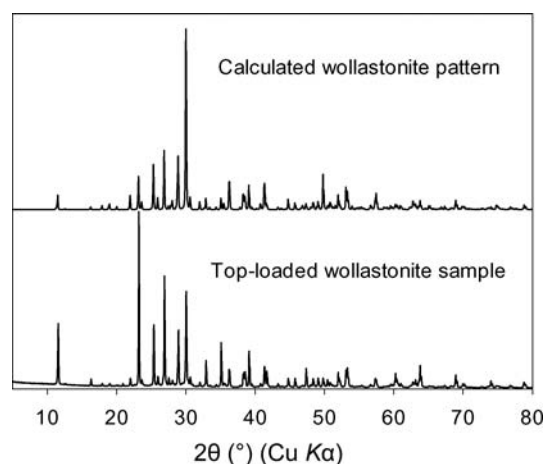
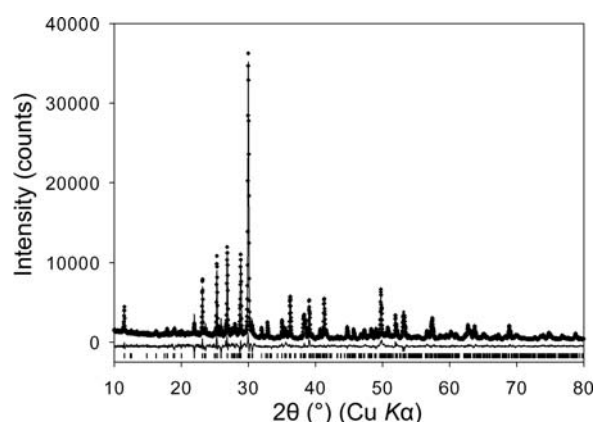


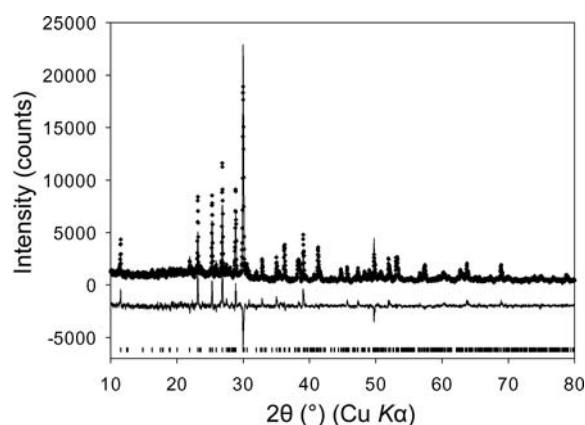
## 2.10. SPECIMEN PREPARATION

**Figure 2.10.26**

Effect of preferential orientation on data from top-loaded wollastonite compared with the calculated pattern from the literature wollastonite-1A structure (Ohashi, 1984).

**Figure 2.10.27**

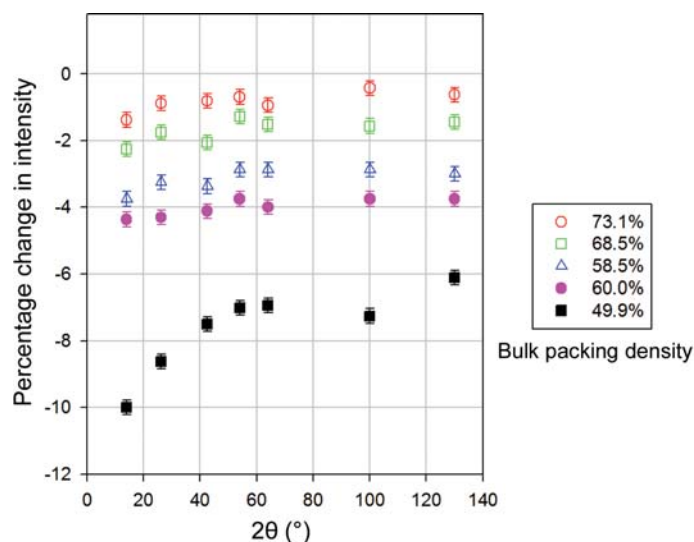
Rietveld refinement fit to the literature wollastonite-1A structure (Ohashi, 1984) with data from a 0.3 mm capillary with no orientation corrections.

**Figure 2.10.28**

Rietveld refinement fit to the literature wollastonite-1A structure (Ohashi, 1984) with data from a 0.2 mm capillary with no orientation corrections.

intact while filling the capillary (Fig. 2.10.23). Fig. 2.10.24 gives a summary of the effectiveness of the different sample-preparation techniques for this particular mica sample in terms of the ratio of the integrated intensities of the 001 and 200 reflections. The spray-dried sample with careful top loading can produce a pattern practically equivalent to the capillary data set.

Plates are not the only problematic morphology. Needle-shaped crystallites such as those exhibited by wollastonite (Fig.

**Figure 2.10.29**

The effect of surface roughness on the intensity compared to that of a bulk copper specimen. Data from Suortti *et al.* (1972).

2.10.25) and some organic compounds can also show significant problems when top-loaded. In fact, lath-like crystallites such as wollastonite can orient in two directions at the same time, so the behaviour can be more complicated than that of materials with plate-like morphology (see Figs 2.10.26, 2.10.27 and 2.10.28).

### 2.10.1.3. Absorption (surface roughness), microabsorption and extinction

Absorption, microabsorption and extinction effects all alter peak intensities, although particularly low absorption (*e.g.* from organics) can give rise to sample transparency in reflection geometry (as discussed in the section on the choice of sample mounting), where a peak shift and change in profiles can occur. Microabsorption and extinction solely affect the peak intensities.

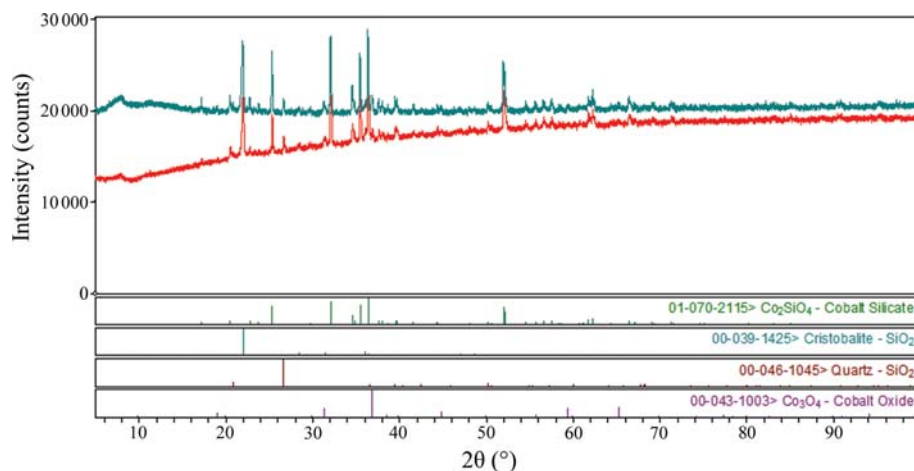
Microabsorption (also known as absorption contrast) and extinction are effects that complicate quantitative phase analysis. They are both still related to size – particles in the case of microabsorption and crystallites in the case of extinction.

#### 2.10.1.3.1. Absorption (surface roughness)

Absorption is an obvious issue when using capillaries in transmission (a convenient calculator is available on the 11-BM web site, <http://11bm.xray.aps.anl.gov>), but absorption can also affect data obtained in reflection using Bragg–Brentano geometry through the mechanism commonly described as ‘surface roughness’. In essence, the increasing packing density with depth leads to lower intensities at low diffraction angles, leading to anomalously low or negative displacement parameters (much as absorption does in capillaries). There are two components to the effect (Fig. 2.10.29, Suortti, 1972). The constant decrease in intensity is generally incorporated into the refined scale factor. The angle-dependent portion becomes more significant as the packing density is reduced.

The effect is greatest with strongly absorbing materials analysed in reflection geometry, so care should be taken to produce a sample with a smooth surface and uniform density where possible. An example is provided by the patterns (Fig. 2.10.30) of a commercial cobalt silicate (which turned out to consist of a mixture of phases). A pattern from a slurry deposited on a zero-background cell – a technique useful for small samples, but which produces a rough surface – yielded significantly lower

## 2. INSTRUMENTATION AND SAMPLE PREPARATION



**Figure 2.10.30**

Powder patterns of a commercial cobalt silicate sample, measured from a (rough) slurry-mounted specimen (red) and from a (flat) conventional front-packed specimen (green). The surface roughness decreases the intensities of the low-angle peaks and background.

peak and background intensities at low angles than a conventionally front-packed specimen. Refinement using the ‘rough’ data yielded unreasonably negative displacement coefficients. Including a surface-roughness model in the refinement resulted in reasonable displacement coefficients, identical to those obtained using the ‘flat’ data.

Models by Suortti (1972) and Pitschke *et al.* (1993) exist in most analysis software. They both yield similar results, but the Suortti correction is generally regarded as slightly more stable at  $2\theta$  angles below  $20^\circ$ .

### 2.10.1.3.2. Microabsorption

Microabsorption is widely regarded as the greatest impediment to the application of quantitative phase analysis with powder X-ray diffraction data. Misapplication of a microabsorption correction can degrade accuracy (Scarlett *et al.*, 2002). The infamous sample 4 in the Commission for Powder Diffraction quantitative phase analysis round robin (Scarlett *et al.*, 2002) was deliberately designed to be difficult to analyse accurately using any wavelengths available to a laboratory X-ray diffractometer because of microabsorption effects.

Brindley (1945) published a theoretical correction (model) for microabsorption, but the range for an appropriate application can be easily exceeded. In the absence of such a correction, relative concentration errors can commonly be 20–30%. The extent of microabsorption for a phase was described by Brindley in terms of  $\mu D$ , where  $\mu$  is the linear absorption coefficient and  $D$  is the particle (not crystallite) diameter. While a crystallite size can be estimated from the profile widths, determining the particle size requires additional information, such as laser light-scattering measurements. Where  $\mu D > 0.1$  the Brindley correction may not be accurate, and ideally  $\mu D$  for every phase present should be less than 0.01, where microabsorption can safely be ignored. Brindley also suggested a rule-of-thumb for the maximum acceptable particle size for quantitative phase analysis, where  $D_{\max} = 1/(100\mu)$ .

The terms  $\mu$  and  $D$  show that microabsorption can be affected by X-ray wavelength and particle size. The easiest approach for the analyst with a troublesome sample is to reduce the particle size by micronizing the sample. Some in-house laboratories may have multiple systems or the flexibility to change wavelengths. As a rule the linear absorption coefficient decreases with increasing

energy, but users should beware of absorption edges that can create a serious discontinuity in this trend. Synchrotron beamlines have more flexibility for avoiding absorption edges and can achieve higher energies that are not practical in laboratory systems. Even when using this high-energy ‘sledgehammer’ approach there is still a benefit to reducing the crystallite size to avoid some of the other effects mentioned in this chapter.

Microabsorption results from differences in linear absorption coefficients and particle sizes, and can sometimes arise in unexpected situations. Adding a NIST SRM 640b silicon internal standard to a micronized mullite sample (Kaduk, 2009) in order to quantify the amorphous content resulted in a significant microabsorption effect, the result of differences in both particle size and absorption coefficients. The microabsorption could be

overcome by micronizing the mullite/Si blend.

Even in cases where the absorption contrast is small, large differences in particle size can result in significant microabsorption effects. For anatase/rutile mixtures ( $\mu = 489.4$  and  $534.2 \text{ cm}^{-1}$ , respectively) in which the anatase and rutile particle sizes were 3 and  $150 \mu\text{m}$ , respectively, concentration errors of 20% relative were observed. The errors were corrected by micronizing the mixtures (Kaduk, 2013). Similarly, mixtures of large-particle ( $23 \mu\text{m}$ ) MFI zeolite ( $\mu = 65.66 \text{ cm}^{-1}$ ) and a quartz internal standard ( $\mu = 96.39 \text{ cm}^{-1}$ ,  $10 \mu\text{m}$ ) resulted in relative concentration errors of 5%; these errors were corrected by micronizing the mixtures.

Neutrons are absorbed much less than X-rays, which means that microabsorption is practically nonexistent in neutron diffraction data. The lack of microabsorption is why neutron diffraction is often regarded as the ‘gold standard’ for quantitative phase analysis, although the beamline proposal process tends to make its application in conventional quantitative phase analysis uncommon. The application of quantitative phase analysis using neutron diffraction data is most often seen when studying phase evolution in an *in situ* experiment. Microabsorption is an issue specific to quantitative phase analysis and a more detailed discussion of the problem is given in Chapter 3.9.

### 2.10.1.3.3. Extinction

Extinction effects are not common in X-ray powder diffraction but may be significant when using neutrons. Extinction is dependent on the size/shape of the coherently diffracting domains, and is a multiple-scattering phenomenon. Primary extinction occurs when a second diffracting event occurs within a single crystallite. Secondary extinction occurs in mosaic crystals and is not seen in powders. When primary extinction occurs, the re-diffracted beam will continue in the same direction as the incident beam but interfere destructively with it. Re-diffraction within a crystallite is not likely to occur where imperfections disrupt the ordering of a crystallite. Consequently, primary extinction is usually only seen in powders of highly ordered and crystalline materials. A classic example is powdered single-crystal silicon as used in studies on extinction such as that by Cline & Snyder (1987). The most commonly encountered phase that can exhibit primary extinction is high-quality natural quartz.