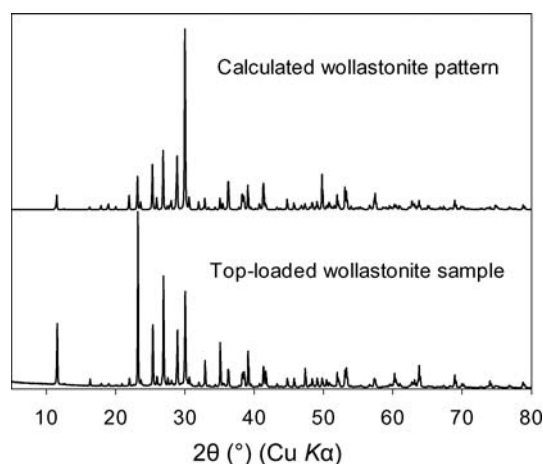
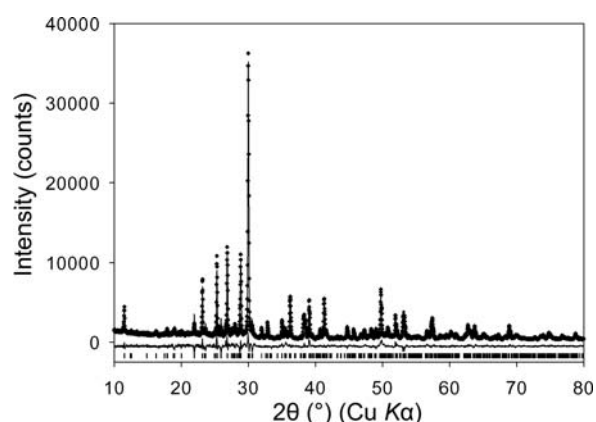


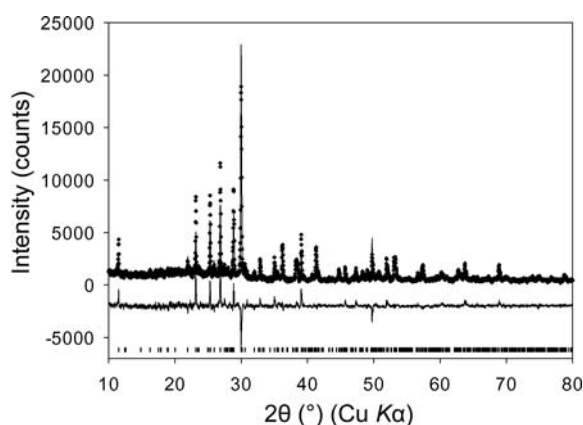
## 2.10. SPECIMEN PREPARATION

**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**

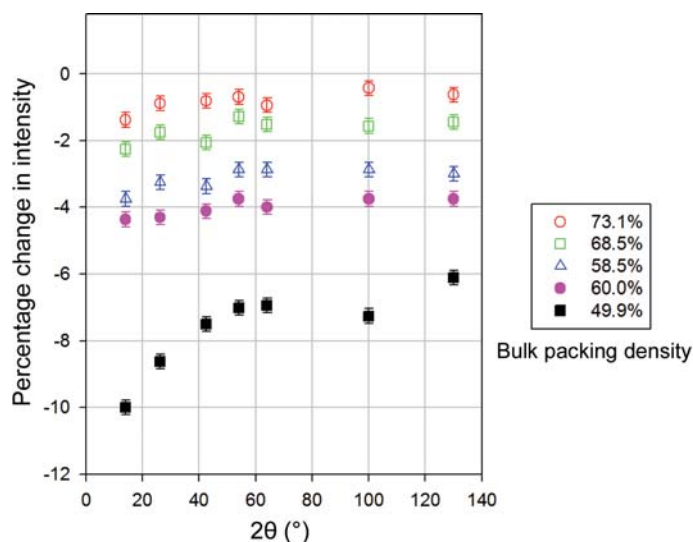
Rietveld refinement fit to the literature wollastonite-1A structure (Ohashi, 1984) with data from a 0.3 mm capillary with no orientation corrections.

**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.

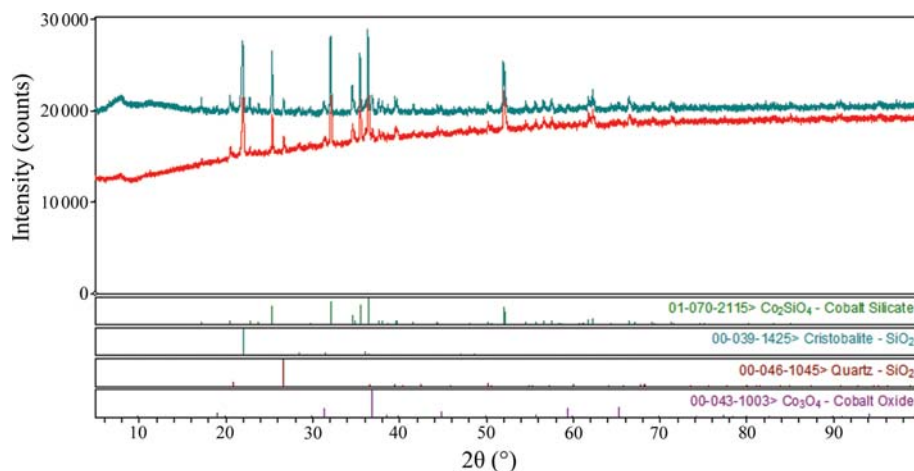
Microabsorption (also known as absorption contrast) and extinction are effects that complicate quantitative phase analysis. They are both still related to size – particles in the case of microabsorption and crystallites in the case of extinction.

#### 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

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**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.

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Zachariasen (1945) described an extinction correction (model) including terms relating to crystallite size, wavelength, structure factor and scattering angle. Extinction effects will be apparent with large crystallites and long wavelengths. Extinction effects are also greater for the more intense (low-angle) reflections, so extinction mimics the effects of small displacement parameters. In a single-phase system, unexpectedly low or even negative displacement parameters may be the only sign that extinction effects are present. In a multiphase system the effects of extinction will reduce the apparent phase fraction of the affected phase with respect to the rest of the sample. In fact, studying extinction experimentally is often done by using its effects on quantitative phase analysis to untangle the different effects (Cline & Snyder, 1987). The frequently high quality of natural quartz makes the quantitative phase analysis of mineral samples the most likely scenario for the appearance of extinction in a practical laboratory setting.

The wide range of wavelengths and wide range of  $(\sin \theta)/\lambda$  used in time-of-flight (TOF) neutron diffraction makes extinction effects particularly pronounced. Consequently TOF data often require the application of an extinction correction (Sabine *et al.*, 1988). Constant-wavelength neutron diffraction frequently uses longer wavelengths than normally used in the laboratory or synchrotron beamlines, so the user must be aware of possible problems.

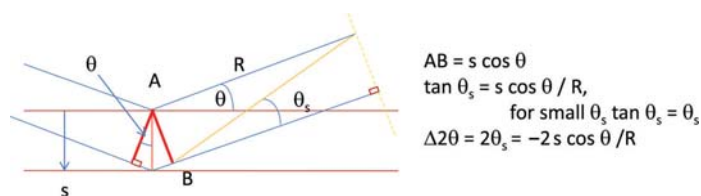
Despite the danger of ‘message fatigue’, the dependence of primary extinction on crystallite size adds yet another reason to reduce the crystallite sizes to the order of 1  $\mu\text{m}$  or so. Theoretically, single-crystal silicon will exhibit extinction with copper radiation with crystallite sizes of 5  $\mu\text{m}$ .

### 2.10.1.4. Holders

#### 2.10.1.4.1. Reflection sample holders

In a laboratory setting these are the most common type of holders – normally for use in a Bragg–Brentano instrument. A wide variety of sample holders for different applications are available. Several different holders and techniques will be described, but there are some issues common to all holders in reflection geometry, particularly with Bragg–Brentano geometry.

In Bragg–Brentano parafocusing geometry care should be taken that the surface of the sample is flat. If the surface is not flat the parafocusing condition is violated and will degrade the peak resolution and positions; in addition, surface roughness can affect the intensities. Where there is a cavity it seems straightforward to make sure that the sample surface is level with the top surface of the holder. The peak positions obtained in Bragg–Brentano geometry are very sensitive to specimen displacement; a vertical displacement of 20  $\mu\text{m}$  in a typical diffractometer will shift the peaks by approximately  $0.01^\circ 2\theta$ . The derivation of the equation for the effect of displacement on peak position is given in Fig. 2.10.31. The minus sign in the equation reflects the convention that the displacement is positive if it increases the radius of the



**Figure 2.10.31**

Derivation of the equation relating peak displacement to sample displacement ( $s$ ) in parafocusing geometry.  $R$  is the goniometer radius.



**Figure 2.10.32**

A home-made top-loading zero-background silicon holder with a 0.5 mm deep cavity.

diffracting circle, *i.e.* the sample is too low. Front-packed specimens are almost always too high, so the analyst needs to refine his/her technique to minimize the displacement errors.

The sensitivity to specimen displacement is such that even dirt between the reference surface of the sample stage and the holder can produce a detectable peak shift. Dust accumulation inside a powder diffractometer is almost inevitable, so occasionally cleaning these surfaces is recommended.

Parallel-beam-geometry diffractometers have become popular in many laboratories because some of these problems are avoided. Although there are often some disadvantages in terms of peak resolution and grain sampling, they allow more flexibility in the mounting of specimens. For instance, rough sample surfaces and displacements do not cause the aberrations that are apparent in data from conventional parafocusing diffractometers when the same samples are analysed with a parallel-beam system.

Many different types of holders for reflection geometry are available commercially from the instrument vendors, but often home-made holders can be equally effective and customized for specific tasks. Most common are the different types of top-loading sample holders made from plastic or metal, often with a cavity to hold the sample. Commonly the cavities are larger or smaller than those offered by the vendors. The cavity may include some form of zero-background plate such as specially cut single-crystal silicon (Fig. 2.10.32) or quartz, although this does add a significant cost. Some quartz plates may exhibit forbidden reflections or contain inclusions, so they should be tested before use in a sample spinner.

In addition to the standard holders, more specialized holders may be bought or built, or indeed fabricated using a 3D printer. These include holders for air-sensitive samples (Fig. 2.10.33), back-loading (Fig. 2.10.34) and side-loading holders, holders for filter papers, clay samples *etc.* Any laboratory with a competent workshop can construct a wide variety of holders, including those for complex *in situ* work, which is discussed in Chapter 2.9. One common theme is that any material in the X-ray beam path must be kept to a minimum to reduce attenuation. Ideally any such material (such as the polymer dome of the air-sensitive holder shown in Fig. 2.10.33) should be as far away from the diffracting plane as possible. A secondary monochromator can be effective in stopping the parasitic scattering from reaching the detector, but with a PSD there is greater reliance on good design to reduce it as much as possible. A common approach with home-designed and -constructed sample holders for air- or moisture-sensitive samples is to cover the sample with a thin Kapton or Mylar film attached with a bead of silicone grease.