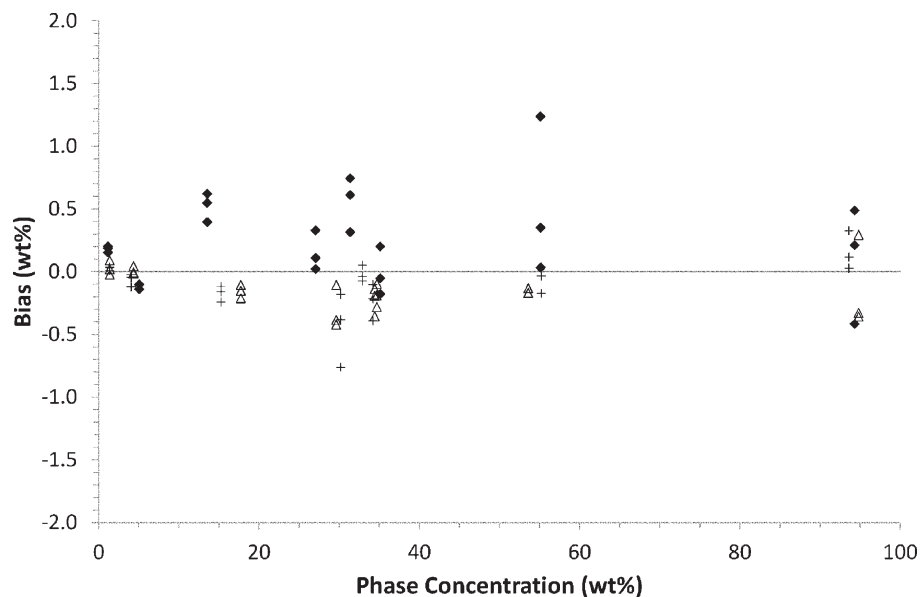
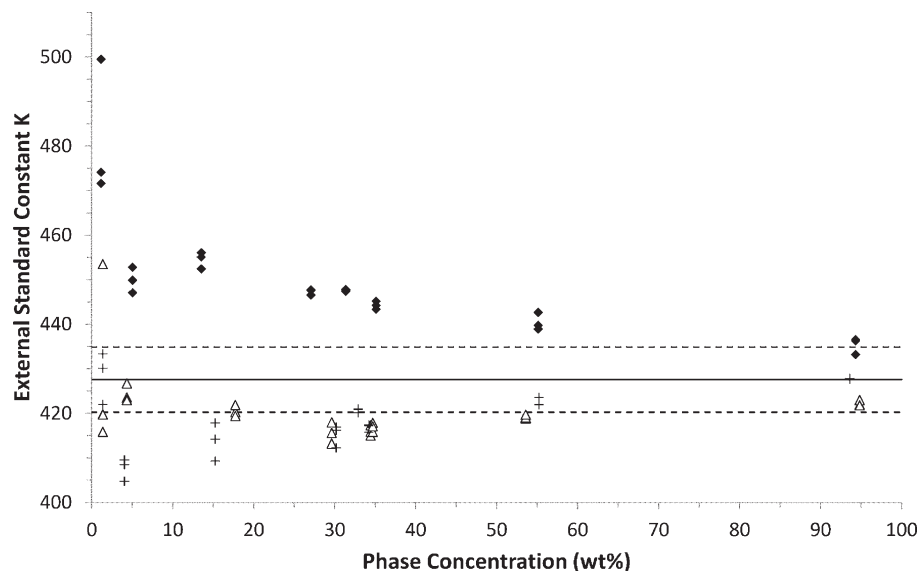


3. METHODOLOGY

**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