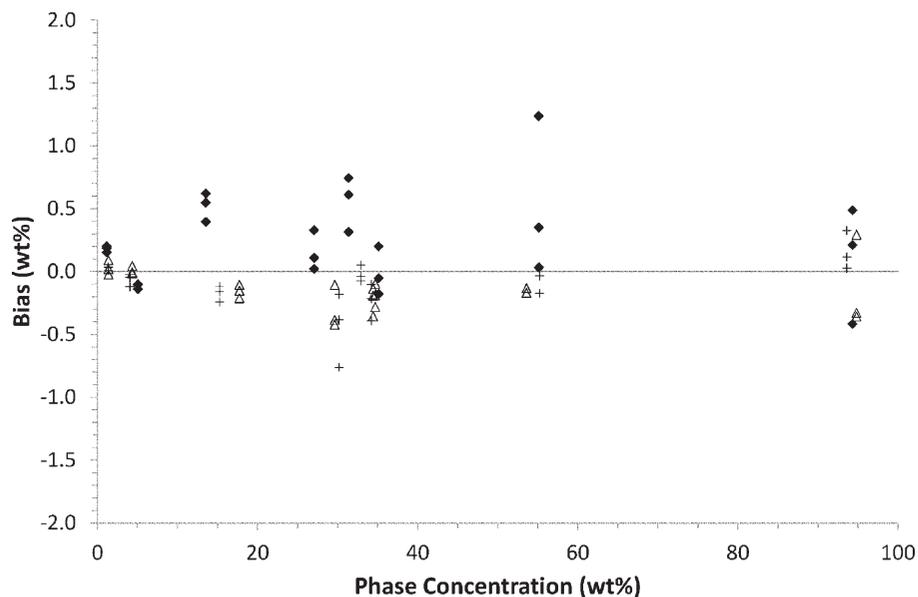


Figure 3.9.9

Plot of the bias (known – determined) in the analysed phase abundances using the Zevin & Kimmel (1995) approach for corundum (black diamonds), fluorite (open triangles) and zincite (crosses). The 72 determinations derive from three replicates of eight mixtures containing three phases each.

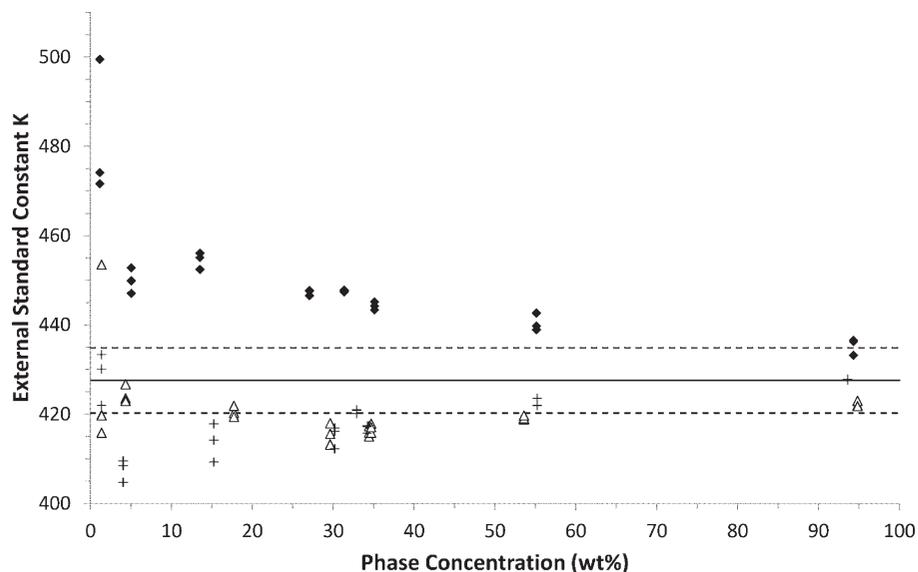


Figure 3.9.10

Plot of the experiment constant K as a function of known phase concentration for corundum (closed diamonds), fluorite (open triangles) and zincite (crosses) using the phase-specific method. The 72 determinations derive from three replicates of eight mixtures containing each of the three phases. The solid line is the mean of 24 values determined using the whole-sample approach. The dashed lines represent ± 2 standard deviations about this mean.

overestimated relative to the fluorite and zincite. This results in an overestimation of the value of K relative to an ideal sample; the magnitude of this difference is about 5% relative. Use of these values for subsequent analysis will result in an underestimation of phase concentrations using equation (3.9.21). The converse is true if fluorite or zincite is used to determine K .

However, if the whole-sample approach embodied in equation (3.9.40) is used for the determination of K , these residual sample-related aberrations can be eliminated; the results of the determination of 24 values of K using this approach are also included in Fig. 3.9.10. The mean of all 24 determinations is 427.6 (3.7) representing a relative error of <0.8%. The important point to note here is that knowledge of the individual phase concentrations is not needed; the only assumption needed relates to the total crystallinity of each sample.

For *in situ* studies, using equation (3.9.40) to calculate K at each step i in the reaction (defined as K_i) can be useful in deriving details of the reaction mechanism. If K_i increases as the reaction progresses, this may be indicative of increasing crystallinity in the sample. Reductions in K_i during the reaction may point to the formation of intermediate amorphous material or unidentified crystalline components, the total concentration of which can be readily calculated using

$$\text{wt\%}_{\text{amorphous}} = 100 \left(1 - \frac{K_i}{K} \right). \quad (3.9.41)$$

Application of this can be demonstrated using sample 3 from the QPA round robin (Scarlett *et al.*, 2002), as it contains the same three crystalline phases as the sample 1 suite with the addition of 29.47 wt% amorphous silica flour. Calculation of K_i for sample 3, based only on the three crystalline phases, results in a value of 301.8. Substituting this into equation (3.9.41) along with the previously determined value of K (427.6) gives a measured amorphous content of 29.42 wt% – this is in good agreement with the known weighed amount. The important point to note here is that the data for sample 3 were collected at the same time, and under the same instrumental conditions, as for sample 1, which ensured that the true value of K was the same for all data.

3.9.6. Quantification of phases with partial or no known crystal structures

While the Rietveld-based methods described in Section 3.9.3.6 work for well ordered phases with known crystal structures, they are limited when published structure data do not accurately represent the phase actually present in the sample, are incomplete or do not exist. Poor agreement with published structure data is a common occurrence in mineralogical research where disorder exists and observed diffraction data deviate significantly from the ideal; this situation occurs with many of the

clay minerals. The issue of incomplete or non-existent structure data can occur in almost any area where new materials are either synthesized or discovered. The growing demand for the analysis of materials from the nanotechnology community, where phases are at the boundary of what can be considered crystalline, serves to further highlight these limitations. Recent developments in diffraction methods have sought to address these issues and have used approaches that include the development of calibrated models or, where appropriate, the extension of existing structure data to incorporate systematic disorder such as stacking faults in clay minerals.

3.9.6.1. Use of calibrated models

Calibrated models are generally developed in one of two ways. The first (which uses what is referred to hereafter as an