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MONTMORILLONITE PSEUDOMORPHS AFTER AMPHIBOLE FROM MELBOURNE, AUSTRALIA

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Abstract—Well developed smectite "crystals" up to 10 mm long, which probably are pseudomorphic after titaniferous hornblende phenocrysts, are present in a weathered dike in a Melbourne clay pit. The pseudomorphs contain 77 per cent of montmorillonite as determined by X-ray powder diffraction, differential thermal analysis, thermo-gravimetric and chemical analysis. The pseudo-hexagonal shape of the pseuodomorphs probably reflects the original crystal habit of the hornblende. The mechanism of alteration of an amphibole to a smectite is discussed.

INTRODUCTION

Highly folded mudstones, siltstones and sandstones of the Melbourne area, Australia, are of Silurian age and are intruded by many dike bodies. Of these Bowen (1967) reported "The Silurian of the Melbourne area has been intruded by a large number of dyke bodies varying in composition. The majority of these dykes are completely decomposed and now consist almost entirely of clay minerals. The presence or absence of quartz in these decomposed dykes is the only indication as to original composition. Occasionally relict feldspar or ferromagnesian phenocrysts are recognisable in thin section and rarely the dykes are fresh enough for complete petrological examination. Because of their decomposed nature it is only in road cuttings, clay pits, building excavations etc. that the dykes are noticeable and hence the extent and strength of the dyke swarm is largely a matter of conjecture."

Dikes that are from 1 to 3 m thick and that extend through the older brick clay pits are both acid and basic in character, frequently porphyritic and their location has been extensively mapped by Bain and Spencer-Jones (1952). Being unsuited for brick-making purposes they are bypassed in the winning of clay. Cole, Lancucki and Nickson (1968), in examining the clay mineralogy of a pit from Preston found that one dike at depths of 27.4 and 42.7 m had some unusual features. Large greenish-grey opaque "crystals" up to 10 mm long, originally of a ferromagnesian mineral or a plagioclase feldspar were pseudomorphed by a smectite mineral. An interesting feature of the replacement was that the peripheries of the crystals were colored but the central cores were white and opaque. The cause of this and the identification of the original crystals were not certain. Also it was not clear as to why the perfect crystal shape had been preserved by the smectite during weathering. The composition of the smectite was not known, nor was the original composition of the rock. The present investigation was aimed at finding answers to some of these questions of composition and origin.

EXPERIMENTAL

The starting material for most of the work was obtained by hand picking the small crystals from the crushed rock. Although laborious and slow this was done fairly easily since the characteristic shape of the pseudomorphs could readily be recognised (Figure 1). At the same time other constituents, such as feldspar and mica phenocrysts also were hand picked for examination. In order to identify non-silicate minerals in the rock and the pseudomorphs, portions of each were treated with HF according to the method of Norrish (1968).

Both the rock and the pseudomorphs were analysed chemically. Before analysis the former was simply crushed but the pseudomorphs were crushed and treated with $CaCl_2$ to Ca-saturate the clay mineral in order to obtain a measure of its cation-exchange capacity.

The X-ray diffraction patterns were taken mainly on a Philips powder diffractometer with monochromatised CuKα radiation. The samples were either packed into aluminum holders or dispersed with water on to glass slides or ceramic plates. Single pseudomorphs and flakes of mica were examined on a single-crystal camera with filtered Cu radiation.

Differential thermal curves were made both on equipment described by Carthew and Cole (1952) and that manufactured by Rigaku Denki. In the latter instrument the loss in weight was determined simultaneously with the differential thermal curve. All runs were made at a heating rate of 10°C/min.

In making a thin section of the rock for petrological examination fragments were first boiled for some hours in Canada balsam in order to consolidate the friable material sufficiently to permit subsequent grinding with kerosene. Although not highly successful one slice was obtained that adequately demonstrated the rock structure.

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Transmission electron microscopy was done on a Siemens Elmiskop 1A operating at magnifications up to 40000 times. Materials were dispersed ultrasonically in absolute ethanol and a drop of the dispersed clay was deposited for examination on standard grids coated with carbon. Selected area electron-diffraction photographs were made of particles for which the electron micrographs had been obtained.

Scanning electron micrographs were done on a Jeol JXA-50A scanning electron microscope which had an electron probe micro-analyser attachment and an energy dispersive spectrometer. For this examination pseudomorphs were embedded in an araldite mixture according to the method described by Glauert and Glauert (1958). After the resin had set the mount was ground away, with fine carborundum wetted with kerosene, to expose a cross section of the pseudomorphs that could be examined in the scanning electron microscope.

RESULTS

The well developed faces of the pseudomorphs (Fig. 1 insert) have interfacial angles (in order of rotation) of 118, 122, 119, 119, 131 and 111 degrees. This indicates a pseudo-hexagonal symmetry perpendicular to the length of the pseudomorphs. Such symmetry can arise from crystals of two likely original mineral classes in the rock: feldspars and amphiboles.

The X-ray diffraction pattern of the crushed pseudomorphs mounted as a dispersion on a glass slide (Fig. 2a) is essentially that of a smectite with a number of weak, sharp lines that can be ascribed to feldspar, mica, kaolinite, apatite and anatase with a line at 2.70 Å ($2\theta = 33.2°$) possibly due to hematite. The anatase and apatite were confirmed by treating the sample with HF to destroy the silicate minerals and running an X-ray diffractometer trace of the residue which clearly shows (Fig. 2b) the presence of both anatase and apatite. The X-ray diffractometer trace of separated and crushed phenocrysts of feldspar is given in Fig. 2c. This pattern is identical with a synthetic feldspar of composition $Na_{0.61}\ K_{0.39}\ AlSi_3O_8$ described by Donnay and Donnay (1952). Isolated mica flakes gave the pattern in Fig. 2d, which is considered to be that of biotite mica.

The simultaneously recorded differential thermal and weight-loss curves for the pseudomorphs together with a differential plot of the weight-loss curve (Fig. 3) are typical of those to be expected from an abnormal smectite mineral (Cole and Hosking, 1957). There is a large low-temperature water loss (10.8%) and endotherm followed by a main hydroxyl loss and endotherm at 550°C with a subsidiary one at 675°C. Part of the 550°C endotherm could be due to the small amount of kaolinite present. The total weight loss was 17.18%. A small water loss and endotherm at 310°C may be due to a final loss of interlayer water from the montmorillonite or to an amount of gibbsite too small to be detected by X-ray diffraction.

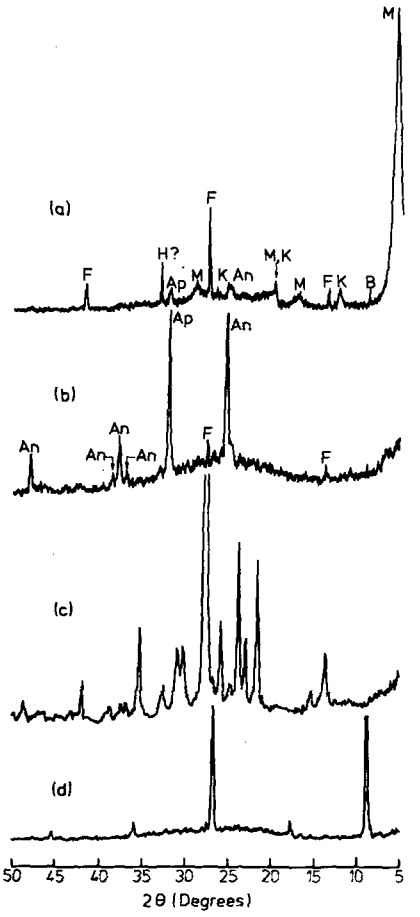


Fig. 2. X-ray diffraction patterns of pseudomorph (a); pseudomorph treated with HF (b); feldspar phenocrysts (c); biotite flakes (d). In (a) and (b), M = montmorillonite, F = feldspar, K = kaolinite, An = anatase, Ap = apatite, H = hematite. Vertical scale is linear.

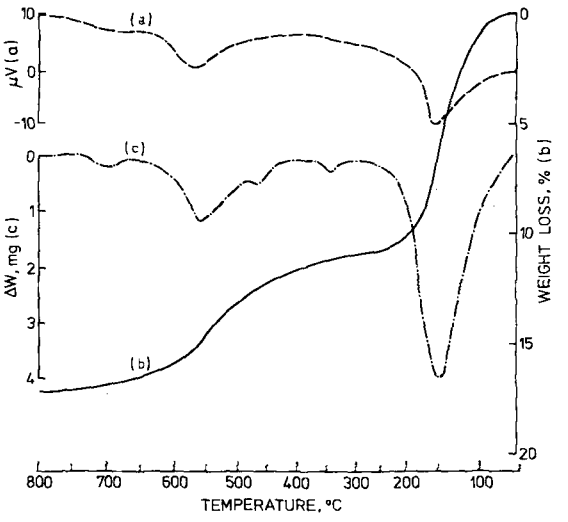


Fig. 3. Simultaneously recorded differential thermal and weight-loss curves. DTA curve (a); weight-loss curve (b); differential of the weight-loss curve (c).

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The chemical analyses of the rock sample and the Ca-saturated pseudomorphs are given in Table 1. Features of the latter are the high total water loss of 22.04%, the high TiO_2 and CaO contents and the presence of a small amount of P_2O_5. In this analysis no Na_2O is reported since for a pure clay mineral saturated with calcium, Na^+ should have been exchanged by Ca^{2+} so that the determination of soda was not included in the analysis. However, since the pseudomorphs contained a soda-potash feldspar some Na_2O must have been present and on the basis of the rock analysis for Na_2O, K_2O and the K_2O content of the pseudomorph this was arbitrarily set at 0.44% on an ignited basis and the analysis re-calculated accordingly (Table 1). Regarding the rock analysis it has a high CO_2 content for which there is no obvious simple explanation.

The electron micrographs of the pseudomorphs show large thin overlapped plates that frequently exhibit *moiré* patterns, similar to those displayed for kaolinite by McConnell and Fleet (1970). Some, however, have banded structures that are reminiscent of the external shape of the pseudomorphs. None of the untreated material gave any evidence of a grid structure of anatase that might have held the pseudomorphs together. Some evidence for this, however, was found in material treated with HF but grid-like structures were rare.

The scanning electron micrograph of a polished cross section of a pseudomorph shows a very granular structure with several prominent areas being rich solely in Al. Titanium also tends to occur as a distinct phase but some is associated with iron probably as ilmenite. Silicon and aluminum correspond to areas of montmorillonite but calcium is only associated with some of these areas. Magnesium could be expected to be the main cation associated with the montmorillonite.

In thin section the rock is composed of phenocrysts of the pseudomorph and feldspar set in a fine grained mass of feldspar laths aligned parallel to a flow direction, with dark granules of iron ore, and glass altered to montmorillonite. The feldspar phenocrysts are badly fractured along narrow zones that are now filled with montmorillonite.

DISCUSSION

The regular pseudo-hexagonal shape of the pseudomorphs (Fig. 1) has been taken as an indication of a primary mineral that the montmorillonite has replaced during weathering. The measured interfacial angles of 118, 122, 119, 119, 131 and 111 degrees are not accurate but they probably correspond to the sequence 118, 124, 118, 118, 124 and 118 degrees given by amphiboles. Feldspars are the most likely of other minerals in the rock that could have been altered to still show pseudo-hexagonal symmetry in sections perpendicular to the *c*-crystallographic axis, but they seldom contain TiO_2 and in the dike body being investigated they have generally resisted weathering. Consequently the montmorillonite is thought to have been derived from phenocrysts of titaniferous hornblende.

No evidence was found that the pseudomorphs were held together by anatase as found for silcretes

Table 1. Analyses of sample 6530 expressed on an air-dry basis

		Pseudomorph		
	Rock Sample* (%)	As reported† (%)	Allowed for Na_2O‡ (%)	Allowing for impurities§ (%)
SiO_2	52.3	42.63	42.43	48.43
Al_2O_3	17.2	18.43	18.34	18.52
Fe_2O_3	3.70	6.71	6.69	0.75
FeO	3.80			
MnO	0.26	0.16	0.16	0.20
CaO	0.59	3.31	3.29	3.30
MgO	1.50	1.75	1.74	1.68
Na_2O	2.85		0.35	
K_2O	5.40	0.67	0.67	
TiO_2	0.27	3.75	3.73	
SO_3	0.40			
Cl	0.20			
CO_2	2.75			
P_2O_5		0.55	0.55	
H_2O^+	2.65	8.45	8.45	9.24
H_2O^-	5.95	13.59	13.59	17.87
Totals	99.82	100.00	99.99	99.99

* Analysis by Amdel.

† Analysis by K. Norrish. Originally reported on an ignited basis with a total of 99.84% and H_2O^+ and H_2O^- relative to the clay dried at 110°C.

‡ 0.44% Na_2O was added to the analysis on an ignited basis before recalculation.

§ After allowing for 1.3% apatite, 4.5% feldspar, 4.7% biotite, 2% kaolinite, 3.7% anatase, 2.0% gibbsite and 5.0% hematite.

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by Milnes and Hutton (1974). The 3.75% TiO_2 content of the pseudomorphs is largely present as anatase and some of it forms a grid structure but there is too little present to hold the montmorillonite together. The same applies to the apatite.

The X-ray diffraction results (Fig. 1) indicate that the pseudomorphs are characterised by a basal spacing of 15.2 Å after being prepared on a glass slide with water. When mounted dry on a ground glass surface, lower spacings are recorded with a minimum of 12.8 Å. This suggests that the original exchange cation of the pseudomorph is probably mainly Na^+ since this is the only common cation to have a single layer of interlayer water, represented by a basal spacing of approximately 12.5 Å, at normal room conditions of about 50% r.h. (MacEwan 1961). Ca–montmorillonite tends to be more highly hydrated than Na–montmorillonite at all relative humidities, so that the total weight loss of the Ca-saturated pseudomorphs (Table 1) is higher (4.86%) than the clay in its natural hydration state with its natural exchange cation (Fig. 3). Impurities detected by X-ray diffraction were feldspar, biotite, kaolinite, hematite, anatase and apatite. Scanning electron microscopy and electron probe micro-analysis indicated that aluminum hydroxide is present also, probably as gibbsite. The amount of the latter was estimated from the small endotherm and weight loss at 310°C (Fig. 3).

To arrive at the chemical composition of the montmorillonite of the pseudomorph, corrections were made to the original analysis of Table 1 according to the methods described by Mackenzie (1960) and Cole and Hajela (1973). The following impurities were allowed for: 1.3% apatite, 4.5% feldspar (soda-potash variety as discussed earlier), 4.7% biotite, 2.0% kaolinite, 3.7% anatase, 2.0% gibbsite and 5.0% hematite. The corrected composition (Table 1) yields the structural formula:-

$$Ca^{2+}_{0.57}\ (Si_{7.80}Al_{0.20})$$
$$(Al_{3.31}\ Fe^{3+}_{0.09}Mg_{0.42}Mn_{0.03})\ O_{20}(OH)_4$$

The tetrahedral layer has a charge of −0.20, the octahedral layer a charge of −0.90 (it is 0.15 atoms deficient) yielding a total of −1.10 balanced by +1.14 from the interlayer cation. The cation-exchange capacity is 118 m-equiv./100 g on an air-dry basis, 144 on an oven-dry basis, and 162 on an ignited basis. The cation-exchange capacity is high, but not excessively so and the composition is that of a montmorillonite rather than of a beidellite. This was confirmed by applying the combined test devised by Greene-Kelly (1953) of Li-saturating the sample, then heating it to 200–300°C followed by glycerol treatment to distinguish beidellite from montmorillonite.

If the composition of the pseudomorphs is compared with that of titaniferous hornblendes it is found that such hornblendes usually have a higher ratio of SiO_2:Al_2O_3 (Deer, Howie and Zussman, 1963) but the kaersutite hornblende from the hornblende monchiquite of the Orkneys (Deer, Howie and Zussman, 1963) have a similar silica–alumina ratio and a comparable TiO_2 content. However, all hornblendes have higher Fe_2O_3, FeO, MgO, CaO, Na_2O and K_2O values than montmorillonite so that a considerable leaching of these components would be required to convert, *in situ*, a hornblende to a montmorillonite clay. As these two minerals differ considerably in density this could be achieved with the montmorillonite maintaining the same volume and shape of the original hornblende as in the present instance.

The transformation of an amphibole to a montmorillonite could take place in a manner similar to that postulated by Eggleton (1974) for the transformation of hedenbergite pyroxene to nontronite. For the latter transformation the *y*-axes are common and the *z*-axis of the pyroxene is aligned parallel to the *x*-axis of the nontronite. Amphiboles differ from pyroxenes in having a doubled *y*-axis which yields a double chain of $(Si,Al)O_4$ tetrahedra extending in the *z*-direction. Their structures are more like clay minerals than pyroxenes in that they contain "talc like" strips made up by five cations in a "brucite" strip sandwiched between two inward pointing bands of tetrahedra (Deer, Howie and Zussman, 1963). If the transformation orientations of amphibole to smectite are the same as that of hedenbergite to pyroxene then the relationship between the amphibole and the smectite would be as shown in Fig. 4. Because alternate chains in the *z*-direction of pyroxenes and amphiboles have (Si, Al) tetrahedra pointing in opposite directions, portions of the structure surrounding the hole occupied by a large cation must be dissolved to allow vertical displacement of tetrahedral and octahedral units to produce a continuous sheet of tetrahedra pointing in the required directions for a smectite (see Fig. 4). In this way, one and a half layers of amphibole in the *x*-direction are required to form one layer of smectite in the *z*-direction. The amphibole considered to be transforming in the present instance has the composition $Ca_2(Na,K)(Mg,Fe^{2+},Fe^{3+})Ti(Si_6Al_2O_{22})(O,OH,F)_2$. Transformation to the smectite pseudomorphs would require considerable leaching of Al from (Si, Al) tetrahedra, and Fe from (Mg,Fe^{2+},Fe^{3+}) octahedra. Some of the leached Al enters the octahedral region of the smectite and the remainder remains as free $Al(OH)_3$ (gibbsite). The leached Fe remains as free hematite. The Ti of the amphibole is freed from the octahedral sites and appears as anatase. As in the case of pyroxenes it would be expected that only small domains of the amphibole would transform to smectite in perfect orientation. Nevertheless such a transformation could yield a pseudocrystal of clay retaining the shape of the original ferromagnesian mineral.

An examination of the rock analysis in the light of the chemical composition deduced for the montmorillonite pseudomorphs and the composition of the impurities indicates that it would be composed of about 50–55% feldspar (some in the ground mass

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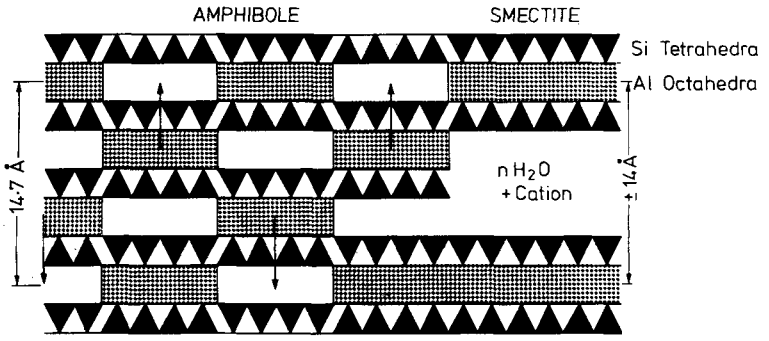


Fig. 4. Postulated boundary region between amphibole and smectite viewed along amphibole *z*-axis. Cations and water not represented (after Eggleston, 1974).

more potash rich than the phenocrysts), 30% montmorillonite, 10% biotite and 5–10% of minor components such as carbonates, chlorides, sulphates, iron and titanium oxides. There is no free silica agreeing with the absence of quartz. Calcium feldspar is also absent. The original rock was probably a soda–potash feldspar, titaniferous hornblende, mica prophyry.

CONCLUSIONS

The pseudomorphs found in a dike body in a Melbourne brick clay pit are composed of 77% pure montmorillonite with impurities of soda–potash feldspar, biotite, anatase, hematite, gibbsite and apatite. The montmorillonite is of the abnormal type with its main hydroxyl water loss on heating at 550°C.

The pseudomorphs investigated probably were formed from titaniferous hornblende in a porphyry which also contained phenocrysts of alkali feldspar and biotite.

The pseudo-hexagonal shape of the pseudomorphs probably reflects the original crystal habit of the hornblende. It cannot be due to a structural grid of anatase. Scanning electron microscopy and electron probe micro-analysis indicate that the montmorillonite is more heterogeneous than expected. Areas rich in iron oxide or hydroxide, aluminum hydroxides and titanium oxide (anatase) are common.

The transformation of an amphibole to a smectite probably takes place similarly to the transformation of hedenbergite to nontronite recently discussed by Eggleton (1974).

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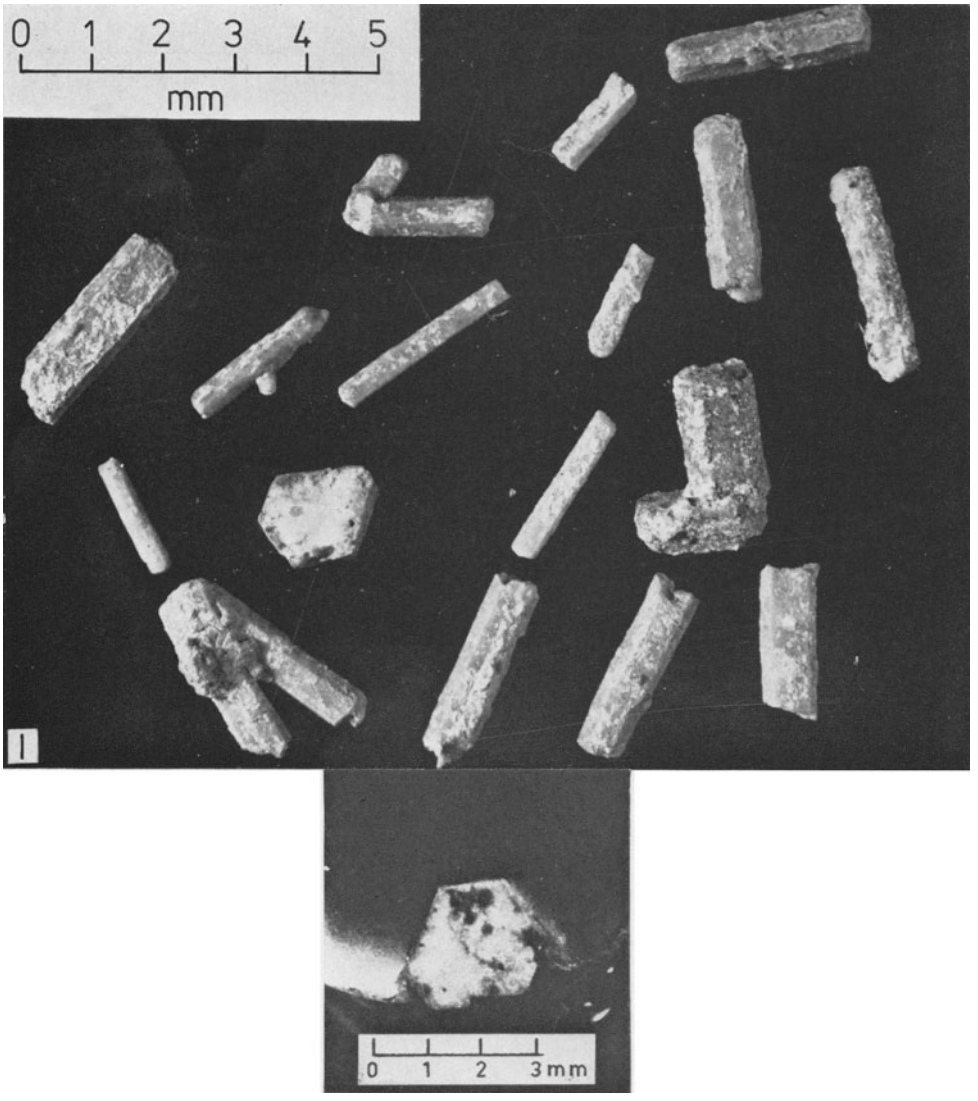


Fig. 1. Montmorillonite pseudomorphs. The insert photograph shows a typical pseudo-hexagonal cross section.

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