3.9. QUANTITATIVE PHASE ANALYSIS

alert the analyst to the presence of non-analysed material in the sample.

3.9.7. QPA from *in situ* experimentation

In situ analysis is a growth area in the field of powder diffraction (Ehrenberg *et al.*, 2013) and is dealt with in depth elsewhere in this volume (see Chapter 2.9). The technique is unparalleled in providing information about reaction mechanisms and kinetics under simulated operational conditions and without the artefacts potentially associated with post-mortem sampling or *ex situ* methods.

An *in situ* experiment collects dynamic, time-resolved data, which present unique challenges for QPA. The phase assemblages formed in such experiments may be quite complex and change dramatically over the course of the experiment. In addition, the data are generally of lower quality than those collected for *ex situ* samples at ambient conditions. This may be due to poor counting statistics resulting from the rapid counting times needed to follow various phase transitions. Data for *in situ* studies are often collected using area detectors, some of which are not photon-counting devices. Care should be taken in the error propagation and hence the weighting used during data analysis.

The data quality may also be affected by components in the sample chamber that are required in order to achieve the environmental conditions (temperature, pressure, solution or gaseous atmosphere, and so on) necessary for the experiment: these components may either attenuate the incident and diffracted beams or contribute features to the pattern resulting from scattering of the beam.

One very important issue that arises from *in situ* studies is the large number of data sets generated. The rapid counting times available at modern synchrotron and neutron facilities mean that hundreds or thousands of diffraction patterns can be collected over the duration of the *in situ* experiment.

3.9.7.1. *Data analysis*

There are usually a series of steps involved in the analysis of *in situ* diffraction data. Given the large number of data sets collected, it is generally not practicable to undertake detailed analysis of every pattern individually. Since any changes to the component phases are transitions generally observed in a sequence of patterns, data analysis focused on extracting QPA could be undertaken using the following steps:

(1) Cluster the data into a number of groups necessary to describe the major phase regions present during the reaction. This can be achieved (i) visually, using software that allows the plotting of three-dimensional data sets of the type shown in Fig. 3.9.14, or (ii) through the use of automatic clustering algorithms using, for example, principal-component analysis.

(2) Select the 'most typical' pattern of each cluster as well as the two 'least typical' patterns at the extreme ends of the cluster. These patterns are often identified by clustering software based on the statistical similarity between patterns in the cluster.

(3) Identify the phases present in each cluster using the most typical pattern. This is not always a trivial task since (i) new phases that are not currently present in databases may have been generated; (ii) effects such as thermal expansion or variation of chemical composition may have changed the peak positions so that search/match procedures are no longer successful; or (iii) impurity elements may have stabilized

phases that are not expected from related phase-diagram studies.

(4) For the discussion here, it will be assumed that the quantification process will be *via* a whole-pattern method.

(*a*) Develop appropriate (crystal structure or PONKCS) models for every phase observed within the data suite.

(*b*) Optimize the pattern and phase-analysis parameters using the most typical pattern selected from each cluster.

(*c*) Set the relevant parameter refinement limits using the least typical patterns. It is necessary to limit the range over which refined parameters can vary to avoid the return of physically unrealistic values.

(5) Owing to the large number of data sets, analysis for QPA will generally be approached as a batch process with limited refinement of structural parameters. This limitation on the total number of refinable parameters is necessary during batch processing in order to avoid instability in the refined values as the phases progress from major to minor concentration.

(6) Batch processing of data suites may be conducted in a variety of ways including:

(*a*) Sequential refinement, beginning with either the first or final pattern of the suite and including all phases present in the entire suite. This methodology must be tempered by a means to either remove or severely restrict refinement of any phases that are not present in all patterns of the suite in order to avoid the reporting of 'false positives' where absent phases have been included. Some software packages allow phases to be removed from the analysis if their abundance is below a selected level or has an error that exceeds some predefined criteria (Bruker AXS, 2013).

(*b*) Parametric Rietveld refinement (Stinton & Evans, 2007), where the entire suite of diffraction data is analysed simultaneously. Selected parameters are constrained to the applied external variable (*e.g.* temperature) with a function describing their evolution throughout the data sequence. For example, the unit-cell parameters for a phase can be constrained to vary according to their thermal coefficients of expansion. This method can bring stability to refined parameters and allows the refinement of noncrystallographic parameters such as temperature and reaction rate constants directly from the diffraction data. This methodology is particularly suited to relatively simple phase systems, but is difficult to develop for complex multiphase mineralogical systems.

(7) In selecting a model for use in QPA, it is highly recommended that one of the approaches that generate absolute phase abundances is used. Many reactions generate intermediate amorphous phases that convert to crystalline components later in the reaction. If relative phase abundances [such as those produced by the *ZMV* approach embodied in equation (3.9.26)] are used, the amounts of the crystalline phases will be overestimated and this will give misleading indications about the reaction mechanism and kinetics.

Whichever method is employed, it is always necessary to examine a sample of individual results as a test of veracity rather than just accepting the suite of numbers for parameter values and QPA resulting from batch processing.

The study of Webster *et al.* (2013) demonstrates many of these points by following the formation mechanisms of the iron-ore
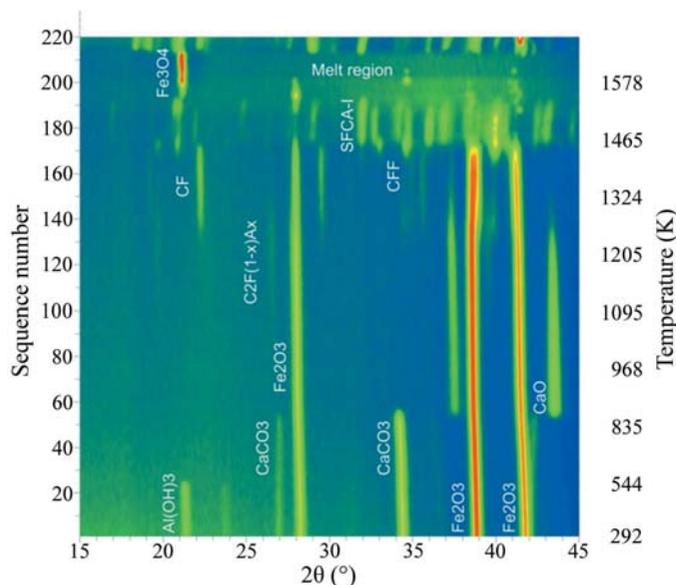
Figure 3.9.14
Raw *in situ* XRD data (Co $K\alpha$ radiation) collected during the synthesis of the iron-ore sinter bonding phase SFCA-I (Webster *et al.*, 2013). The data, collected as a function of heating temperature, are viewed down the intensity axis with red representing the highest intensity and blue the lowest intensity. The identified phases include gibbsite $Al(OH)_3$, calcite $CaCO_3$, haematite Fe_2O_3, lime CaO, calcium ferrites CF and CFF, calcium alumina-ferrite $C_2F_{1-x}A_x$, magnetite Fe_3O_4, and SFCA-I.

sinter bonding phase, SFCA-I, where SFCA = silico-ferrite of calcium and aluminium (Scarlett, Madsen *et al.*, 2004; Scarlett, Pownceby *et al.*, 2004; Webster *et al.*, 2013). The starting material, comprising a synthetic mixture of gibbsite, $Al(OH)_3$, haematite, Fe_2O_3, and calcite, $CaCO_3$, was heated to about 1573 K using an Anton Paar heating stage. The laboratory-based XRD data, collected using an Inel CPS120 diffractometer, are shown in Fig. 3.9.14, while the QPA results are shown in Fig. 3.9.15. Both figures show that there are several phase changes, including the formation of transient intermediate phases before the final production of SFCA.

In Fig. 3.9.15(*a*) the QPA results are derived using the Hill/Howard algorithm (Hill & Howard, 1987) in equation (3.9.26): this is the 'default' value reported by most Rietveld analysis software and normalizes the sum of the analysed components to 100 wt%. The apparent increase in haematite concentration at about 533 and 868 K results from the decomposition of gibbsite and calcite, respectively. There are no possible mechanisms in this system that could lead to an increase in haematite concentration at these temperatures; the reported increases are an artefact derived from normalizing the sum of all analysed phases to 100 wt%. Fig. 3.9.15(*b*) shows the correct result derived using the external-standard approach (O'Connor & Raven, 1988) embodied in equation (3.9.21), which has placed the values on an absolute scale. Fig. 3.9.15 demonstrates the importance of putting the derived phase abundances on an absolute scale for a realistic derivation of reaction mechanism and kinetics.

3.9.8. QPA using neutron diffraction data

One of the early papers detailing the application of the Rietveld method to quantitative phase analysis used neutron diffraction (ND) data (Hill & Howard, 1987). The reasons stated within this work define many of the advantages of neutrons over X-rays for diffraction in general and QPA in particular. One of the most significant advantages for QPA derives from the fact that

neutrons interact weakly with matter, hence there is very little microabsorption with ND even in samples comprising a mixture of high- and low-atomic-number materials.

The high penetration capability of neutrons also enables the use of larger sample environments in *in situ* studies, thus enabling studies to be undertaken at, for example, higher pressures than would be possible with many X-ray sources. In addition, larger sample volumes can be investigated, which in turn produces better particle statistics and makes the technique less sensitive to grain size. It also makes ND a bulk technique in comparison with XRD, which is effectively surface-specific with a penetration depth of the order of microns or tens of microns.

The different strengths of ND and XRD mean that they can be exploited in combination to provide complementary information. For example, XRD generally has higher angular resolution and is therefore better at resolving small lattice distortions and heavily overlapped phases. However, the observed intensities in ND do not decrease as strongly with decreasing *d*-spacing. This results in ND providing more accurate determination of atomic displacement parameters and therefore the Rietveld scale factors; this then improves the accuracy of QPA derived from these scale factors (Madsen *et al.*, 2011).

Hill *et al.* (1991) have investigated the phase composition of Mg-PSZ (partially stabilized zirconia) using both ND and XRD. The surfaces of these materials were subjected to various treatments, which meant that they were no longer representative of the bulk. From the more highly penetrating ND data they obtained bulk properties including crystal structure and size and strain parameters of the components along with QPA. From XRD they were able to examine the surface of the samples to investigate the effects of surface grinding and polishing.

The majority of Rietveld-based QPA still relies on the use of accurate crystal structure models; consequently, it is of increasing importance that powder diffraction methods used for structure solution be robust and reliable. Combining laboratory or synchrotron XRD and ND has been shown to be of considerable benefit in the solution of complex structures *via* powder diffraction (Morris *et al.*, 1992). This joint-refinement approach has been used to determine the crystal structure of a component phase of Portland cement (De La Torre *et al.*, 2002) for subsequent use in Rietveld-based QPA.

One of the disadvantages of neutron sources is that they are much less accessible than laboratory X-ray sources and of much lower flux than either laboratory or synchrotron X-rays sources. In addition, larger samples are generally required; this is not always practical in the investigation of many materials.

In many phase systems, the presence of severe microabsorption in XRD data serves to limit the accuracy that can be obtained. The collection of ND data, where microabsorption is virtually absent, from selected samples provides more accurate QPA; selected ND-based values can therefore act as a benchmark for the more routine XRD-based studies.

3.9.9. QPA using energy-dispersive diffraction data

Energy-dispersive diffraction (EDD) involves the use of high-energy white-beam radiation, often from a synchrotron source. This provides very high penetration and is, therefore, ideal as a probe to examine the internal features of relatively large objects (Barnes *et al.*, 2000; Cernik *et al.*, 2011; Hall *et al.*, 1998, 2000). In an experimental arrangement such as that in Fig. 3.9.16, diffraction data can be measured by energy-dispersive detec-

references