Microstructures and mixed layering in intergrown wonesite, chlorite, talc, biotite, and kaolinite

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Abstract

Macroscopically intergrown chlorite, wonesite (sodium trioctahedral mica), and potassium biotite from the Post Pond Volcanics, Vermont, have been studied with transmission electron microscopy and diffraction. The chlorite occurs in intergrown 1-layer and disordered polytypes, the wonesite occurs in 1-layer, 2-layer, 3-layer, and disordered forms, and the biotite occurs as 1-layer and 2-layer polytypes with minor stacking disorder. In addition, both chlorite and wonesite are twinned on (001) by a law involving layer rotations of 30° or angles very close to 30°. IN wonesite, this constitutes a sort of "chemical twinning," with twin planes containing fewer interlayer sites than normal mica interlayers. Some of the wonesite also exhibits turbostratic stacking.

Low-angle grain boundaries occur within chlorite and wonesite and also between pairs of the sheet silicate phases. The structures at these grain boundaries can be discontinuous, or the structural layers can be continuous across them, depending on the grain boundary orientation.

Parts of the chlorite exhibit perfect alternation of the talc-like and brucite-like layers, but in other places, there are extra or missing brucite-like layers. Likewise, occasional brucite-like layers are found in most of the wonesite. In both chlorite and wonesite, these extra layers are in some cases observed to terminate. In some places, the chlorite and mica structures intergrow freely, either in almost total disorder or as slabs of chlorite and mica up to several hundred ångströms thick. Thin slabs of kaolinite, talc, and potassium biotite also intergrow with the chlorite and wonesite. The mixed layering phenomena in this specimen demonstrate that chlorite that appears normal in thin section can, at least in places, deviate substantially from ideal chlorite stoichiometry.

Introduction

Mixed layering, the phenomenon in which a crystal contains two or more structurally and chemically distinct types of layers, is common in sheet silicate clay minerals. The distinct types of layers can be arranged in either periodic or nonperiodic sequences, leading to both ordered and disordered mixed-layer structures. Ordered mixed layering has also long been recognized in macroscopically-crystalline layer minerals, such as chlorites, which consist of alternating talc-like and brucite-like layers. With few exceptions, however, disordered mixed layering has not been described from these rock-forming sheet silicates.

Fine-grained mixed-layer micas have been recognized by Frey (1969, 1978) in low-grade metapelites; they were identified by using powder X-ray diffraction techniques. In addition, there have been several high-resolution transmission electron microscopy (HRTEM) studies relevant to the occurrence of mixed layering in rock-forming sheet

minerals. Iijima and Buseck (1977, 1978), Spinnler, Buseck, and Iijima (personal communication, 1982), and Buseck and Iijima (1974), for example, did not recognize any mixed-layering disorder in studies of muscovites, biotites, and chlorites; Amouric *et al.* (1981) did not observe mixed-layering in several mica specimens; and Schreyer *et al.* (1982) found no disorder in the sequence of talc-like and brucite-like layers in a chlorite specimen. Page and Wenk (1979) did, however, observe relatively fine-scale intergrowths of micas, clay minerals, and chlorite in fine-grained alteration products of plagioclase. Page (1980) observed planar features in muscovite that he interpreted as zones of occupied and unoccupied interlayer sites. Veblen and Buseck (1979, 1980, 1981), Buseck and Veblen (1981), and Veblen (1980) observed mixed layering in several specimens. Features noted in these studies included mixing of serpentine, talc, and chlorite layers; missing brucite-like sheets in chlorite; and intercalation of brucite-like layers in talc to form local chlorite-like structural configurations. In addition to these obser-
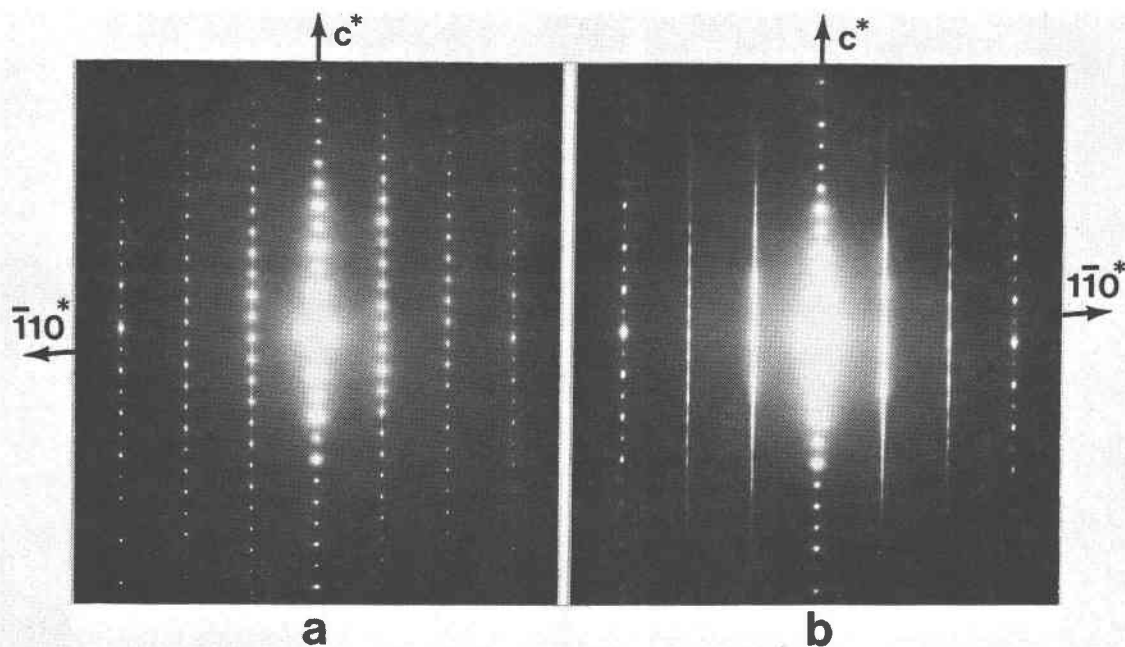
Fig. 1. [110] electron diffraction patterns of chlorite with c^* vertical. a. 1-layer chlorite with minor streaking parallel to c^* due to stacking disorder. b. Chlorite with extreme stacking disorder, exhibiting streaking for diffraction rows with $k \neq 3n$. $1\bar{1}0^*$ and $\bar{1}10^*$ refer to the reciprocal lattice directions $[1\bar{1}0]$ and $[\bar{1}10]$.

vations of disordered mixed layering in relatively fine-grained alteration products, there have been two recent reports of limited intergrowth of brucite-like layers in coarsely crystallized biotite (Iijima and Zhu, 1982; Olives Baños *et al.*, 1983).

In this paper, results of HRTEM and electron diffraction experiments on macroscopically-crystalline sheet silicates from the Post Pond Volcanics, Vermont (Spear *et al.*, 1981), are presented. These results demonstrate that disordered mixed layering can be important in chlorite and in the sodium mica wonesite. In addition, fine intergrowths of these minerals with talc, kaolinite, and potassium biotite are described. Exsolution phenomena and microstructures in the wonesite from this locality are discussed in a companion paper (Veblen, 1983).

In addition to the mixed layering phenomena, several other interesting structural variations occur in the sheet silicates from this Post Pond locality. These include the occurrence of ordered polytypes in wonesite and chlorite, as well as disordered stacking; twinning and turbostratic stacking; and low-angle grain boundaries.

Specimen description, experimental techniques, and image interpretation

The specimen employed in this study is number 68-432E of Spear *et al.* (1981), who reported electron microprobe analyses of the macroscopic wonesite and potassium biotite. A microprobe analysis of the chlorite in this specimen was also kindly provided by Dr. Frank S. Spear

(pers. comm.). The analysis, recalculated with all iron as FeO, yields the formula $(Mg_{3.83}Fe_{0.78}Al_{1.35})_{5.96}[Si_{2.70} Al_{1.30}]_{4.00}(O_{10}OH)_8$. The chlorite is thus a sheridanite (Deer *et al.*, 1962, p. 137).

Experimental techniques and image interpretation methods utilized in this paper are described by Veblen (1983). The interpretation of chlorite images, however, requires further clarification. As shown by Iijima and Buseck (1977), under favorable imaging conditions, sites in the chlorite structure between the talc-like and brucite-like layers and in the positions of the rings of the silicate sheets can be imaged as white spots; these can be used to determine the detailed layer stacking sequences. In the present work, these white spots were also observed in many TEM images. It was more usual, however, to image only the 00*l* reflections, which results in images containing a broad black fringe in the position of the talc-like layer and a narrower fringe in the position of the brucite-like layer. In some cases, image quality was reduced by electronic problems with the TEM so that the brucite-like layer was resolved only poorly, or not at all; interpretation of such images was still possible in favorable cases, however.

Careful measurement of the talc-like and brucite-like layers in the TEM images of chlorite gives anomalously small values for the talc-like parts and anomalously large values for the brucite-like parts. Similar discrepancies, but of lesser magnitude, occur in micrographs obtained by Iijima and Buseck (1977) from a clinochlore specimen
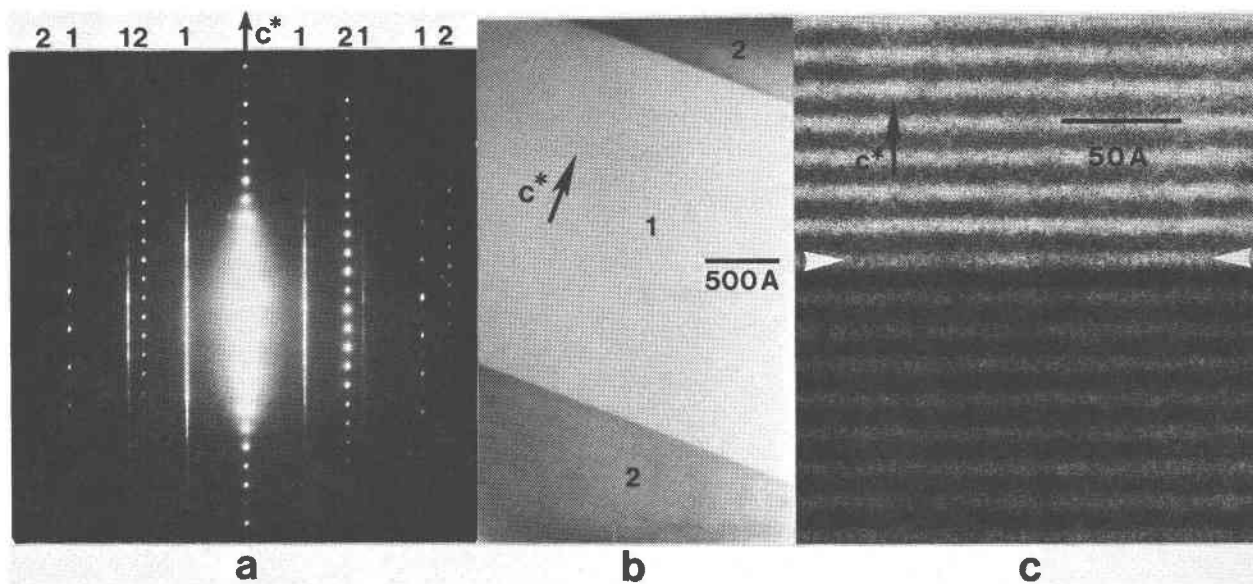
Fig. 2. Approximately 30° twinning in chlorite. a. Composite electron diffraction pattern from the two orientations. Both orientations contribute to the 00l row (vertical). One of the crystals produces the rows labeled "1," which exhibit extreme streaking for $k \neq 3n$. The other orientation produces the rows labelled "2." b. Low-magnification images of a 30° twin lamella ("1") surrounded by chlorite in the other orientation ("2"). c. High-resolution TEM image showing the 14Å chlorite periodicity at an interface (arrowed) between the orientations 1 and 2 shown in b. The continuity of the periodicity across the interface indicates that there are no missing structural layers at the twin boundary.

(the difference in magnitude is apparently the result of the different microscopes used in the two studies and/or minor differences in imaging conditions). Image calculations by Spinnler, Buseck, and Iijima (pers. comm., 1982) demonstrate that apparent layer thickness variations arise from electron optical effects like those described by Spence *et al.* (1977) for germanium. These anomalous layer thicknesses do not impair the interpretation of chlorite HRTEM images.

Stacking phenomena

In most, if not all, sheet silicates, the layers can be stacked in a variety of ways. For example, in a crystal of chlorite, there are virtually an infinite number of ways in which the tetrahedral–octahedral–tetrahedral (TOT) and brucite-like octahedral (O) layers can be stacked. Different ways of stacking the layers result in different polytypes, stacking disorder, and twinning.

Chlorite

The chlorite in the Post Pond specimens contains regions of both ordered stacking and disordered stacking, which can be recognized in either diffraction patterns or high-quality electron images. Figure 1a is a [110] electric diffraction pattern from an area of chlorite with relatively little stacking disorder. The pattern is consistent with a one-layer polytype having $\beta = 97°$; this chlorite is probably the 97° polytype IIb-2, which is by far the most common chlorite polytype (Brown and Bailey, 1962), although it is not possible to rule out other polytypes having the same unit cell parameters.

Much of the Post Pond chlorite produces electron diffraction patterns as in Figure 1b, with heavy streaking in reciprocal lattice rows with $k \neq 3n$. Diffraction patterns from other orientations demonstrate, however, that rows with $h \neq 3n$ contain sharp diffractions, indicating that the stacking disorder primarily involves layer shifts or rotations of 120°, rather than 60° (Ross *et al.*, 1966). Stacking disorder was also observed in some HRTEM images of chlorite. Such images are similar to those of Iijima and Buseck (1977), which were obtained from a clinochlore specimen (see the section "Specimen description, experimental techniques, and image interpretation"). As in the study of Iijimi and Buseck, no long-period polytypes were observed, in contrast with the study of Schreyer *et al.* (1982), who found 2-layer and 5-layer chlorites in a metamorphosed dolomite.

Most twinning in sheet silicates occurs on the composition plane (001), and the twin operations can be described as layer rotations of $\pm 60°$, $\pm 120°$, or 180°. For example, the common [310] twinning in micas is simply a 60° layer rotation. In addition to rotations of this sort, a new type of twinning operation was observed in both the chlorite and wonesite in this study. This twinning involves a layer rotation of 30°, or an angle that is very close to 30°. Figure 2a is a diffraction pattern from such a twin, with the two
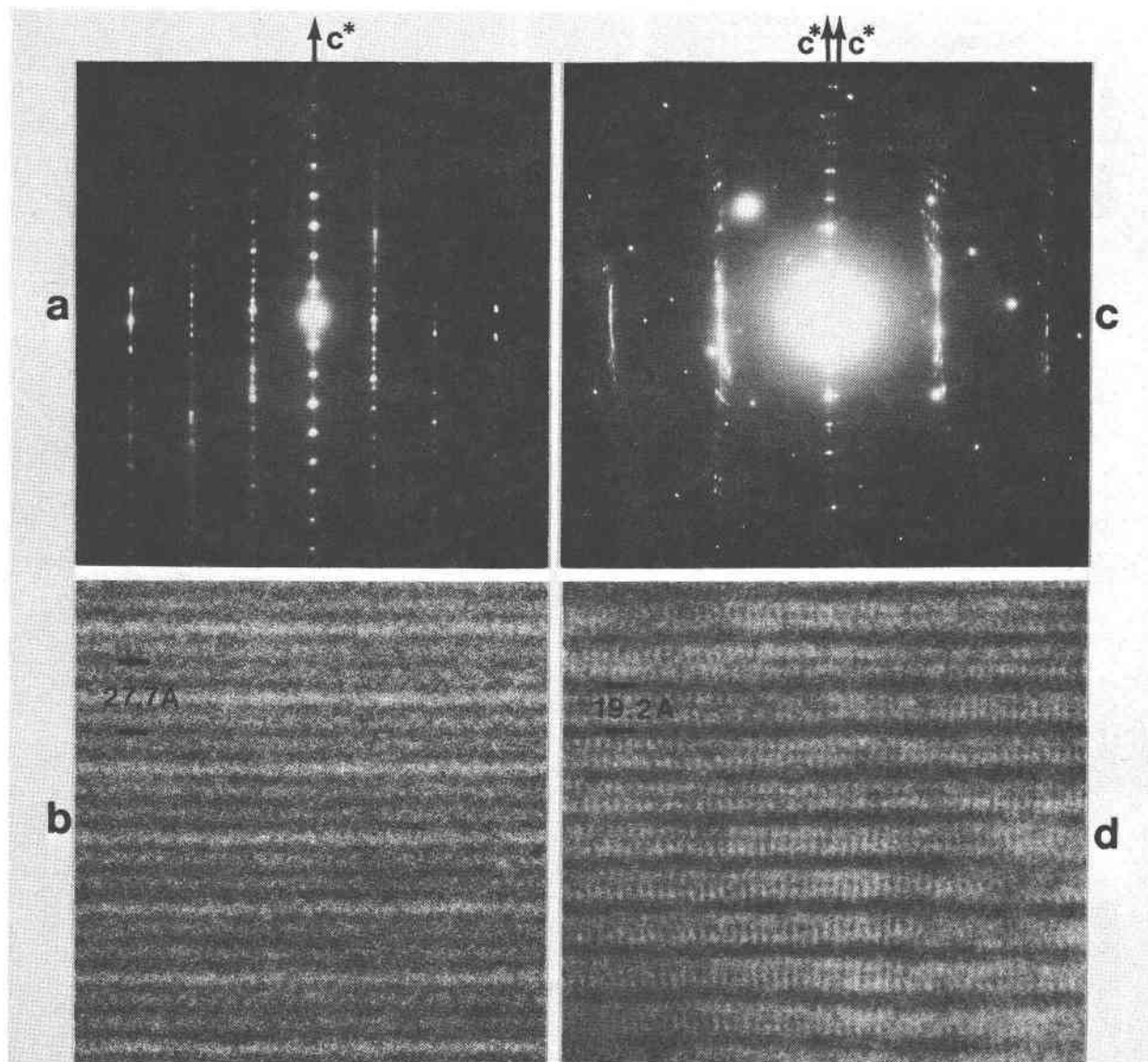
Fig. 3. a,b. Electron diffraction pattern and image of 3-layer wonesite (c^* vertical). c,d. Diffraction pattern and image of 2-layer wonesite. Many of the sharp diffractions are from intergrown plagioclase in irrational orientation, and the absence of a single c^* direction indicates rotational disorder of the wonesite layers about an axis parallel to the layers. The images in b and d were produced by rotating the crystals so that c^* was not perfectly normal to the TEM axis, to enchance the periodicity due to the polytypism.

crystal orientations sharing a common c^*. The ($1\bar{1}l$), ($2\bar{2}l$), and ($3\bar{3}l$) rows from one of the orientations appear, with heavy diffuse streaking of the ($1\bar{1}l$) and ($2\bar{2}l$) diffractions; diffraction rows from this crystal are designated "1" in the figure. The other orientation (designated "2") produces uniformly sharp ($20l$) and ($40l$) diffractions, consistent with stacking sequences containing no 60°, 180°, or 300° rotations. Although at first glance this pattern might appear to be a composite containing an ordered crystal and a disordered crystal, both members of the twin are disordered (as indicated by tilting experiments), but the

effects of 120° stacking disorder are visible in only one of the orientations.[1]

Figure 2b is a low-magnification image of a region twinned by 30° rotation. The twinning in this case is lamellar, with a lamella 0.24 μm thick in twin orientation (orientation "1") with respect to the surrounding chlorite (orientation "2"). The higher-magnification image of Fig-

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[1] For random 0°, ±120° rotations, hkl: $k = 3n$ sharp, $k \neq 3n$ diffuse. For random 0°, ±60°, ±120°, 180° rotations, hkl: h and k = 3n sharp, h and/or $k \neq 3n$ diffuse.
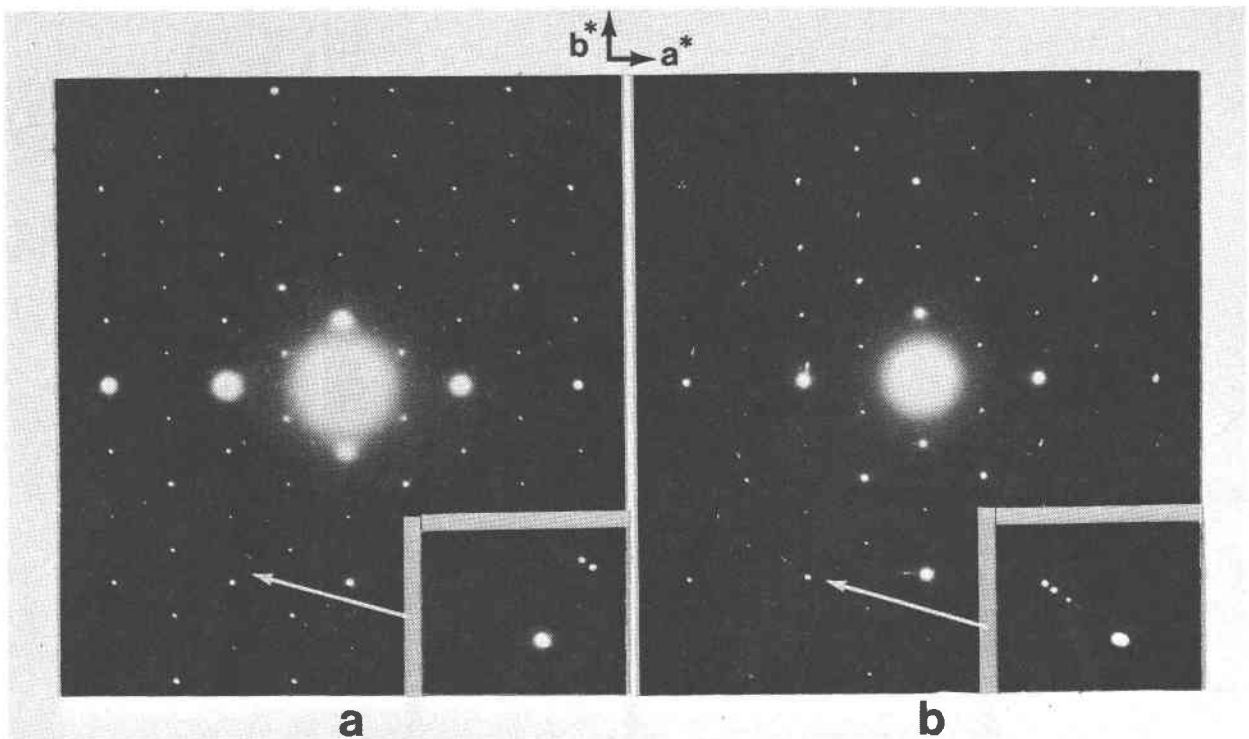
Fig. 4. c-axis electron diffraction patterns of thin cleavage fragments of wonesite. a. Crystal with nearly 30° twinning. b. Crystal with turbostratic stacking. The insets are expanded views of the regions indicated by arrows.

ure 2c further suggests that the twinning is structurally coherent and that no brucite-like or talc-like layers are omitted from the chlorite at the interfaces, since the periodicity of the 14Å fringes is not disturbed. The twinning operation must therefore consist of a 30° rotation between a talc-like layer and a brucite-like layer. This is a different structural relationship from that resulting from the same sort of twin in mica, as discussed in the next section.

Wonesite

Single-crystal and powder X-ray studies of wonesite (Spear *et al.*, 1978, 1981) suggested that this sodium mica is a disordered 1-layer polytype ($1M_d$). Selected-area electron diffraction and high-resolution imaging experiments show, however, that ordered polytypes, as well as disordered material, occur in wonesite.

Although the common 1M biotite polytype predominates in ordered regions of wonesite, there are also smaller regions with larger periodicity. Figures 3a, b, for exmaple, show a diffraction pattern and image from a region of 3-layer wonesite. The non-orthogonal diffraction pattern is not consistent with the trigonal 3T polytype, which has been reported for both triotahedral (Ross *et al.*, 1966) and dioctahedral (Güven and Burnham, 1967) micas. Thus, this diffraction pattern must be from a region of 3-layer triclinic structure, since 3-layer polytypes other than 3T are all triclinic (Ross *et al.*, 1966).

Figure 3c is a diffraction pattern from a small region in which wonesite and plagioclase occur together in lamellar intergrowth, possibly as the result of replacement of one by the other. The plagioclase is a single crystal, here in an irrational orientation, but the wonesite layers are not everywhere parallel, leading to a range of orientation for c^*. The periodicity along c^* indicates that this portion of the wonesite crystal is a 2-layer polytype (either $2M_1$ or $2M_2$). Figure 3d is an image of 2-layer wonesite, showing the doubled periodicity (relative to the 1M polytype) parallel to c. Figures 3b and 3d were obtained by tilting the crystals so that c^* was not perfectly normal to the TEM axis, thus enhancing the modulations due to the polytypism.

As in the chlorite, perhaps the most interesting stacking phenomenon in the wonesite is the presence of layer rotations that are not an integral multiple of 60°. As noted by Veblen (1983), structural distortions and other complications arising from the exsolution of talc lamellae lead to difficulties in the interpretation of diffraction patterns obtained with the electron beam parallel to the layers of the structure. It is, however, possible to study layer rotations by using c-axis diffraction patterns from specimens that have been crushed and mounted on holey carbon grids. Diffraction patterns taken in the orientation indicate that layer rotations of 30°, or very close to 30°, do occur in wonesite. Figure 4a, for example, shows a diffraction pattern from a very thin crystal with weak
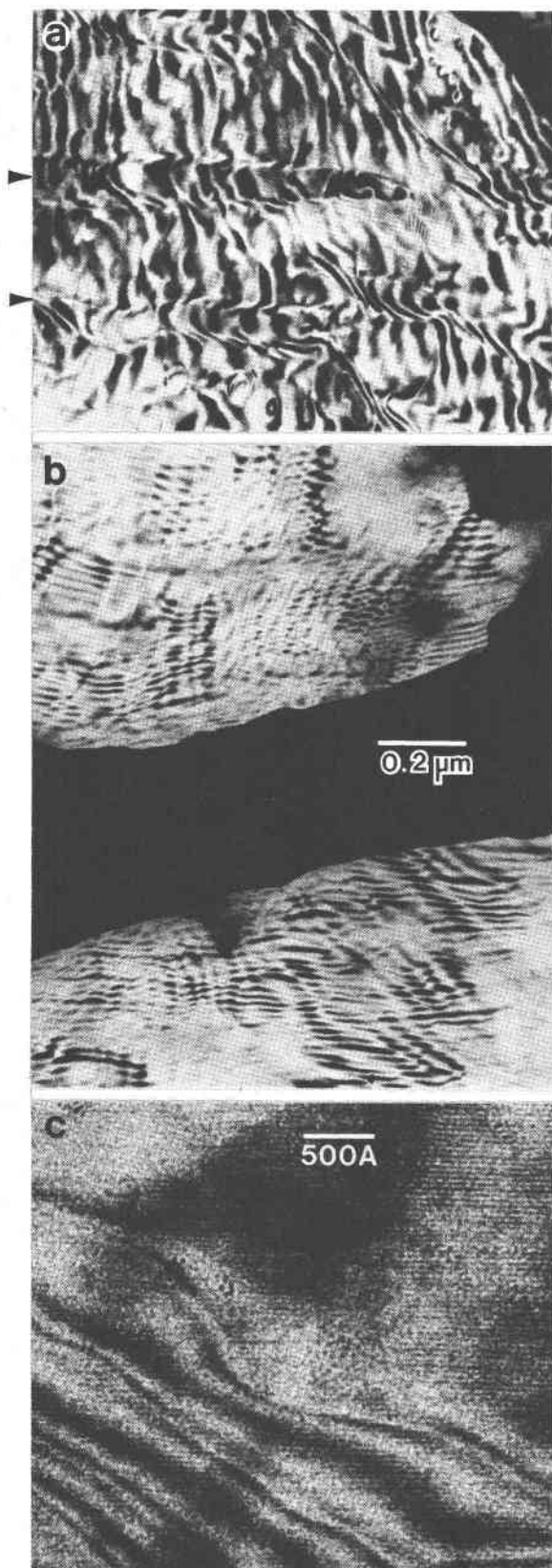
reflections in two orientations that are rotated approximately 29° with respect to the main part of the crystal. Because the crystal is quite thin, these rotated portions may be only one or a few mica layers thick.

Another type of layer rotation that is unusual for macroscopically-crystalline sheet silicates is illustrated in the diffraction pattern of Figure 4b. Here, the pattern is split into a number of different orientations that are rotated by non-integral amounts. This is reminiscent of the turbostratic stacking that is common in many clay minerals; in extreme turbostratic stacking, as observed in some smectites, there is virtually no relationship between adjacent layers in the structure (see Gard, 1971, for example). In the present case, some of the orientations probably contain at least several mica layers, indicating that there is greater structural control of the stacking. Turbostratic stacking in smectites in some cases may result when TOT talc-like layers that were separated in the presence of water are brought together upon desiccation. This is presumably not the case in the wonesite, since the mica was not prepared with an aqueous solvent, and this sort of diffraction pattern was observed in areas containing talc exsolution lamellae (see Fig. 5 in Veblen, 1983), which were formed long before sample preparation.

Both bright- and dark-field images of wonesite crystals having non-integral layer rotations exhibit pronounced moiré fringes from interaction of the overlapping layers in different orientations. An example is shown in Figure 5a, where the contrast is complicated by the presence of talc lamellae. The curving of the moiré fringes suggests that the orientation relationships between layers are not exactly identical across the crystal. In Figure 5b, there is a two-dimensional moiré pattern, resulting from two sets of interacting reflections being in a strong diffraction condition simultaneously. Figure 5c is a further example of such moiré patterns, in which one set of fringes is perfectly periodic and quite straight, indicating rigid structural control between the rotated layers giving rise to these fringes.

The presence of twinning by a 30° rotation and turbostratic stacking raises the question of the structural relationships between the TOT layers by such rotations. In the case of apparently non-integral rotations, there is obviously no one structure for all cases. We may speculate, though, that since at least some of the pseudohexagonal rings in one tetrahedral sheet of one layer must overlie rings in the adjacent tetrahedral sheet, there will be some sites between the layers that are suitable for

Fig. 5. a. Moiré fringes from turbostratic stacking. The arrows indicate two talc exsolution lamellae (horizontal). b. Two-dimensional moiré pattern. c. Two sets of moiré fringes. The very fine horizontal set of fringes is from a 30° twin, and the coarse, irregular fringes are from turbostratic stacking. The scale in a is the same as in b.
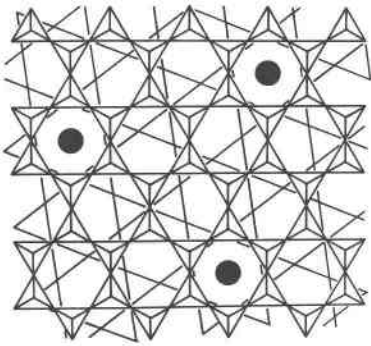
Fig. 6. Idealized representation of the structural relationship between adjacent tetrahedral sheets at a 30° mica twin plane. One seventh of the hexagonal rings of the sheets provide reasonable sites for interlayer cations (indicated by black circles).

occupancy by interlayer cations, such as sodium. Whether these sites really are occupied or not is a question not accessible to present experimental techniques.

In the case of layer rotations of exactly 30°, there is probably a more rigorous structural relationship between the adjacent tetrahedral sheets. Figure 6 is an idealized (unrotated tetrahedra) drawing of the expected structure. Just as in normal mica structure with relative layer rotations of n(60°), there are large cage sites in the structure with 30° layer rotation; like the interlayer sites of normal mica structure, these are capable of holding interlayer cations, although the geometry of these sites is

not exactly like those of micas. There are, however, only one-seventh as many sites compared with the number of alkali sites in a normal mica interlayer. If these sites are occupied by sodium, the chemical composition would thus be less sodium-rich than in other interlayers of the wonesite structure. These 30° twins therefore represent a form of chemical twinning (Andersson and Hyde, 1974; Takéuchi, 1978).

There are several chemical consequences of the 30° twins in chlorite and wonesite. In chlorite, since there are no interlayer cations, there is probably no compositional change associated with the twin planes, although these planes could form zones of weakness in the structure. In wonesite, the low-sodium composition of these planes could conceivably explain a small amount of the nonstoichiometry of this mineral. However, the numbers of such twin planes observed in most parts of the wonesite that was studied are much too small to affect the overall chemical composition appreciably. Another probable chemical effect of both irrational and 30° layer rotations is that the tetrahedral sheets that participate in such junctions are more silicon-rich than those of the average structure. This assertion follows from local charge-balance requirements; where there is a paucity of interlayer cations, neutrality can be maintained by the exchange $\square SiNa_{-1}Al_{-1}$.

Biotite

Only small amounts of potassium biotite were observed in the electron microscope specimens used in this study.
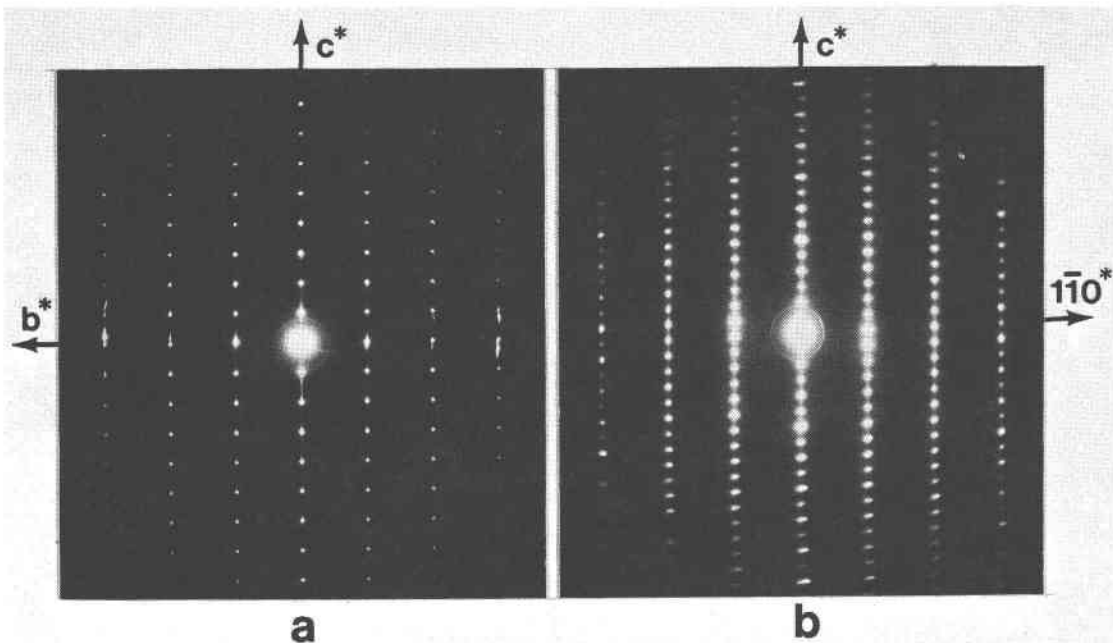

Fig. 7. Electron diffraction patterns from potassium biotite (c^* vertical). a. 1-layer biotite. b. 2-layer biotite. 110* refers to the reciprocal lattice direction [1$\bar{1}$0].
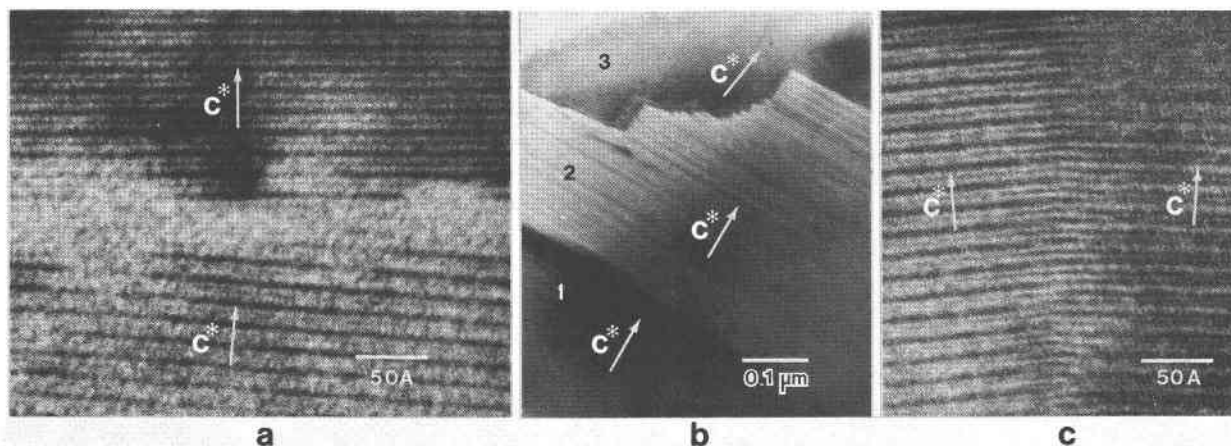
Fig. 8. Low-angle grain boundaries in chlorite. a. A boundary that is parallel to the crystal on the top. b. A low-magnification view of an irregular boundary. 1, 2, and 3 indicate separate crystals in different orientations. c. A boundary that is nearly normal to the chlorite layers. Individual layers are apparently at least partially continuous across the boundary. Contrast differences result from differences in crystal orientation.

The stacking of the layers of the biotite is similar to that of the chlorite and wonesite, in that multiple polytypes, as well as stacking-disordered material, occur in fine intergrowth in the same specimen. Figure 7 shows electron diffraction patterns from both 1-layer and 2-layer biotites intergrown in wonesite. These patterns are free of the complications exhibited by diffraction patterns of wonesite that arise from exsolution of talc from the mica (see Fig. 2 in Veblen, 1983, for example).

Low-angle grain boundaries

Low-angle grain boundaries are a common feature of the Post Pond sheet silicates. Most commonly observed are boundaries that are parallel to (001) of one crystal and close to (001) of the other, although boundaries in other orientations and with variable orientation are also present. Low-angle grain boundaries occur both between crystals of the same phase and between crystals of different minerals. A few representative examples are shown below.

Figure 8a is a HRTEM image of a grain boundary between two chlorite crystals. The boundary is parallel to (001) of one crystal and inclined 8° to (001) of the other. There is a difference in contrast for the two crystals that results from a difference in orientation; the layers of one crystal are parallel to the electron beam, while those of the other are slightly inclined to the beam. The boundary is relatively "tight," especially considering that the structure along the interface had been partially destroyed by electron radiation damage before the image was recorded. This is similar to the case of a mica grain boundary observed by Page (1980).

Another grain boundary between two chlorite crystals is shown in Figure 8b. In this case, the boundary is irregular in form, with parts that cut across the chlorite

layers at high angles. Figure 8c is a HRTEM image from such a boundary. The image suggests that the layers of the structure are at least partially continuous across the boundary, although rigorous interpretation is hampered by contrast differences for the two crystals and at the boundary itself, as described for Figure 8a. As noted above, low-angle grain boundaries also occur between different phases. An example of such a boundary between chlorite and wonesite is shown in Figure 9.

Intergrowth phenomena

Intercalation defects in chlorite and wonesite

Much of the chlorite examined in this study contained only perfectly alternating brucite-like and talc-like layers,
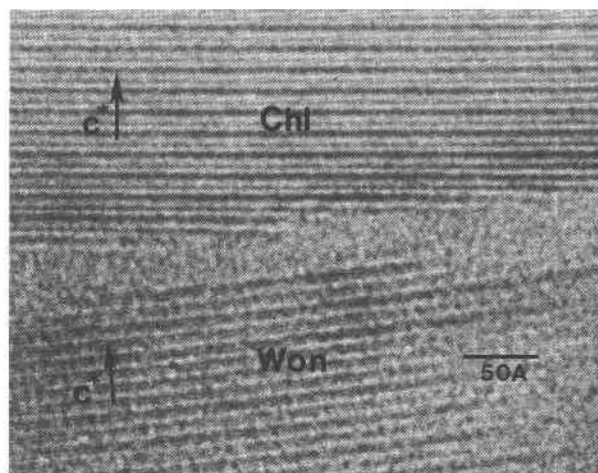

Fig. 9. A low-angle grain boundary between wonesite and chlorite.
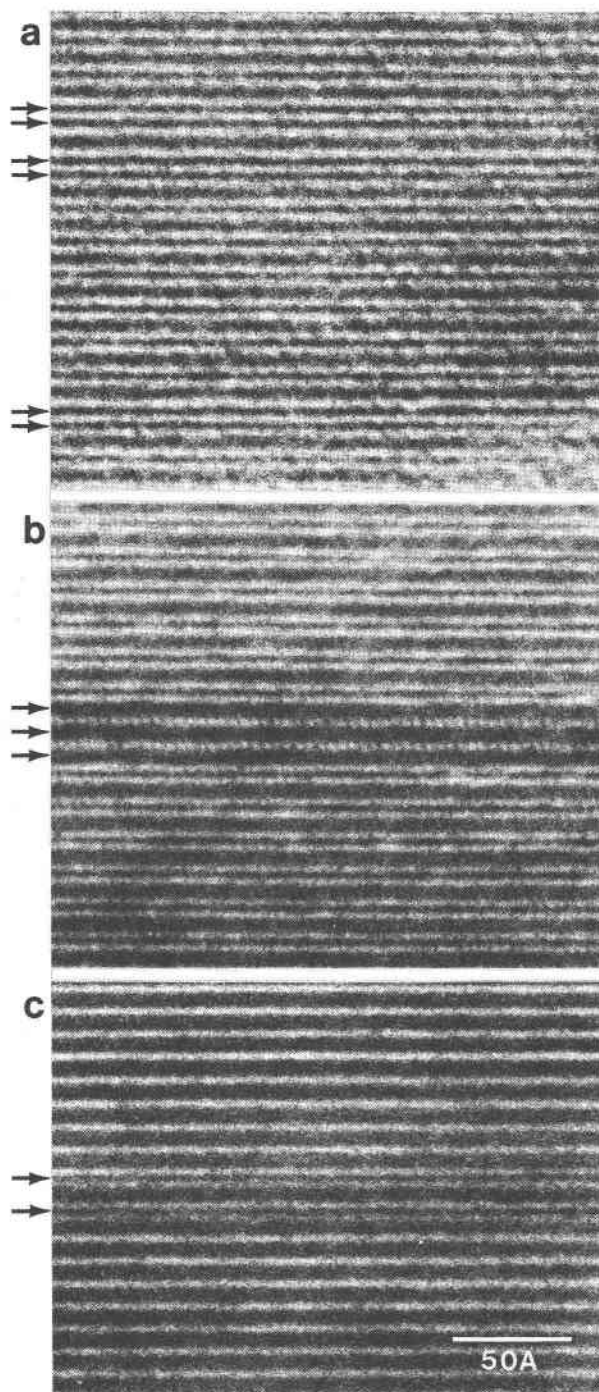
Fig. 10. Mixed layering defects. a. Extra brucite-like layers (or missing talc-like layers) in chlorite. The arrows indicate pairs of adjacent brucite-like layers. b. Extra talc-like layers in chlorite (or missing brucite-like layers). The arrows indicate three adjacent talc-like (TOT) layers. c. Brucite-like layers (arrowed) intercalated in wonesite.

without any indication of disordered mixed layering. Substantial regions of the crystals examined did, however, exhibit significant mixed-layering. This contrasts with the observations of Iijima and Buseck (1977) on a clinochlore specimen, for example. The difference may represent a true difference in the specimens examined, or it may reflect the sample preparation methods employed: whereas Iijima and Buseck used ultramicrotomy and were therefore precluded from examining large amounts of material, the present study used specimens prepared by ion milling, which produced relatively vast thin areas that were examined with HRTEM.

Figure 10a shows an example of the simplest type of mixed layering observed in the Post Pond chlorite. In this case, extra brucite-like layers occur, resulting in planes with adjacent brucite layers (these defects alternatively could be described as missing talc-like layers). Chemically, these defects represent silica-poor, hydroxyl-rich layers in the structure. Another type of planar mixed-layering defect is illustrated in Figure 10b, where brucite layers are missing from the chlorite structure (alternatively described as extra talc-like layers). These defects are relatively silica-rich zones.

Individual planar defects such as those of Figure 10 are smaller than the resolution of any chemical analytical technique presently available, so that it is possible to obtain only the defect stoichiometry, which can be derived from the observed defect structure. However, x-ray chemical analyses of regions containing numerous talc-like layers do indicate sodium and minor potassium, suggesting that these layers should, in fact, be considered to be layers of the mica wonesite intercalated in the chlorite, rather than talc (for x-ray analyses of wonesite, see Fig. 3 in Veblen, 1983). Since the observed Na and K clearly are not located in the tetrahedral or octahedral sites, the interlayer sites created between adjacent tetrahedral sheets in such defects are apparently at least partially filled with alkali cations.

Planar mixed-layering defects occur in small numbers (< a few percent) in almost all of the wonesite examined with HRTEM in this study. These defects take the form of intercalated brucite-like layers (Fig. 10c). The local configuration of such defects is that of chlorite. Similar interlayering of chlorite structure has previously been observed in talc (Veblen, 1980; Veblen and Buseck, 1980, 1981) and in potassium biotite (Iijima and Zhu, 1982; Olives Baños et al., 1983), but not to the extent seen in wonesite.

One curious observation in a region of chlorite with extra talc-like layers (or missing brucite-like layers) is shown in Figure 11. Here, the two "defects" are separated by one normal chlorite layer. The specimen has partially pulled apart along each of the talc-like or mica-like interlayers, but not within the chlorite itself. This behavior apparently implies that the layers of the chlorite structure are more strongly bonded together than those of the mica-like intercalated structure, even though it is
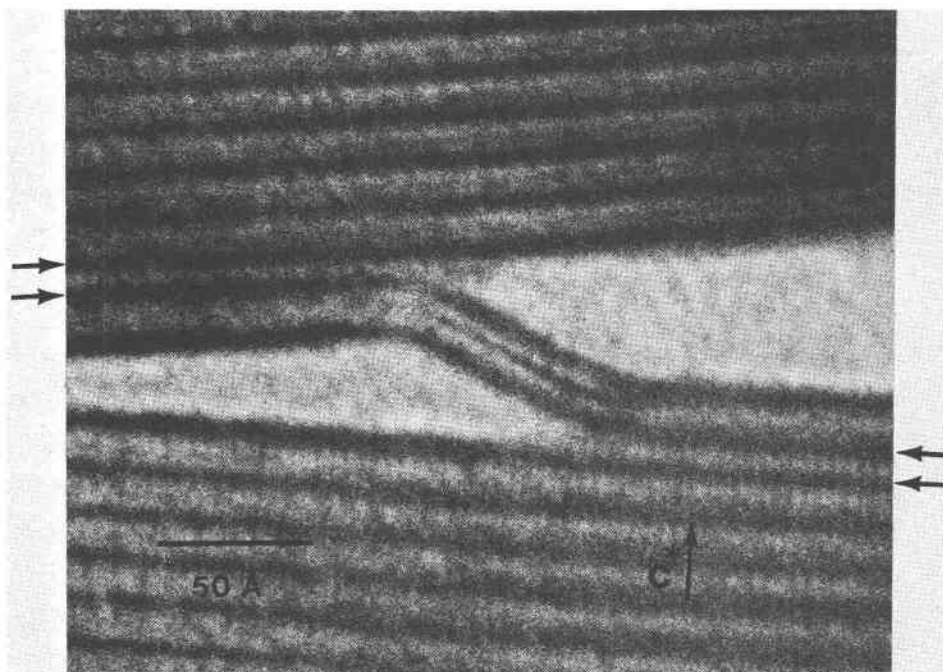
Fig. 11. Chlorite crystal that has partially pulled apart at the interlayers between adjacent talc-like layers (*i.e.*, along interlayers with missing brucite-like layers). Adjacent talc-like (TOT) layers are indicated by arrows.

likely that the mica-like interlayers contain cations, as noted above, while there are no interlayer cations between the layers of the chlorite. This attests to the relatively strong electrostatic and hydrogen bonding between the talc-like and brucite-like parts of the chlorite structure, as demonstrated by Bish and Giese (1981).

Extensive mixed-layering and incipient exsolution

The mixed-layering defects described above occur in relatively small numbers, so that the parts of the specimens that contain them can still be considered to be chlorite or wonesite. In some areas, however, there are similar numbers of chlorite and sodic mica layers, so that the sheet silicate cannot reasonably be referred to as either chlorite or wonesite. In some such areas, mica and chlorite layers are quite finely intergrown, as in Figure 12a. The numbers in this figure are the numbers of mica ("M") and chlorite ("C") layers occuring in sequence. Because a given talc-like layer, for example, can be connected on one side to a brucite-like layer (producing a chlorite configuration) and on the other side to another talc-like layer (producing a mica configuration), it is not always possible to state that a given TOT layer is chlorite or mica. It is therefore necessary, as has been done in Figure 12, to split the structure into unconventional layers. These layers are sectored in the planes of the octahedrally-coordinated cations of the conventional talc-like layers, and it is the interlayers that are designated as mica or chlorite. A chlorite "interlayer" consists of a

brucite-like layer, whereas a mica interlayer lies between two back-to-back tetrahedral sheets and may or may not contain interlayer cations (Fig. 12c).

In other regions of mixed-layer material, packets of mica layers are intercalated with packets of chlorite, forming what could be considered to be an extremely fine-grained lamellar intergrowth of the two minerals (Fig. 12b). Regions such as those shown in Figure a, b are stoichiometrically intermediate between the mica and chlorite compositions and would presumably be recognizable in high-quality electron microprobe analyses. Analysts of chlorites should be alert to this possibility; analyses that are apparently faulty on the basis of stoichiometry might, in fact, simply be from areas of extensive mixed layering involving either extra or missing brucite-like layers.

As explored in detail by Veblen (1983), macroscopic wonesite crystals from this specimen have exsolved pervasively to a lamellar mixture of talc and sodium trioctahedral mica. In regions where narrow lamellae of wonesite are intergrown on or near (001) with chlorite, this exsolution microstructure is not so well developed, although the initial stages of phase separation have still occurred on a scale of a few hundred angstroms. In cases where the wonesite lamellae are only a small number of mica layers thick, separation into two phases is not obvious. However, a curious microstructure in which the wonesite layers curve is commonly present in such cases.
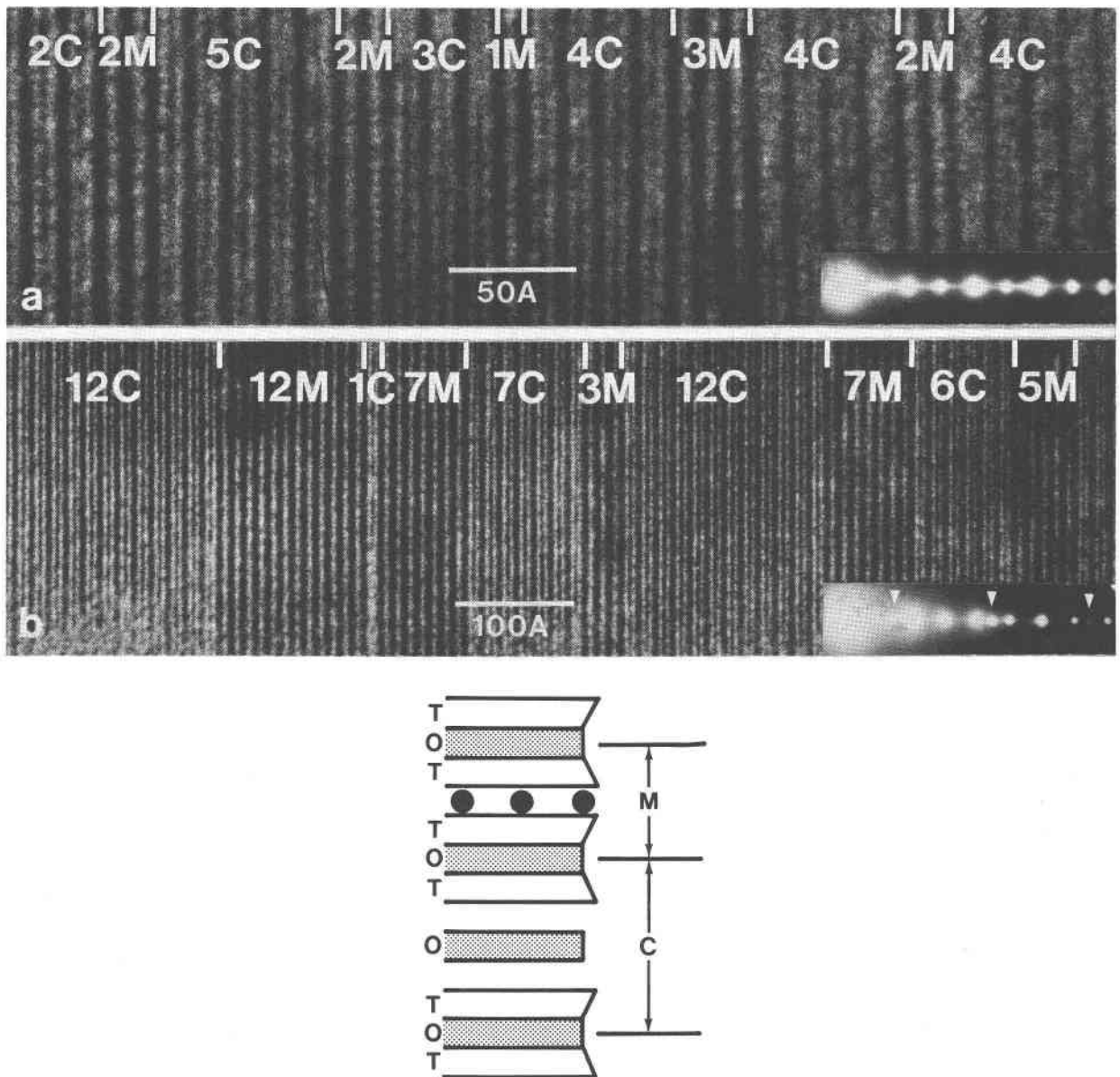
Fig. 12. Mixed-layer chlorite-mica (c^* horizontal). a. Mica ("M") and chlorite ("C") slabs are quite narrow. The numbers indicate the number of adjacent layers of each structure; the layers are defined in an unconventional way, as described in the text and shown in c. The inset diffraction pattern shows the heavily streaked 00*l* row resulting from extremely fine intergrowth. b. Intergrowth of thicker slabs of mica and chlorite. In addition to streaking, the diffraction pattern shows additional reflections from wonesite. Note the different scales of the images in a and b. c. Diagram showing the structures of the nonconventional C (chlorite) and M (mica) slabs. T and O refer to tetrahedral and octahedral sheets, respectively, and circles represent interlayer sites.

This "pinch and swell" structure, as seen in Figure 13, may well be the result of incipient exsolution that has been prevented from further development by the encasing chlorite structure. In this interpretation, bending of the TOT layers occurs because the talc-like regions depleted in sodium have a smaller (001) spacing relative to the high-sodium mica regions with larger basal spacing. If this

pinching and swelling of the wonesite lamellae does, in fact, result from incipient phase separation, it indicates that the chemical forces that drive the exsolution process operate even when the wonesite "crystal" is only a few layers thick. The pinching and swelling effect may be enhanced by minor composition-dependent expansion of the interlayer region resulting from hydration.
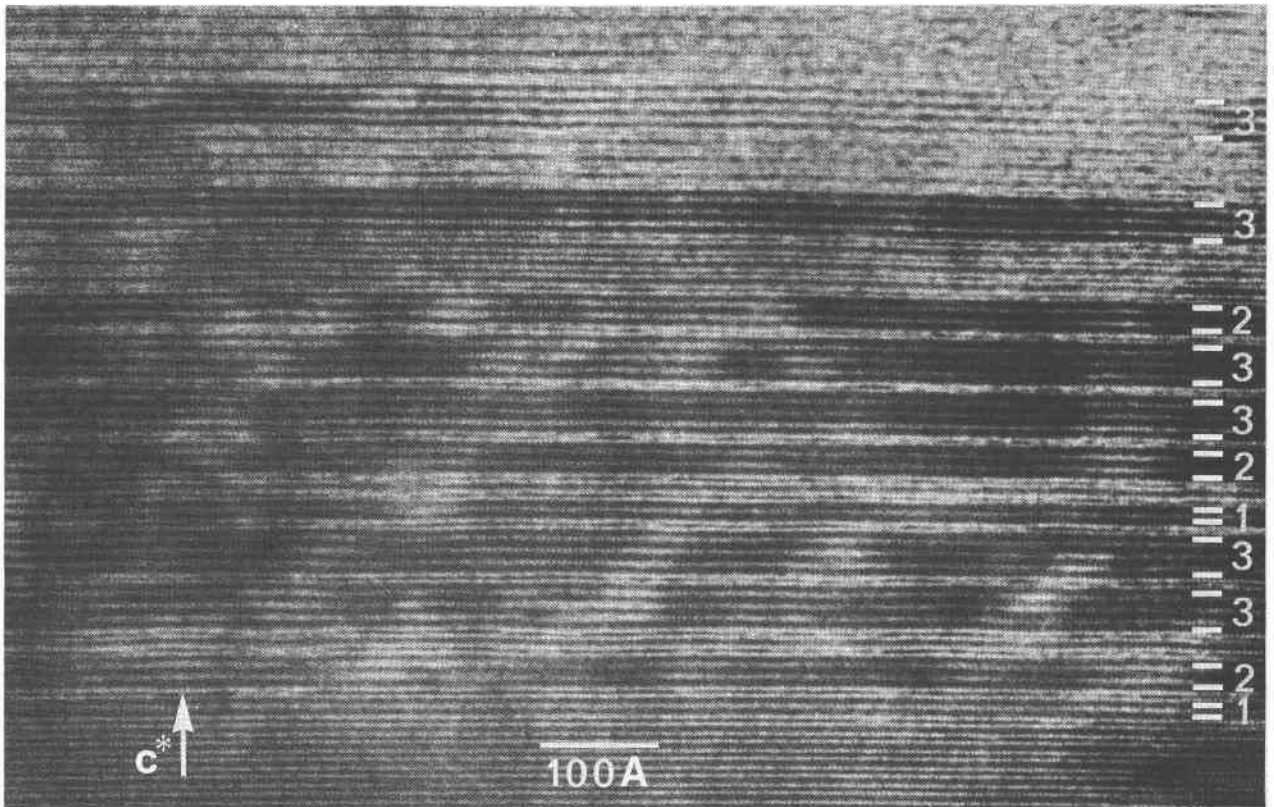
Fig. 13. "Pinch and swell" in finely intergrown chlorite and wonesite. Deviation of the layers from planarity can be seen best by viewing at a low angle parallel to the layers. The bending apparently results from incipient exsolution in the mica. Numbers of adjacent mica layers, as defined in Fig. 12 and the text, are indicated.

Intergrowth of chlorite and wonesite with other sheet silicates

In addition to the intergrowths of chlorite and wonesite described above, both minerals also have been observed to intergrow with other sheet silicates on (001) or planes near this orientation. These other intergrown minerals include kaolinite, talc, and potassium biotite; both talc and biotite had been previously recognized in this rock from TEM, X-ray, and electron microprobe studies (Veblen, 1983; Spear et al., 1981).

Two examples of these further intergrowths are shown in Figure 14. The intercalation of kaolinite in wonesite occurs in limited amounts but was observed in a number of parts of the specimens examined (Fig. 14a). The identity of the intergrown phase was established by its interlayer spacing (approximately 7Å), combined with X-ray analyses that indicated the presence of Al and Si, and not Mg (thus ruling out serpentine).

Intergrowth of wonesite, chlorite, and talc is illustrated in Figure 14b. The talc, which can be recognized by X-ray analyses and its interlayer spacing that is slightly smaller than that of wonesite, does not exhibit the mottled texture seen in the mica. This contrast in wonesite apparently

results from the initial stages of exsolution into talc plus mica.

Discussion

The above descriptions of the stacking and intergrowth phenomena observed in the Post Pond sheet silicates would be incomplete without some consideration of the origins of the microstructures and their petrologic significance. First, the polytypic variations, stacking disorder, and low angle grain boundaries are presumably features acquired during primary growth of the sheet silicates. Although reactions that transform one polytype to another are known from other systems, there is no reason to suppose that similar reactions have occurred in the present case; no microstructures indicative of such transformations were observed, and it is known that all of the stacking modifications that have been noted can form during growth. At the same time, it is clear that the exsolution lamellae of talc in the wonesite are a secondary, postcrystallization feature (Veblen, 1983).

The origins of the mixed-layering defects in chlorite and wonesite and the extreme mixed-layering of these minerals and other sheet silicates are not so clearly
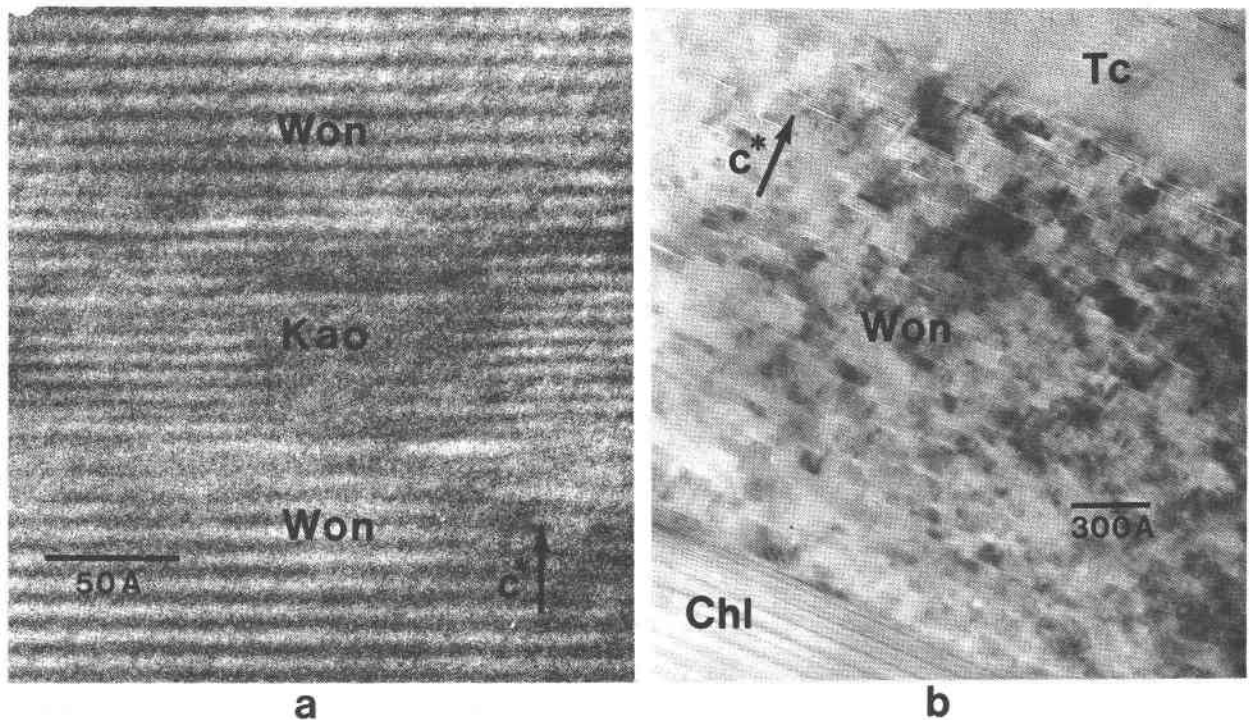
Fig. 14. a. A thin lamella of kaolinite intergrown in wonesite. b. An intergrowth of chlorite, wonesite, and talc. The wonesite exhibits mottling and gaps in the layers characteristic of incipient exsolution of talc and mica.

ascertained. Because kaolinite is a common alteration product of aluminous minerals, and because its chemistry appears to be incompatible with the Mg–Fe silicates of this assemblage, it seems likely that this clay mineral formed by alteration or weathering of the micas and chlorite; textural relationships do not contradict this origin. The careful chemical study of Spear *et al.* (1981) suggests, however, that at least the macroscopically-crystalline wonesite, potassium biotite, talc, and chlorite formed by equilibrium growth under metamorphic conditions. There is no reason to suppose that the smaller crystals of these phases had an alternative origin, but the mode of formation of mixed-layering disorder is more complicated.

Relationships among interacting microstructures have been used in other systems to determine temporal relationships among various structural features. For example, it has been established that post-crystallization reactions can give rise to polysomatic intergrowths in biopyriboles (Veblen, 1981; Veblen and Buseck, 1980, 1981), although similar intergrowths can also form by primary growth processes (Veblen, 1981). Some of the same sorts of defects that have proven useful in other systems are, in fact, present in the mixed-layer sheet silicates from the Post Pond Volcanics. Figure 15 shows the termination of a talc-like layer in chlorite, termination of a chlorite layer in the mica of an intergrowth, and the

coupled terminations of brucite layers in wonesite and talc-like layers in chlorite. It is possible that these terminations are the remnants of arrested reactions in which the terminating layers were either growing or shrinking. In the absence of other, interacting microstructures, however, it is impossible to distinguish this explanation from the possibility that the terminations formed during primary crystal growth.

In the chlorite, such interacting microstructures are entirely absent. In the wonesite, brucite-like layers typically pass through the exsolution lamellae of talc without interruption. It might be argued that non-termination of these layers by the talc lamellae indicates that the brucite-like sheets formed prior to exsolution, perhaps during crystal growth. It is also conceivable, however, that a brucite-like sheet growing at a later stage could continue its growth unimpeded through the talc lamellae. Thus, it is not possible to establish the formation mechanism of the mixed layering, and the terminations of structural layers remain as interesting structural phenomena, rather than being useful temporal markers.

Possibly the most important result of this study of stacking phenomena and mixed layering is that substantial mixed layer disorder can occur in macroscopically-crystalline, rock-forming sheet silicates. If such mixed layering is a common phenomenon, it will have important implications for the interpretation of microprobe analyti-
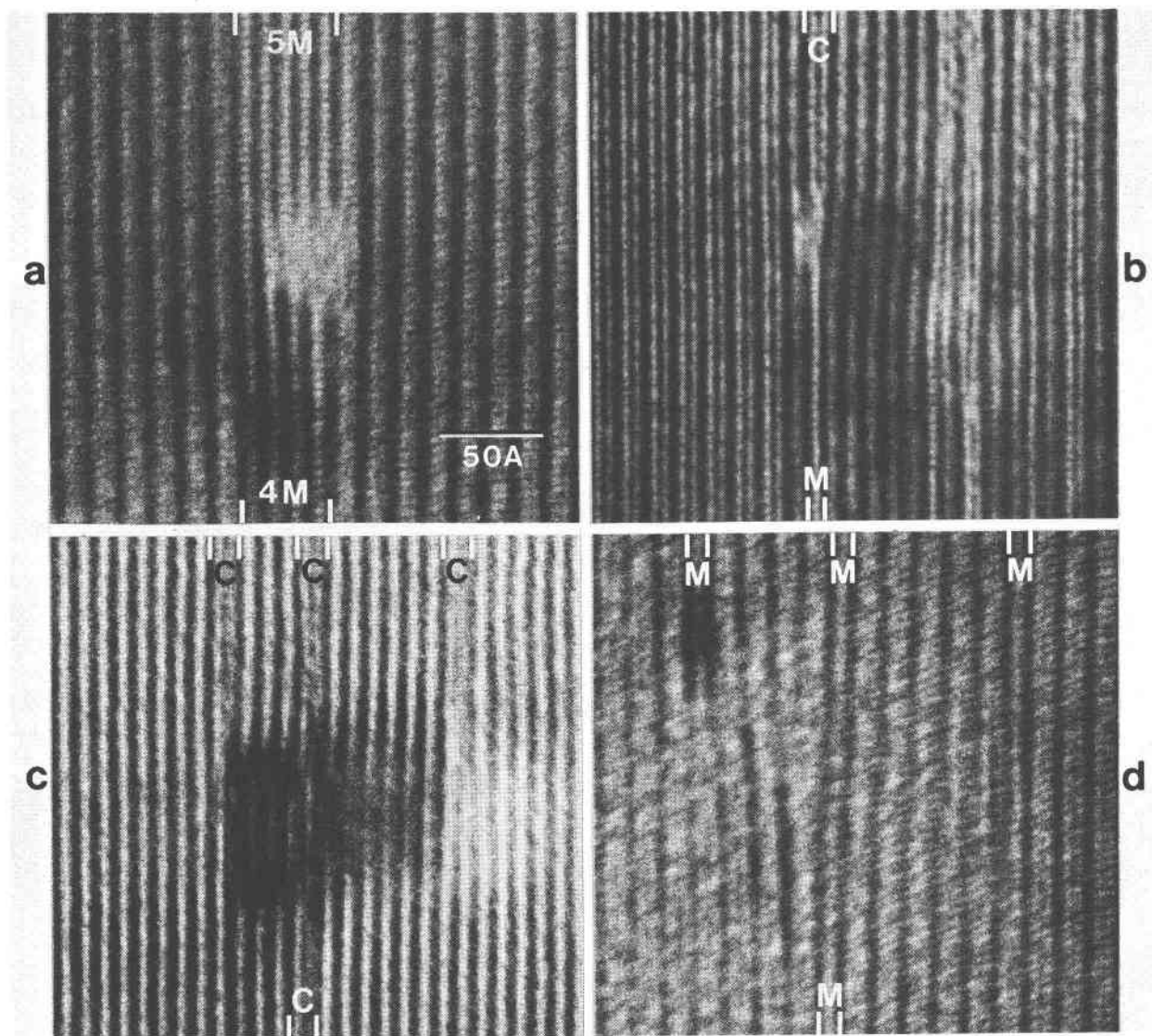
Fig. 15. Termination of layers in mixed-layer materials. a. Termination of a mica layer in chlorite. At the top, there are 5 mica layers (as defined in Fig. 12 and the text), while there are only 4 at the bottom. b. Termination of a brucite layer in intergrown wonesite and chlorite. This results in a chlorite layer at the top ("C") becoming a mica layer at the bottom ("M"). c. Cooperative termination of two brucite layers in wonesite. At the top, three brucite layers produce three local chlorite configurations ("C"), while there is only one at the bottom. Strain contrast in the middle of the figure results from the termination. d. Two of the three mica layers intergrown in chlorite at the top ("M") terminate cooperatively, leaving only one at the bottom of the figure.

cal results in sheet silicates, because polysomatism of this sort affects both stoichiometry and apparent cation partitioning trends. Such disordered intercalation of different structural units can be difficult to recognize in powder X-ray diffraction experiments, and high-quality single-crystal X-ray results are difficult to obtain because of severe crystal deformation. Thus, the sheet silicates of ordinary igneous and metamorphic rocks provide fertile ground for petrologically significant future studies employing HRTEM and X-ray microanalysis techniques. Such studies should be aimed at statistically valid characterization of these minerals by the observation of relatively large areas on ion-milled specimens.

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