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TRANSMISSION ELECTRON MICROSCOPY OF FINE-GRAINED PHYLLOSILICATES IN ULTRA-THIN ROCK SECTIONS

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Abstract—A method is described for preparing electron-transparent sections of fine-grained argillaceous rocks suitable for making transmission micrographs. A sediment and a slate are used as examples. Sections perpendicular to bedding or cleavage yield diffraction patterns with clearly defined 00*l* reflections. These allow immediate identification of 7, 10 and 14 Å structures. The combination of detailed textural information with structural identification of individual phyllosilicate particles affords a powerful method for the investigation of late diagenetic and early metamorphic changes in sediments.

INTRODUCTION

In his review of the applications of transmission electron microscopy to mineralogy, McConnell (1967) states, "Traditionally, it has been usual to examine mineralogical specimens by making use of finely ground material, which may be deposited from suspension on a suitable supporting film on a standard electron microscope grid." Fine-grained phyllosilicates prepared in this way inevitably end up with their basal planes parallel to the grid plane. The well-developed basal cleavage in all phyllosilicates also ensures that electron-transparent sections produced by grinding are all morphologically alike.

As well as denying the possibility of obtaining textural information, therefore, these methods make it virtually impossible to set up diffraction conditions such that phyllosilicate (00*l*) reflections may be observed. These reflections are of the greatest interest to clay mineralogists. Diagnostic procedures rely to considerably extend on documenting the response of (00*l*) reflections (X-ray powder diffractometry) to various thermal and chemical treatments.

ION BOMBARDMENT THINNING

Carefully prepared cleavage flakes have been used successfully in substructure investigations of minerals. McLaren and Phakey (1965) and McLaren *et al.* (1967) studied quartz, Fleet and Ribbe (1965) and Nissen (1967) studied feldspars, and glasses were investigated by James and McMillan (1968). The particular problems associated with phyllosilicates, however, are well illustrated by Eckhardt's (1958) work on possible superlattice structures in chlorite. He observed two chlorite electron diffraction patterns rotated by 32·2° about [001] from what appeared to be a single grain. In addition to the expected two sets of spots he found new ones, supplementing the two patterns to produce a new pseudo-hexagonal pattern. He found it impossible to decide conclusively whether this is due to a superlattice of a single crystal or to double diffraction by twins with twinning on the basal planes.

Paulus and Reverchon (1961) laid the foundations for solving these problems by perfecting the technique of ion bombardment thinning. The method is described in considerable detail by Barber (1970) and has been used in a number of investigations of mineral substructure by Tighe (1970), McLaren *et al.* (1970), Blacic and Christie (1972), and also of lunar rocks by Radcliffe *et al.* (1970), Christie *et al.* (1971), Barber *et al.* (1971), and Barber and Price (1972). To our knowledge, however, the technique has not previously been applied to the study of fine-grained phyllosilicate rocks. The potential of the method in this field would seem to be considerable. Textures may be observed directly, and selected area electron-diffraction allows for rapid identification of different phyllosilicate groups as a consequence of large differences in *c*-dimension from one group to another.

Two rock types were chosen for study. The first is a carbonate concretion in a shale of West-

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phalian age taken from a fresh exposure in industrial clay quarrying operations by the Hepworth Iron Company at Hazlehead, near Penistone, England (Sample CHH8). The shale contains quartz, illite, and kaolinite with subsidiary chlorite. In the concretion, grains of these minerals are cemented by diagenetic siderite. The sample was cut normal to bedding, thus providing the greatest possible number of phyllosilicate grains at right angles to the section.

The second is a Middle Cambrian purple slate taken from a quarry of the Dorothea Slate Quarry Company, near Nantlle, Caernarvon, North Wales (Sample W22). The slate consists of muscovite, chlorite, quartz, albite, and hematite. The specimen is again so oriented that the greatest possible number of muscovite and chlorite grains have their basal planes normal to the section.

EXPERIMENTAL

Technique

Rock slices, 30 μm or thinner (depending upon the friability of the material) and polished on both sides, are prepared by normal petrographic methods. It is essential that the slice be mounted by some readily soluble medium; Canada balsam is adequate. The thin sections are then examined by normal petrographic microscopy and areas selected for further thinning. Three-millimeter cores are taken of the selected areas by ultrasonic drill. Copper electron-microscope grids (75 mesh) are then attached to the upper disc surface by some rapidly setting cement which is insoluble in alcohol or acetone. The whole rock slice is then immersed in one of these solvents until the grid-supported discs separate from the glass base. When removed and dried these discs are ready for ion beam thinning.

The disc is mounted in a stainless steel holder within the ion beam thinning unit (Fig. 1) and tilted about 15° to the plasma beam (Heuer *et al.*, 1971). A direct current, glow discharge, argon plasma provides two ion beams which impinge simultaneously on both surfaces of the specimen. This is rotated slowly to provide uniform thinning. The ion bombardment removes an average of three to four microns of the specimen surface every hour. From time to time throughout the thinning by ion bombardment, the specimen is examined through a low-power microscope mounted as part of the apparatus. Specimen thinning is ceased when a few small holes appear between the copper grid bars (Fig. 2). Examination under the petrographic microscope then shows the presence of very thin areas surrounding the perforations of the sample. A thin layer of carbon is evaporated onto this ultra-thin specimen to avoid surface charging during electron optical examination (JEM 120KV instrument used in this work). The camera constant (λL) for the electron microscope must be determined using a suitable standard foil to allow calculation of d-values for individual grains in the specimens. Cementing of a copper grid on the specimen not only provides a mechanical support to the specimen but is also advantageous because it usually leads to multiple perforations of the specimen in

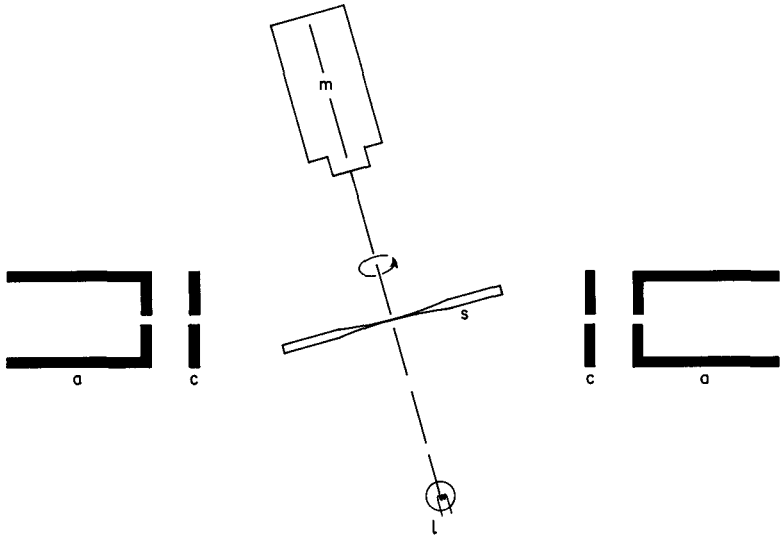


Fig. 1. Schematic diagram of ion bombardment assembly: a = anode, c = cathode, s = specimen, l = light, m = microscope.

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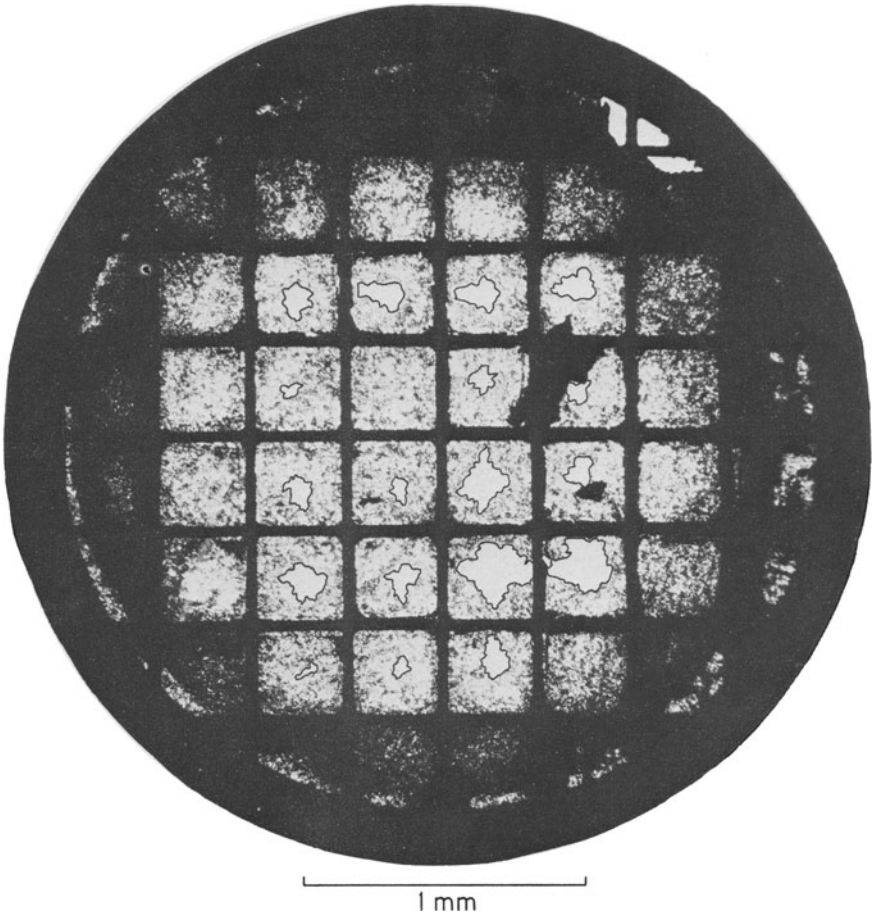


Fig. 2. Ultra-thin section of portion of a siderite nodule in shale through the petrographic microscope. The sample is thinnest near the holes (outlined with an ink line) in the central regions of squares between copper wires of supporting grid.

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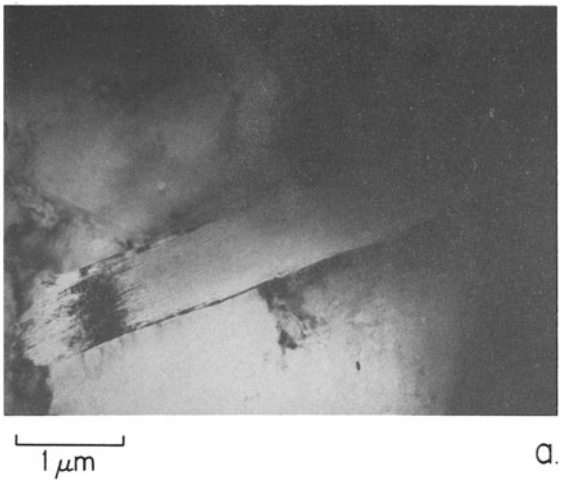
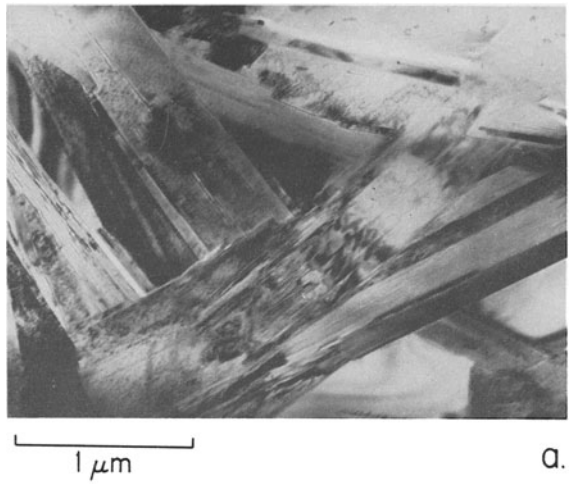
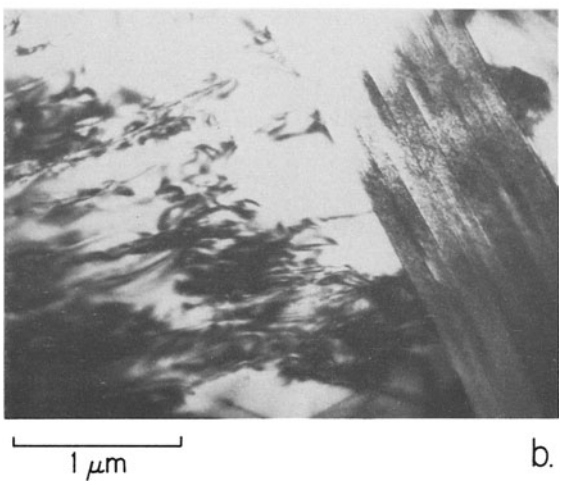


Fig. 3. Transmission electron micrographs of detrital mica grains in siderite matrix. Clay-ironstone concretion, Westphalian, from quarry of Hepworth Iron Company, Penistone, England, Sample CHH8.





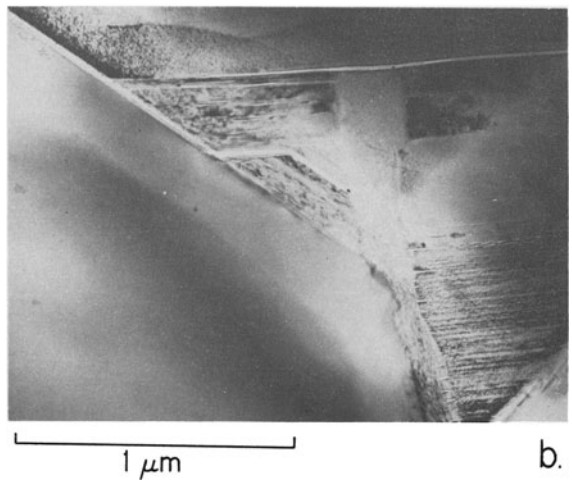


Fig. 4. Transmission electron micrographs of slate, cut normal to cleavage. Middle Cambrian purple slate, Dorothea Slate Quarry Company, Nantlle, Caernarvon, North Wales, Sample W22: (a) muscovite, chlorite, and quartz in the interstitial spaces; (b) quartz grain surrounded by muscovite and chlorite.

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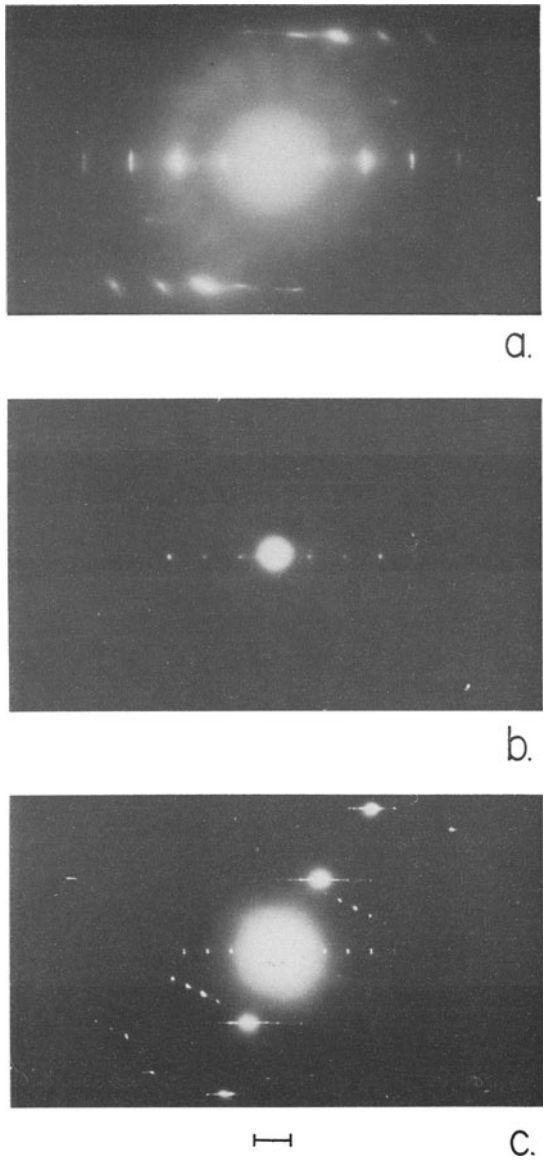


Fig. 5. Selected area electron diffraction patterns showing 00*l* reflections from phyllosilicates with, (a) 7·1 Å, (b) 10·0 Å, (c) 14·2 Å basal spacings. The grains producing the patterns were (a) kaolinite, (b) a member of the mica group, (c) a member of the chlorite group. The scale bar shows the reciprocal of 10 Å.

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several grid squares and thus provides many thin areas throughout the specimen. When unsupported specimen foils are thinned they attain a biconcave shape with a single central hole, and the total thin area is less. The grid squares can also be used as markers to help in positioning a selected mineral grain in the electron microscope. Sometimes the copper grid bars themselves become electron transparent by thinning, this then provides a convenient internal standard to allow diffraction studies.

Siderite concretion

Transmission electron micrographs of the concretion (Sample CHH8) reveal the presence of a large number of phyllosilicate flakes with thicknesses ranging from less than 0·1 to about 3 μm embedded in the siderite matrix. The identification of these flakes using the selected area diffraction patterns is described later in this section. The flakes have various orientations in the siderite matrix, but a considerable number of them were found to have their basal planes normal to the plane of the section (see Figs. 3a and b). We investigated such phyllosilicate flakes in particular because their selected area diffraction patterns reveal clearly defined (00*l*) diffraction spots of the type shown in Fig. 5. Fig. 3a is the transmission electron micrograph of a mica grain embedded in a large single crystal of siderite. The grain is probably detrital and has worn, frayed-looking boundaries. It gives an electron diffraction pattern of the same type as the one shown in Fig. 5b. The pattern has a 10 Å basal *d*-value, can be indexed, and shows that the crystal is a mica. The spots are somewhat diffuse, and this may be due to weathering alteration. The matrix is siderite. Although the grain boundaries of the mica show signs of mechanical attrition, they are not strained and are free of inclusions. There is no evidence of chemical corrosion at the time when the mica grain was included into the siderite.

Figure 3b shows another mica grain according to the selected area diffraction pattern proving spacing along [001] of $d = 10$ Å. The spots in the pattern are sharp, and it seems that the grain is not affected by chemical alteration. Although the mica flake is probably detrital, no signs of mechanical wear can be seen along its sharp, strain-free boundaries parallel to the basal plane.

Slate

Figure 4a is a transmission electron micrograph of a cluster of mica and chlorite grains, all with basal planes nearly orthogonal to the section. Interstices between phyllosilicate flakes, forming triangular areas without fine internal structure patterns, consist of quartz. Sharp, smooth, grain boundaries are almost exclusively determined by the basal plane of one of the neighboring grains. They indicate recrystallization, followed by growth of quartz, filling left-over spaces. Mica and chlorite were identified in selected area electron diffraction patterns like those of Fig. 5, taken in a subarea of the area of illustration. However, there is no way of distinguishing the photographic images of individuals of one of these two mineral species from those of the other.

Figure 4b shows a large quartz grain with smooth, angular boundaries. Variously oriented muscovite and chlorite grains abut against a single, straight quartz surface. It seems that the quartz grain, possibly an original detrital grain, acquired idiomorphic faces by recrystallization, either before the growth of neighboring phyllosilicate grains or at their expense. The interrelations between the phyllosilicate individuals are as in Fig. 4a. Two generations of quartz may thus be distinguished tentatively in the slate, one grown before, another after the bulk of the phyllosilicates attained their present shapes and configuration. Other structural and textural aspects of Sample W22 are described by Oertel *et al.* (1972) and Oertel and Phakey (1972).

Selected area diffraction

Since selected area of microdiffraction enables electron diffraction patterns to be obtained from chosen areas as small as 0·2 μm in dia., very small phyllosilicate crystals can produce adequate electron diffraction patterns. Hence, a particular phyllosilicate particle seen at high magnification in the electron microscope may be selected from a number of other particles. Thus, it is possible to obtain an analysis of the relationship between crystallography and morphology for selected areas of interest.

The electron diffraction patterns shown in Fig. 5 were obtained from phyllosilicate grains in the concretion (CHH8, Fig. 5a) and slate (W22, Fig. 5b and c) following the procedure described by Agar (1960). Since these crystals have their basal planes nearly normal to the section, the systematic row of (00*l*) reflections is very pronounced. The interplanar spacing, *d*, of the planes giving rise to the (00*l*) reflections is readily obtained from the relation $d = \lambda L/R$, where λL is the camera constant and R the distance of the diffraction spots from the center of the pattern. The camera constant λL was determined using a thin foil of polycrystalline copper as a standard. The (00*l*) reflections in Fig. 5a, b, and c are caused by spacing of $d = 7{\cdot}1$, 10·0 and 14·2 Å, respectively; hence, the phyllosilicates could be kaolinite, mica and chlorite. These determinations have been confirmed in a number of cases when the electron diffraction

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patterns were indexed more fully. All three 7, 10, and 14 Å phyllosilicate structures were observed in the shale concretion (CHH8), only 10 and 14 Å structures in the slate (W22).

CONCLUSIONS

Ion bombardment thinning can yield electron transparent thin foils of shales and slates without preferential loss of any of the constituent grains and without structural changes. When thin sections are prepared perpendicular to bedding or cleavage, the selected area diffraction patterns yield clearly defined (00*l*) reflections with the help of which one can easily identify 7, 10, and 14 Å structures. Hence, it is possible to investigate the density, distribution, and texture of phyllosilicates in rocks by comparing the transmission electron micrographs and their selected area diffraction patterns. The technique also allows the textural study of fine-grained shales and slates. It is also significant that one can with this technique study crystal structure aspects of single clay particles as opposed to X-ray powder patterns which average structural data over normally inhomogeneous bulk samples. Another advantage is the possibility of studying clay flakes *in situ* without danger of structural modifications induced by sample preparation.

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Résumé—On décrit une méthode pour préparer, à partir de roches argileuses à grain fin, des coupes transparentes aux électrons adaptées à la micrographie par transmission. On prend comme exemples un sédiment et une ardoise. Des coupes perpendiculaires à la stratification ou au clivage donnent des diagrammes de diffraction comportant des réflexions 00*l* clairement définies. Ces réflexions permettent l'identification immédiate des structures à 7, 10 et 14 Å. La combinaison d'une information texturale détaillée et de l'identification de la structure des particules individuelles de phyllosilicate constitue une

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méthode puissante dans l'étude des modifications subies par les sédiments à la suite d'une diagenèse avancée et d'un métamorphisme faible.

Kurzreferat – Es wird eine Methode beschrieben für die Herstellung elektronentransparenter Schnitte feinkörniger Tongesteine, die geeignet sind für die Erzeugung von Transmissionsmikrographien. Als Beispiele werden ein Sediment und ein Schiefer verwendet. Schnitte in Normalrichtung zum Lager oder Spalt ergeben Beugungsbilder mit klar definierten 00*l* Reflexionen. Diese gestatten unmittelbare Identifizierung von 7, 10 und 14 Å Gefügen. Die Kombination detaillierter Information über das Gefüge mit struktureller Identifizierung individualler Phyllosilikatteilchen ergibt eine wirksame Methode für die Untersuchung spät diagenetischer und früh metamorphischer Veränderungen in Sedimenten.

Резюме — Описывается метод приготовления «прозрачных» для электронов шлифов тонкозернистых глинистых пород пригодных для электронномикроскопических снимков в проходящем пучке. Для примера применялись осадок и сланец. Профили перпендикулярные к наслоению или сланцеватости дали диффракционную картину с ясно выраженными отражениями 00*l*-го порядка, которые допускают непосредственную идентификацию структур 7, 10 и 14 Å. Это сочетание детальной информации о текстуре со структурной идентификацией индивидуальных частиц филлосиликата представляет отличный метод для изучения последних диагенетических и ранних метаморфических изменений в осадках.

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