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MICROBEAM X-RAY DIFFRACTION IN THE ANALYSIS OF MINERALS AND MATERIALS

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ABSTRACT

The microbeam X-ray camera records diffraction patterns from small amounts of loose or *in situ* material. It was used in many areas of materials research, including mineralogy, but did not find wide acceptance. Since the microbeam X-ray diffractometer was developed in the 1970s, it has evolved to a variety of commercially available and individual custom instruments. The microbeam camera has been used for *in situ* mineral identification and texture characterization of layer silicates and fine-grained products of alteration. Its use in conjunction with the electron microprobe and the transmission electron microscope has been particularly effective, in the first case, in the study of chrysotile asbestos deposits and, in the second case, in relating TEM images to larger-scale mineral textures. The microbeam diffractometer has found wider application than the microbeam camera. It is used for identification of minerals and other crystalline materials in fine-grained man-made materials ranging from paints to complex electronic components. The technique of strain measurement in fine-grained polycrystalline aggregates has been developed in the electronics industry; its application in the Earth Sciences to rocks such as mylonites, ultramylonites and fall-back breccias will give increased understanding to the processes that produce these rocks.

Keywords: microbeam X-ray diffraction, microbeam X-ray camera, microbeam X-ray diffractometer, diffractometry, position-sensitive detector, strain analysis, paint analysis, serpentine, clay minerals.

SOMMAIRE

La chambre de diffraction X conçue pour utilisation avec micro-faisceau produit des spectres de diffraction de quantités infimes de matériau en particules ou *in situ*. Cette technique a été utilisée dans plusieurs domaines liés à la caractérisation des matériaux, y inclus en minéralogie, mais son usage n'a jamais été répandu. Depuis le développement d'un diffractomètre à micro-faisceau, il y a une vingtaine d'années, la technique a beaucoup évolué, et est maintenant disponible sous forme d'instruments sur le marché ou construits sur mesure. La chambre à micro-faisceau permet une identification minéralogique *in situ* et une caractérisation des phyllosilicates et des produits d'altération à granulométrie fine. Elle a été utilisé comme complément aux études par microsonde électronique dans l'étude de gisements de chrysotile asbestiforme, et aussi aux études par microscopie électronique à transmission, pour réconcilier les observations faites à cette échelle aux observations faites à plus faible grossissement. L'utilisation du diffractomètre à micro-faisceau est plus répandue. Il a servi à l'identification de minéraux et autres phases cristallines dans des pigments de peinture et des composants électroniques. La technique de mesure de déformation dans les agrégats polycristallins à granulométrie fine a été développée dans l'industrie électronique; son utilisation dans les sciences de la terre pour étudier les mylonites, les ultramylonites et les brèches attribuées à un impact météoritique augmentera sans doute nos connaissances des processus impliqués dans la formation de ces roches.

(Traduit par la Rédaction)

Mots-clés: diffraction X avec micro-faisceau, chambre de diffraction X à micro-faisceau, diffractomètre X à micro-faisceau, diffractométrie, détecteur sensible de position, analyse de déformation, analyse de peinture, serpentine, argiles.

INTRODUCTION

Microbeam X-ray diffraction is a technique for the study of small samples of polycrystalline aggregates, fibers, single crystals and powders. An X-ray beam 5 to 100 μm in diameter is used in a specially designed camera or diffractometer, or in a standard camera. Samples may be very small and lie completely within the beam during irradiation, or may be much larger than the microbeam so that only a selected part of the sample is irradiated. In this second case, comparative studies of orientation, grain size and degree of strain of grains can be made within a single sample. It is this capability for *in situ* studies of grain-to-grain and textural relations that is the strength of the technique. Microbeam X-ray diffraction has been used in research in metallurgy (Hirsch & Kellar 1952, Gay & Kelly 1953, 1954, Gay *et al.* 1954), textile studies (Bergmann *et al.* 1948), medicine (Grynpas *et al.* 1991, Lucas *et al.* 1993), dentistry (Klein *et al.* 1951), petrology (Carrigy & Mellon 1964, Wicks & Whittaker 1977), mineralogy (Wicks & Zussman 1975) and materials science (DeHaven *et al.* 1991, DeHaven 1994).

Microbeam cameras were developed in the 1940s, but most were custom-built instruments that were never commercially produced. The camera most commonly used was designed by Chesley (1947) and produced commercially by Philips and Norelco (Bergmann 1959); it was used in several areas of research, but was overshadowed by the electron microscope in the 1950s. The microbeam camera was not used in mineralogical work until Carrigy & Mellon (1964) and Carrigy *et al.* (1964) used it to study clay-mineral cements in sandstones. Later, Wicks & Zussman (1975) and Wicks & Whittaker (1977) used it for identification of serpentine textures in serpentinized ultramafic rocks. Use of the microbeam camera in conjunction with the electron microprobe, to obtain information on both crystal structure and crystal chemistry (Wicks & Plant 1979), and with the transmission electron microscope (TEM), to provide information at an intermediate level of magnification (Wicks 1986), has proved particularly effective.

A microbeam diffractometer was designed and manufactured by Rigaku in the mid-1970s, and this generated a renewed interest in the technique, particularly in materials science (DeHaven *et al.* 1991). The addition of computers for instrumental control, data collection and analysis has opened exciting new possibilities for microbeam X-ray diffraction, and has brought the technique into the current mainline of X-ray diffraction. Because of its unusual geometry, the original instrument was difficult to align, and had flawed software. These problems discouraged use of the equipment. Redesign of the instrument in the late 1980s to incorporate a position-sensitive proportional-counter has significantly improved the instrument.

X-ray powder diffraction has long been the principal method for identification of minerals and other crystalline materials. In recent years, the technique has been further strengthened with the use of computers for data collection and analysis, and with the development of techniques such as Rietveld crystal-structure analysis. In contrast, X-ray microbeam diffraction has not been applied extensively in the Earth Sciences in spite of the development of new equipment and computer software. The purpose of this paper is to bring the potential of X-ray microbeam diffraction to the attention of Earth scientists.

INSTRUMENTATION

Microbeam camera

The Philips–Norelco microbeam X-ray diffraction camera (Fig. 1), was developed in the early 1950s (Bergmann 1959), and is still in use (Wicks & Zussman 1975); it is based on Debye–Scherrer geometry. The front of the camera contains the Pb-glass collimator and a specimen holder that pivots about a fixed axis (parallel to the X-ray beam) and traverses in one direction (perpendicular to the beam). The back contains a flat-plate film (35 × 40 mm) holder, a fluorescent screen and a Pb-glass direct-beam stop. The X-ray microbeam is collimated by a 10-mm long Pb-glass capillary (either 50 or 100 μm in diameter) cemented in a metal frame. Scattering of the X rays by air is significantly reduced by operating the camera in vacuum during long exposures.

The X-ray microbeam camera is ideal for the identification of fine-grained aggregates because the fine grain-size and random to semirandom distribution produce random to semirandom X-ray diffraction patterns. However, the sample is stationary in the X-ray microbeam, so that single grains produce randomly oriented single-crystal patterns that are difficult to interpret. Fragments of rocks up to 10 × 10 mm can be removed from thin sections and mounted on Mylar film in the sample holder, so that mineral grains and textural features can be studied *in situ* (Fig. 1). Fibers, small bundles of fibers, fragments and fine-grained powders can be mounted on double-sided tape in the sample holder. The relationship between 2θ and the position of a reflection on the film is given by $L = R \cot 2\theta$, where L is the sample-to-film distance, and R is the radius of the Debye–Scherrer ring. The recorded transmission diffraction patterns extend out to 45° 2θ (~2 Å with Cu radiation, 0.9 Å with Mo radiation) using the film holder with a sample-to-film distance of 15 mm, and to 56° 2θ (1.6 Å with Cu radiation, 0.75 Å with Mo radiation) with a sample-to-film distance of 10 mm. Although the latter gives a more complete pattern, it is tightly compressed so that resolution is low for closely spaced reflections. Diffraction patterns can be used for mineral identifica-

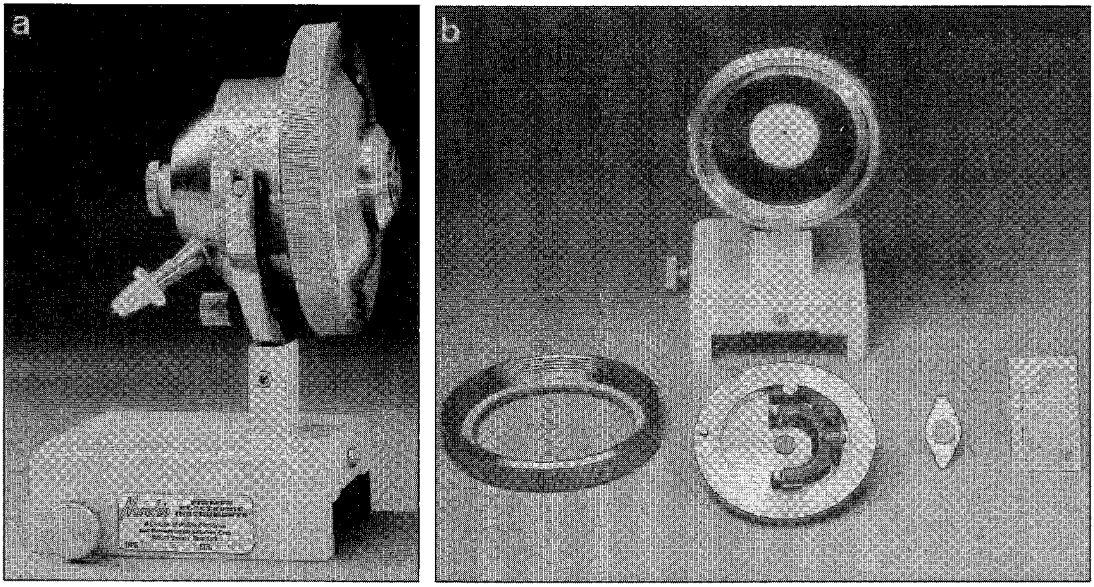

FIG. 1. a) Microbeam X-ray camera; the bottom edge of the stand is 8.4 cm. The back of the camera (left) contains the direct-beam trap and a tube for attaching a vacuum pump. b) The microbeam X-ray camera components, left to right, front row: 1) knurled ring that holds the two parts of the camera together, 2) front of the camera containing the specimen holder and the collimator (center), 3) fragment of thin section glued to Mylar film on an aluminum frame, and 4) thin section with fragment removed. Back row, the back of the camera containing the film holder with film.

tion, for analysis of mineral or fiber textures, and for estimates of grain size. The small size of the diffraction pattern, the short sample-to-film distance, and the irregular internal structure of the X-ray microbeam (see below) mean that measurements are of a semi-quantitative nature.

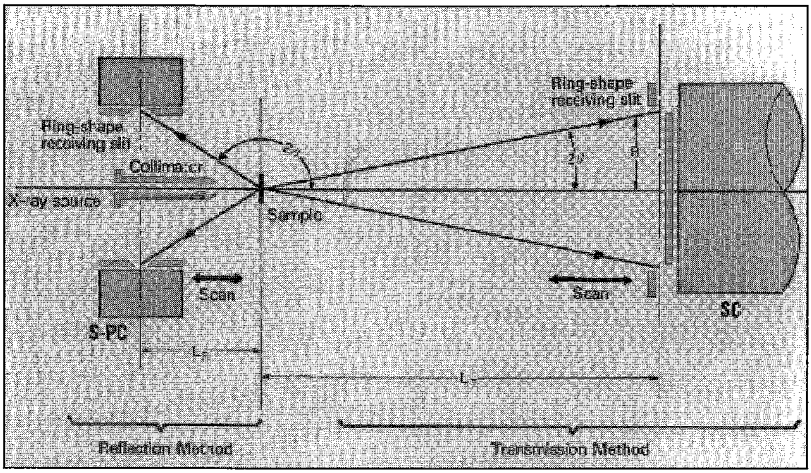

FIG. 2. A schematic drawing of the geometrical arrangement of the microbeam diffractometer showing the transmission mode to the right. SC is the scintillation counter. The back-reflection mode is shown to the left. S–PC is the sealed proportional counter. Courtesy of the Rigaku Corporation.

Scintillation microbeam diffractometer

The microbeam diffractometer developed by Rigaku is based on the same geometry as the microbeam camera (DeHaven *et al.* 1991). In the second generation of this instrument, the maximum sample-size is 10 × 10 × 10 mm. The position of the sample in the X-ray microbeam can be adjusted along *X*, *Y* and *Z* while observing the sample with a permanently mounted ×160 microscope. Thus, each sample can be placed at the same spot with respect to the microbeam, the horizontal axis of the diffractometer and the detector. The sample holder can be oscillated about the horizontal axis, and oscillated or rotated about the vertical axis. In transmission mode (Fig. 2), a scintillation counter with a circular receiving slit records each successive diffraction ring in its entirety over a 2θ range from 5 to 60° (~17 to 1.54 Å with Cu radiation, and ~8 to 0.71 Å with Mo radiation). In this mode, the diffractometer is similar to the microbeam camera, but has the added advantage that the sample can be oscillated and rotated so that useful diffraction patterns can be recorded from some single grains, although in general they are problematic. The diffractometer can also be operated in reflection mode (Fig. 2) using a sealed proportional counter that records 75% of a Debye–Scherrer ring through a 2θ range of 30 to 150° (~3.0 to 0.80 Å with Cu radiation, and ~1.4 to 0.37 Å with Mo radiation). The diffractometer is equipped with two 100-mm pinhole collimators 30 and 100 µm in diameter, which allow sample areas approximately 35 and 120 µm in diameter to be irradiated.

The transmission mode is better for general identification, and the reflection mode is better for the analysis of strain (DeHaven *et al.* 1991) and for texture analysis using pole figures (Steinmeyer 1986). The $\sin^2\psi$ method of strain analysis (Cullity 1978) is commonly used in microbeam diffractometry. The use of a computer for data analysis is essential with this instrument. Intensities recorded in this unusual geometry have to be recalculated to the intensity values of standard Debye–Scherrer camera or Bragg–Brentano diffractometer geometry so that phases can be identified using search–match routines of the powder diffraction files (PDF) produced by the International Centre for Diffraction Data (ICDD).

Position-sensitive microbeam diffractometer

The third-generation Rigaku microbeam diffractometer (Fig. 3) was extensively redesigned to take advantage of a curved position-sensitive proportional counter and standard Debye–Scherrer geometry (Araki 1989, DeHaven *et al.* 1991). The proportional counter can measure intensities simultaneously over 150° of arc, and through a 2θ range of –30° to +150°. As intensities are collected simultaneously over the entire range of the detector, exposure times are shorter. DeHaven *et al.* (1991) found that for the same sample and identical conditions of operation, a diffraction pattern could be collected in 1 hour with the position-sensitive microbeam diffractometer compared to 4.5 hours with the second-generation diffractometer. A third oscillation axis was added to the instrument (Fig. 3), and the resulting wide range of motions allows a full diffraction pattern to be collected from a single grain (Araki 1989). The sample holder can accommodate a sample up to 6 × 6 × 6 mm or as small as 5 µg. A motorized sliding stage permits two-dimensional analysis of the distribution of orientation and strain. There are four pinhole collimators 10, 30, 50 and 100 µm in diameter that irradiate sample areas 11, 31, 52 and 103 µm in diameter. Internally reflecting Pb-glass collimators also are available. Further details of operation, and assessments of the advantages and disadvantages of the instrument, are given in DeHaven *et al.* (1991).

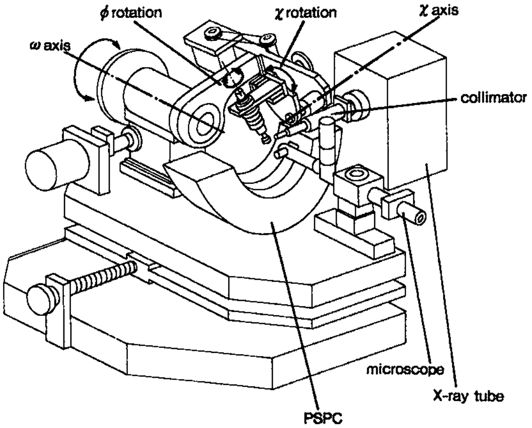

FIG. 3. Drawing of the third-generation microbeam diffractometer. PSPC is the curved position-sensitive proportional counter. Courtesy of the Rigaku Corporation.

X-ray sources

Microbeam cameras and diffractometers can be operated on sealed tube or rotating-anode X-ray sources. Exposures for the microbeam camera using sealed-tube Ni-filtered Cu radiation and the 50 µm collimator range between 8 to 18 hours for serpentine minerals (Wicks & Zussman 1975). The intensities of the diffracted X-rays from most mineral samples are just strong enough for the operation of the scintillation counter on the early versions of the microbeam diffractometer, although rotating-anode X-ray sources frequently have been used to significantly increase intensities and reduce exposure times. However, the new position-sensitive detectors, produced by several manufacturers (*e.g.*, Enraf-Nonius, Rigaku, Siemens), operate quite satisfactorily on sealed-tube generators, so the option is available to avoid the operational and maintenance costs of rotating-anode generators. Synchrotron radiation shortens exposure times further, and microbeam diffraction facilities are being developed at synchrotron radiation sources (Ohsumi & Miyamoto 1994).

Collimators

There are two types of collimators: pinhole collimators and internally reflecting collimators. Pinhole collimators are constructed in the same manner as the pinhole collimators used in any X-ray diffraction camera (Klug & Alexander 1954), except that the pinholes are smaller. Beam diameters of 30 to 100 μm are routinely used, but collimators down to 5 μm have been manufactured. Internally reflecting collimators were initially made of Pb-glass drawn into fine capillaries, usually between 20 and 100 μm in diameter. Recently, glass capillaries 500 mm long with parabolic inner surfaces and initial and final diameters of 22 and 7.5 μm, respectively, have been produced (Yamamoto & Hosokawa 1988).

Several factors must be assessed to determine the type of collimator to be used. These include the intensity of the X-ray source, the degree of beam divergence that can be tolerated, and the required uniformity of the internal structure of the beam. Pinhole collimators allow only X rays that are parallel (or very slightly subparallel) to the collimator axis to pass through to the sample. Internally reflecting collimators allow all X rays entering the collimator, many of them divergent from the collimator axis, through to the sample because the X rays are reflected off the internal glass surface and spiral through the collimator to increase the intensity of the beam. Thus, internally reflecting collimators produce beams that may be 3.5 (DeHaven *et al.* 1991) to 10^3 (Yamamoto & Hosokawa 1988) times more intense than a pinhole collimator of the same outlet-diameter. The beam produced by short internally reflecting collimators, such as the 10-mm collimators used in the microbeam camera, may have a complex internal structure (Bergmann 1959), but this is minimal in longer collimators. Internally reflecting collimators produce a beam with slightly more divergence than an equivalent pinhole collimator.

The type of experiment dictates the choice amongst these factors. If the objective is simple identification by comparison with known diffraction patterns, then the very short length (~10 mm), the complex and non-uniform internal structure of the beam (Bergmann 1959) and the greater angular divergence of the Pb-glass collimators in the microbeam camera are not significant factors (Wicks & Zussman 1975). If the objective is to accurately measure and map strain in a polycrystalline aggregate, beam intensity must be maximized, possibly by evacuating the collimator (DeHaven 1994), and beam divergence must be minimized, usually by using a long collimator placed close to the sample. Several long collimators have been built for this purpose, including a 371-mm-long pinhole collimator by DeHaven (1994), and internally reflecting collimators from 200 and 500 mm long by Nakazawa (1983), Nozaki & Nakazawa (1986), Yamamoto & Hosokawa (1988) and York & Xiao (1993). Commercially available collimators tend to be in the 100-mm range and are a reasonable length for routine identification and strain analysis.

Other microbeam X-ray techniques

Microbeam X-ray studies do not have to be confined to specialized cameras or diffractometers. The pinholes in the standard collimators in Gandolfi or Debye–Scherrer cameras can be modified to produce an X-ray microbeam. In the ROM laboratory, we use a modified collimator with an exit diameter of 100 μm for X-raying small samples. Grains or powder aggregates to 200 μm in diameter are stuck with silicone grease to the tip of a glass fiber 10 μm in diameter. A 100-μm (1 – 10 μg) sample typically requires 12 – 24 hours of exposure time with a small (57.3) mm camera. A 10-μm (1 – 10 ng) sample requires 5 days or longer, depending on sample crystallinity. Evacuating the camera during these long exposures reduces scattering of X rays and produces a cleaner pattern. Such small samples require care in centering, but they produce diffraction patterns of quite high resolution. Consequently, there is little to be gained by using a camera of larger diameter.

A standard Rigaku diffractometer also has been adapted to microbeam diffractometry for automated mapping of strain in samples up to 625 mm^2 by DeHaven (1994). The 371-mm evacuated pinhole collimator described above is used in conjunction with an automated *XYZ* sample stage. This instrument was developed to measure strain in thin-film read–write heads for high-density magnetic-disk drives, thin-film wiring on multichip carriers, metal–ceramic composite structures, and semiconductor gate electrodes, but it has obvious application to mineralogical problems.

Several laboratories have developed instruments for simultaneous identification of phases with microbeam X-ray diffraction and energy-dispersion analysis for elements present in the phases (Yamamoto & Hosokawa 1988, Nakazawa *et al.* 1990, York & Xiao 1993). These instruments use a ~10 μm microbeam to produce both diffracted and fluorescent X-rays, which are measured with solid-state detectors. An image plate can also be used for recording the diffraction pattern on the Nakazawa *et al.* (1990) instrument. The Yamamoto & Hosokawa (1988) instrument uses Bragg–Brentano geometry, and the Nakazawa *et al.* (1990) instrument uses Debye–Scherrer geometry. These instruments have features similar to an analytical high-resolution transmission electron microscope but operate at lower magnification, with the advantage of operating in air and on larger samples.

Small-sample X-ray techniques

Diffraction patterns can also be obtained from small samples using a variety of modified standard instruments. Hill & Madsen (1991) have modified a Philips Bragg–Brentano diffractometer to hold <2 mg of sample in a 0.5-mm-diameter Lindemann glass capillary mounted along the central θ axis of the diffractometer, converting it to Debye–Scherrer geometry. Counting times are about five times longer than in Bragg–Brentano geometry, owing to the smaller sample-size, but excellent patterns, suitable for Rietveld analysis, are obtained. F.C. Hawthorne (pers. comm.) has found that diffraction patterns of a quality good enough for phase identification can be obtained from a Siemens diffractometer in transmission mode with a sample as small as 5 mg.

Clay minerals are usually characterized with a diffractometer. A standard series of tests is applied at various humidities and in different solutions to expand the clays; the samples are also heated to various temperatures to collapse the clays. Clays usually occur in great abundance, but in some cases only small amounts of material are available. As little as 10 μg can be placed in a 0.1-mm-diameter Lindemann glass capillary (producing a volume of sample ~0.01 mm^3) and X-rayed in a standard 114.6-mm Debye–Scherrer camera using a line focus X-ray source. All the standard expansion and moderate-temperature heating X-ray studies can be done on the sample while it is in the glass capillary. The clay-mineral particles are in a random (or near-random) orientation in the capillary, and produce a significantly more complete diffraction-pattern than the highly preferred orientation of the clay particles on a diffractometer mount.

SAMPLE PREPARATION

In situ studies are one of the main strengths of the microbeam diffraction technique, and thus procedures of sample preparation have been developed that cause minimum disruption to the sample. The sample size is limited by the sample holders, 10 × 10 mm in the microbeam camera (Wicks & Zussman 1975), 10 × 10 mm or 6 × 6 mm in commercially designed microdiffractometers (DeHaven *et al.* 1991), and 25 × 25 mm in a microdiffractometer specially designed by DeHaven (1994). Samples of the appropriate size are cut from electronic components and mounted directly in the microdiffractometer (DeHaven 1994). Samples of rock are removed from thin sections made with an adhesive like Lakeside 70 and mounted in a microbeam camera (Carrigy & Mellon 1964, Wicks & Zussman 1975) or microdiffractometer. The advantage of the microbeam camera is that the front of the camera fits on the stage of a petrographic microscope so that the part of the sample to be X-rayed can be precisely aligned with the collimator. The alignment of textural features through ×160 microscope in the microdiffractometer is less certain.

The preparation of samples from painted objects is usually done in one of two ways (Corbeil & Sirois 1994). Paintings usually have a few layers of paint, but other painted works, such as polychrome sculptures or architectural elements, may have been repainted several times, and have ten or more layers. A small sample of paint is removed from an object, embedded in a polyester-casting resin and polished flat on one side to reveal the sequence of paint layers. It can then either be mounted directly in the microdiffractometer, or a thin section, approximately 10 μm thick, can be made with a microtome.

APPLICATIONS

There is great potential for the application of microbeam X-ray techniques in the Earth Sciences, particularly as a greater selection of X-ray microbeam equipment is now available than ever before. Also, the technique is complementary to many other microbeam analytical techniques described in this volume.

Layer silicates

The first microbeam X-ray work in mineralogy was done on authigenic kaolinite, illite, chlorite and montmorillonite cements in sandstones by Carrigy & Mellon (1964). On the basis of their success, microbeam-camera techniques were applied to the long-standing problem of the identification of serpentine minerals in the complex textures observed in thin sections of serpentinized ultramafic rocks (Wicks & Zussman 1975, Wicks & Whittaker 1977, Wicks *et al.* 1977). As a result of this work, criteria for the visual identification of serpentine minerals in thin section were established (Wicks & Whittaker 1977). Most serpentine pseudomorphic after olivine, pyroxene, amphibole, talc and chlorite is composed of lizardite or, less commonly, lizardite intimately associated with brucite. Antigorite and chrysotile also form pseudomorphic textures, but much less commonly than lizardite. Nonpseudomorphic serpentine textures are more varied. Antigorite occurs most commonly in nonpseudomorphic textures in serpentinites in prograde metamorphic terranes. In chrysotile asbestos deposits, textures are extremely complex, with chrysotile, lizardite and antigorite forming a host of textures either separately or intimately associated with one another, and demonstrate the subtle differences in conditions of crystallization that produce each of the three minerals. Microbeam X-ray studies are still essential for any comprehensive study of serpentine minerals in chrysotile asbestos deposits (Wicks & Whittaker 1977, Wicks & O'Hanley 1988, O'Hanley & Wicks 1995).

The microbeam X-ray camera and the electron microprobe offer a powerful combination that provides both crystal-structure and crystal-chemical information on the same mineral. Wicks & Plant (1979) showed that many samples of antigorite, chrysotile, and lizardite have significant substitution of Fe and Al for Mg and Si. Chrysotile has the smallest range, and lizardite, the greatest range, with maximum FeO contents of 9% and 16 wt%, respectively. Antigorite is intermediate, with up to 12% wt% FeO. Aluminum is less abundant (<1% Al_2O_3) than Fe in most serpentine minerals. However, lizardite, with up to 19% Al_2O_3, and antigorite, with up to 3% Al_2O_3, were analyzed, but few samples of chrysotile with more than 1% Al_2O_3 were found. In addition to establishing compositional ranges for the serpentine minerals, a great deal was learned about the migration of elements during both prograde and retrograde serpentinization. Also, the complex and unique environment of serpentinization in chrysotile asbestos deposits was shown for the first time. The success of this study led to similar combined studies of the Cassiar chrysotile asbestos mine (Wicks & O'Hanley 1988, O'Hanley & Wicks 1995). This would not have been possible without microbeam X-ray diffraction.

Detailed studies of lizardite-1T formed by pseudomorphic replacement of enstatite, made with a microbeam camera and single-crystal rotation camera, have been used to provide a basis for interpreting TEM observations from similar materials (Wicks 1986). Lizardite occurs in several orientations (including random) with respect to the host enstatite. The microbeam camera produces results at a scale of observation intermediate between those of traditional X-ray diffraction and TEM. The resulting understanding of the relation of product to parent provides a framework for the interpretation of the TEM results.

Ilmenite alteration

Meglio (1979) and Mathis & Sclar (1982) used a microbeam X-ray camera in conjunction with electron diffraction, electron-microprobe analysis, and Gandolfi and powder diffraction to study detrital grains in titanium-rich black-sand deposits. They showed that oriented polycrystalline aggregates or pseudo-single crystals of pseudorutile had formed as pseudomorphs after ilmenite that had contained exsolved hematite.

Paint analysis

Analysis of paint from an early eighteenth century sculpted décor is a more recent example of applied mineralogy using a third-generation Rigaku microbeam diffractometer mounted on a rotating anode generator (Corbeil & Sirois 1994). The original paint materials and successive layers of paint were analyzed to document changes in the materials used over time. The décor, of which the main components are two retables and a pulpit, was sculpted and assembled between 1726 and 1736 by Pierre-Noël Levasseur for the chapel of the Ursulines convent in Québec City. The samples typically were found to contain five to twelve layers, ranging in thickness from 10 to several hundred µm. It was possible to analyze an area of each layer (using a 30-µm collimator) without significant interference from adjacent layers.

Figure 4 illustrates the diffraction patterns of the

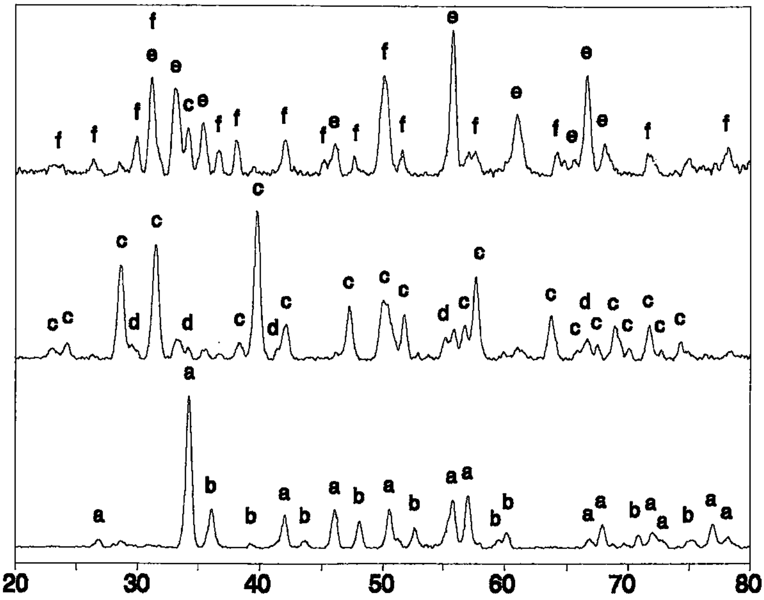

FIG. 4. Microbeam diffraction patterns from 20 to 80° 2θ obtained from calcite (a) and dolomite (b) in the first layer, lead white (c) and lead carbonate (d) in the fourth layer, and zinc sulfide (e) and barium sulfate (f) in the fifth layer of the paint sample. Typical operating conditions for Co $K\alpha$ radiation were 45 kV, 160 mA, and collection times of 1 to 2 hours.

first, fourth, and fifth layers of paint obtained from a sample from the pulpit containing five layers of paint. The first layer, a ground directly applied to the wood, contains a filler of calcite and dolomite; the fourth contains the pigment lead white [$Pb_3(CO_3)_2(OH)_2$] and lead carbonate ($PbCO_3$); the fifth layer is made primarily of lithopone, a mixture of zinc sulfide (ZnS) and barium sulfate ($BaSO_4$).

An interesting feature is the change in materials used in the successive layers. The paint (layer 2) applied immediately over the ground is made up of lead white. The object was repainted twice using lead white (layers 3 and 4), but the final overpaint (layer 5) contains lithopone rather than lead white. As lithopone was first introduced in the paint industry at the end of the nineteenth century (Wilkinson 1973), the last repainting of the décor was done after that time. This reflects the change in paint formulation that occurred owing to the growing health-related concerns about the use of lead-based paints.

Strain in electronic components

Scientists active in the semiconductor industry have made extensive use of microbeam diffractometry to study strain in polycrystalline metal–ceramic composites and other materials in electronic devices. Strain has been measured in a microelectronic package with 125-µm-diameter pads composed of successive layers of Au–Ni solid solution, Ni and Mo fused to alumina (Goldsmith & Walker 1984). In another study, a problem of cracking and component failure in an alumina substrate that held contact pads at 100 or 250 µm intervals was solved after measuring the strain around the pads using a microbeam diffractometer with a 30-µm collimator and Cu radiation (Goldsmith & Walker 1984). The same study using conventional diffractometry gave strain measurements near zero. Strain measurements have been made on spots as small as 10 µm in an alumina substrate adjacent to a Mo-to-alumina interface of Mo-dots 25 µm in diameter (Walker & Goldsmith 1978). Tangential strain was recorded in the alumina around Mo-dots, and linear strain was found in alumina between Mo-dots. All the studies described above were made using scintillation or proportional counters. Several studies of strain have been made using film or an image plate in back-reflection mode (Fujii & Kozaki 1993).

The advantages of microbeam diffractometry over conventional diffractometry in the measurement of strain in small electronic and industrial devices has been demonstrated by DeHaven *et al.* (1991) in a comparative study of the two techniques. A test sample was manufactured, composed of successive elongate layers of Cu, followed by a second Cu-layer and capped with a Ni-layer, all on a ceramic substrate. Each layer of metal was several micrometers thick, and defects were introduced into the second layer. Strain was measured across the width and along the length of the structure using a conventional diffractometer and a microbeam diffractometer with a 50-µm collimator. Strain was shown to be much greater along the length of the structure than across the width with both techniques. However, where the conventional diffractometer gave a single average measurement across the width of the structure, the microbeam diffractometer results clearly showed a strain gradient with a sharp drop in strain at the edge.

Strain in minerals

The success of these studies in the semiconductor industry indicates that this technique can be applied to significant problems in the Earth Sciences. For example, strain in fine-grained polycrystalline aggregates such as mylonites, ultramylonites and fall-back breccias could be measured using microbeam diffractometry and mapped by customized microbeam X-ray diffractometry such as the automated instrument developed by DeHaven (1994). Much could be learned about the processes that produce these rocks using this technique.

SUMMARY

Microbeam X-ray diffraction is a powerful tool for studies in the Earth Sciences, particularly if supported by other microbeam techniques. Its use for *in situ* identification of fine-grained mineral aggregates in thin section is well established. Recent developments in microbeam X-ray instrumentation have expanded the nature of the problems that can be studied. Coarse-grained aggregates and single crystals can now be manipulated so that complete diffraction patterns can be obtained. This means that almost any crystalline material can be studied, but these developments have not yet seen extensive use in the Earth Sciences. The use of microbeam X-ray diffraction for the measurement of strain has the potential for important new studies of geological materials. The technique has been extensively developed by material scientists, and its application in the Earth Sciences should give new insight into the extent and mechanisms of deformation in rocks and minerals.

Although Rietveld structure analysis has not been done using microbeam X-ray diffraction as yet, the increasing quality of the diffraction data being produced with the microbeam approach should soon make it possible in the near future.

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