Special Techniques

10.1
Introduction

10.2
Techniques to Study Deformation Fabrics

10.3
Methods to Measure Lattice-Preferred Orientation

10.4
Chemical and Isotope Analysis

10.5
Fluid Inclusion Studies

10.6
Image Analysis

This book is mostly concerned with the study of microstructures in normal thin sections under the petrographic microscope. This is a fast, cheap method which gives a lot of information on rock deformation, but other techniques are also available for the study of small scale structures. In this chapter we give a short outline of all these techniques, some of which are relatively new. The aim is not to give a full introduction to each technique, or to allow the reader to use these techniques independently. Rather, we wish to introduce alternative techniques up to a level where the reader will be able to decide if a particular technique is useful and applicable to his specific type of samples and scientific problem. A choice of literature is provided for further reading on each subject. Information is also given on methods of sample preparation. Since this book deals with microstructures, we restrict ourselves to analytical laboratory techniques that use minerals in their original arrangement in the rock, similar to that in a thin section, excluding techniques that use powdered or dissolved rocks or minerals for analysis. The chapter treats the following themes; cathodoluminescence, Raman spectroscopy, SEM, TEM, X-ray tomography, U-stage, goniometers, electron microprobe, proton microprobe, mass spectrometry, in situ age dating techniques and fluid inclusion studies.

10.1

10.1 Introduction

The study of microstructures in thin section can give a lot of information for thematic and tectonic studies but has its limitations. In many cases, additional information has to be gathered by other techniques. In this chapter we wish to give the reader an outline of some other analytical laboratory techniques that use minerals in their original arrangement in the rock, similar to that in a thin section, excluding techniques that use powdered or dissolved rocks or minerals for analysis. Analysis may concern the fabric, the arrangement of minerals in the rock, the mineral chemistry and isotope composition, fluid inclusions, age of minerals and parts of minerals and lattice preferred orientation. We only discuss methods that study minerals in their original arrangement in the rock. We indicate what problems can be studied by these techniques, which type of materials can be studied and what type of sample is needed, and, finally, what the limitations of the different techniques are. The aim is to allow the reader to assess whether other techniques can help him to solve his problem and, if so, what material has to be prepared.

Finally a warning: it is not difficult to obtain data using unfamiliar techniques, but it is difficult to interpret the reliability of such data in any specific geological setting.

10.2 Techniques to Study Deformation Fabrics

10.2.1 Cathodoluminescence

Many minerals show luminescence when being excited with a beam of electrons. The impact of a primary electron beam on a sample causes processes like backscattering of electrons, energy transfer to the lattice resulting in local heating, and the generation of X-rays and secondary electrons. The latter are low enough in energy to transfer electrons of lattice ions to an excited energetic state. The return of ions from the excited to the basic state may cause a portion of the initial energy to be emitted as light photons in the visible range of the electromagnetic spectrum (Figs. 5.1b, 10.1, 10.9a). Because electron beams are commonly produced in cathodes, this type of electron beam-induced luminescence is referred to as *cathodoluminescence* (CL). One characteristic of CL is that the excited location and the location from which the CL is emitted may be several micrometres apart. As a result, CL images commonly have a somewhat blurred or "out-of-focus" appearance when compared with backscattered electron images (Sect. 10.2.4.3).

The CL signal emitted by an excited mineral is mostly complex in nature. The emission can be related to the mineral structure itself and this type of CL is mostly in the ultraviolet part of the spectrum. However, CL of many rock-forming minerals is mainly controlled by the presence of

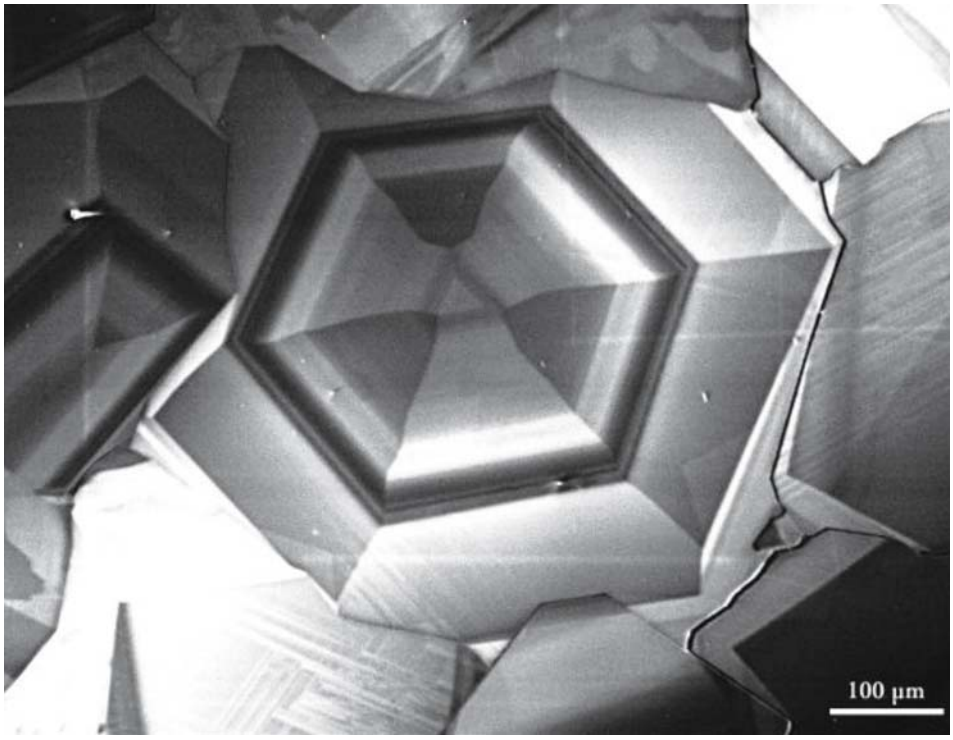


Fig. 10.1.
Example of a SEM-cathodoluminescence image showing both sector and concentric zoning in hydrothermal vein quartz, possibly due to Al variation. The sample has been polished flat and is viewed looking down the (0001) axis. The sector zoning appears related to the positive and negative rhomb orientations and may therefore have potential for indicating dauphiné twinning. Note that the true trigonal symmetry at the very centre has been replaced by a pseudo-hexagonal symmetry throughout much of the grain. (Courtesy E. Condliffe, Leeds University)

point defects. These may include ions of *3d* elements (transition group metals, such as Mn^{2+}, Cr^{3+} and Fe^{3+}), ions of *4f* elements (rare earth elements, such as Dy^{3+}), other ions [e.g., $(S_2)^-$ in sodalite and haüyne] and vacancies and related defect centres in the crystal lattice (Richter and Zinkernagel 1981; ten Have and Heynen 1985; Solomon 1989; Barbin and Schvoerer 1997; Götze 2000; Pagel et al. 2000; Nasdala et al. 2004a).

A large number of mineral species has been studied using CL, including carbonate minerals (Spötl 1991; El Ali et al. 1993; Yang et al. 1995; Habermann et al. 1996, 1998; Barbin and Schvoerer 1997; Gillhaus et al. 2000), diamond (Smirnova et al. 1999; Mineeva et al. 2000; Davies et al. 2003), zircon (Ohnenstetter et al. 1991; Cesbron et al. 1993; Hanchar and Miller 1993; Hanchar and Rudnick 1995; Nasdala et al. 2003), monazite (Seydoux-Guillaume et al. 2002), apatite (Barbarand and Pagel 2001; Kempe and Götze 2002), quartz and silica (Fig. 10.1; Matter and Ramseyer 1985; Shimamoto et al. 1991; Gorton et al. 1996; Götze et al. 2001), feldspar group minerals (Mora and Ramseyer 1992; Mariano and Roeder 1989; Finch and Klein 1999), and clay minerals (Götze et al. 2002). Cathodoluminescence is a well-established technique in sedimentology to study mineral growth processes and provenance of sediments (Marshall 1988; Augustson and Bahlburg 2003) but is also useful in microtectonic studies. The intensity distribution pattern and colour of CL may be independent of optically visible microstructures and can reveal mineral growth from solutions, e.g. in microcracks (Narahara and Wiltschko 1986; Laubach et al. 2004), in veins and along grain boundaries and details of the microstructure of cataclasites (Stel 1981; Blenkinsop and Rutter 1986). In veins, CL can reveal growth surfaces that are invisible in ordinary light (Dietrich and Grant 1985; Urai et al. 1991). Fracture patterns can be easily distinguished (Kanaori 1986). Overgrowth structures along grain boundaries, which are invisible in normal transmitted light, can be used for strain analysis (Onasch and Davis 1988). Dislocation networks can be made visible in some cases (Grant and White 1978).

Cathodoluminescence analysis can be carried out using either "hot cathode" or "cold cathode" systems attached to an optical microscope (then called OM-CL) and in a SEM or electron microprobe (called SEM-CL; (Fig. 10.9a, Photo 10.9; Yacobi and Holt 1990; Shimamoto et al. 1991; Lloyd 1994; Götze 2000; Nasdala et al. 2003). In both cases ordinary polished sections covered with a thin conductive layer (carbon or gold) are used. The CL technique involves the analysis of spectra or the generation of images. Cathodoluminescence spectroscopy provides information about the spectral composition of the emitted light, which is needed for the sound interpretation of causal CL-active defects etc. Cathodoluminescence imaging, in contrast, is predominantly used to reveal internal structures of minerals, for which it may not be absolutely necessary to know the causes for local variations of the CL. A combination of both types of analysis is monochromatic CL imaging. Here, distribution patterns are obtained separately for certain wavelengths. Most studies apply panchromatic (or integral) imaging, which uses the entire detected CL signal independent of its wavelength composition. One advantage of OM-CL imaging is that colour variations within minerals are easily observed, which provides a rough indication of the wavelength. A combination of trace element analysis and CL spectroscopy promises to become a powerful tool for mapping of trace element distribution in microstructures (Yang et al. 1995; Barbin and Schvoerer 1997).

10.2.2 Raman Spectroscopy

Raman spectroscopy is based on the interaction of the (vibrating) electric field vector of light with vibrations in the sample (molecule, crystal lattice). Light can be absorbed by a sample upon the excitation of a vibration, provided that its photon energy corresponds to the phonon quantum energy of an allowed vibration in the sample (vibrational quanta are called phonons). This is the case for light in the infrared range, and such absorption is used in infrared absorption analysis. In contrast, the phonon energy of visible light is too high to be transferred to the sample through the excitation of a vibration. However, it is possible that a small fraction of the photon energy of visible light is taken to excite the sample to vibrate. After such interaction, a scattered light photon will be lowered in energy and shifted in wavelength towards the red end of the electromagnetic spectrum, a process known as *Stokes-type Raman scattering*. Alternatively, it is possible that the vibrational state of the sample be lowered in which case the scattered light has gained energy and is blue-shifted. This is called *anti-Stokes Raman scattering*. In the case of *Rayleigh scattering* no energy shift of the light results. Raman analyses are mostly done in the Stokes region because of the higher intensity of Stokes-type Raman scattering compared with anti-Stokes scattering.

Raman scattering is a weak effect. Only a small fraction of the incident light interacts with vibrations in the sample as described above. The Raman shift is measured as the wave number difference between incident and scattered light. The wave number is defined as the reciprocal wavelength and is given in cm^{-1} (McMillan and Hofmeister 1988; Marfunin 1995; Smith and Carabatos-Nédelec 2001; Loudon 2001; Nasdala et al. 2004b).

Raman spectroscopy is nowadays generally done with a laser beam, which is directed at a sample using high-resolution objective lenses. Powerful Raman microprobe systems have a depth resolution as good as 2 μm when the beam is focused at the sample surface and a real lateral resolution of 1–1.5 μm, which may result in a real volume resolution better than 5 μm^3 (Markwort et al. 1995). The scattered light is analysed in a spectrometer. Apart from the analysis of single spectra, Raman is also

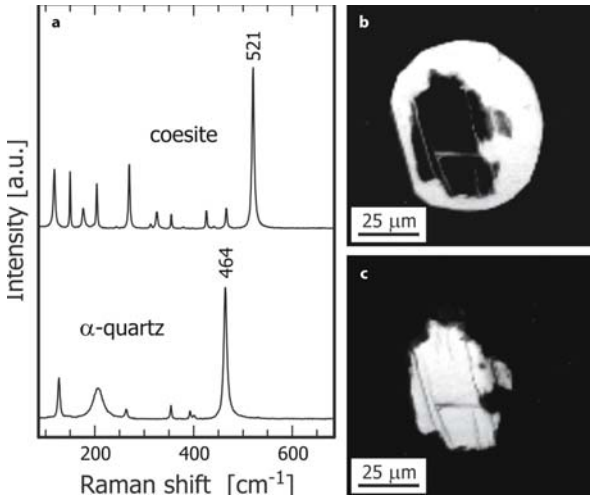


Fig. 10.2. Raman mapping applied to reveal the distribution of SiO_2 polymorphs within an inclusion in garnet. **a** Raman spectra of coesite and alpha quartz. **b** Distribution pattern obtained for the 464 cm^{-1} Raman band, showing the distribution of alpha quartz in white. **c** Analogous distribution pattern of the intensity of the 521 cm^{-1} coesite Raman band. The two images show that the central part of inclusion still consists of coesite whereas transformation to alpha quartz has started at the outer rim and at cracks. Ultrahigh-pressure gneiss from the Seidenbach reservoir, Saxonian Erzgebirge, Germany (Massonne 2001). (Photograph and diagram courtesy Lutz Nasdala and Hans-Joachim Massonne)

used to generate images of the internal structure of samples, using global illumination imaging and point-by-point mapping techniques (Lehnert 2000; Nasdala 2002).

Raman signals, usually referred to as "bands", reflect vibrations in the sample. These vibrations, in turn, are controlled by the size, valence and mass of atomic species in the sample, the bond forces between them, and their geometrical arrangement in the crystal lattice. As a consequence, each molecule and crystal structure is characterised by its own particular pattern of Raman bands. Spectral parameters of Raman bands, their variations (for instance, shifts, broadening, and relative intensity changes of bands) and other spectral peculiarities (for instance, band splitting and the observation of additional bands) may be used to identify a sample and characterise its structure. Particularly useful is the possibility to recognise polymorphs with identical chemical composition, for example quartz and coesite (Fig. 10.2). The main advantage of the technique is the possibility to analyse small samples non-destructively and without the need for sample preparation. Nearly all important minerals have been studied, and many institutions worldwide build-up reference databases. Apart from the analysis of solid minerals, Raman spectroscopy has a long history in the study of fluid inclusions (van den Kerkhof and Olsen 1990; Beny et al. 1982; Dubessy et al. 1989, 2001; Boiron et al. 1999; Giuliani et al. 2003). For a review see Nasdala et al. (2001, 2004b).

10.2.3 Electron Microscopy – Introduction

At magnifications exceeding 1 000 ×, objects seen by the optical microscope become fuzzy. This is a direct consequence of the use of light as a medium to transport information; the wavelength of visible light varies from 400 to 750 nm and no objects smaller than 100 nm can be observed. Depending on their velocity, electrons have much smaller wavelengths and can therefore be used to carry information about smaller objects. Two types of electron microscope are commonly used in geology; the scanning electron microscope (SEM), and the transmission electron microscope (TEM).

10.2.4 Scanning Electron Microscopy (SEM)

10.2.4.1 Introduction

Although this book deals with the interpretation of structures visible with the optical microscope, the scanning electron microscope (SEM) is now an important tool in the study of microstructures. Its accessibility in many laboratories and relatively easy use makes the SEM a powerful tool to complement and sometimes replace the optical microscope. In the SEM, a sample is placed in a specimen chamber under vacuum, and investigated by scanning a beam of electrons across the sample (Fig. 10.3). Only the surfaces of samples can be studied. The electrons are either scattered back from the surface of the sample (Lloyd 1987) or cause the sample to emit secondary electrons. Both types of electron signal are collected by detectors. The electrons that strike the detectors are used to build up an image of the sample on a monitor (Fig. 10.3). This technique allows magnifications significantly greater than those achieved via optical microscopy, depending on electron emission signal (e.g. >100 000 × for secondary electrons, or 100 times more than the optical microscope). This is an obvious advantage, but a disadvantage is that SEM images are always in grey tones. The recognition of minerals by their interference colour, as in the optical microscope, is therefore not possible. However, recognition of minerals with the SEM is usually not problematic. The amount of electrons that are emitted or back scattered in a volume of material struck by the electron beam is directly proportional to the atomic number (Z) of the constituent elements in the minerals, with heavier elements yielding more electrons. It is therefore possible to identify individual minerals in a sample by their grey tone on the screen (atomic number or Z contrast). For example, in most cases the following sequence can be observed

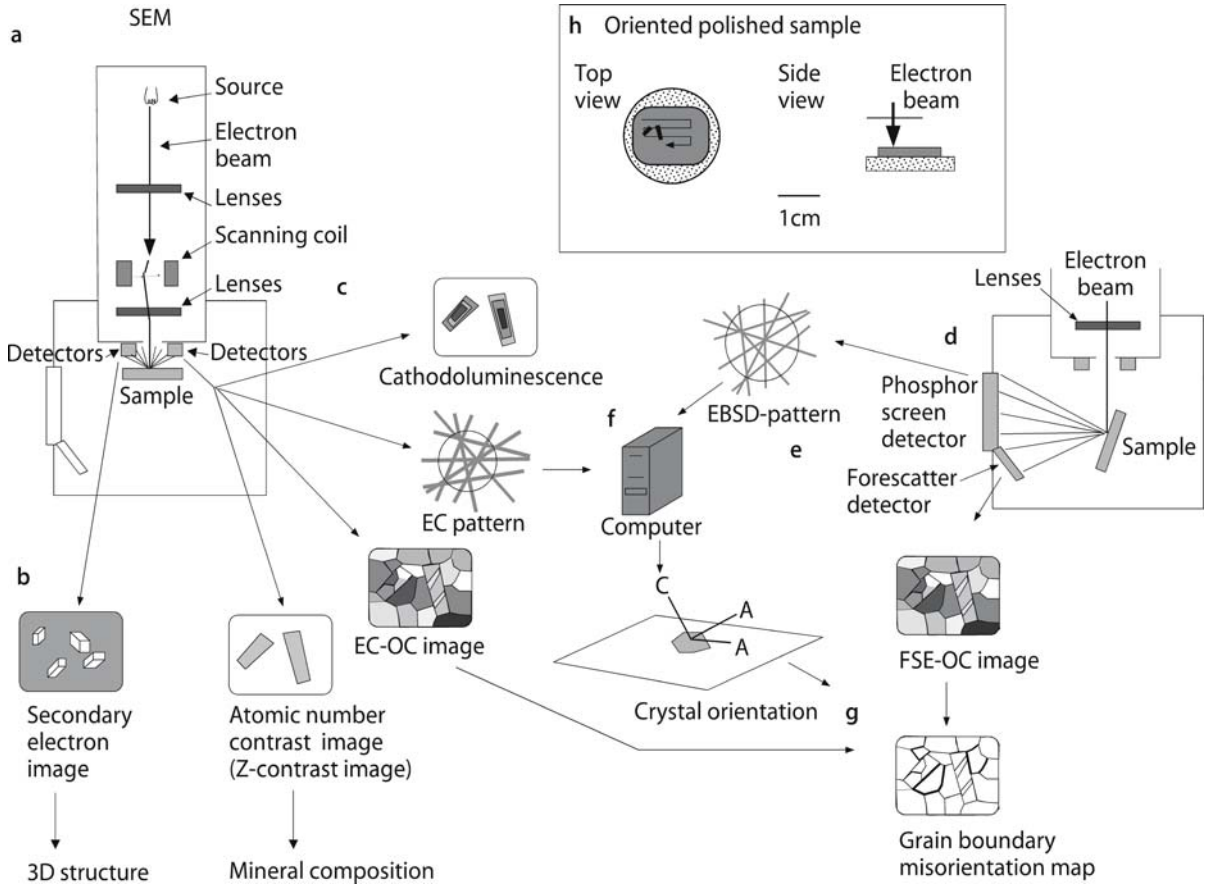


Fig. 10.3. Schematic presentation of a modern SEM with modes of operation. **a** Simplified cross-section through the SEM showing the operation of detectors in the top of the specimen chamber and a horizontal specimen close to the detectors to monitor secondary and backscattered electrons. Results are **b** secondary electron images and **c** cathodoluminescence-, atomic number contrast- and orientation contrast (OC) images produced by backscattered electrons. OC images produced from a horizontal sample high in the specimen chamber as shown in **a** are known as electron channelling orientation contrast (EC-OC) images. Electron channelling (EC) diffraction patterns can also be obtained. **d** operation of phosphor screen- and forescatter detectors at the side of the specimen chamber. For the use of these detectors, the sample is deeper in the specimen chamber and highly tilted. These detectors can be used to monitor **e** forescatter detector orientation contrast (FSE-OC) images and electron backscatter diffraction (EBSD) patterns. **f** Computer programmes can be used to index EBSD or EC patterns in order to obtain crystal orientations. **g** These in turn, combined with FSE-OC images, can be used to make grain boundary misorientation maps. **h** Typical oriented polished SEM sample and scanning motion of the electron beam over the sample

from dark to light; serpentine – quartz – feldspar – biotite – rutile – ilmenite – zircon. A more detailed list is given in Hall and Lloyd (1981).

Most SEMs have linked energy dispersive X-ray analysis (*EDAX*) facilities available (Goldstein et al. 1992). This tool measures the energy of X-rays emitted by the irradiated sample, and can identify the elements that occur in the sample. With this tool, minerals cannot only be easily identified, but their chemical compositions can be determined, either qualitatively or fully quantitatively. If a few grains in a sample have been analysed by EDAX, the rest can be recognised by their respective grey tones. Notice that EDAX cannot be used to analyse grains smaller than 5 μm as the X-rays are produced in a pear-shaped volume in the sample where the electron beam hits the surface. The diameter of this volume is much larger than the diameter of the electron beam.

10.2.4.2 Secondary Electron Mode

In secondary electron emission mode (Figs. 5.35, 10.4, 10.5), electrons, which are detached from the sample, are caught by a detector and used to build up a picture. This mode is useful to study topography in samples, and can also be used to get some information on the composition of minerals using grey-tones. This method has been much used to study fossils, the 3D geometry of small crystals, fluid inclusions, stylolite surfaces and other structures where 3D information is essential.

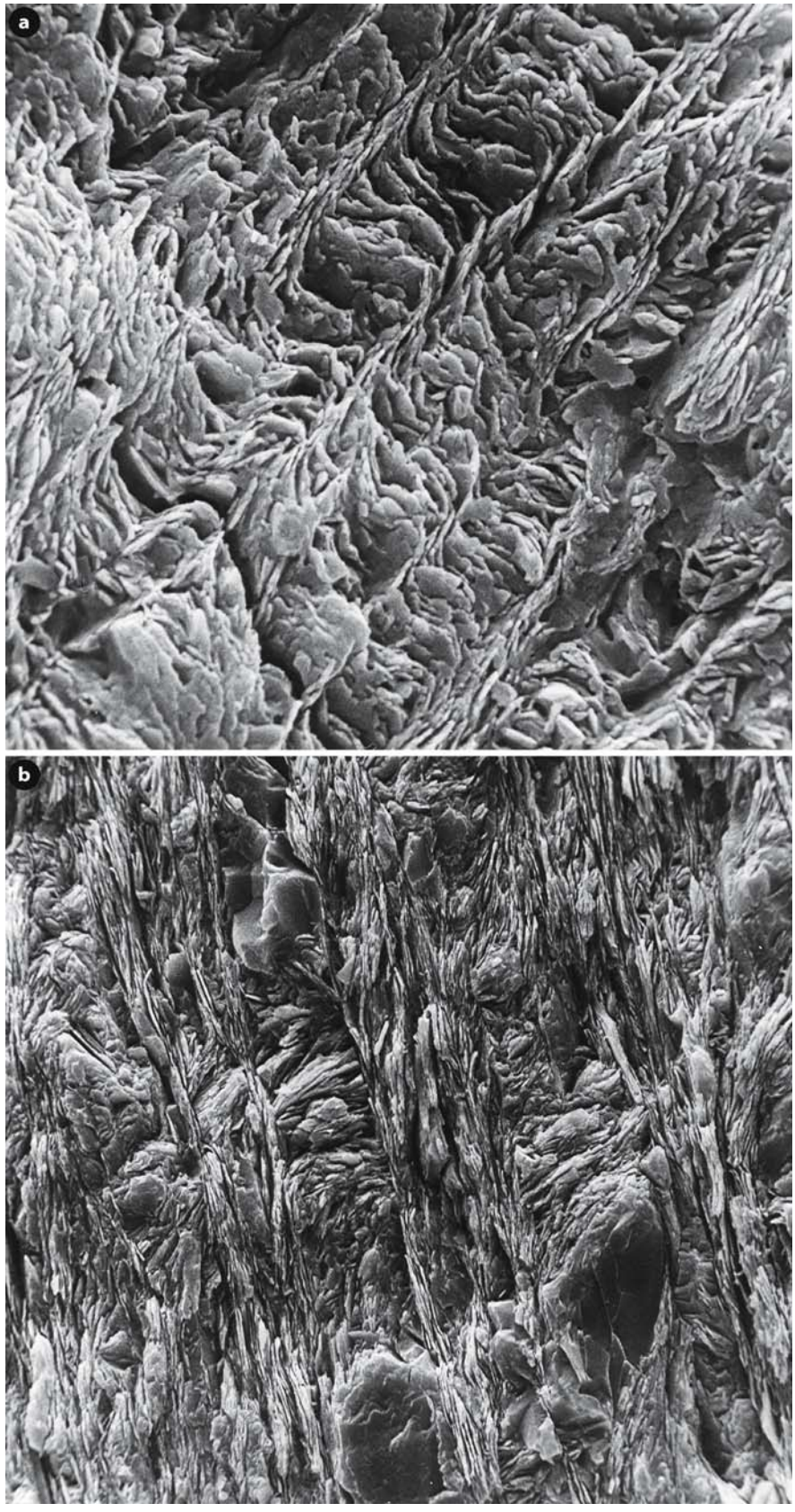


Fig. 10.4a,b.
Secondary electron images of a series of fracture surfaces (see text) of a slate sample observed by SEM. Details of the structure can be seen, but grey tones cannot be used to distinguish mineral composition because of the rough surface. **a** Bedding parallel foliation is folded and fold limbs define a first slaty cleavage S_1. **b** Spaced slaty cleavage S_1. Microlithons contain micas that are truncated against micas in the cleavage lamellae. This slaty cleavage formed at slightly higher metamorphic grade than **a**. Massive grains in microlithons probably consist of quartz. Rheinisches Schiefergebirge, Germany. Width of view **a** 20 μm; **b** 95 μm. (Photographs courtesy K. Weber 1981)



Fig. 10.4c.
Secondary electron image of a fracture surface (see text) of a slate sample observed by SEM. S_2 crenulation cleavage in slate overprinting an S_1 slaty cleavage. Rheinisches Schiefergebirge, Germany. Width of view 95 µm. (Photograph courtesy K. Weber 1976)

10.2.4.3 Backscatter Electron Mode

Backscatter electron mode (BSE) uses electrons from the primary beam, which penetrate the sample and are reflected back from crystals at the surface. The characteristics of the backscattered electrons depend on both the elements and crystal structure of the minerals in the sample. Backscattered electrons therefore carry information on the composition of the sample and crystal orientation (Randle 1992; Dingley and Field 1997; Prior et al. 1999; Wheeler et al. 2003; Trimby et al. 2000). The backscatter electron mode of SEM operation is most useful if fine details of mineral composition, texture or LPO are the subject of study (Humphreys et al. 1999; Lloyd et al. 1997). However, SEM backscatter electron mode operation requires a number of different electron detectors and configurations depending on the specific backscatter electron signal. These are (Fig. 10.3):

1. *Atomic number* or *Z contrast*, where different grey tones represent different mean atomic weights of elements in the mineral phases (Figs. 10.5, 10.6). In general, the mineral will appear darker when lighter elements are present. In this mode, only parts of the sample with different composition will show different grey tones.
2. *Orientation contrast* (OC). Here, parts of a mineral with different crystal orientation will show different grey tones (Fig. 10.7). Unfortunately, the intensity of the grey tone is not dependent on degree of misorientation, which means that subgrains and grains will show the same aspect. Nevertheless, OC patterns show a lot more detail than optical microscope images of the same domain. OC images can be obtained in two ways. *Electron channelling orientation contrast* (EC-OC) (Fig. 10.9b, Photo 10.9) involves horizontal (i.e. beam normal) samples positioned very close to the objective lens and backscatter electron detector such that the incident electron beam maintains a large angle during the scanning process that satisfies the Bragg conditions for diffraction. *'Forescattered' electron* OC images (FSE-OC; Fig. 10.7) involve highly tilted (typically 60–75°) samples relative to the incident electron beam and only electrons that are reflected or scattered forward are caught on a fluorescent screen and a forescatter detector (Fig. 10.3; Prior et al. 1996, 1999; Fliervoet et al. 1997). In this configuration, the angle of incidence of the electron beam and the tilted sample also satisfy the conditions for diffraction.
3. *Electron diffraction patterns*. These patterns appear as patterns of crosscutting lines (Fig. 10.8). They are in fact parts of very flat cones of diffracted electrons,

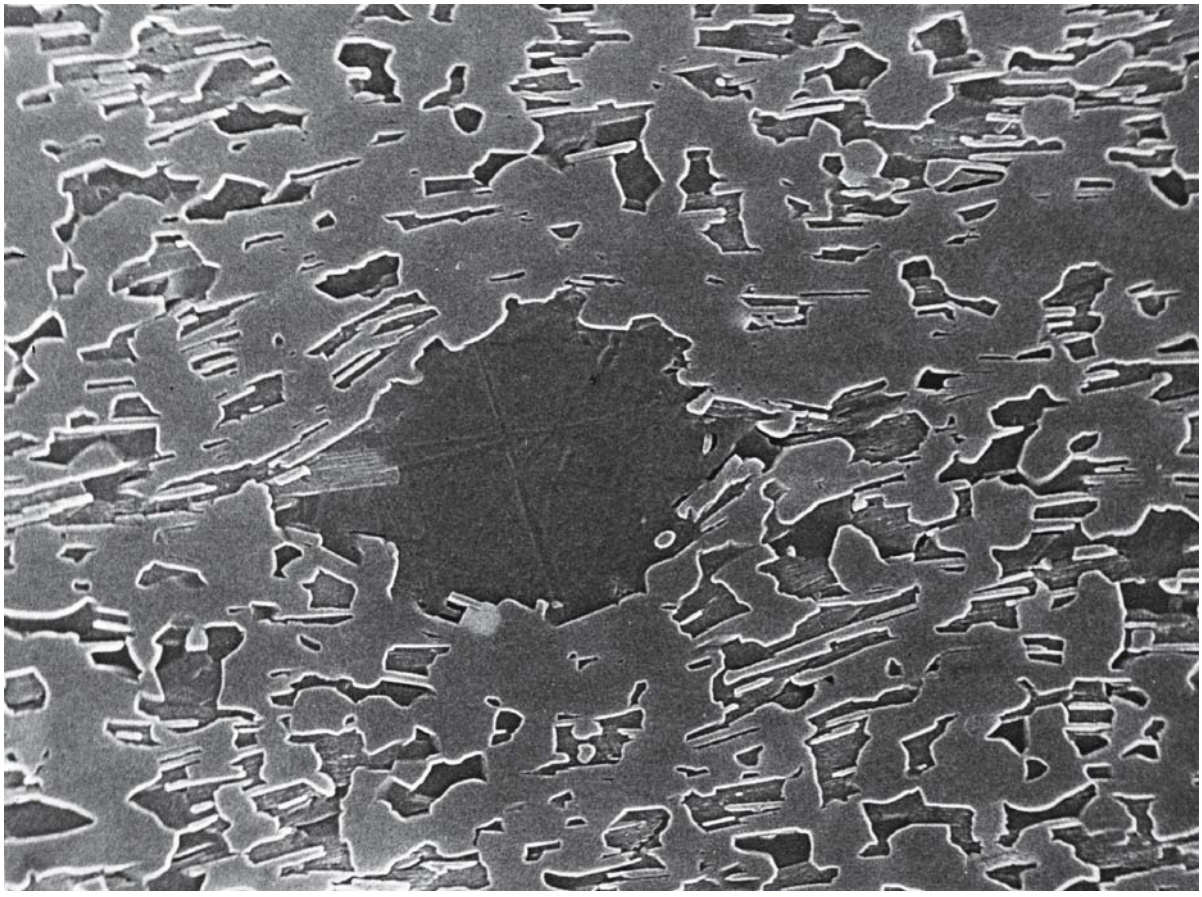


Fig. 10.5. Polished sample of ultramylonite, etched with HF vapour. Secondary electron mode. Gold cover. Fine detail is visible through the presence of *etch pits* and different *grey-tones* for the three minerals present. Quartz has not been etched much and forms the matrix (*light grey*). Feldspar and biotite have been etched. Feldspar is *dark grey* and forms the central porphyroclast. The etched *medium grey* elongate grains with cleavage are biotite. Biotite seems to replace feldspar at the left-hand side of the porphyroclast. St. Barthélemy Massif, Pyrenees, France. Width of view 40 μm

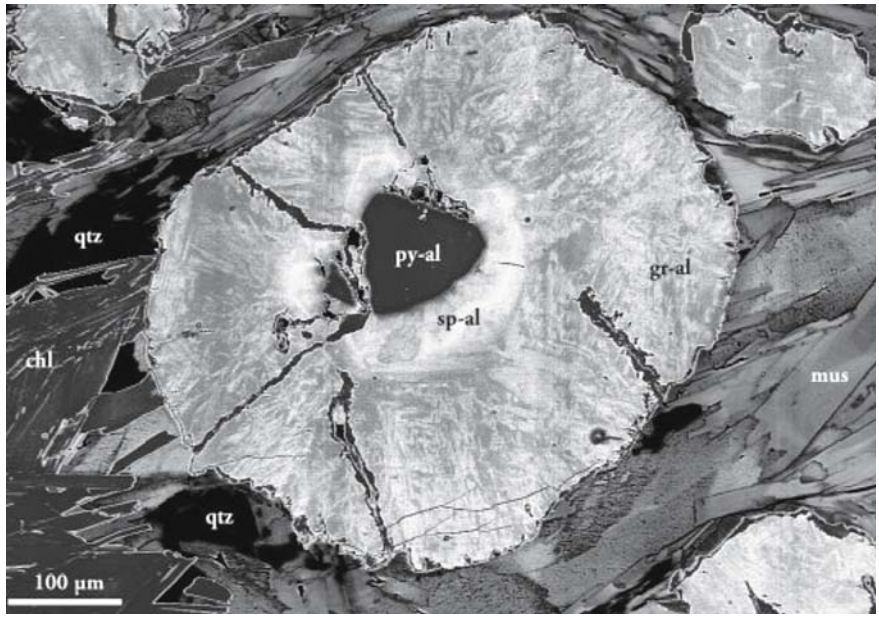


Fig. 10.6.
Atomic number or Z contrast images are based on the relationship between backscattered electron emission characteristics and sample composition (e.g. Lloyd 1987). The example shows a typical Z contrast image obtained from low-grade metasediments of the Clew Bay Complex, S. Achill Island, Mayo, Ireland (Yardley et al. 1996). Polyphase garnets have a detrital pyrope-almandine (*py-al*) core surrounded by spessartine-almandine (*sp-al*) and then grossular-almandine (*gr-al*), which is unmixing to a grossular-rich and an almandine-rich component. They sit in a matrix of quartz (*qtz*), chlorite (*chl*) and white mica (*mus*), with the latter zoned for Mg+Fe as revealed by the image contrast variations (Fe-rich compositions appear brighter). (Photograph courtesy Eric Condliffe and Geoffrey Lloyd)

which scatter at a small angle from lattice planes in a crystal. Such a diffraction pattern carries all information necessary to determine the exact orientation of a crystal with an error of less than 1°, provided the type and composition of the mineral is known (Krieger-Lassen 1996; Prior 1999). In order to find the crystal orientation from the pattern, the lines in the pattern must be *indexed*, i.e. the corresponding lattice planes should be identified. There are two different methods to obtain electron diffraction patterns:

3a. with the sample in the position for EC-OC (i.e. horizontal), diffraction patterns can be obtained if the incident electron beam is focused on a fixed position on the sample and rocked back- and forward (Figs. 10.3, 10.8a). The diffraction patterns produced in this way are known as electron channelling (EC) patterns and have a spatial resolution of >1–10 μm but an angular resolution of <1°. The angular spread of EC patterns is typically <20°, which makes identification relatively difficult (Fig. 10.8a).

3b. with the sample in the position for FSE-OC (i.e. highly inclined), diffraction patterns can be obtained simply by focusing the incident electron beam on a fixed position on the sample. The diffraction patterns produced in this way are known as electron backscattered diffraction (EBSD) patterns and have a spatial resolution of 0.1–1.5 μm with an angular resolution of ~1°. The angular spread of EBSD patterns is typically >50°, which makes identification relatively easy (Fig. 10.8b).

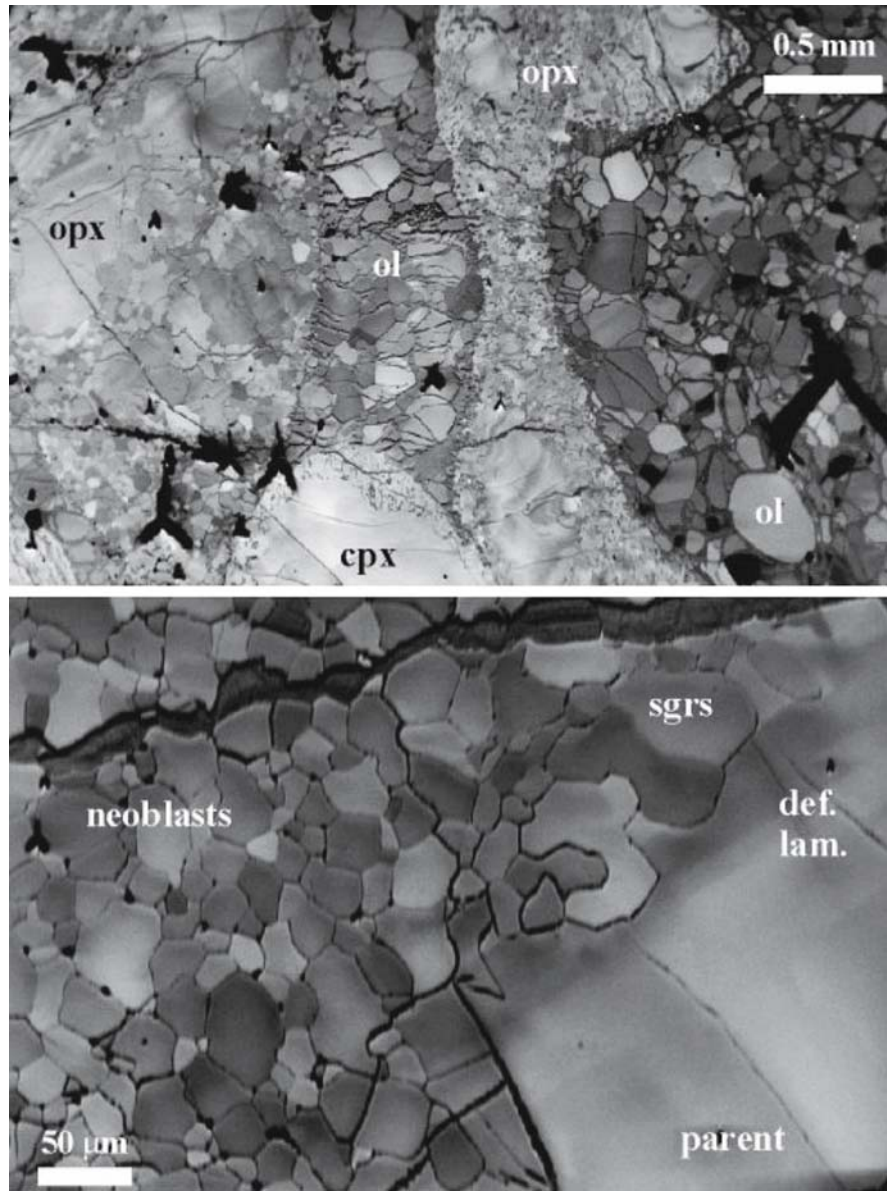
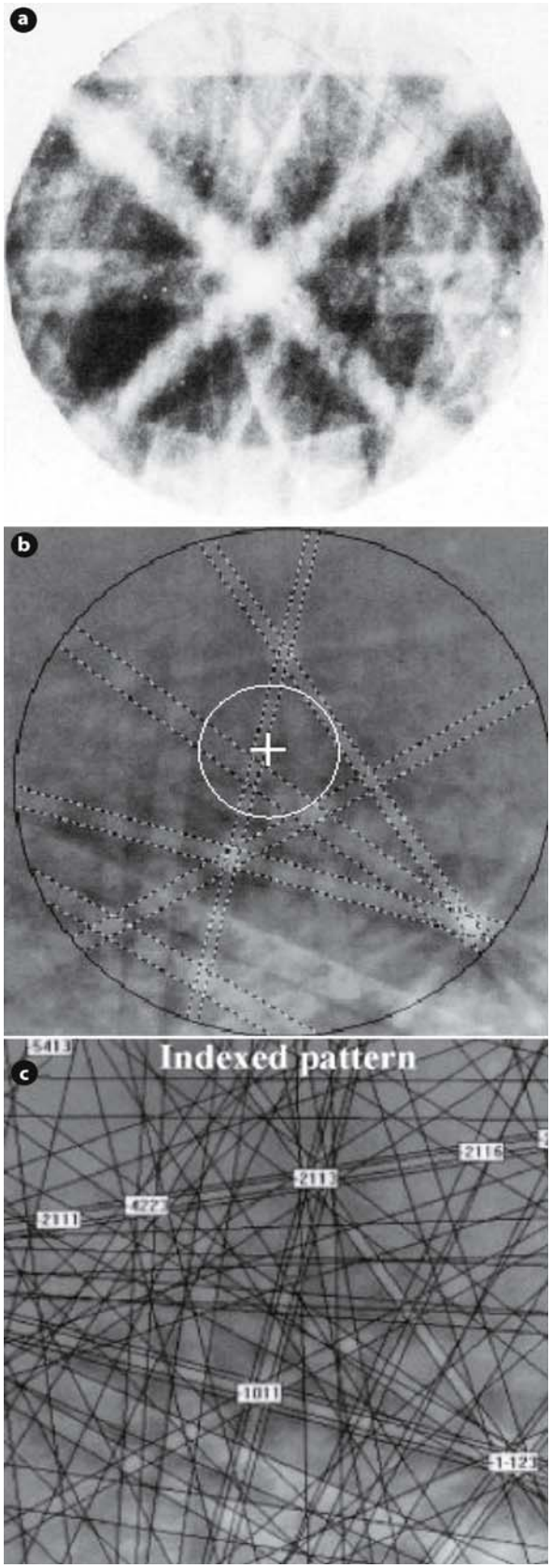


Fig. 10.7.
Examples of 'forescattered' electron orientation contrast (FSE-OC) images from an uncoated lherzolite mantle nodule, Lhesoto, South Africa. *Top*, olivine (*ol*), orthopyroxene (*opx*) and clinopyroxene (*cpx*) crystallographic microstructure in lherzolite. *Bottom*, detail of dynamic recrystallisation in orthopyroxene achieved by the progressive development of deformation lamellae (*def. lam.*), subgrains (*sgrs*) and new grains. (Photographs courtesy Geoffrey Lloyd)



EBSD is a very powerful method to investigate microstructure in rocks, and presently more popular than EC patterns since resolution is higher and patterns are easier to determine (Photo 10.3a–e). The interpretation of the diffraction patterns through indexing of lines in the diffraction patterns is now highly automatised and can be carried out by a number of computer programs (Fig. 10.8c, Photo 10.3d,e).

Combinations of atomic number contrast, OC and EBSD-pattern information for a sample provide a powerful tool in microtectonics. It is standard practice to make atomic number contrast and OC images of a microstructure, and then select a large number of points where EBSD patterns are determined and translated into orientation data. In this way, the complete crystallographic preferred orientation of a microstructure can be obtained quickly, and linked to a spatial image (Photo 10.3a–e). A useful way to present such data is through a *grain boundary misorientation map*, where grain boundaries are marked by the angle of misorientation separating neighbouring grains and subgrains (Trimby and Prior 1999). Attempts are being made to automatise the process completely, to make complete maps of the atomic number contrast and the orientation of the material over a fine, regular grid.

10.2.4.4 Sample Preparation

Samples used in the SEM are studied under vacuum, and should therefore be dry. This is no problem with most rock samples, but clay samples may have to be dried before use. One specific problem of the SEM is that the electron beam, which hits the specimen, tends to cause local electrostatic charging which can cause beam deflection, thereby distorting the image. It is therefore necessary that samples are conductive. This is a problem in most rock samples, which have to be coated with a thin conductive layer of a metal such as gold (secondary electron-mode images) or carbon (back-scatter electron-mode images).

Fig. 10.8. a Electron channelling (EC) pattern from quartz; the *white cross* defines the pole to a positive rhomb ($10\bar{1}1$) plane (Lloyd 1987). The diameter of the pattern covers ~20°. **b** Electron backscattered diffraction (EBSD) pattern from quartz. The pattern extends over a significantly larger angular area (~80° square in this case) than the EC pattern, indicated by a *white circle*, and is therefore much easier to index. **c** EBSD pattern indexing (e.g. quartz). A number of commercial computer-based systems are available to index EBSD patterns. They are all based on a comparison between the configuration of Bragg lines/bands in the observed pattern (**b**) with those predicted by theory (**c**) and stored in a database of crystal diffraction characteristics for each mineral phase (see Prior et al. 1999). Indexing can be either manual or automatic and can be used to define the complete crystal orientation (via three spherical Euler angles), provide mineral identification (i.e. quartz), the spatial coordinates of the pattern within the sample, a numerical indication of pattern quality (i.e. 'band contrast') and the mean angular deviation ('goodness-of-fit') between observed and predicted patterns. (Images courtesy Geoffrey Lloyd)

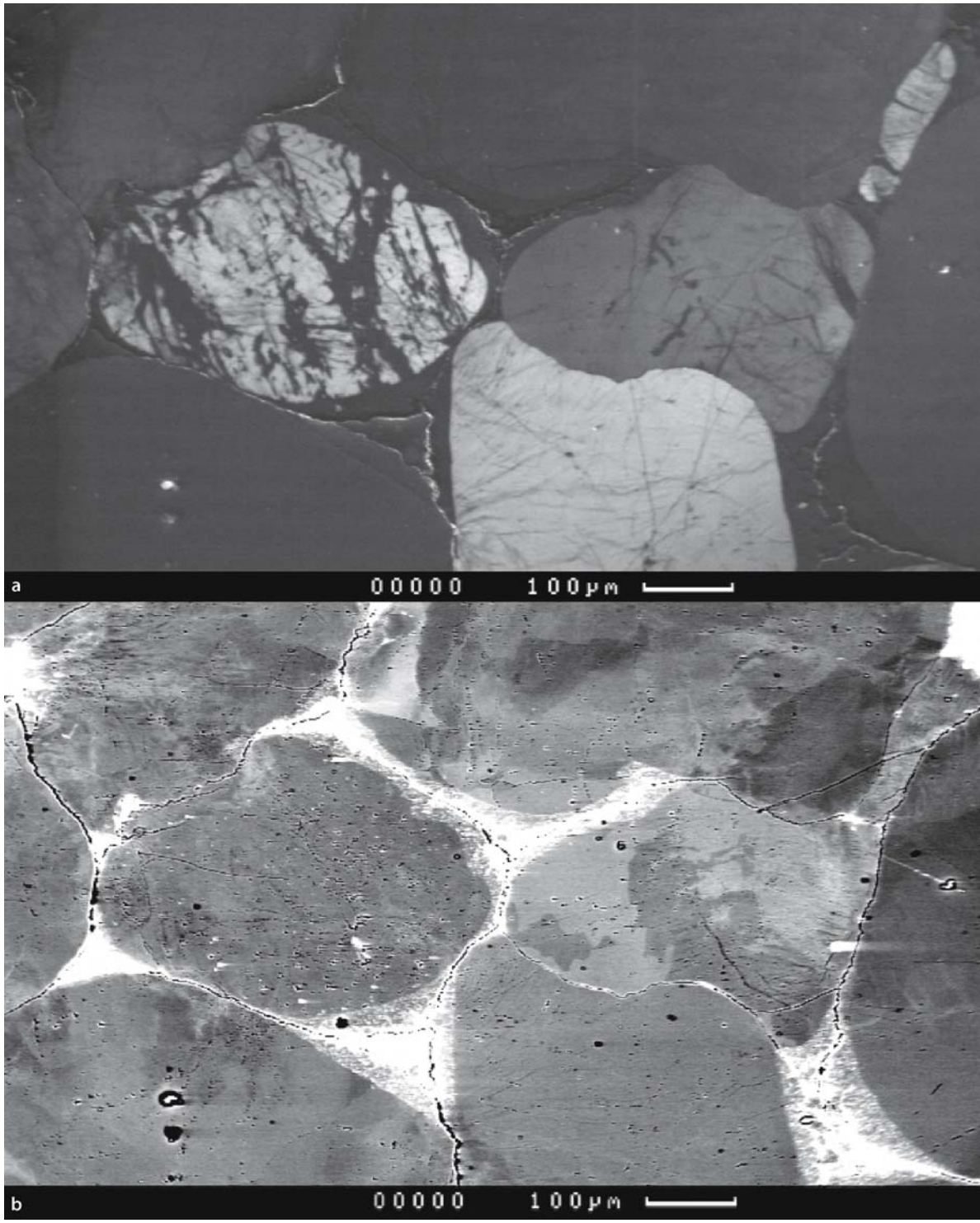


Fig. 10.9. a SEM cathodoluminescence (CL) image and **b** electron channelling orientation contrast (EC-OC) image of the same sample, where both images show different but complementary information. The images are of quartz grains in Cambrian quartzite, Assynt, NW Scotland (Lloyd 2000). The CL image clearly shows the different grains with different CL characteristics; one grain contains many microfractures healed by authigenic (*black*) quartz. The OC image shows the crystallographic related microstructures in the grains; the *light* and *dark areas* in the *right central* grain are dauphiné twin microstructures, whilst other grains show deformation lamellae and subgrains. All microstructures are due to mutual indentation of grains, a precursor to the development of cataclastic microstructures on through-going fractures. (Photographs courtesy Geoffrey Lloyd)

There are several methods to prepare samples for the SEM; as only the surface of the sample is studied, it is possible to use either polished thin sections or small chips of rock (Fig. 10.3). Small chips can be polished or broken. The advantage of a broken surface is that it is free of contaminations and usually breaks along grain boundaries; it therefore shows a lot of information on grain shape, grain size and internal structure of grains (Fig. 10.4; Weber 1981). A disadvantage is that the surface is irregular and difficult to interpret by scientists familiar with the interpretation of planar sections through a material. This problem can be overcome by using a polished thin section or polished chip of rock (Hall and Lloyd 1981); this will give familiar geometries as in thin section, which is an advantage if one wishes to compare optical and SEM microstructures. A disadvantage of this kind of sample preparation is that polished samples will only show structures if sufficient atomic number contrast or difference in orientation contrast exist between grains. Polishing also destroys the crystal lattice in a thin surface layer of the specimen, which may result in a blurred image of the grains. These problems can sometimes be solved by etching the specimen briefly in hydrofluoric acid (HF)[1]; this will remove the damaged top layer and may also etch some minerals more than others, generating a topography which outlines the fabric in the specimen (Fig. 10.5). Such a topography, however, is not wanted if backscatter electron mode is used. A more advanced technique, necessary for EBSD work, is therefore a second round of polishing using a silicone fluid, which removes the damaged top part of the sample without creating a relief (Sect. 10.3.6). The surface that is going to be studied should not be touched; this may spread grease over the sample and can decrease visible detail. Specimens are mounted on a special holder to fix it in the SEM with a special conductive glue. After surface preparation, the specimen is coated with a thin conductive layer.

10.2.4.5 SEM and Optical Microscopy

This book deals almost exclusively with optical microscopy, but it seems unavoidable that scanning electron microscopy will become an irreplacable tool alongside and partly replacing optical microscopy. This is especially the case where use of polished thin sections can provide an ideal combination of optical and SEM observations (Trimby and Prior 1999).

The SEM provides higher resolution than optical microscopy, more complete information on twin-, grain- and subgrain boundary structures and on chemistry of minerals. Moreover, it provides easy and complete texture analysis, in contrast to the incomplete and more time-consuming optical techniques. Optical microscopy, however, also has a number of advantages, which will not make it obsolete in the near future. Large-scale structures and coarse-grained rocks are difficult to study by SEM, and are better served by optical microscopy. In an optical microscope, subgrains and grains are easier to distinguish than in an OC image. The thickness of a thin section provides a certain amount of 3D information, like the presence of fluid inclusions and tilt of grain boundaries, while the SEM is a purely two-dimensional tool. Organic substances used in analogue experiments and ice, are difficult although not impossible to study by SEM.

Although the large magnifications obtainable by SEM are an obvious advantage, it also means that it can be difficult to find a specific feature in a sample that was easily recognisable under the optical microscope. Turning the SEM to low magnification usually does not help, since very little detail will be visible. Therefore, if a specific feature in a sample such as a porphyroblast or a fault is to be studied, it is advisable to mark it under a reflected light microscope with an electrically conducting marker, or to use a photograph or sketch of the sample; once the sample is in the SEM, it may be very difficult to find the object.

Despite its restrictions, optical microscopy has the advantage that preparation is fast and easy and can be carried out at low cost. SEM is more versatile, but much more expensive and complex to acquire and maintain.

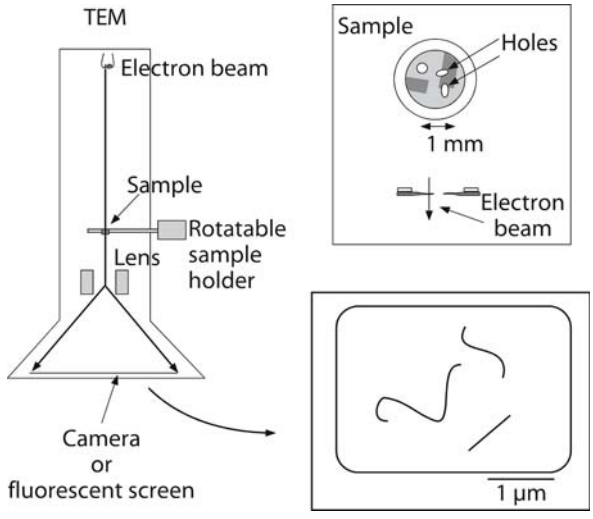


Fig. 10.10. Simplified cross-section through a TEM showing the path of the electron beam and the nature of the samples used

[1] WARNING: Take great care when etching in HF; it is usually sufficient to clean the polished surface with alcohol, then hold it several seconds over the vapour of a small reservoir of HF using a pair of tweezers; use suitable gloves and only work in a fume cupboard! HF is a very dangerous acid and should never be touched. It is useful to study the etched surface under a reflected light microscope; after a roughness becomes visible under the microscope, the sample is sufficiently etched. It is rarely necessary to submerge the specimen in the HF.

10.2.5 Transmission Electron Microscopy (TEM)

10.2.5.1 Introduction

Transmission electron microscopy (TEM) allows observation of structures as small as a few nanometres at magnifications of up to 350 000×. Dislocations, deformation lamellae, subgrain and grain boundaries and twins can be studied with the TEM, since it allows interpretation of their nature and their orientation with respect to the crystal lattice (Figs. 3.13, 3.14, 3.24, 10.11). Although TEM analysis of intracrystalline structures is very powerful, considerable experience is needed before it can be applied, and a description of TEM techniques is outside the range of this text. However, a short outline is given to allow readers to assess whether TEM work can help to solve their problems. Reviews can be found in McLaren (1991), Buseck (1992) and Champness (2001).

In a TEM a beam of high velocity electrons passes through a thin foil of sample material suspended in a high vacuum (Fig. 10.10). The electron beam is deflected by electronic lenses, which enlarge the image, and the result is focused onto a fluorescent screen, photographic plate or CCD camera. An intact crystal lattice is transparent for the electron beam, but a crystal defect such as a dislocation, either isolated or in a (sub) grain boundary is visible as a shadow on the image (Figs. 3.13, 3.14, 3.24, 10.11). A TEM has sample-holders in which a sample can be rotated in all directions (Fig. 10.10). In certain orientation and observation modes, a crystal will show diffraction patterns that can be interpreted in terms of crystal structure and orientation (Fig. 10.11, insets). Dislocations will

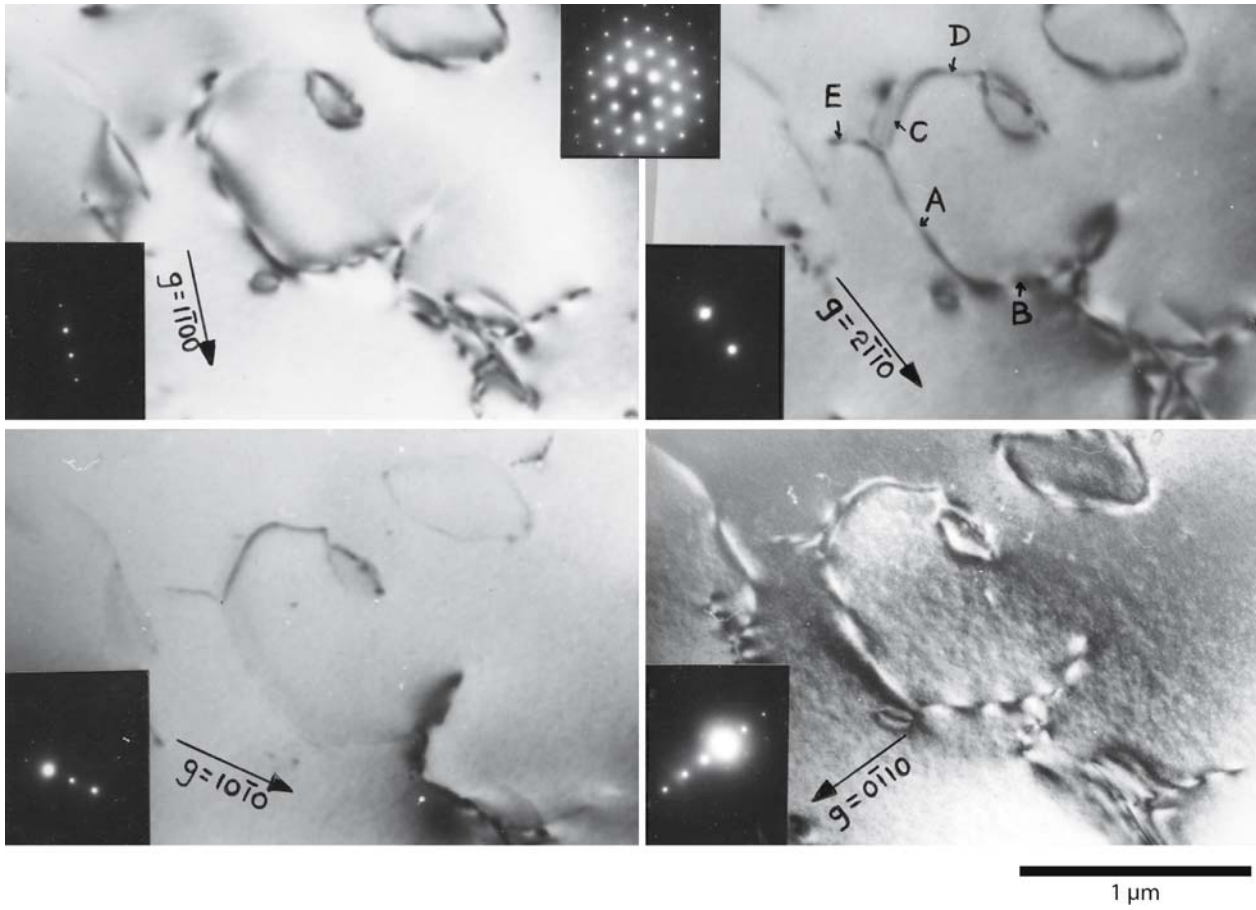


Fig. 10.11. TEM images of the same area in a quartz grain showing free dislocations. The four photographs were taken at four different orientations of the sample in the specimen holder. For each orientation, a diffraction pattern was obtained for the quartz grain under different diffraction conditions (insets). In each case, the diffraction vector is labelled as g on the photograph. The diffraction pattern at the *top centre* is the pattern taken with the [0001] direction parallel to the electron beam. The other images are taken by tilting away from this orientation so that only one set of lattice planes are diffracting. The Burgers vector of dislocation segments can be established from images where the segment produces no contrast in the image, such as at lower left for dislocation segment A–B. In this case the dislocations produce no constrast when the crystal is diffracting on {10$\bar{1}$0} planes. This means that the Burgers vectors are perpendicular to the diffraction vector (g), with $b = <1\bar{2}10>$ parallel to the <a> directions in quartz. Image of free dislocations in quartz mylonite from St. Barthélemy massif, France. (Photographs courtesy Martyn Drury)

be visible in the TEM only if their Burgers vector (Sect. 3.4) has a particular orientation with respect to the electron beam; rotation of a crystal until a dislocation becomes invisible, together with determination of the diffraction pattern of the crystal in that orientation allows determination of the Burgers vector for that dislocation (Fig. 10.11). Similarly, the orientation of other intra- and intercrystalline structures can be determined with great accuracy using diffraction or Kikuchi patterns (Gapais and White 1982; Fitz Gerald et al. 1983). TEMs usually also have equipment for energy dispersive X-ray analysis and scanning (Sect. 10.2.4.1); therefore, the chemical composition of grains can also be determined, although it is time consuming to conduct quantitative analyses.

The TEM is most useful to identify and study microstructures on the grain scale, or to determine the mineral content and microstructure of very fine-grained rocks (<1 μm) that are difficult to study by SEM. However, although the TEM is a very powerful devise for microstructural studies, it has its limitations. The volume of material which can be studied in a single session on the TEM is very small. Although it is possible to determine the orientation of single crystals, it is a rather tedious and time-consuming job to use the TEM to measure LPO patterns unless the microscope is equipped with on-line diffraction pattern indexing software. EBSD with the SEM (Sect. 10.2.4) is usually a better technique for LPO measurement unless the grain size is less than one micron.

Not all minerals can be studied by TEM; in general, minerals with a large water content such as clay minerals and muscovite are less suitable since they disintegrate in the electron beam; water-free minerals such as olivine and pyroxenes are most stable in the TEM.

10.2.5.2 Sample Preparation

TEM samples are small fragments of the rock slice of a thin section, attached to metal grids with a diameter of a few mm (Fig. 10.10). The thin section should be prepared with a resin or glue such as 'lakeside' that is dissolvable in alcohol; metal grids are glued with araldite onto interesting parts of the sample as determined by optical microscope; a single grid is insufficient since many samples fracture, or are otherwise damaged during further preparation. The rock slice is then removed from the glass by submersion in alcohol, and broken into fragments to remove the metal grids and small attached rock chips. The chips must be thinned to a few nm before they are transparent for the electron beam, and since the sample should not be mechanically damaged during the process of thinning, the superfluous material is evaporated by bombardment with Ar-ions in a vacuum. This process of *ion thinning* continues till small holes are visible in the sample; observation in the TEM is only possible adjacent to these holes, where the sample is sufficiently thin (Fig. 10.10). After thinning, coating of the sample with carbon is necessary to avoid charging. Because of this sample preparation method and thinning procedure, it is difficult to select a particular small grain or object in a thin section for observation by TEM; the chance that it will be located exactly on the edge of one of the 'observation holes' is rather small. SEM work is probably more effective if a particular isolated structure is to be stud-

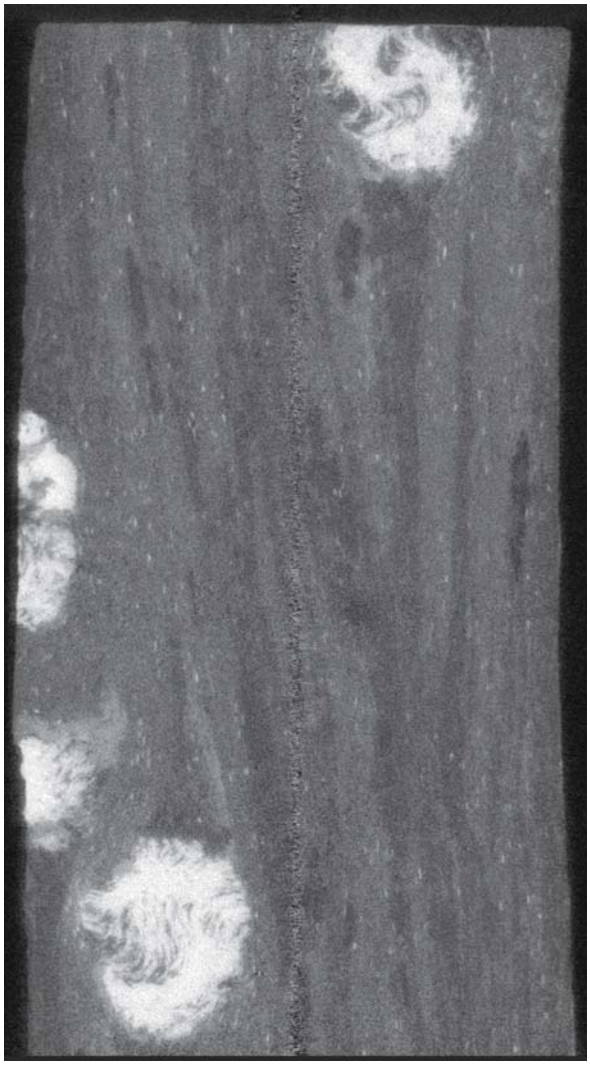


Fig. 10.12. High resolution computed micrograph produced by X-ray microtomography of a garnet-bearing schist from the Main Central Thrust zone, Nepal Himalaya. *Light-coloured* areas are garnet porphyroblasts with spiral inclusion trails, which are wrapped by the principal foliation in the thrust zone. Image represents a slice through a rock cylinder 20 mm in length and 10 mm in diameter. The data were collected at the Consortium for Advanced Radiation Sources, University of Chicago, USA. Resolution is 17.2 microns per pixel. (Image courtesy of Scott Johnson and Richard Spiess)

ied. However, a new technique of preparing TEM samples using a focused ion beam (FIB) within a SEM allows precise selection of areas for TEM study.

10.2.6 Tomography

It is presently possible to make direct 3D observations of microstructures *inside* a small rock sample using tomography techniques (Fig. 10.12, Video 10.12a–c; Carlson et al. 2003). Because of the high density and presence of heavy elements in rocks, and the demand on calculation capacity for 3D analysis, only small samples can be investigated by this method at present. Available equipment ranges from small desktop X-ray tomographs for small samples (up to 2 cm^3) and low resolution (down to 5 µm), to large-scale machines attached to a particle accelerator for larger samples and high-resolution.

A great advantage of tomography is that the method is non-destructive. Any small rock sample can be directly analysed without special preparation, although samples should preferably be circular or square in cross-section. Best results are obtained for high density contrast or high atomic number contrast. This means that pores in a sandstone, or e.g. galenite grains in carbonate are easy to resolve, but feldspar grains in quartz mylonite, or leucosomes in a gneiss, are difficult to see.

10.3 Methods to Measure Lattice-Preferred Orientation

10.3.1 Introduction

Several methods are used to measure lattice-preferred orientation in rocks (Leiss et al. 2000; Sects. 4.4.3–4.4.5). The classical method is the use of a *U-stage*, which allows rotation of a thin section or sample in three directions to determine the orientation of fabric elements. Other methods are optical bulk analysis, texture goniometry, and electron microscope techniques (Ullemeyer et al. 2000). For goniometry, the term texture is commonly used instead of LPO in the literature and therefore maintained here (Box 1.1). All methods require rather expensive equipment and each has its advantages and disadvantages.

10.3.2 U-Stage Measurements

In a universal stage or *U-stage* a thin section is mounted between two glass hemispheres (Fig. 10.13). The complete setting of hemispheres and thin section can be turned around several axes in such a way that a single crystal in the thin section at the centre of the half-spheres

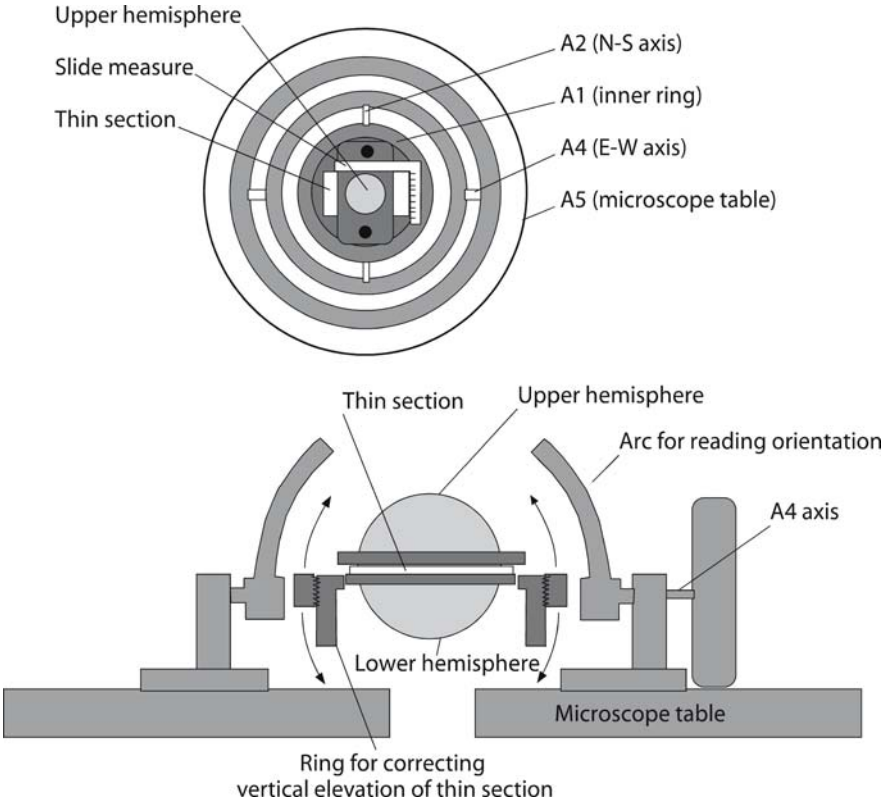


Fig. 10.13. Schematic top view and cross-section of a U-stage, showing the various parts. The thin section is wedged between two halfspheres, and the internal part can be tilted and rotated until specific features have a vertical orientation, after which the orientation can be read from the arcs and rings of the stage. *Detailed explanation on the CD*

can be focussed in orientations up to 40° from the horizontal. In this way, crystals or microstructures such as twins, lamellae and inclusions can be rotated until they lie in a particular orientation with respect to the axes of the microscope. If the orientation of the U-stage axes is now read, these data can be used to calculate the orientation of the structure with respect to thin section axes, and eventually to geographic orientation. Modern versions of the U-stage have been modified to allow automatic storage of measurements in a computer.

Although the U-stage has a long history, it is still an important instrument to measure LPO patterns, especially for quartz. For those who do not have access to goniometers and electron microscopes it is the only means to assemble data on lattice-preferred orientation of minerals. A U-stage is also quite useful for study of microstructures such as twins, inclusions and cleavage planes which have been obliquely cut by a thin section. These will appear unsharp in a normal thin section, but in the U-stage they can be observed in a more suitable orientation, and their orientation can be measured with reasonable accuracy.

The U-stage can also be a useful tool to establish the shape of grain boundaries (Kruhl 2001; Kruhl and Peternell 2002) and the relative orientation of subgrain boundaries and the crystal lattice of quartz on both sides. This method has been used to determine the orientation of slip systems in minerals like quartz; the orientation of a subgrain boundary depends on the orientation of the slip system of the dislocations, which accumulate in it (Christie and Green 1964; Trepied et al. 1980; Mainprice et al. 1986). However, there is some doubt about the reliability of this method, and additional TEM analysis is always necessary.

U-stage measurements of LPO are inexpensive and can be done on a normal microscope. Notice, however, that some modern microscopes have insufficient working space to fit a U-stage. Full LPO can be determined for olivine, calcite and orthopyroxene, and with some difficulty also for minerals with lower symmetry like amphiboles and feldspars, provided that grains are large and that sufficient cleavage or twin planes can be measured. Full LPO of quartz cannot be measured with a U-stage, only the orientation of the c-axis. Nevertheless, U-stage measurements are very popular for quartz since they are relatively easy and fast to obtain, and normally the c-axis pattern is sufficient to determine shear sense. If fluid inclusions are present, it may be possible in some cases to use their negative crystal shape to determine the orientation of a-axes as well (Fig. 10.17a; Rosin et al. 2004).

Disadvantages of the U-stage are the laborious and time-consuming nature of the work and a minimum diameter of about 20 μm for grains to be measured. Strong undulose extinction also hampers measurement. U-stage measurement of LPO patterns does not allow a statistically unbiased analysis of the fabric; the volume of minerals with a particular orientation is difficult to determine since normally only one measurement per grain is taken, and the relative size of the grains is not taken into account. AVA diagrams (Sect. 4.4.3) have been constructed based on U-stage measurements but these tend to be inaccurate.

10.3.3 U-Stage Sample Selection

The presence of an LPO in an aggregate can be checked for minerals with low birefringence by inserting a gypsum plate with crossed polars; if a preferential colour occurs in some orientations when the microscope table is turned, an LPO is probably present. It is important that a thin section used for LPO analysis does not contain too many minerals other than the one to be measured, since such minerals will have influenced the LPO and inhibit comparison with standard patterns measured for monomineralic rocks. Grain size should not be less than 30 μm, otherwise it is better to use a texture goniometer. The thin section should have a basal glass plate of less than 1 mm thick; presence of a thick basal glass plate makes focussing on single grains difficult. Make sure that the thin section is properly oriented. The range of measurements is usually restricted to 30% of the thin section in the centre; grains in the periphery cannot be measured. Interesting parts should therefore lie in the centre of the thin section. It is important to realise that several populations of grains with different LPO may be present even in a monomineralic rock. For example, course grains may represent an older generation, and fine grains a new, recrystallised phase. It is therefore usually advantageous to try to distinguish several groups of grains on the basis of size, shape and content of inclusions or intracrystalline deformation structures. In many cases it is useful to have enlarged photographs of a thin section before an attempt is made to measure the fabric. This will also be helpful in the construction of AVA diagrams. The method to measure quartz-LPO using a U-stage is described in item "U-stage" on the CD.

10.3.4 Optical Semiautomatic Methods

A technique to measure LPO in an ordinary thin section with computer-integrated polarisation microscopy (CIP method) was devised by Heilbronner-Panozzo and Pauli (1993) and described in Heilbronner (2000). An ordinary microscope is used with added tilt stage and rotating polarising filters. A digital camera records the brightness of all grains in the field of view while the polarising filters are rotated and the thin section is stationary. Images

for each rotation increment are stored in a computer and used to calculate the LPO orientation of each pixel in the image. A colour code (colour look-up table) is devised to colour-code the c-axis orientation of each pixel, thus creating an orientation image where each coloured pixel indicates a particular orientation. Such an image is a high resolution AVA diagram which can be used for accurate analysis of the grain scale fabric with image analysis techniques (Fig. 10.14 (in colour on CD); Photo 10.14).

Fueten (1997) devised a similar automatic rotating stage where a control box is connected to two rotating polarisers, one of which is fixed below the thin section. Rotation of the polarizer, acquisition with a digital camera and processing of the images is guided by a PC (Goodchild and Fueten 1998). This method can determine the trend and plunge angle, though not plunge direction for the c-axis of quartz grains.

Another tool for this type of analysis was developed by Wilson (Wilson et al. 2003). Here, a specially adapted microscope and stage is required, fitted with three digital cameras that can be linked to a laptop computer. The device slowly moves the thin section with respect to the microscope lens and thus scans the section mechanically with a resolution of up to one μm; it can measure the orientation of c-axes of each pixel. This device gives an accurate and high-resolution image of c-axis orientations of quartz or other uniaxial minerals.

Besides AVA, the three methods discussed above can also be used to produce other types of orientation images such as misorientation images, relating pixel orientation to some reference direction, or to that of its direct neighbours (e.g. Wilson et al. 2003). This marks grain and subgrain boundaries. Volume weighted pole figures can be derived and therefore statistically balanced analysis of the fabric can be carried out on the orientation, as in goniometer data. Some techniques allow automatic recognition and mapping of different minerals. The advantages of these methods are relatively low costs, the possibility to use normal thin sections, and high resolution. A disadvantage is that the methods only apply to uniaxial minerals such as quartz, calcite, dolomite, ice, and norcamphor and can only determine and plot the orientation of c-axes.

10.3.5 Texture Goniometers

Two types of goniometers are commonly used to study fabrics in rocks; the X-ray and neutron texture goniometers. The X-ray goniometer is most accessible and is most easily operated on monomineralic rocks, although bimineralic rocks can be studied in some cases (Braun 1994). Samples should be relatively fine-grained (<200 μm) and homogeneous, preferably with a high crystal and lattice symmetry. Neutron texture goniometry can only be carried out with a

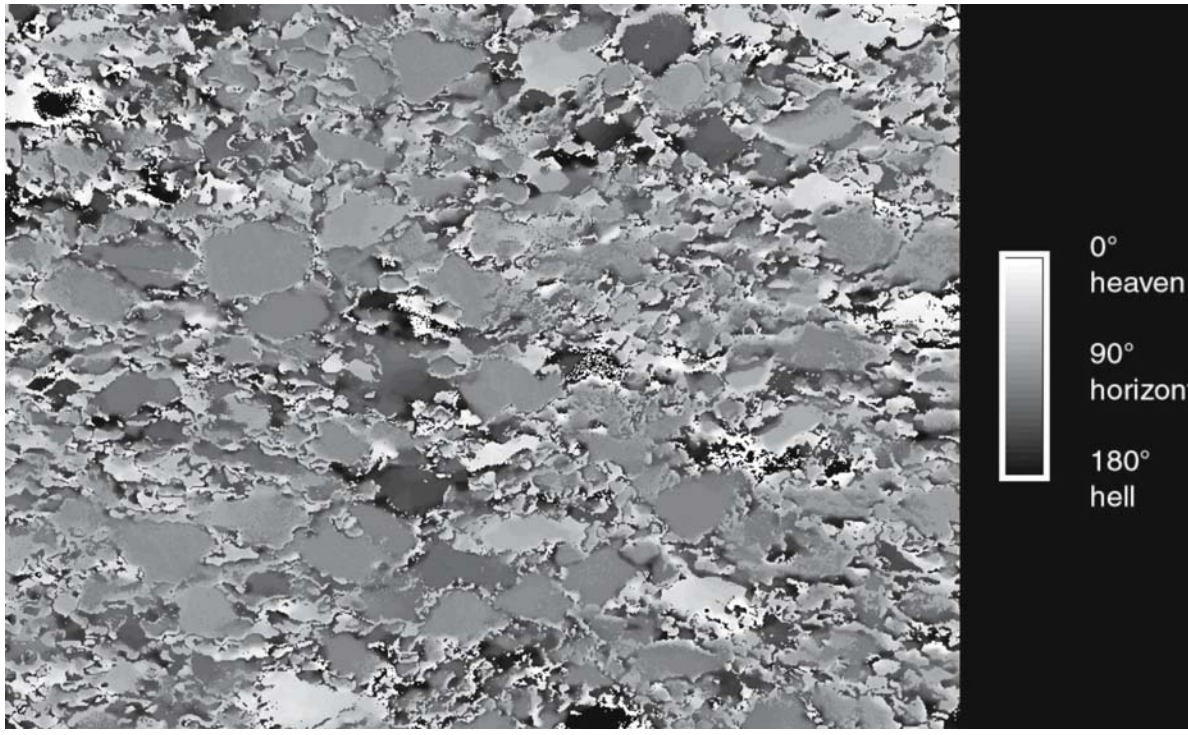


Fig. 10.14. AVA diagram produced by the CIP method. Only the plunge of C-axes is shown in this grey tone image. Experimentally deformed Black Hills quartzite. Deformation conditions 900 °C, 15 kbar and 10^{-5} s^{-1} (Regime 3 – Hirth and Tullis 1992). (Image courtesy Renee Heilbronner). Complete colour version of this AVA as Fig. 10.14 on the CD (see also Photo 10.14)

neutron diffractometer and suitable neutron source, few of which are presently available, and is rather time-consuming (Brokmeier 1994). The method has great advantages, however, since large and therefore coarse-grained samples can be used (Brokmeier 1994); samples can be up to 4 cm in diameter and need not be polished, although spherical or cylindrical samples are preferred. Neutron goniometry is suitable for polymineralic aggregates containing minerals with low symmetry such as amphiboles and plagioclase, and for measurement of weak fabrics (Wenk et al. 1986b; Brokmeier 1994; Siegesmund et al. 1994; Ullemeyer et al. 1994, 2000). Both types of goniometers can give full LPO patterns, which are statistically balanced for the volume of each of the present directions. Goniometers have been used to study the LPO of micas in foliated rocks for finite strain analysis (Sect. 9.2; Tullis and Wood 1975; Wood and Oertel 1980; van der Pluijm et al. 1994; Ho et al. 2001) and even sense of shear from the skewness of the fabric (O'Brien et al. 1987). For minerals like quartz and calcite goniometry has been used to determine full ODFs (Sect. 4.4.3; Casey 1981; Schmid and Casey 1986). A disadvantage of goniometers is that they cannot show how the different orientation peaks are distributed over the sample. This implies that no AVA diagram can be constructed and that no link can be made to microstructures, which could give information on the mechanisms by which the LPO originated. For this reason, additional U-stage observations are commonly made on thin sections prepared from a sample that was analysed by goniometry.

10.3.6 SEM-Techniques

EC and EBSD pattern observation modes in the SEM are possibly the most promising tool for determination of preferred orientation of minerals in thin sections (Fig. 10.8, Photo 10.3d,e). Although SEMs with equipment for EC and EBSD are still scarce, the method has many advantages; full LPO patterns for many minerals can be measured automatically in a complete sample, and maps can be made of the distribution of these LPO over the sample. Details are described in Sect. 10.2.4. (Lloyd and Hall 1981; Lloyd et al. 1981; Joy et al. 1982; Lloyd 1987; Lloyd and Freeman 1991, 1994; Mainprice et al. 1993).

Since the orientation of the fabric at the surface of the crystal is analysed, "superpolished" specimens are used. Normal polishing with diamond paste or similar abrasives damages the surface layer of a specimen, and this means that no good channelling patterns can be made. Therefore, ordinary polished rock chips, mounted in epoxy, are repolished using a silica solution in a special polishing rig to remove the damaged surface layer. Such "superpolished" sections are also useful to do careful work on small-scale structures in a normal SEM, since they give much better resolution than ordinary polished sections.

10.4 Chemical and Isotope Analysis

10.4.1 Electron Microprobe

The electron microprobe has been a standard analysing tool in most laboratories for 40 years to determine main-element composition of mineral grains in a polished thin section. A high-energy focused beam of electrons is used to generate X-rays characteristic of the elements in a sample. The resulting X-rays are diffracted by analyzing crystals and counted in detectors. The electron current in an electron microprobe is up to 1 000 times higher as in a SEM, because the purpose of the machine is to generate X-rays, rather than study topography or texture (Reed 1996). Chemical composition is determined by comparing the intensity of X-rays from standards (known composition) to those from materials in investigated samples, normally polished thin sections.

Polished sections are coated with carbon to reduce charging by the electron beam, and introduced in a specimen chamber that is operated in vacuum. Spot analyses and profiles of series of spot analyses give accurate main element compositions in each part of the sample with a resolution of a few micrometres. Normally, sites to be analysed are found and coordinates marked before introducing the samples in the machine in order to save time during the analysis steps. Parts of a sample as small as 3 μm can be analysed. Elements from fluorine ($Z = 9$) to uranium ($Z = 92$) can be analysed routinely down to 100 ppm. Both electron-generated images, similar to those in the SEM and optical microscope images of the sample can be seen during the analysis. The method is virtually non-destructive, fast, relatively cheap and uses normal polished thin sections.

Modern microprobes permit *high-resolution compositional mapping* of mineral phases often allowing the distinction between newly grown rims around older cores. This is a powerful method to study metamorphic reactions and mass transfer e.g. during cleavage formation (Williams et al. 2001).

10.4.2 Proton Microprobe

The proton microprobe, also known as the *nuclear microprobe* is a powerful tool for the analysis of trace elements and their distribution in the microstructure of a rock (Ryan and Griffin 1993; Ryan 1995; Ryan et al. 2001). Trace elements can be analysed with very low detection limits, down to sub-ppm, and with a high horizontal resolution. Samples can be up to thin-section size and should have a smooth surface. The sample is irradiated by a beam of high energy (several MeV) protons from a particle ac-

celerator, leading to emission of protons, ions, X- and gamma rays, which can all be analysed. Several analysing techniques are presently available with the proton microprobe, the most important of which are mentioned below, notably Proton Induced X-ray Emission (*PIXE*) (Fig. 10.15).

Fast protons induce X-rays by dislodging electrons from the inner electron shells of atoms, which are replaced by outer-shell electrons with the emission of X-rays. The PIXE spectrum can be used to determine the sample composition down to the trace elements at ppm level and below. This is similar to EDAX in the SEM or electron microprobe, but much more accurate while standards are not needed. However, PIXE is generally only used for elements heavier than Al ($Z > 13$). Special approaches can be used down to Na ($Z = 11$), but commonly filters are used to absorb intense major element lines to improve trace element detection typically for elements above Ca-Fe ($Z = 20–26$).

Energetic protons approach atomic nuclei closely and cause nuclear reactions in light elements and emission of particles and gamma rays. Proton Induced Gamma-ray Emission (*PIGE*) is suitable for the analysis of light elements such as Li, Be, B, F, Na, and Al. This fills part of the gap left by PIXE. Analysis of the secondary reaction products also gives information on light element concentrations. This is known as Nuclear Reaction Analysis (*NRA*). NRA with reaction product particle detection is particularly useful for lighter elements that cannot be analysed with PIXE, especially for analysis of C, N and O.

The energy loss of the backscattered protons gives direct information about the three dimensional distribution of target nuclei. This is known as Rutherford Backscattering Spectrometry (*RBS*).

Fast protons can also produce secondary electrons, which can be used to determine the topography of a sample, as in the SEM. Visible or infrared emissions from the sample, known as Ionoluminescence (IL) can be used on the same structures and give similar information as cathodoluminescence.

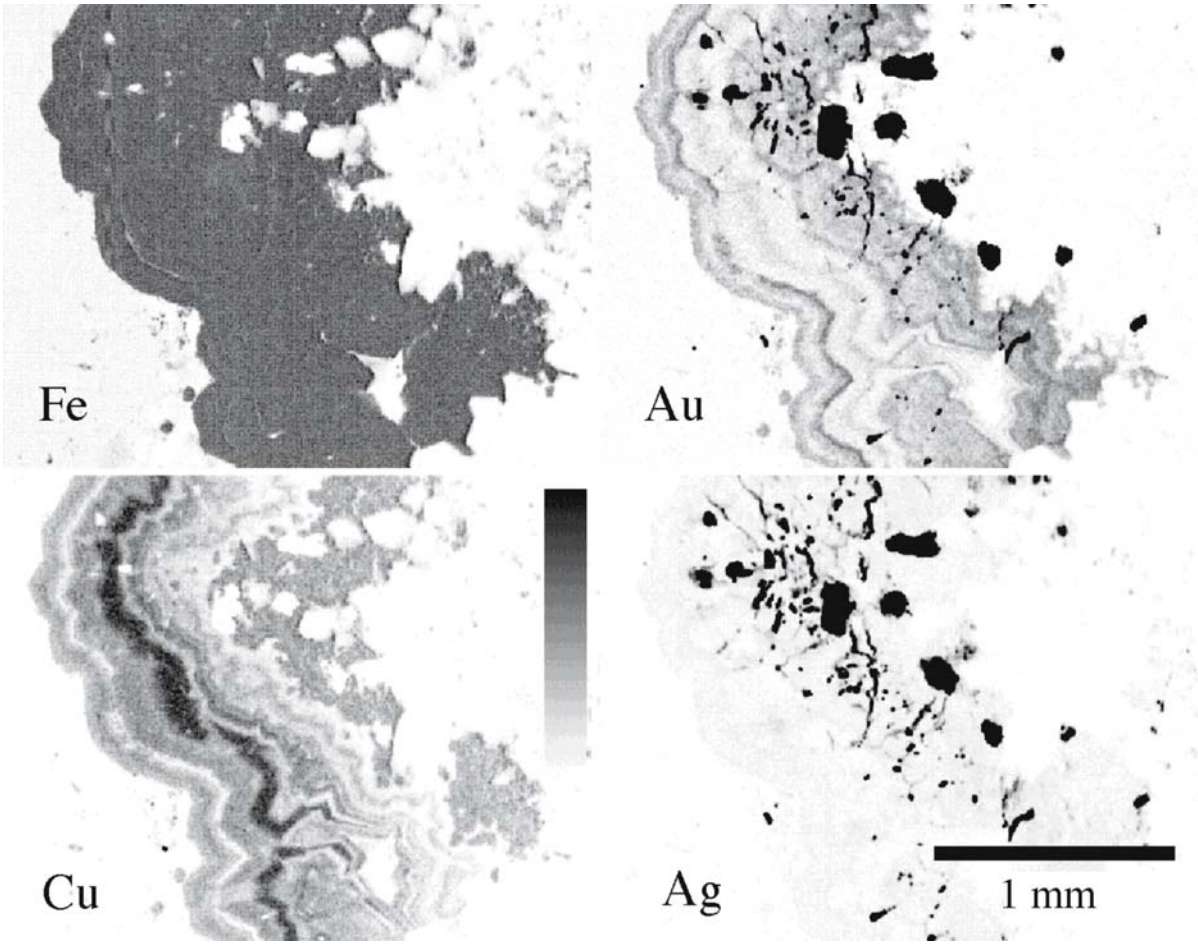


Fig. 10.15. Trace element zonation in a pyrite vein in quartz as observed using proton induced X-ray emission (PIXE). The data were collected using a 6 nA beam of 3 MeV protons focused into a 1.6 μm beam spot in the CSIRO nuclear microprobe in Clayton, Australia. Sample from the Emperor mine in Vatukoula, Fiji. (Photos courtesy Chris Ryan at CSIRO)

A proton microprobe is particularly suited for the study of *fluid inclusions*, since the high-energy protons can penetrate down to more than 40 μm into a sample.

Advantages of the proton microprobe are the high resolution and accuracy, the fact that the proton beam does very little damage to the sample, the high penetration depth, and the fact that low-vacuum can be used when needed for delicate samples. Disadvantages are that the high penetration depth precludes the analysis of small grains, and the high costs and limited availability of the equipment.

10.4.3 ERDA and RToF Heavy Ion Microprobes

Several types of ion microprobes are currently available, using ions heavier than protons (Breeze et al. 1996). In principle, the same analytical methods can be used as in the proton microprobe but the lighter elements can be more easily investigated. By using a beam particle heavier than the target atoms of interest, the lighter target atoms can be knocked forward in the collision and recoil out of the target. The target-derived particles are caught in a detector, set up at a high angle to the incident beam after rejection of the scattered beam. The method is especially powerful for the analysis of light elements and is known as Elastic Recoil Detection Analysis (*ERDA*). The approach is especially useful for hydrogen analysis (Sie et al. 1995). A more sophisticated technique, known as Recoil Time-of-Flight spectrometry (RToF) measures the time particles take to reach the detector. This also allows assessment of the distribution of phases with depth in the sample. A disadvantage of the ion probe over the proton probe is the larger size of the spot, 10–15 μm, which means that less detail can be seen in the sample. Also, the irradiation damage to the sample is larger than for the proton probe.

10.4.4 Mass Spectrometry – Introduction

Mass spectrometers differ from ion microprobe techniques described above in that ionized atoms or molecules are dislodged from the sample and not directly scattered into a detector, but sent to a mass spectrometer where they are analysed using their difference in mass-to-charge ratio (m/e) to separate them from each other. In contrast to the ion microprobe, the method is more destructive and, for laser sampling, evaporates material from the surface of the sample, creating small craters. A mass spectrometer consists of an ion source, a mass-selective analyzer, and an ion detector. Since mass spectrometers create and manipulate gas-phase ions, they operate in a high-vacuum system.

10.4.5 SIMS, TIMS and SHRIMP

In Secondary Ionization Mass Spectrometry (SIMS) analysis, a focused beam of "primary" ions bombards the surface of a polished sample. The bombardment removes atoms from the surface of the section, some of which are ionized and can be accelerated into a mass spectrometer. The method is useful for in situ quantification of many elements at sub-ppm concentrations. Like the ion microprobes, the method is an extension of the information that can be obtained from the electron microprobe. The method is used for measurements of isotope ratios for major and minor elements and in situ mapping of isotopic and trace element abundances in thin sections or individual grains. SIMS are in routine use for U-Pb zircon dating, measurements of trace element abundances, and stable isotope measurements including those of O, C and S. While the lateral spatial resolution can be submicron for major element mapping, it is more typically in the 5 to 25 μm range for most isotopic and trace element measurements. However, craters are shallow and depth profiling can be used to investigate micron-scale gradients in isotope composition. SIMS is also referred to as "ion microprobe".

The sensitive high-resolution ion microprobe (SHRIMP) is a SIMS-type instrument that can reach very high precision needed for dating portions of minerals such as zircon that are used for dating. Presently, spatial resolution of a few μm is reached and most elements can be analysed down to 5 ppb and isotopic ratios to a few ppm.

Thermal Ionization Mass Spectrometry (TIMS) usually uses mineral separates, but a small amount of material can be isolated from a thin section using a micro drill. Thermal ionization means that the sample is deposited on a metal ribbon, such as Pt or Re, and an electric current heats the metal to a high temperature. TIMS is more cumbersome in sample extraction and preparation, and is destructive, but more accurate than LA-ICPMS and SIMS; isotope ratios can be measured better than 15 ppm.

10.4.6 ICPMS and LA-ICPMS

In *Inductively Coupled Plasma Mass Spectrometry* (ICPMS) the sample is dissolved and then exposed to a high temperature argon plasma, which dissociates molecules and ionizes atoms, which are then passed into a mass spectrometer. Here, the ions are sorted by mass and detected using a scanning electron multiplier. Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICPMS) is more versatile since it allows use of thin sections, albeit with a thickness of 80–100 μm. This tech-

nique combines laser ablation and ICPMS techniques and can be used to measure trace elements; especially the rare earth elements of minerals in a thin section can be measured directly. The laser ablates a small amount of material from the surface of the section, producing ablation-pits of 10–200 µm. Detection limit is sub-ppm. The method is useful to measure profiles over large mineral grains.

The advantage of a laser to ablate material from a sample is that the sample does not charge, and both conducting and non-conducting materials can be used, without need for a conductive coat and/or other charge balancing techniques, as in SIMS and the electron microprobe. The sample must be in an airtight chamber, but is not exposed to a vacuum. The ionization step is separate from the sampling step by laser ablation, and the ablated material is transported in Argon to the ICPMS.

Although LA-ICPMS is a very versatile method, it is still less accurate than SIMS or TIMS for determination of isotopic ratios analyses, but this is not a serious problem for the heavier isotopes. However, multidetector ICP-MS can measure isotopes more accurately.

10.4.7 In-Situ Age Determinations

Most age dating techniques are based on isotopic ratios of radiogenic elements, which can be measured with one of the mass spectrometer types described above. Some of these techniques allow dating of minerals or even parts of minerals in their original fabric, in a thin section (Johnson 1999b). Most important and allowing highest resolution is the SHRIMP for dating zircon and monazite in thin section, although LA-ICPMS, SIMS and similar methods can also give good results. Examples are monazite inclusions in garnet dated by SIMS (Zhu et al. 1997) and monazite and K-feldspar using LA-ICPMS, (Möller et al. 1998; Christensen et al. 1995).

Particularly useful is Ar-Ar dating in thin section of micas, amphiboles or feldspars where the entire thin section is irradiated before analysis (Kelley et al. 1994). A laser is used to evaporate some material from the surface of the crystals, after which it is sent to a mass spectrometer for analysis.

An alternative but not generally accepted method is *chemical age dating*, where concentrations of Y, U, Th and Pb in monazite (Williams et al. 1999; Williams and Jercinovic 2002), xenotime, uraninite, zircon and staurolite (Lanzirotti and Hanson 1997) measured by electron microprobe are used for dating. The method is especially promising for monazite since this contains virtually no original lead, so all lead can be assumed to be radiogenic, while lattice diffusion is apparently slow, preserving delicate chemical zoning patterns. The method can be used for crystals older than about 200 Ma. The method uses a type of least-squares regression or plane fitting through a data cloud and needs a considerable spread in order to give workable results. Errors are in the range of 20–50 Ma. Advantages are high spatial resolution (down to 2–3 µm), the possibility to analyse parts of complexly zoned crystals and the non-destructive analysis compared with mass spectrometers which need to evaporate material. Analyses can be done in a relatively short time at low expense (Suzuki et al. 1991; Rhede et al. 1996; Montel et al. 1994; Terry et al. 2000). A particular advantage is the possibility to date monazite crystals in their relationship with porphyroblasts and foliations, and thus to date parts of the microstructure (Williams and Jercinovic 2002). Problems are Pb-contamination during sample preparation, analytical problems, uncertainties of the original composition and zoning of monazite growth and the possibility of lead loss (Scherrer et al. 2000).

Chemical dating cannot replace isotope dating, but is presently at least useful for first-approach dating and has the advantage that it can date zoning in crystals and inclusions in porphyroblasts. In the SHRIMP, resolution is a few µm and crater depth 1 µm. In the electron microprobe less than 1 µm and little damage is done to the specimen. In situ dating promises to aid precise dating of deformation phases, tectonic processes, mineral growth rates and to refine general *P-T-t* paths for metamorphic rocks.

10.5 Fluid Inclusion Studies

10.5.1 Introduction

Fluid inclusions are small pockets of fluid inside crystals. They are assumed to be samples of the fluid that was present in the rock during deformation and metamorphism, although the original composition and density may have been modified by leaking and preferential removal or addition of certain components (Roedder 1984; Shepherd et al. 1985; Crawford and Hollister 1985; de Vivo and Frezzotti 1994; Goldstein and Reynolds 1994; Boullier et al. 1997). Fluid inclusions of CO_2, H_2O, N_2 and CH_4 are relatively common (Figs. 10.16, 10.17a). Usually, inclusions contain more then one phase (Fig. 10.17b); many contain a gas bubble and some contain also solid phases such as small salt or graphite crystals (Fig. 10.17d).

It is possible to determine the composition and density of the fluid in inclusions without destroying the sample. To a first approximation, H_2O rich inclusions in quartz can be recognised by the presence of a small salt crystal and gas bubble, and by a small contrast in refractive index with quartz (Figs. 10.16, 10.17c,d). CO_2-rich

inclusions may have a gas bubble but lack salt crystals, and have a stronger contrast in refractive index with quartz, leading to thick 'shades' along the contacts (Figs. 10.16, 10.17b,c).

Fluid inclusions either occur isolated or as swarms that commonly lie along a plane. Isolated inclusions, many with a negative crystal shape (Fig. 10.16), may represent inclusions that were captured when the host grain grew from a solution; they are therefore also known as *primary fluid inclusions* (Figs. 10.17a,b). Planes of inclusions commonly contain inclusions of similar composition and density, and are thought to represent healed fractures on which fluid has been present (Figs. 3.18, 10.16, 10.17c,e); they are also known as *secondary fluid inclusions*. Such fractures can normally be followed over long distances in a section, and may transect grain boundaries or even mineral boundaries (Figs. 10.16, 10.17f). The ratio between the diameter of fluid inclusion and the length of fluid inclusion planes as measured in thick sections is around 10^{-2} when the average aspect ratio of microcracks in rocks is 10^{-3} after Kranz (1983). The lower aspect ratio (10^{-2} versus 10^{-3}) may be explained by dissolution crystallization processes during healing of mode I microfractures. Thus, the relative age of inclusions in the healed crack and structures or minerals in the rocks can be established; the composition and density of the inclusions can be related to deformation phases or metamorphic conditions. Where healed cracks transect grain boundaries, it is possible to determine whether they were tension fractures (without a shear component) or shear fractures. Tension fractures are most common. If their orientation is known, they can then be related to a stress tensor of a particular orientation and, in the case of tension fractures, an upper limit can be placed on the magnitude of the differential stress (Sect. 9.6). In many cases, several sets of healed cracks occur in a rock (Fig. 10.17e), and their relative age can be established at the intersection point, since inclusions of the older phase will have been destroyed by the younger fracture (Fig. 10.16). Thus, sequences of fracturing and associated fluid compositions and densities can be linked to phases of deformation and, in some cases, metamorphic conditions. Since fluids play a major role in deformation of rocks, such information is extremely valuable. However, there are also some disadvantages in the use of fluid inclusions:

1. inclusions are usually relatively young; the older inclusions are destroyed by deformation;
2. inclusions may have leaked or changed shape, composition and density, and this is difficult to check; especially inclusions with strongly irregular shape, or with surrounding swarms of small inclusions may have leaked, decrepitated or imploded.

In healed cracks the situation is probably relatively safe, since any inclusions with strongly deviant composition and density can be regarded as suspect. For these reasons, any work on fluid inclusions in metamorphic rocks should take into account their topology: shape, fluid composition, density and mutual relationships. For example,

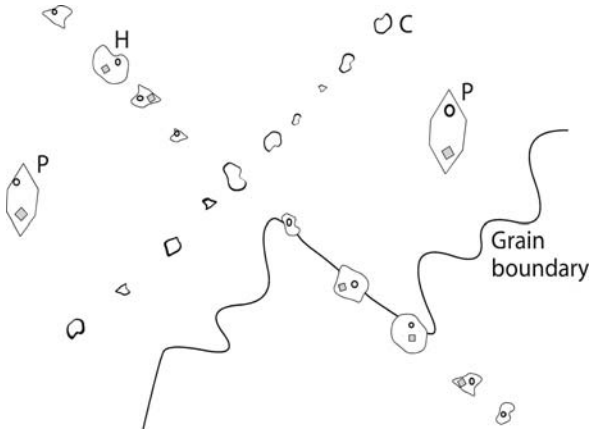
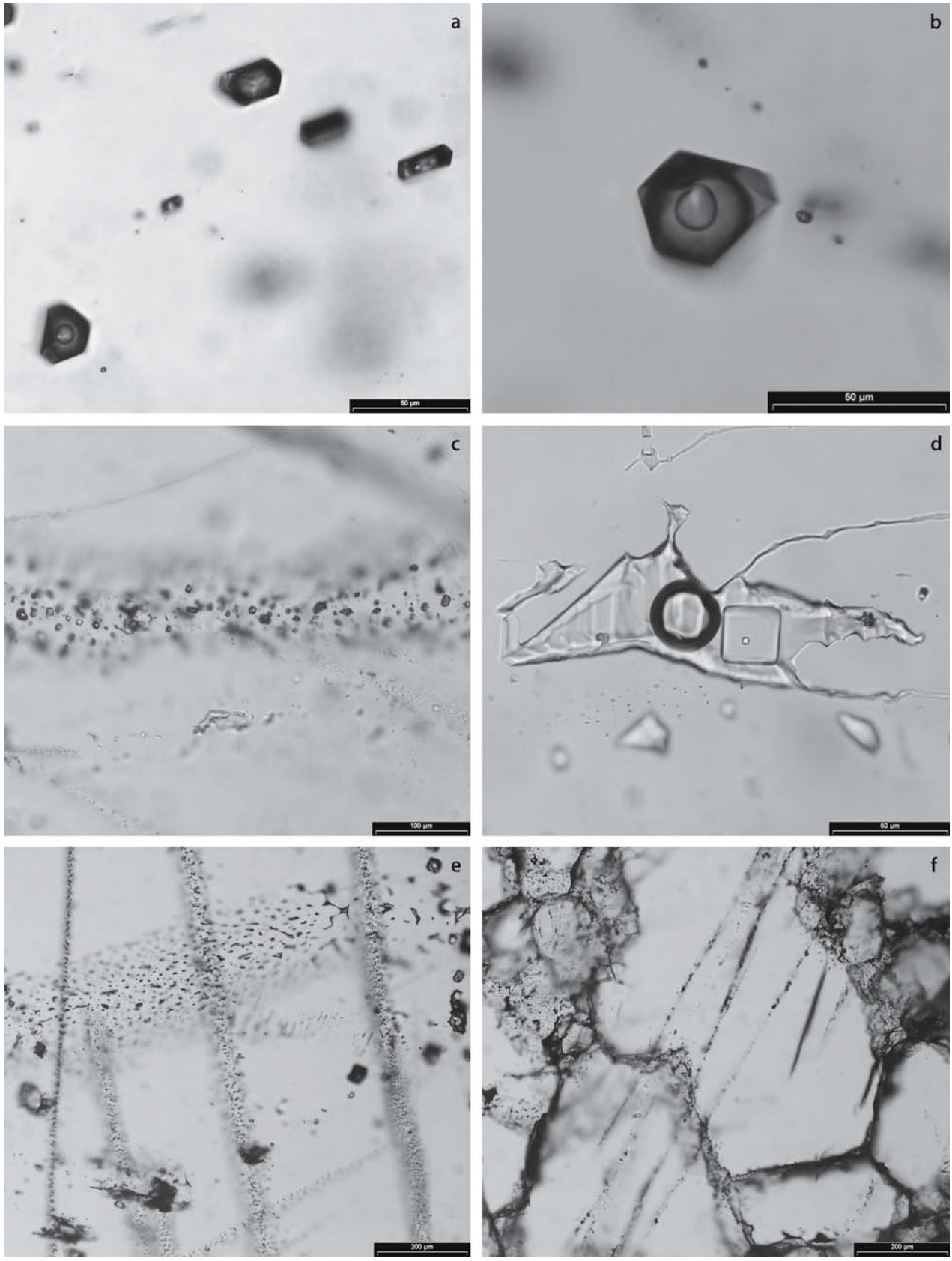


Fig. 10.16. Schematic drawing of fluid inclusions as they may appear in a thin section; large isolated inclusions with a negative crystal shape can be primary (*P*). Secondary inclusions occur in arrays that represent healed fluid-filled cracks, and have similar composition within one array; two types are shown, H_2O-rich inclusions (*H*) with gas bubbles and small salt cubes, and CO_2-rich inclusions (*C*), with thick shades along the edge due to a difference in refraction with surrounding quartz. The H_2O inclusion array cuts a grain boundary, and the CO_2-rich array cuts the H_2O rich array, thus establishing the relative age of the structures

Fig. 10.17. a Typical primary CO_2-H_2O fluid inclusions containing three phases. Camperio, Swiss Alps. **b** Primary CO_2-H_2O fluid inclusion containing three phases: from *centre* to *margin*: a bubble of CO_2 gas and CO_2 liquid (*centre*), and H_2O liquid (*lighter part* at the *right-hand side*). The well-developed negative crystal shape is typical of primary fluid inclusions. Camperio, Swiss Alps. **c** Two planes of secondary fluid inclusions in quartz. The *top* one of dark inclusions contains CO_2. The *lower* one, of low-relief inclusions contains H_2O. High-grade gneiss from the Grenville Province, Canada. **d** H_2O-NaCl fluid inclusion in a quartz crystal. A gas bubble and salt cube are present in the inclusion; the salt cube contains itself a small inclusion. The fluid inclusion formed late and indicates the percolation of seawater through the rock. Zabargad Island. (Red Sea, Egypt). **e** Quartz crystal with several sets of planes of secondary fluid inclusions. Bands of variable width composed of small inclusions are thin inclusion planes; width of the band increases with decreasing angle between the inclusion plane and the thin section. All are CO_2-H_2O inclusions. Some of the larger inclusions have an annular shape due to late differential stress increase and implosion of the inclusions. The planes of small fluid inclusions are probably formed from imploded large (now annular) inclusions. The two large irregular dark inclusions at *bottom left* are decrepitated, empty inclusions. Main Central Thrust, Himalaya. **f** Fluid inclusion planes transecting grain boundaries in quartzite. All are CO_2-H_2O inclusions. Grain boundaries also contain fluid inclusions, but these are now mainly empty. Main Central Thrust, Himalaya. 100 μm thick doubly polished section. PPL. (Photographs courtesy A-M. Boullier)


a
50 µm
b
50 µm
c
100 µm
d
50 µm
e
200 µm
f
200 µm

some fluid inclusions have a ring-shaped geometry (Fig. 10.17e). They are known as *annular fluid inclusions* (Boullier et al. 1991). These inclusions form from large primary or secondary inclusions by increased differential stress after their formation event; this causes the inclusions to implode and reduce to a ring shape while the expelled fluid forms planes of secondary small inclusions.

The relationship between healed cracks of fluid inclusions and other microstructures in a rock can be studied in ordinary thin sections or polished sections, although many inclusions will have leaked and are now empty; they appear as dark inclusions with unusually thick shades along the rims due to refraction of light through the empty space (Fig. 10.17e,f). For precise fluid inclusion studies, thick (100 μm) doubly polished sections are generally used. Intact inclusions can be recognised by a clear image and the presence of an included bubble or small crystals. The presence of fluid in an inclusion is proven by rapid Brownian movement of the included gas bubble, especially when approaching the homogenisation temperature. Fluid inclusions are mostly studied in quartz, but can be found in many minerals. Minerals with a strong mineral cleavage such as calcite and micas are less suitable for analytical purposes since they are likely to have leaked; similarly, minerals that are likely to have reacted with water or CO_2 are to be avoided.

10.5.2
Non-Destructive Techniques to Study Fluid Inclusions

10.5.2.1
Introduction

Several techniques can be used to study fluid inclusions. Some of these are destructive, opening and destroying the inclusions, and are not treated here. Others can be carried out without damaging the sample, although in many cases special thick polished sections are needed. The most important techniques to study fluid inclusions are thermal analysis (Sect. 10.5.2.2) and Raman spectroscopy (Sect. 10.2.2), proton microprobe (Sect. 10.4.2), ultraviolet microscopy for inclusions, which contain oil (Sect. 10.5.2.3), and infrared microscopy (Sect. 10.5.2.4) for opaque minerals.

10.5.2.2
Thermal Analysis – the Heating-Freezing Stage

For inclusions with a simple composition (less than four major components) composition and density are determined by thermal analysis on a *heating-freezing stage* that fits under a normal microscope. A chip of rock less than 1 cm in diameter, 100 μm thick, and polished on both sides without attached glass plates is heated to 300 °C, or even up to 600 °C if additional equipment is used. The sample can also be cooled down to –160 °C using liquid nitrogen (Roedder 1984; Shepherd et al. 1985). A single inclusion is observed during heating and cooling and the temperature at which a phase change occurs in the inclusion (melting, homogenisation to the liquid or vapour phase, or dissolution of a solid phase) is noted. Synthetic fluid inclusions can be used for calibration. If the precise composition of the inclusion is known, e.g. by Raman spectroscopy, the density can now be accurately determined. This density defines an *isochore*, a line of constant volume for the fluid in *P-T* space. If the inclusion did not leak, the metamorphic conditions at which the inclusion was sealed lie on this line; if either pressure or temperature during sealing is known, the other can be determined.

10.5.2.3
Ultraviolet Microscopy

When exposed to ultraviolet light (365 nm) the aromatic portion of a hydrocarbon fluoresces within the visible spectrum. The presence of fluid hydrocarbons (oil) in fluid inclusions can therefore be checked with ultraviolet microscopy. The colour is diagnostic of physical properties of oil such as composition and maturity or density, the latter expressed as degrees *API gravity* (Burruss 1987, 1991; Burruss et al. 1985; George et al. 1997, 2001). Fluorescence colour tends to change from yellow to blue as maturity or API gravity increases.

Differences in fluorescence colour of oil in different inclusions can be used to infer oil migration or oil mixing. If different types of fluorescence are observed in different trails or groups of inclusions, it is likely that several discrete water/oil migration events took place through the sample, e.g. due to hydrocarbon fractionation from a maturing source rock. This, in turn, may be used to predict gas or oil ratios within a reservoir. The method is powerful when used in combination with microthermometry.

10.5.2.4
Infrared Microscopy

Fluid inclusions also occur in opaque mineral phases but cannot be studied in transmitted light when inside a crystal. Fluid inclusions in some opaque minerals can be studied in transmitted near infrared light using microscopes with special infrared facilities (light source, lenses, objectives) and an infrared sensitive TV camera to transmit the infrared image to a monitor. This microscope can be fitted with a heating-freezing stage so that fluid inclusions in the opaque minerals can also be analysed for homogenisation temperature. The quality of infrared transmittance of a mineral strongly depends on its crystal structure and chemistry (Lüders 1996; Lüders and Ziemann 1999).

Inclusions, which are placed on the infrared path, partially absorb the light beam that is collected by an MCT detector. An infrared spectrum in absorbance units is obtained and can be Fourier transformed to produce the absorbed frequencies, and therefore the masses of the ions present. This is known as *Fourier Transform Infrared Microspectroscopy*.

10.6 Image Analysis

10.6.1 Introduction

Several powerful computer programs have become available over the last few years that allow 'automatic' analysis of certain microstructures (e.g. Masuda et al. 1991; Heilbronner-Panozzo and Pauli 1993; Heilbronner and Herwegh 1997; Heilbronner-Panozzo and Pauli 1994; Bartozzi et al. 2000). Microfabrics can be monitored with a video camera and the digitised image can be fed into a computer. The image can then be analysed in terms of the intensity and distribution of different colours. An image analysis program allows the calculation of percentages of particular colours visible in an image, and recognises sharp transitions in colour. Such transitions are commonly grain boundaries, and it is possible in some samples to identify individual minerals and mineral grains. With the use of filters, a single mineral may be selected, and the total percentage of this mineral in the image can be determined. In addition, the size and shape of the grains can be determined and plotted. Such techniques are obviously useful if large numbers of grain shapes, grain sizes and volumetric fractions of minerals have to be determined, e.g. the percentage, shape, size and orientation of plagioclase grains in a basalt. Unfortunately, even the best presently available programs have difficulties with samples in which the contrast between minerals is small, or where grain boundaries are of variable sharpness and lattice misfit angle, as in dynamically recrystallised rocks. Best results are obtained in rocks that consist of few, clearly distinct phases, e.g. pyrite grains in quartz, or quartzite with pores. Another disadvantage of image analysis is that most commercially available software is expensive, sometimes difficult to operate, and not adapted for geological applications[2]. However, *image analysis* programs are continuously being improved and are an important tool in microtectonic analysis. A single method is described below because it can be applied without access to expensive programs.

10.6.2 SURFOR and PAROR

A simple method to determine grain shape and orientation in a grain aggregate can be used without expensive software on a desktop computer (Panozzo 1983, 1984; Schmid et al. 1987). Drawings of grain boundaries are made from photographs or directly on a computer screen, and subdivided into segments of a fixed length, e.g. 2 mm on photographs. A projection line is then defined, all line segments are projected onto this projection line, and the total length of projections is added. This process is repeated after rotating the projection line over a small angle, e.g. 1°. In this way, 180 total projection lengths $A_{(\alpha)}$ are obtained for 180 angles of projection (α). This process can easily be automated with simple programming (program SURFOR: Panozzo 1983, 1984; Schmid et al. 1987). When $A_{(\alpha)}$ is plotted against (α) in a diagram, the symmetry of the distribution can be assessed. If grains are elongate and define a simple shape preferred orientation, the ratio of $A_{(\alpha)\max} / A_{(\alpha)\min}$ defines the elliptical ratio of the aggregate, which may be a measure of strain if grain boundaries were immobile (Sect. 9.2). The orientation (α) of $A_{(\alpha)\max}$ is the orientation of the foliation defined by the longest axis of the grains (program PAROR: e.g. Heilbronner and Bruhn 1998; Molli and Heilbronner 1999).

[2] For Macintosh users, there is a public domain image analysis program called "NIH Image", developed by the Research Services Branch (RSB) of the National Institute of Mental Health (NIMH), part of the National Institutes of Health (NIH). For PC and LINUX users there is now a similar Java program called "ImageJ".