Minerals and the electron microscope

THE HALLIMOND LECTURE, 1986

J. ZUSSMAN

Department of Geology, University of Manchester, Manchester M13 9PL

Abstract

The transmission electron microscope is now used in a great variety of mineralogical and petrological contexts. The development of such applications over the past thirty years is illustrated by reference mainly to studies on serpentine and amphibole minerals.

KEYWORDS: electron microscope, serpentine, amphiboles.

MY original intention was to give a rather broad review of the very wide range of useful applications of electron microscopy to Earth science in general and mineralogy and petrology in particular. An illustration of this range is provided in Table 1 which lists many aspects of mineralogy that have been studied by electron microscopy. Another tabulation could have been by minerals, but it is probably true that all the main mineral groups have been subjected to some sort of electron microscopic study by now.

The grouping in Table 1 is not precise and exclusive; some topics would fit in more than one group and there are obvious inter-connections, e.g. dislocations and grain boundaries with strain, stacking faults with polytypes, anti-phase domains with polymorphic transformations, chain-width errors with super-structures.

After realising that some particular aspects of electron microscopy are being reviewed by other contributors to this conference (e.g. high-resolution work, convergent beam methods, deformation, and elemental analysis) I decided to be more selective in my own coverage and deal with those areas closer to my own research interests and experience, some recent and some rather ancient! To some extent then my talk will have a historical perspective and be autobiographical, but 'auto' in a very broad sense, since the work I recount has depended very much on research students, and other co-workers who have used electron microscopy in Manchester at one time or another. Among these I would mention particularly Maryla Dorling, Barbara Cressey, Martin Hampar and Jim Chisholm. I need

also to restrict myself to transmission as distinct from scanning electron microscopy.

My paper will thus be mainly, not entirely, about serpentine and amphibole minerals, but although this may seem restrictive, it will allow me to illustrate a fairly wide range of those features observable by electron microscopy listed in Table 1.

When I first chose (around 1953) to work on the serpentine minerals it was purely as a mineralogical or even crystallographic curiosity. I had been advised that the serpentines were little understood. I had little idea of their widespread occurrences,

Table 1.

Some uses of Electron Microscopy

Phase recognition	Dislocations
Determination of symmetry	Stacking faults
High resolution of structures	Antiphase domains
Superstructures	Chain-width errors
	Chain-repeat errors
Exsolution	Textures of aggregates
Twins	Crystal sizes & morphology
Polytypes	Grain boundaries
Mixed layers	Voids
Polysomes	Strains

Polymorphic transformations

Reactions (metamorphic, hydrothermal,

alteration).
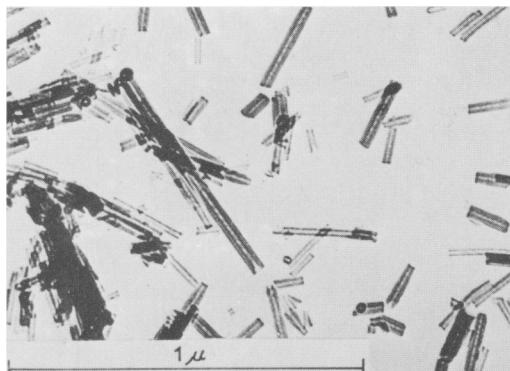
FIGS. 1 and 2. FIG. 1 (left). Electron micrograph of synthetic chrysotile (from Whittaker and Zussman, 1971).
FIG. 2 (right). High-resolution electron micrograph of cross-section of chrysotile asbestos (Yada, 1971).

and the question of health hazards from asbestos did not loom as large. I certainly did not expect to hear of the presence of serpentines in meteorites. The structure of chrysotile was known and that of antigorite had been hinted at, but there were many varieties of serpentine that did not fall clearly into either category. Conventional methods of study (optical and X-ray diffraction) were hampered by fine grain size and disorder of various kinds. It became apparent that electron microscopy and diffraction lent themselves well to the examination of such specimens, and I had access to an instrument and help from Dr Joe Comer at Pennsylvania State University while working there with the late Professor G. W. Brindley in 1956.

At about this time, although some electron micrographs of minerals had been published, mineralogists (e.g. Malcolm Ross in the U.S.A.; Alan Gard, U.K.; and Boris Zvyagin, U.S.S.R.) were just beginning to use electron diffraction in addition, and of course without the involvement of diffraction only a superficial interpretation of micrographs is possible.

I would like to recount briefly the story of serpentine structures. For chrysotile, in spite of some convincing theory and X-ray work by E. J. W. Whittaker (e.g. 1953, 1954) indicating the tubular structure, the longitudinal views of fibrils in electron micrographs (Fig. 1) though they looked like hollow or partially filled tubes, were still treated with caution, some suspecting that they were artefacts of specimen preparation. All doubts were dispelled however by the first high-resolution electron micrographs (e.g. Fig. 2) of cross-sections produced by Yada (1967).

X-ray diffraction patterns had been obtained from bundles of fibrils; in contrast, electron diffraction patterns were obtained from single fibrils
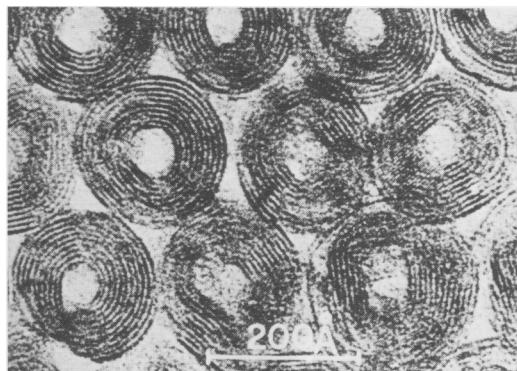
(Zussman et al., 1957) and readily showed for each one of them whether it had an 'ortho' or 'clino' sequence of layer stacking.

The flat-layer variety of serpentine, lizardite, exists commonly in fine-grained massive serpentine and less frequently in reasonably sized 'single crystals'. For these, X-ray work (Rucklidge and Zussman, 1965) showed the basic $5 \times 9 \times 7$ Å cell and structure, and the presence of some saucer-like distortion and stacking disorder. The more common fine-grained lizardites were suitable only for powder X-ray methods, but simple electron diffraction patterns were readily obtained from their platy single crystals.
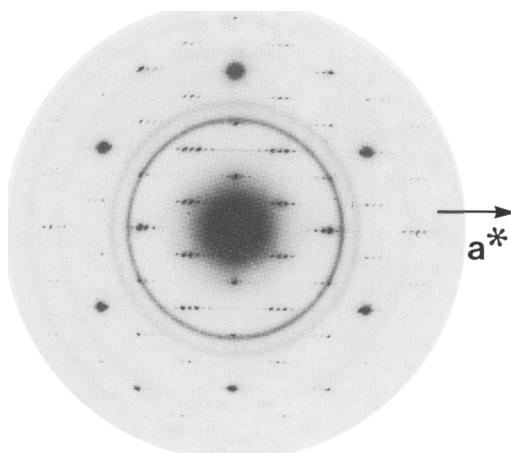

FIG. 3. Electron diffraction pattern of antigorite (Glen Urquhart, Scotland) with a 35 Å. Closely spaced lines of spots in the a^* direction are in clusters relating to the simple cell with a 5.3 Å, b 9.2 Å. Powder rings are from Pt coating.

A third variety, antigorite, is usually more crystalline and is characterized by a super-cell (not superlattice) with a in the range of 33–43 Å generally, according to its electron diffraction pattern (Fig. 3). The 'wavy layer' structure was shown to fit by X-ray diffraction work (Fig. 4) but only recently has it been directly imaged by high resolution electron microscopy (Yada et al., 1980; Akai, 1985a; Cressey and Hutchison, 1983; and others). In some cases methods of image enhancement have been employed.

In the super-structures of antigorites one would not expect the large a cell parameter to be exactly and simply related to a for the small cell, because the former is measured along chords and the latter along arcs. However an approximate relationship exists leading to a parameters clustered around certain values, e.g. approximately 38, 40.5, 43 Å for different antigorites depending upon where layer inversions occur. Some electron micrographs show clearly that even within a single-crystal of one antigorite the large a parameter can vary. X-ray values of a and even some electron diffraction values can be averages and in the latter case streaky spots in the e.d. patterns appropriately indicate the structural disorder. There is the danger, pointed out by Cressey and Hutchison (1983), in one of the methods of image enhancement, that it tends to
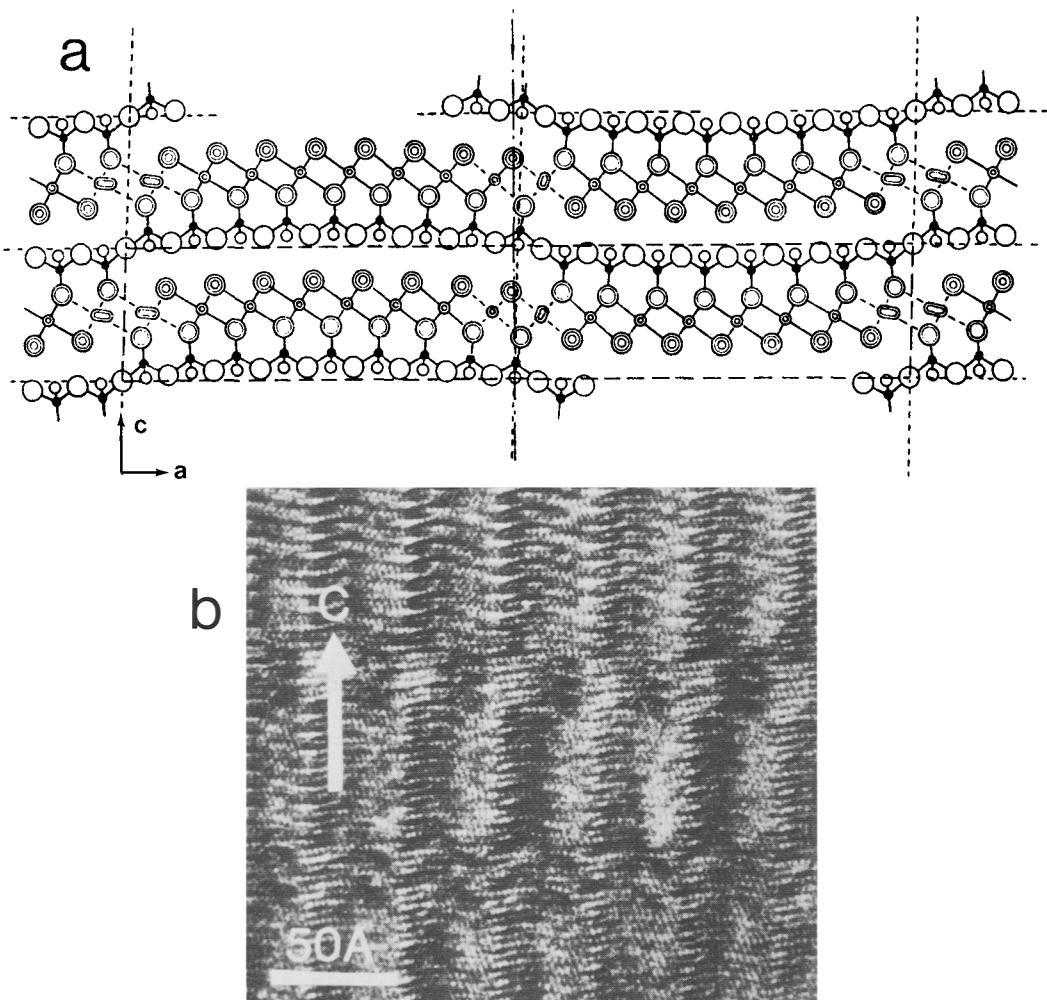

FIG. 4. (a) Corrugated layer structure of antigorite as viewed along the y axis (X-ray determination; Kunze, 1956). (b) High-resolution electron micrograph of antigorite; electron beam parallel to y axis (Cressey and Hutchison, 1983).

force a regular repeat on the structure which is not necessarily present.

Recent high resolution electron microscopy (Yada *et al.*, 1980) has revealed different layer stacking sequences for antigorite as well as for chrysotile.

Still further strange structures have been revealed for the serpentine minerals by electron microscopy (Cressey and Zussman, 1976). In Fig. 5 is shown a serpentine specimen containing flat layers (end-on views of laths) of limited extent making up the sides of polygonal prisms. Some of these have cores of cylindrical chrysotile; some do not. This texture was first deduced for the so-called 'Povlen' variety of chrysotile (Middleton and Whittaker, 1976), but it has since been observed in many more specimens and is better referred to as 'polygonal serpentine'. It is perhaps strange that polygonal serpentine has proved to be not uncommon, and yet it has been observed only recently, and the explanation must lie in specimen preparation techniques. The earlier work on serpentines was carried out on dispersions of crushed grains whereas more recently ion-thinning methods have been used; the former method probably destroyed the polygonal structures.

The curvature of the polar structural layers which occurs so often in one way or another is generally explained by the misfit between tetrahedral and octahedral components, the latter having a larger natural repeat distance. Several workers (e.g. Crawford *et al.*, 1978 by analytical electron microscopy) have demonstrated that the flat layered lizardites contain more Al substituting
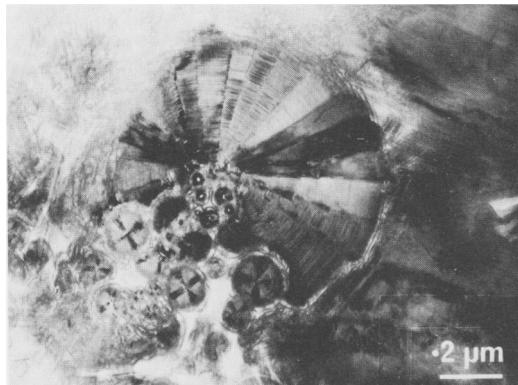

FIG. 5. Electron micrograph of polygonal chrysotile (Cressey and Zussman, 1976).

for both Si and Mg, thereby reducing the misfit. More recently some serpentine specimens have exhibited inhomogeneity even on the electron microscope scale, with parts cylindrically curved, parts wave-like and some flat. Whether such variations are also a consequence of chemical differences has not been demonstrated.

When curvature does occur it takes place about one axis or another, a ($\simeq 5.3$ Å) in most chrysotiles, b ($\simeq 9.3$ Å) in para-chrysotile and in antigorite, but not about both, except for the larger scale bending of lizardite (Kennack) platelets (Rucklidge and Zussman, 1965).

If Fe or Mn replace Mg in a serpentine-like structure, one would expect the misfit problem to
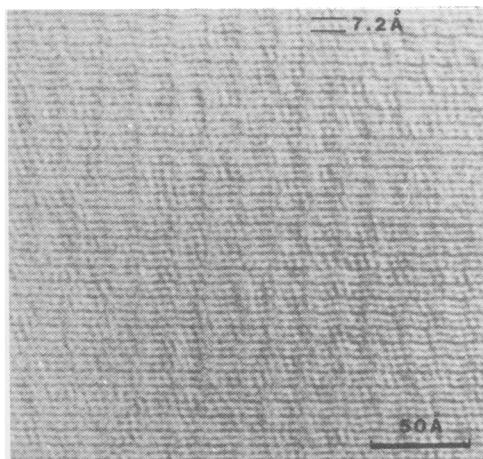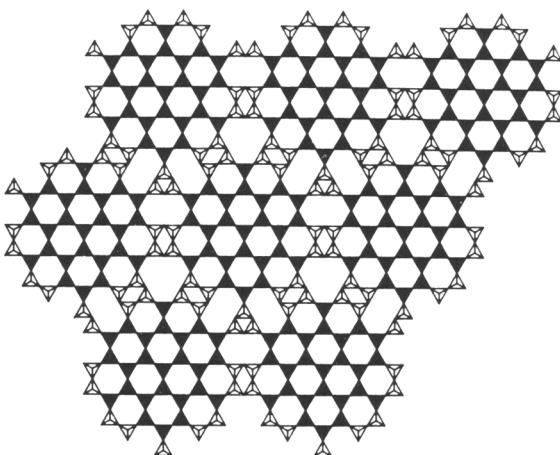
FIGS. 6 and 7. FIG. 6 (*left*). Idealized version of the tetrahedral component of the structure of greenalite or caryopilite. FIG. 7 (*right*). High-resolution electron micrograph of caryopilite showing corrugated layer structure (both from Guggenheim *et al.*, 1982).

be further demonstrated. Work by Guggenheim *et al.* (1982) shows that this does indeed happen in the minerals greenalite and caryopilite respectively. In these, 'islands' of saucer-shaped serpentine structure are linked by tetrahedra in other configurations (Fig. 6). The diameter of such saucers is approximately 23 Å and 17 Å for greenalite and caryopilite respectively, values reminiscent of the most common half-wavelength for antigorite ($\simeq \frac{1}{2} \times 40$ Å). Electron micrographs (e.g. Fig. 7) of end-on views of the layered structure show the curved elements directly. As with antigorite, the structure implies deviations from the ideal serpentine formula, and inversions of tetrahedra probably occur.

In recent years, the occurrence of serpentine as a major phyllosilicate phase in certain carbonaceous chondrite meteorites has been reported (e.g. Mackinnon and Buseck, 1979; Akai, 1980; Barber, 1981). Some were of the usual Mg-rich composition, others more Fe-rich and some had appreciable Ni content. Nearly all of the known morphological variations (hollow tubes, partially filled tubes, polygonal forms and even antigorite) have been represented in meteoritic serpentines. Akai (1985*b*) published high-resolution micrographs of Fe-rich serpentine from the Murchison meteorite showing directly stacking faults with *b*/3 displacements (Fig. 8), and Mackinnon and Buseck (1979) observed regions with regular sequences of serpentine and two brucite layers giving a repeat distance of approximately 17 Å [7 + (2 × 5) Å]. Recognition of these minerals and their intergrowths has helped to understand the origins and formations of their host meteorites, indicating a probable aqueous low-temperature alteration process occurring in the regolith of the parent body.

The direct observation by electron microscopy, of (001) spacings in layered silicates or in regular or randomly inter-layered specimens, and of layer displacements, as illustrated above, is clearly of great potential for the study of clay minerals, as long as specimens providing suitable end-on views of layers can be prepared. This possibility provides a very attractive alternative to the use of indirect evidence provided by non-Bragg X-ray diffraction (streaky diffraction spots, reflection profiles in powder patterns, etc.) which will in any case yield information 'averaged' over a wider region of the specimen.

Returning to antigorite, the study by Brindley *et al.* (1958) was probably the first to draw attention to and make use of the so called 'lattice fringes' in an electron micrograph of a mineral specimen (Menter had reported on lattice fringes with 11.97 Å spacing from Pt-phthalocyanin in 1956). Although the electron microscope used for the study of antigorite
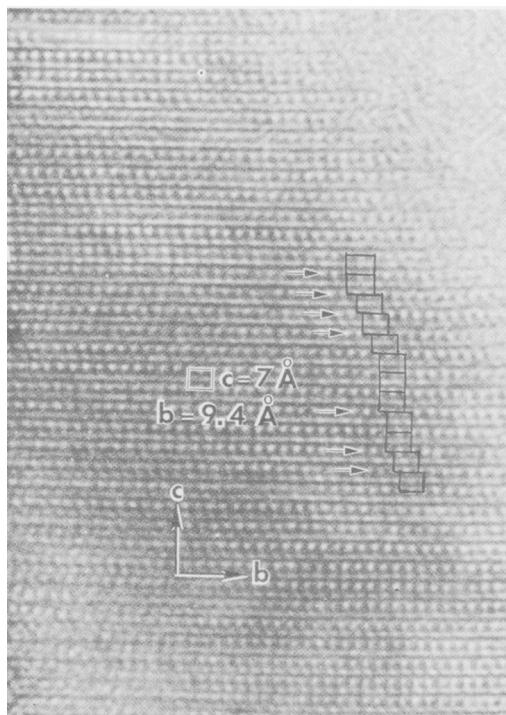

FIG. 8. High resolution electron micrograph showing *b*/3 layer stacking faults in chamosite (from Barber, 1985; micrography by J. Akai).

was of only moderate capability, the observation of fringes was not remarkable, since the antigorite in question had a wave-structure repeat of about 100 Å! It may seem surprising that the number of reports of lattice fringes in other minerals did not increase and their spacings decrease gradually as microscope performances improved. This was probably because rather few of the minerals studied had crystals lying in favourable orientations, with relatively long spacings and reasonable diffraction intensities. Once the resolution commonly obtainable came down to around 2 to 5 Å, however, many of the more common lattice spacings became observable and were reported.

Antigorites from various localities had given electron diffraction patterns indicating *a* parameters mainly in the range 33 to 43 Å, plus the one at about 100 Å and, it seemed, one showing approximately 19 and 17 Å fringes (Chapman and Zussman, 1959). Recently, however, (Mellini and Zussman, 1986) the assignment of these smaller values to antigorite has been shown to be mistaken, since the specimen, assumed to be a fibrous variety of antigorite ('picrolite') was in fact carlosturanite.
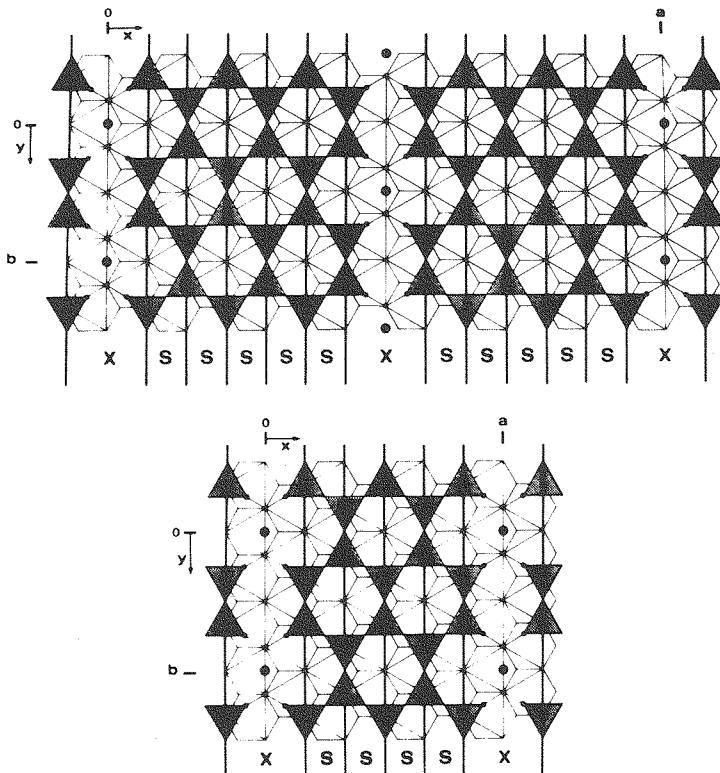
FIG. 9. The structure of a carlosturanite layer containing elements of serpentine structure (S) regularly interrupted by Si-deficient strips with OH (small circles) and H_2O (large circles). (From Mellini *et al.*, 1985.)

The structure of this new mineral (Fig. 9) described by Mellini *et al.*, 1985 (see also Compagnoni *et al.*, 1985) has, like serpentine, layers of Mg octahedra but the attached tetrahedral component instead of being continuous, is interrupted at regular intervals by strips (parallel to *y*) where silicons are missing and oxygens replaced by hydroxyl ions. The interval is about 17 Å and gives a super-structure effect. The superstructure *a* depends upon the number of normal serpentine repeats before each Si-poor, OH-rich strip, thus allowing the possibility of a polysomatic series, and the possibility of faults similar to the chain-width errors in 'pyriboles'.

Electron probe analysis of the supposed picrolite yielded a formula close to that of carlosturanite: $M_{21}T_{12}O_{28}(OH)_{34}.H_2O$ as compared with ideal serpentine: $M_{21}T_{14}O_{35}(OH)_{28}$. ($M$ = Mg, Fe, etc.; T = Si, etc.)

The close relationship of the two structures makes the X-ray powder patterns similar though not identical, and the same is true of single-crystal electron diffraction patterns. In the light of this work, other specimens which appear to be picro-

lites (fibrous antigorite with *y* as fibre axis) need to be carefully studied to see whether or not they are indeed antigorites.

Another mineral group with which we have been closely concerned in Manchester is the amphiboles, particularly in relation to asbestos. The electron microscope has of course been much used in recognising and identifying the presence of asbestos in dusts and in determining the shapes and sizes of fibrils. Without electron microscopy together with chemical analysis either by an analytical attachment or in an electron probe, there had been some quite erroneous descriptions of the nature and quantity of particles in dusts, meaning either over- or under-estimation of the health hazards involved.

The properties of non-fibrous amphiboles are also of interest in this context. Inhalation of fibres of crocidolite is known to be hazardous; does the same hold for dusts of crystalline glaucophane, riebeckite or arfvedsonite? Similar questions may be posed for amosite asbestos and crystalline grunerite, and for tremolite–actinolite fibres and crystals of these minerals or of hornblendes.

More fundamental studies of asbestos by electron microscopy have been carried out by ourselves and by others. The conditions necessary for fibrous development remain somewhat elusive, but by giving close attention to non-fibrous and fibrous specimens we can perhaps answer a different question, that is, why many amphibole specimens are *not* fibrous. Our most detailed work here (Dorling and Zussman, 1980, 1987) has been on the tremolite–actinolite series of calcium amphiboles. In hand specimens there are four morphologically distinct varieties—prismatic, acicular (byssolite), massive and asbestos.

Of particular interest were the massive nephrite varieties. Optical and SEM studies had established a fine scale intergrowth of acicular crystals, but the SEM is not the best method of determining orientations of crystallites or their sub-structure. Previous TEM work was on dispersions of crushed nephrite. We have used ion-thinned specimens which revealed the *in situ* texture and included views of crystallites down the z axis (Dorling and Zussman, 1985). We observed a texture of bundles of lath-like crystallites. Within a cluster there is more or less parallel orientation but azimuthal disorder. We deduced that each bundle is the successor to a pre-existing grain. Such grains have been subjected to strain and re-crystallization and the new crystals inherit the z-axis of the old. The clusters (like the original grains) are not in any particular orientation (Fig. 10). Cross-sections of clusters show the azimuthal disorder by means of readily observable planar defects on (010). Both kinds of misorienta-
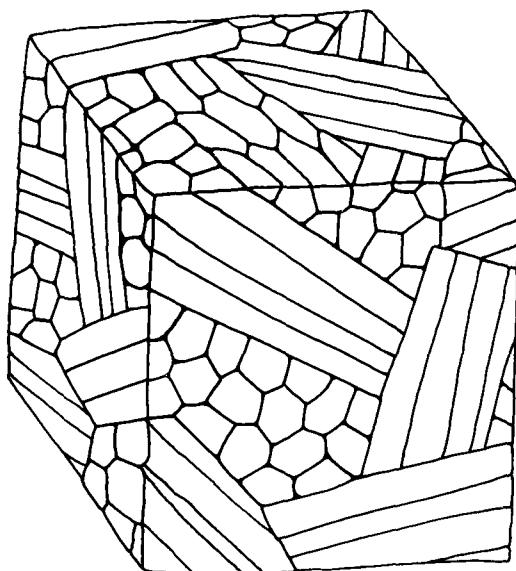

FIG. 10. Sketch illustrating the texture of crystallites in nephrite as deduced from transmission electron microscopy.

tion (within and between clusters) contribute to the toughness of nephrite, additional factors being the small grain size and irregular boundaries within and between clusters.

The identification of the (010) defects as chain-width errors (Fig. 11) (more common in nephrites
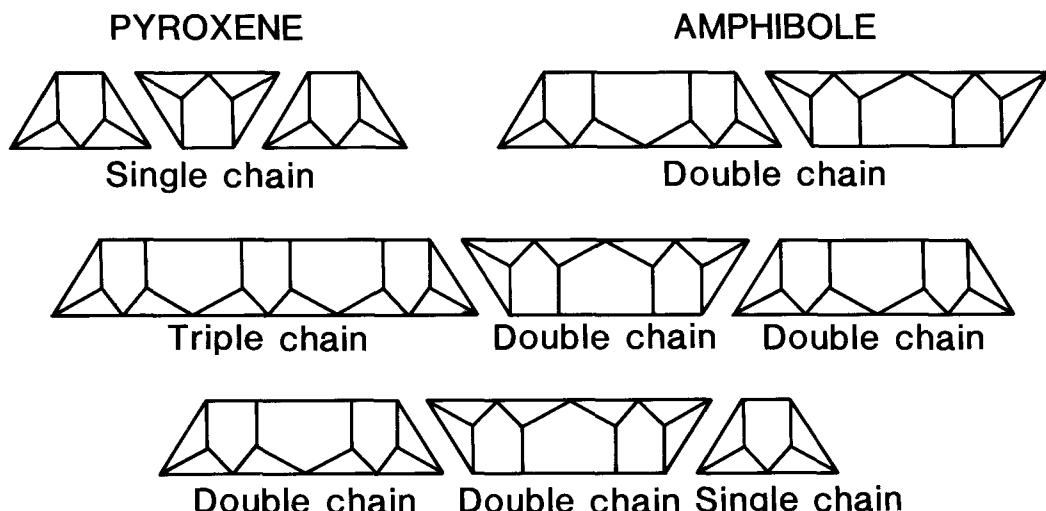

FIG. 11. Schematic illustration of chain-width errors. Above: normal sequence of amphibole 'double chains' seen end-on. Below: amphibole chains interrupted by triple chains and single chains.

than in other kinds of amphibole) was first suggested by Chisholm (1973) and subsequently confirmed by high resolution electron microscopy (e.g. Hutchison *et al.*, 1976). Three- and four-chain errors in the normal 2-chain amphibole matrix are quite common. In nephrite, these errors, plus the combination of curved and planar interfaces are indicative of relatively rapid re-crystallization during an annealing process.

Chain-width errors mostly occur randomly, but sometimes, as for example in a Zn-rich asbestos (Fig. 12) regular sequences are found. How many regular repeats of an 'error' are needed before a specimen is described in terms of two minerals in parallel intergrowth rather than as a single mineral with a fault?
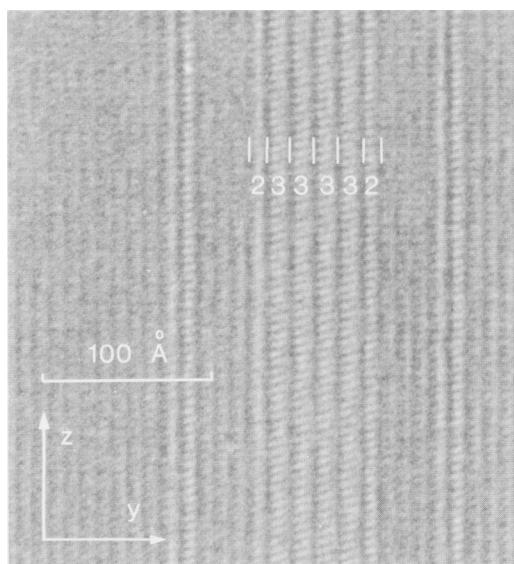

FIG. 12. High-resolution electron micrograph of Zn-tremolite asbestos showing an ordered region of triple chain structure (Dorling and Zussman, 1984).

When studying the texture of an aggregate of fibrils in an asbestos specimen views with the electron beam perpendicular to the fibrils' length suffer from overlap of individual fibrils. The most useful views are those of cross-sections of fibre bundles which have the added advantage of showing planar features on both (010) (chain-width errors) and (100) (twinning or stacking faults). The preparation of asbestos for TEM work on cross-sections has set a special problem and some of the most satisfactory results have been obtained using an ultramicrotome method.

Chain-width errors are observed to be very common in some tremolite asbestos, less common in astinolites and least of all in byssolites and prismatic specimens. However, it is dangerous to generalise in this manner; one prismatic specimen showed abundant (010) defects.

Chain-width errors have been cited (e.g. Veblen and Buseck, 1979) as a possible cause of asbestiform morphology. This seems very unlikely since one would then expect individual fibrils to be in similar crystallographic orientations rather than considerably rotated (about z) with respect to one another. Similar reasoning would apply to the fibrils forming by the splitting of otherwise prismatic crystals along cleavage or twin planes. The observed azimuthal disorder seems to indicate rather a process of multiple nucleation and relatively rapid growth in the z direction.

The elongation of most amphibole specimens (prisms, needles and fibrils) parallel to z is well recognised. We have observed in addition that growth in the y direction is generally greater than that along x, so that lath-like (in nephrites and byssolites) and ribbon like (in asbestos) morphology is common.

Because of the ribbon-like morphology of asbestos most fibrils in a dispersed preparation lie on or near the (100) plane so that (100) twinning is not often directly observable. In these circumstances, however, the electron diffraction pattern can be used indirectly as evidence of twinning. End-views of fibrils provided by microtomed sections do not reveal (100) twinning if the beam is strictly along z, but do so when slightly tilted from this position.

Some strange features have been observed in byssolites (Fig. 13) which have not been positively identified but are assumed to be fluid inclusions or voids occurring along planar features.

Beam-damage effects are not as prevalent with amphiboles as with serpentines but they can nevertheless mar attempts to obtain high-resolution images. They can, however, be turned to good use since they occur most readily at grain boundaries and planar defects and enhance their visibility, thus helping to identify grain orientation even at low magnifications when lattice fringes are not visible.

Electron microscopic studies of amphiboles are continuing at Manchester, with emphasis shifting to alkali amphiboles, and results will be reported elsewhere.

A review of the application of electron microscopy to mineralogy would not be complete without mention of progress over the years with specimen preparation. Historically, early work was restricted to observations of particle sizes and shapes. The common preparation techniques involved dispersions of crushed grains or shadowed
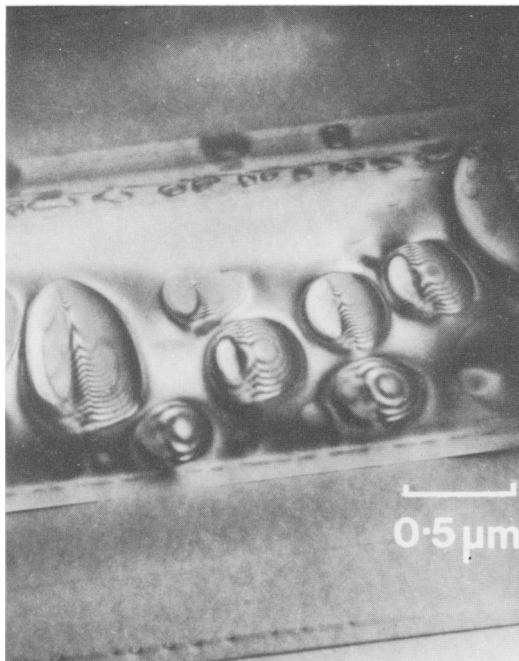
FIG. 13. Electron micrograph of ion-thinned 'byssolite' crystal showing what are probably fluid inclusions or voids.

(b) better point resolution through less chromatic aberration

(c) less beam damage

(d) decreased beam broadening in the analysis mode.

Concluding remarks

Crystals in their ideal form are the essence of regularity and perfection and in this respect structure determination by X-ray diffraction gives very complete information. But in practice, by concentrating mainly on X-ray reflections and less on the gaps between them we see an enforced perfection and we average out imperfections. Non-Bragg scattering holds the information about departures from regularity but is not easily interpreted. The electron image, on the other hand is not yet good at revealing to us completely unknown crystal structures but it is very good at revealing imperfections on a unit cell or sub-unit cell scale, such as dislocations, sub-grain boundaries, stacking faults and chain-width errors. It is no doubt an over simplification, but broadly speaking X-rays are particularly good at showing us what is 'right' with crystals and electrons at showing what is 'wrong', and the latter is at least equally important to the Earth scientist.

carbon replicas of surfaces. Dispersed grains have of course lost the relationships which pertained in their parent rock. They do present a selection of orientations but because of grain morphology these are not always so random that a desired view is always available. A vital step forward came with the method of ion-beam thinning, pioneered by D. Barber and N. Tighe in the mid 1960s, in which a beam of energetic argon ions is used to erode a hole in a thin section prepared as for optical microscopy, and use is made of the thin margin to the hole. This procedure provides strict correlation between the optical images of the rock, its textures and associations of minerals, and electron microscopic and electron probe observations. Still more powerful is the now increasingly used combination of all the above with elemental analysis in the electron microscope itself.

Another important development in electron microscopy which will enhance its use in the study of minerals is the more common availability of higher voltage (300–400 kV) instruments. These give the advantages of

(a) dealing with thicker specimens (thinning is not always feasible)

References

Akai, J. (1980) *Mem. Nat. Inst. Polar Res. Tokyo.* Special Issue No. 17. 299–310.
——(1985) *The World of Fine Textures and Structures in Rock-Forming Minerals through High Resolution Electron Microscope (I).*
——(1985) *Proc. 10th Symp. on Antarctic Meteorites.* Nat. Inst. Polar Res. Tokyo.
Barber, D. J. (1981) *Geochim. Cosmochim. Acta,* **45,** 945–70.
——(1985) *Clay Minerals,* **20,** 415–54.
Brindley, G. W., Comer, J. J., Uyeda, R. and Zussman, J. (1958) *Acta Crystallogr.* **11,** 99–102.
Chapman, J. A. and Zussman, J. (1959) Ibid. **12,** 550–2.
Chisholm, J. E. (1973) *J. Mater. Sci.* **8,** 475–83.
Compagnoni, R., Ferraris, G. and Mellini, M. (1985) *Am. Mineral.* **70,** 767–72.
Crawford, E. S., Jefferson, D. A., Thomas, J. M. and Bishop, A. C. (1978) *J. Chem. Soc., Chem. Comm.* 986–7.
Cressey, B. A. and Hutchison, J. L. (1983) *Inst. Phys. Conf. Ser.* No. 68. 409–12.
——and Zussman, J. (1976) *Can. Mineral.* **14,** 307–13.
Dorling, M. and Zussman, J. (1980) *Fourth International Conference on Asbestos, Turin.* Preprints, **1,** 317–33.
————(1985) *Mineral. Mag.* **49,** 31–6.
————(1984) *Mineral. Pol.* **15,** 11–20.
————(1987) *Lithos,* **20** (in press).

Guggenheim, S., Bailey, S. W., Eggleton, R. A. and Wilkes, P. (1982) *Can. Mineral.* **20**, 1–18.

Hutchison, J. L., Jefferson, D. A., Mallinson, L. G. and Thomas, J. M. (1976) *Mater. Res. Bull.* **11**, 1557–62.

Kunze, G. (1956) *Z. Kristallogr.* **108**, 82–107.

Mackinnon, I. D. R. and Buseck, P. R. (1979) *Nature*, **280**, 219–20.

Mellini, M. and Zussman, J. (1986) *Mineral. Mag.* **50**, 675–9.

——Ferraris, G. and Compagnoni, R. (1985) *Am. Mineral.* **70**, 773–81.

Middleton, A. P. and Whittaker, E. J. W. (1976) *Can. Mineral.* **14**, 301–6.

Rucklidge, J. C. and Zussman, J. (1965) *Acta Crystallogr.* **19**, 381–9.

Veblen, D. R. and Buseck, P. R. (1979) *Am. Mineral.* **64**, 687–700.

Whittaker, E. J. W. (1953) *Acta Crystallogr.* **6**, 747–8.

——(1954) Ibid. **7**, 827–32.

——and Zussman, J. (1971) *The Electron-optical Investigation of Clays* (ed. J. A. Gard), Mineralogical Society, London, 159–91.

Yada, K. (1967) *Acta Crystallogr.* **23**, 704–7.

——(1971) Ibid. A **27**, 659–64.

——Tanji, T. and Nissen, H. U. (1980) *Fourth International Conference on Asbestos*, Preprints, **1**, 347–57.

Zussman, J., Brindley, G. W. and Comer, J. J. (1957) *Am. Mineral.* **42**, 133–53.