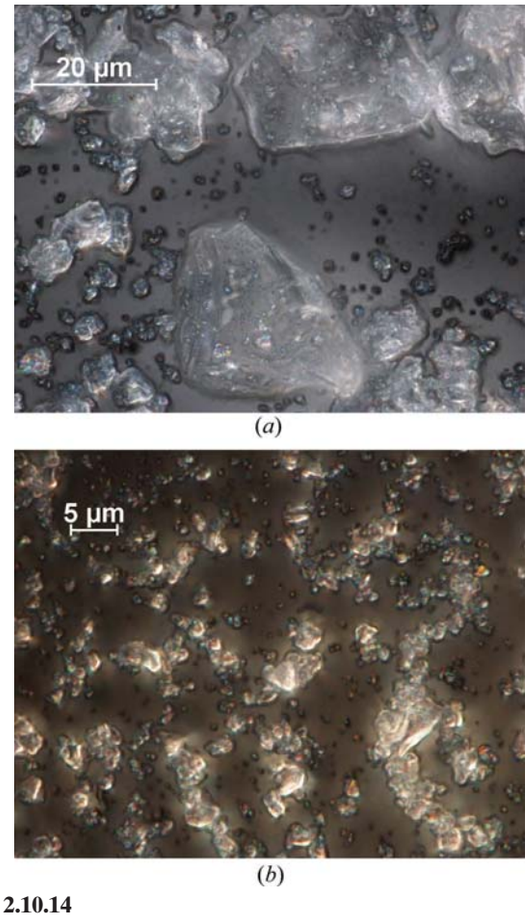

Figure 2.10.14
Optical micrographs of (*a*) -400 mesh quartz at 100× magnification and (*b*) quartz milled in a McCrone micronizer for 15 min in isopropyl alcohol at 150× magnification.

elements (corundum or agate in the micronizing mill; possibly iron, WC, SiC *etc*. in other types of mill).

Obviously, a reduction of the crystallite size to the µm-sized region will produce size broadening if the instrument has sufficient resolution to detect it. It is worth bearing in mind that micronizing does not guarantee a problem-free sample. Micronized specimens almost always exhibit some microstrain broadening. In principle, this could be decreased by an annealing treatment, but this step is rarely practiced. When a mixture contains both very hard and very soft phases, the hard phases may not mill properly. This has been observed in mixtures containing organics and a minor quartz fraction. Despite milling for 30 min or more, the classical split 101 quartz reflection (such as seen in Fig. 2.10.11) was still visible in some data sets, an indication of the 'rocks in dust' phenomenon. Although the McCrone mill is designed to minimize microstructural damage to samples, damage can still occur with very soft materials, and ductile materials may weld as opposed to mill. With very soft and pliable materials a possible alternative could be to cryo-mill the samples, taking advantage of the increased brittleness of materials at low temperature.

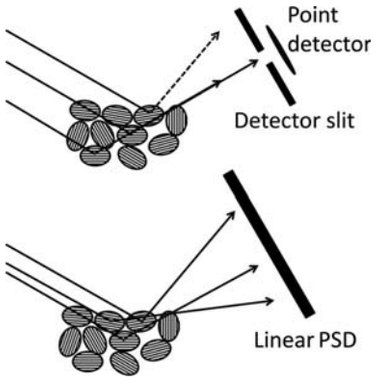

Figure 2.10.15
Diagram showing the source of improved particle statistics in reflection geometry using a 1D position sensitive detector (PSD) *versus* a point detector.

2.10.1.2. *Preferred orientation*

Preferred orientation is usually undesirable in a powder diffraction pattern, although sometimes it *is* the information required, as in texture studies. One of the exceptions is the analysis of clays, where orientation is deliberately induced to identify related reflections. Preferred orientation manifests itself as continuous but non-uniform intensity in the Debye rings, and so is easily characterized with 2D detectors. Preferred orientation does not change the total diffracted intensity, but renormalizes some classes of reflections with respect to others.

Reference is commonly made to a preferred-orientation 'correction'. Strictly speaking, what is done is 'modelling' of the preferred orientation. The proper way to correct preferred orientation is through better specimen preparation.

Models for preferred orientation exist in many analysis packages, specifically the March–Dollase (Dollase, 1986) and spherical-harmonics (Järvinen, 1993) formalisms. Apparent severe preferred orientation may be a sign of large crystallites, which may result in one or more of the other problems outlined in this section.

Additional care must be taken where software corrections are used during quantitative phase analysis, where overlapping reflections can cause serious correlations and erroneous results. The March–Dollase correction is less prone to this, as an orientation direction must be supplied by the analyst. The spherical-harmonics correction has no such constraint. It behaves properly where peak overlap is not extensive, but negative peak intensities are not uncommon (especially when too high an order is used) when applying it without thought in complex mixtures. Negative peak intensities are obviously impossible, so the results of such an analysis must be viewed with great suspicion.

The presence of preferred orientation can be most easily discerned by comparing the observed pattern to a calculated pattern (random) of the same phase from the Powder Diffraction File or other source. The likelihood of preferred orientation can be assessed by calculating the Bravais–Friedel–Donnay–Harker (Bravais, 1866; Friedel, 1907; Donnay & Harker, 1937) morphology from the crystal structure using *Mercury* (Sykes *et al.*, 2011) or other tools.

Orientation tends to occur in materials where the crystallites have either a needle or plate-like morphology. Plates are common in the analysis of mineral samples, such as the commercial phlogopite mica used here as an example. Conventional top-loading of such samples can result in very few reflections being visible because of almost perfect orientation of the plates during pressing, as seen in Fig. 2.10.16. Where the aspect ratio of the crystallites is large, micronizing the sample does not reduce the preferred orientation significantly (Fig. 2.10.17).

The most common approach to decrease preferred orientation of troublesome samples such as this mica is a technique known as back-loading. [Others are discussed in Buhrke *et al.* (1998).] The concept is that the surface of the sample is not subjected to

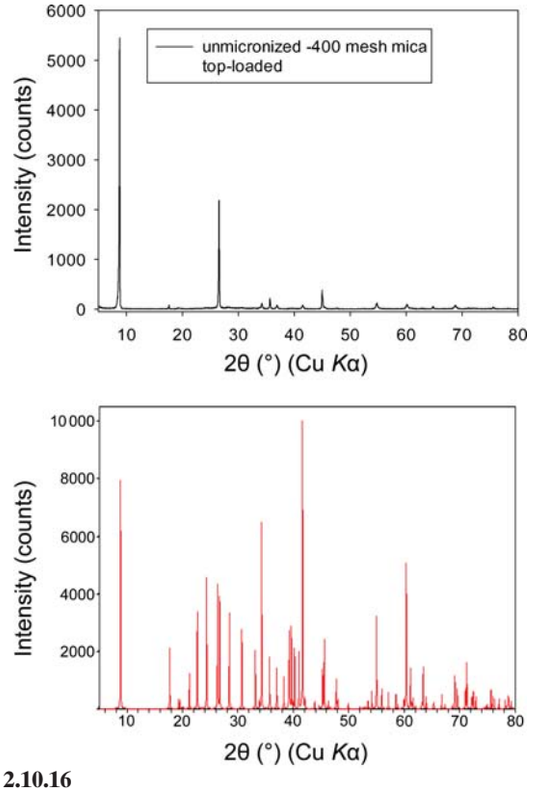

Figure 2.10.16
Top: diffraction pattern of top-loaded 400 mesh phlogopite mica. Bottom: calculated random pattern.

significant compression, yet remains flat. An example of a commercial back-loading holder is shown in Fig. 2.10.34. These holders are filled while upside down with the back removed. The cavity is filled with sample using minimal pressing, the back of the holder is replaced, and then the whole assembly including specimen is flipped the right way up. Generally, the deeper the holder the lower the compressive force on the analysed surface, but the trade-off is the requirement for large amounts of sample. Many of the samples exhibiting plate-like morphology possess low-angle reflections (such as mica and illite) so the sample area cannot be reduced too much to reduce sample volume, or beam overspill may occur.

A variation of the back-loading sample holder is the side-loading sample holder. These are less common, although the sample is still loaded against some surface in the same fashion as the back-loading variant. As the name implies, the difference is that the sample is introduced from a hole in the side as opposed to the back, and the hole is then plugged after filling.

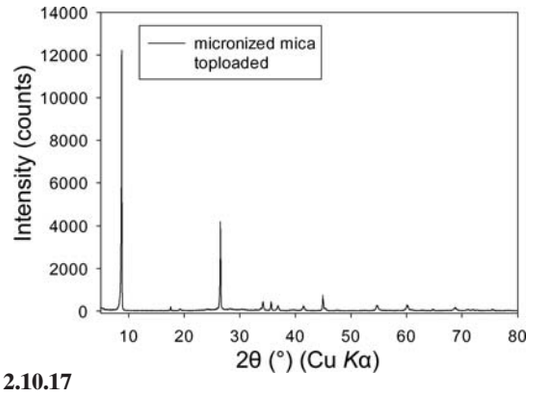

Figure 2.10.17
Diffraction pattern of top-loaded miconized phlogopite mica.

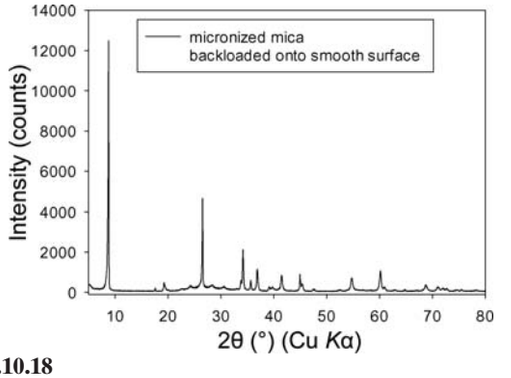

Figure 2.10.18
Diffraction pattern of miconized phlogopite mica when back-loaded onto a smooth surface.

Simple back-loading of samples in itself is not always sufficient for very platy samples such as the high-aspect-ratio mica used here. Fig. 2.10.18 shows the result from back-loading a micronized sample of the mica onto a smooth surface.

Although the result is improved, the specimen is still not a random powder. A useful approach in these circumstances is to make the surface of a back-loaded sample deliberately rough to break up the orientation of the plates. An easy way to achieve this is to load the sample onto the surface of sandpaper or a coarse ground glass slide. Sandpaper has the advantage of being disposable so avoiding cross-contamination among samples. Not all sandpaper has the desired jagged surface, so it may be necessary to experiment to find the best. The paper used for the data shown here was a 400-grit carborundum paper, the surface morphology of which is shown in Fig. 2.10.19. The rough surface will cause some slight defocusing in a parafocusing setup and reduce the count rates somewhat, but in many cases the advantages outweigh the disadvantages.

The result of back-loading the micronized mica onto the 400-grit carborundum paper is shown in Fig. 2.10.20. The dominance of the 00*l* reflections is reduced even further than when mounted onto a smooth surface. The approach is simple enough that it is used routinely in at least one laboratory dealing with large numbers of mining and mineral samples (Raudsepp, 2012). Back-loading samples is more time consuming than top-loading. Consequently, where high sample throughput is required, back-loading can be reserved for those samples where orientation is a problem.

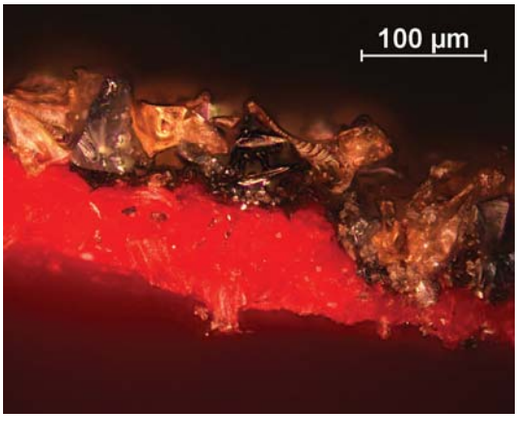

Figure 2.10.19
20× optical micrograph of a cross section of the 400-grit carborundum paper used for back-loaded mica.

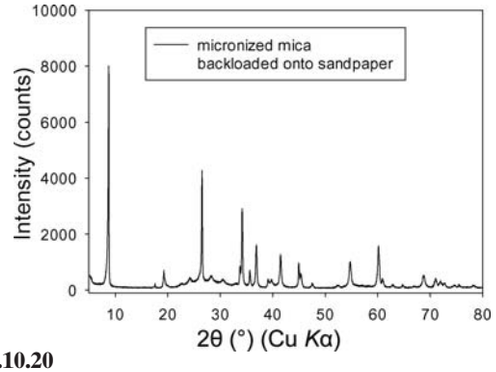

Figure 2.10.20
Diffraction pattern of micronized phlogopite mica when back-loaded onto 400-grit carborundum paper.

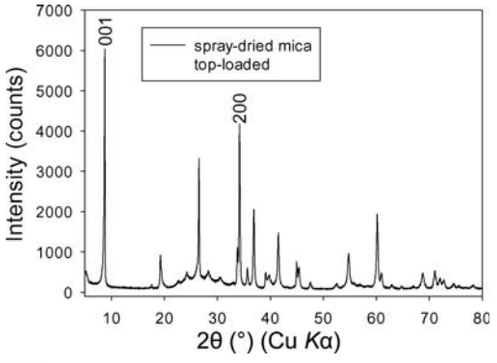

Figure 2.10.21
Diffraction pattern of top-loaded spray-dried phlogopite mica. The sample was not pressed; instead, a flat surface was produced by lightly scraping off excess material with a microspatula.

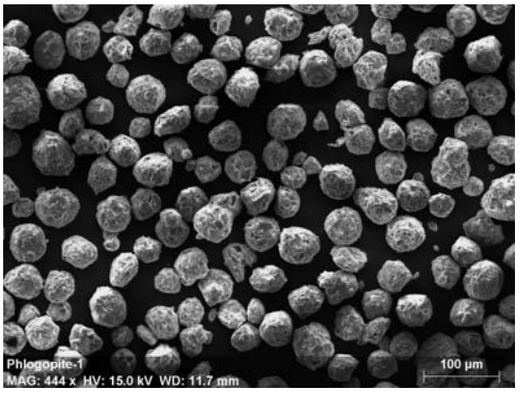

Figure 2.10.22
SEM micrograph of spray-dried micronized phlogopite mica (courtesy of M. Raudsepp, University of British Columbia).

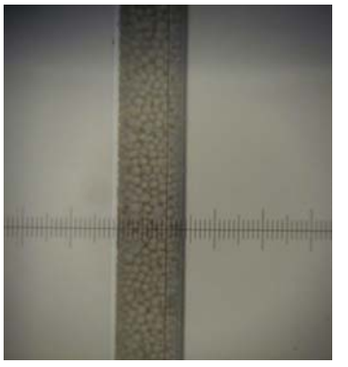

Figure 2.10.23
View through the alignment scope of the spherical spray-dried mica inside a 0.5 mm capillary.

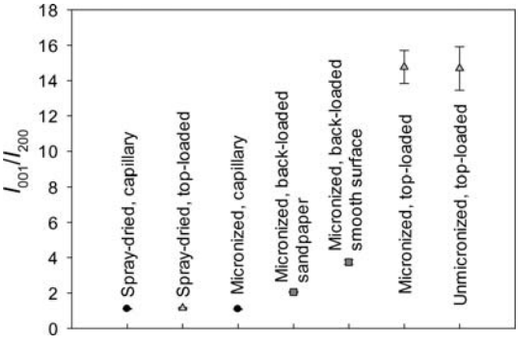

Figure 2.10.24
Plot of the ratio of the integrated intensities of the 001/200 reflections of the mica using different sample-preparation techniques.

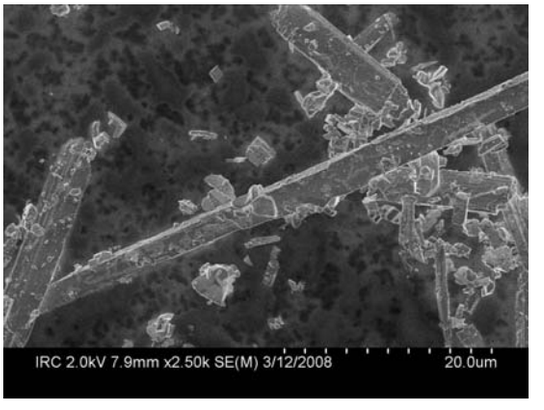

Figure 2.10.25
SEM micrograph of wollastonite needles.

Without resorting to transmission measurements, preferred orientation from platy samples may be almost, if not completely, eliminated by spray drying micronized samples (Hillier, 1999, 2002; see Fig. 2.10.21). This process produces spherical agglomerates (Fig. 2.10.22) that have no tendency to orient if handled gently. The disadvantage is that a relatively large amount of sample is often required because of inefficient sample recovery. Equipment optimized to reduce sample loss for spray-dried XRD samples may be bought in kit form (http://www.claysandminerals.com/spraydrykit), or constructed in house using a small air-brush and heated oven.

One potential practical problem when using spray-dried material with $\theta-2\theta$ geometry instruments is that the spherical particles can start to roll out of the specimen holder at higher 2θ angles (Raudsepp, 2012). The effectiveness of spray drying can be seen as the relative intensities from the top-loaded spray-dried material are almost identical to those in data obtained from the capillary experiments. The spray-dried spheres are very delicate and pressing of the sample must be avoided where possible.

It is worth noting that the platy nature of this mica was so extreme that the micronized mica tended to orient slightly inside the capillary if too much energy was applied during the filling process (*e.g.* using ultrasonics). Arguably, a capillary measurement using a spray-dried material is the ultimate precaution against preferred orientation effects, and the excellent flow characteristics of the spheres mean that the agglomerates remain

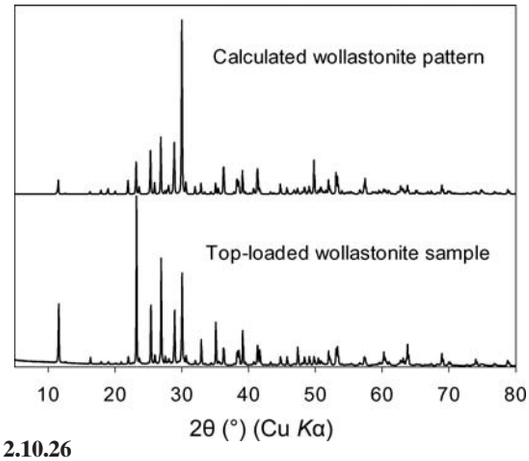

Figure 2.10.26
Effect of preferential orientation on data from top-loaded wollastonite compared with the calculated pattern from the literature wollastonite-1A structure (Ohashi, 1984).

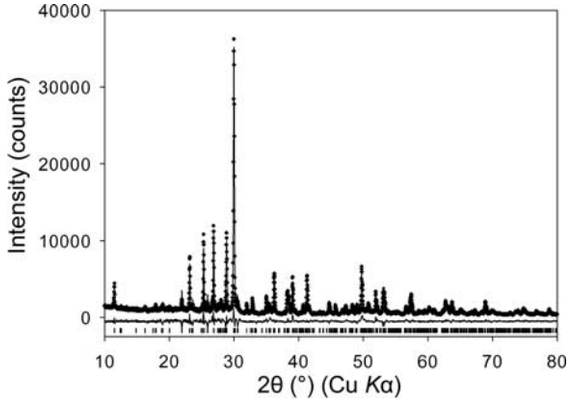

Figure 2.10.27
Rietveld refinement fit to the literature wollastonite-1A structure (Ohashi, 1984) with data from a 0.3 mm capillary with no orientation corrections.

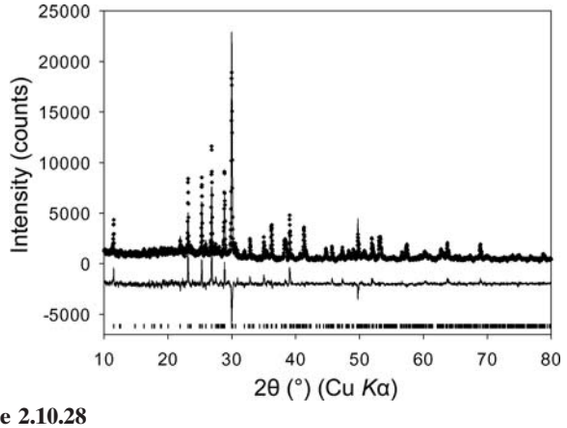

Figure 2.10.28
Rietveld refinement fit to the literature wollastonite-1A structure (Ohashi, 1984) with data from a 0.2 mm capillary with no orientation corrections.

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. 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).

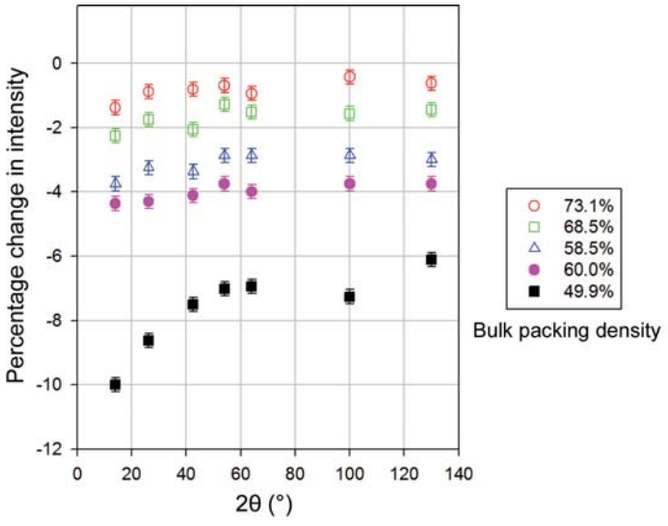

Figure 2.10.29
The effect of surface roughness on the intensity compared to that of a bulk copper specimen. Data from Suortti *et al.* (1972).

2.10.1.3. *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