

On stacking disorder and polytypism in pectolite and serandite

By WOLFGANG FRIEDRICH MÜLLER

Institut für Kristallographie und Mineralogie der Universität Frankfurt am Main*

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Auszug

Die isotypen Minerale Pektolith, $\text{Ca}_2\text{NaHSi}_3\text{O}_9$, und Serandit, $\text{Mn}_2\text{NaHSi}_3\text{O}_9$, wurden mit transmissionselektronenmikroskopischen Methoden untersucht, um zu sehen, ob sich ihre strukturelle Verwandtschaft mit Wollastonit, CaSiO_3 , auch in ähnlichen Polytypie-Erscheinungen äußert. Pektolith und Serandit weisen wie Wollastonit Stapelfehler parallel zu (100) mit einem Verschiebungsvektor von $\frac{1}{2}b$ auf. Ein Polytyp von Pektolith mit Beugungsmaxima und Auslöschungen entsprechend denen des pseudomonoklinen Parawollastonits wurde gefunden; er wurde vorläufig Parapektolith genannt. Submikroskopische Verzwilligung nach (100) ist häufig in Pektolith wie in Wollastonit, kam dagegen nur selten in Serandit vor. Ein „Paraserandit“ wurde nicht beobachtet.

Abstract

The isotypic minerals pectolite and serandite have been studied by transmission electron microscopic methods in order to examine if their structural similarities to wollastonite are reflected in their polytypic behavior. Pectolite and serandite exhibit like wollastonite stacking faults parallel to (100) with a displacement vector of $\frac{1}{2}b$. A polytype of pectolite, tentatively called parapectolite, with diffraction maxima and extinctions analogous to pseudomonoclinic parawollastonite was found. Submicroscopic twinning on (100) is frequent in pectolite like in wollastonite. It occurred only rarely in serandite and no “paraserandite” was observed.

Introduction

The isotypic minerals pectolite, $\text{Ca}_2\text{NaHSi}_3\text{O}_9$, and serandite, $\text{Mn}_2\text{NaHSi}_3\text{O}_9$, are chain silicates. Their crystal structures are characterized by single chains of SiO_4 tetrahedra which extend parallel to

* Present address: Mineralogie, Fachbereich 11, Technische Hochschule Darmstadt, 6100 Darmstadt.

b and have repeat units of three tetrahedra. Crystal-structure determinations of pectolite¹⁻³ and of serandite^{4,5} have shown that both minerals are closely related to wollastonite, CaSiO₃, which is also a chain silicate with a Dreier-Einfachkette (cf.⁶). Their structural relationships have been discussed by several authors^{2,7,8}. Unit-cell information for wollastonite, pectolite, and serandite is given in Table 1.

Table 1. *Unit-cell data for wollastonite, pectolite, and serandite*

	wollastonite ²	pectolite ²	serandite ⁵
<i>a</i>	7.94 Å	7.99 Å	7.68 Å
<i>b</i>	7.32	7.04	6.89
<i>c</i>	7.70	7.02	6.75
α	90.03°	90.52°	90.53°
β	95.37	95.18	94.12
γ	103.43	102.47	102.25

The present transmission electron-microscopic study was started in order to examine whether the structural similarities between wollastonite, pectolite, and serandite are also reflected in their polytypic behavior and their crystal defects. Before the results on pectolite and serandite are presented, a brief review of results on wollastonite is given in order to facilitate a comparison between the three minerals.

¹ M. J. BUERGER, The determination of the crystal structure of pectolite, Ca₂NaHSi₃O₉. *Z. Kristallogr.* **108** (1956) 248–262.

² C. T. PREWITT and M. J. BUERGER, Comparison of the crystal structure of wollastonite and pectolite. *Min. Soc. Amer. Spec. Paper* **1** (1963) 293–302.

³ C. T. PREWITT, Refinement of the structure of pectolite, Ca₂NaHSi₃O₉. *Z. Kristallogr.* **125** (1967) 298–316.

⁴ Y. TAKÉUCHI, Y. KUDOH and N. HAGA, The interpretation of partial Patterson functions and its application to structure analyses of serandite Mn₂NaHSi₃O₉ and banalsite BaNa₂Al₄Si₄O₁₆. *Z. Kristallogr.* **138** (1973) 313–336.

⁵ Y. TAKÉUCHI, Y. KUDOH and T. YAMANAKA, Crystal chemistry of the serandite-pectolite series and related minerals. *Amer. Mineral.* **61** (1976) 229–237.

⁶ F. LIEBAU, Silicon. In: *Handbook of Geochemistry*, Vol. II/3. Springer, Berlin, Heidelberg, New York, 1972.

⁷ C. T. PREWITT and D. PEACOR, Crystal chemistry of the pyroxenes and pyroxenoids. *Amer. Mineral.* **49** (1964) 1527–1542.

⁸ M. A. PEACOCK, On wollastonite and parawollastonite. *Amer. J. Sci.* **30** (1935) 495–529.

Polytypism and stacking disorder in wollastonite have already been discussed in several x-ray diffraction studies^{2,9-15} and also very recently in transmission electron-microscopic studies¹⁶⁻¹⁹. The common characteristic feature of most natural wollastonite crystals are diffuse streaks parallel to \mathbf{a}^* of $k = 2n + 1$ reflections. JEFFERY¹¹ attributed this streaking to stacking faults parallel to (100) with a displacement vector of $\frac{1}{2}b$ and WENK¹⁴ suggested that polytypism of wollastonite could be explained by periodic (100) stacking faults with a $\frac{1}{2}b$ displacement vector. A study of wollastonites from different localities showed that the predominant polytypes are either triclinic wollastonite, untwinned or twinned, or parawollastonite¹⁸. All samples displayed stacking disorder in varying degrees, and submicroscopic intergrowth of different polytypes was frequently observed. Contrast experiments in the transmission electron microscope proved that the displacement vector of the stacking faults is indeed $\frac{1}{2}b$. A structural model for parawollastonite has been proposed^{18,19}: A fault along (100) associated with every pair of unit cells of triclinic wollastonite displaces the next pair of unit cells by $\frac{1}{2}b$, thereby creating a new triclinic unit cell whose \mathbf{a} is four times larger than that of the original cell. Professor TAKÉUCHI

⁹ K. S. MAMEDOV and N. V. BELOV, Crystal structure of wollastonite. *Doklady Akad. Nauk SSSR* **107** (1956) 463-466.

¹⁰ T. ITO, *X-ray studies on polymorphism*. Maruzen, Tokyo, 1950.

¹¹ J. W. JEFFERY, Unusual x-ray diffraction effects from a crystal of wollastonite. *Acta Crystallogr.* **6** (1953) 821-825.

¹² K. DORNBERGER-SCHIFF, F. LIEBAU and E. THILO, Zur Struktur des β -Wollastonits, des Maddrellschen Salzes und des Natriumpolyarsenates. *Acta Crystallogr.* **8** (1955) 752-754.

¹³ F. J. TROJER, The crystal structure of parawollastonite. *Z. Kristallogr.* **127** (1968) 291-308.

¹⁴ H. R. WENK, Polymorphism of wollastonite. *Contrib. Mineral. Petrol.* **22** (1969) 238-247.

¹⁵ D. A. JEFFERSON and M. G. BOWN, Polytypism and stacking disorder in wollastonite. *Nature Physical Science* **245** (1973) 43-44.

¹⁶ T. AKAI, Direct observation of stacking faults in wollastonite. *Memoirs Faculty of Science, Kyoto University, Ser. Geology and Mineralogy* **41** (1975) no. 2, 1-14.

¹⁷ D. A. JEFFERSON and J. M. THOMAS, The resolution of disordered polytypic silicates. *Acta Crystallogr. A* **31** (1975) Suppl. S 295.

¹⁸ W. F. MÜLLER and H. R. WENK, Transmission electron microscopic study of wollastonite (CaSiO_3). *Acta Crystallogr. A* **31** (1975) Suppl. S 294.

¹⁹ H. R. WENK, W. F. MÜLLER, N. A. LIDDELL and P. P. PHAKEY, Polytypism in wollastonite. In: *Electron microscopy in mineralogy* (H. R. WENK, coord. ed.), p. 324-331. Springer, Berlin, Heidelberg, New York, 1976.

has kindly brought to the attention of the present author a very similar proposal²⁰. He derives parawollastonite from the wollastonite structure by shifting only the silicate chains of every third and fourth cell by $\frac{1}{2}b$.

Material and techniques

The two pectolite samples studied come from Kinzigtal (Black Forest, Germany) and Rauschermühle (near Niederkirchen, Pfalz, Germany). A serandite sample from the Tanahota mine, Japan, was kindly donated by Professor TAKÉUCHI. Its chemical composition⁵ is $(\text{Mn}_{1.88}\text{Ca}_{0.17}\text{Mg}_{0.11})\text{Na}_{1.00}\text{HSi}_{2.97}\text{O}_9$. The other serandite sample was kindly supplied by Professor JAGODZINSKI. Its locality is Demix Quarry, Quebec, Canada. Specimens for transmission electron microscopy were prepared by crushing crystals about 0.5 mm in size between two glass slides, adding a drop of ethyl alcohol, and dipping a copper grid covered with a carbon-coated formvar film into the suspension. The transmission electron microscopic methods of bright-field and dark-field imaging, selected area electron diffraction, and lattice imaging were employed in this study^{21,22}. The instrument used was a JEM 100 B equipped with a side-entry goniometer.

Results

Pectolite

Typical $hk0$ electron-diffraction patterns of selected areas of pectolite $1\ \mu\text{m}$ in diameter are shown in Fig. 1. Figure 1a represents triclinic pectolite without diffuse streaks along \mathbf{a}^* in the layers $k = 2n + 1$. Figure 1b shows slightly diffuse diffraction maxima in layers $k = 2n + 1$ connected by streaks along \mathbf{a}^* ; these indicate stacking disorder with faults parallel to (100). (Weak diffuse streaks may also be seen in the layers $k = 2n$; they are due to dynamic diffraction effects.) The pattern of Fig. 1c arises from a crystal submicroscopically twinned on (100). Because of the geometry of the unit cell the reflections of the twin are only observed in the layers $k = 2n + 1$ and coincide with the matrix reflections in the layers $k = 2n$.

²⁰ Y. TAKÉUCHI, Polymorphic or polytypic changes in biotites, pyroxenes and wollastonite. *J. Mineral. Soc. Japan* **10**, Spec. Paper **2** (1971) 87–99. [In Japanese.]

²¹ P. B. HIRSCH, A. HOWIE, R. B. NICHOLSON, D. W. PASHLEY and M. J. WHELAN, *Electron microscopy of thin crystals*. Butterworths, London, 1965.

²² H. R. WENK (coord. ed.), *Electron microscopy in mineralogy*. Springer, Berlin, Heidelberg, New York, 1976.

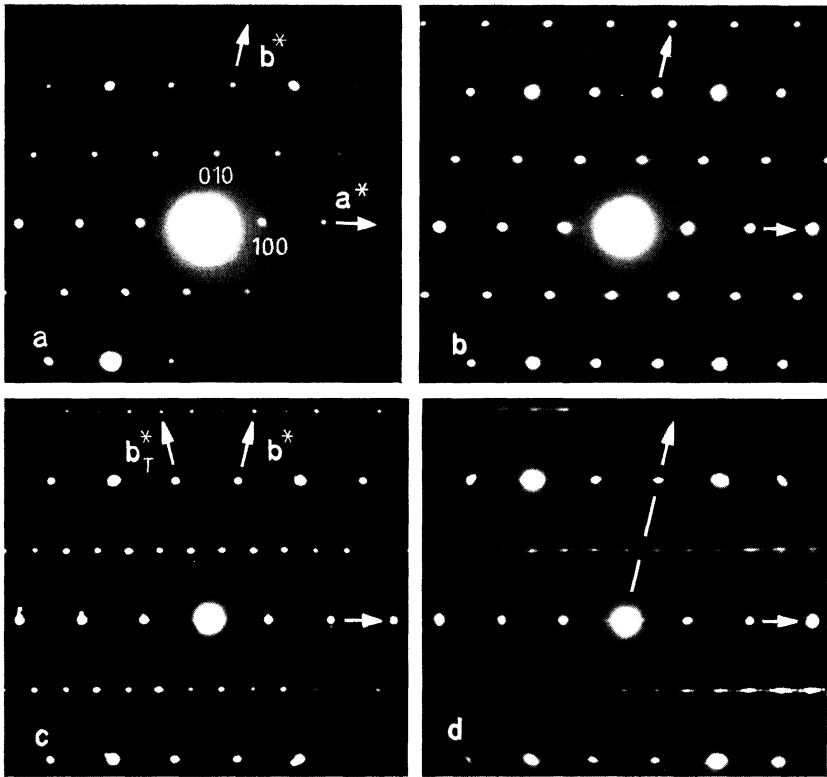


Fig. 1. Selected area $hk0$ electron-diffraction patterns of various pectolite crystals. (a) Pectolite, ordered (no streaks along a^* in the layers $k = 2n + 1$). (b) Pectolite, slightly disordered (note the streaking along a^* in the layers $k = 2n + 1$). (c) Twinned pectolite. (d) Parapectolite

The pattern of Fig. 1d differs from the previous ones. By comparison with Figs. 1a–c it becomes obvious that the diffraction maxima of triclinic pectolite in layers $k = 2n + 1$ are extinguished. Instead of that additional reflections occur at $\frac{1}{2}a^*$ in these layers. The diffraction pattern of Fig. 1d with its maxima and extinctions is analogous to that of parawollastonite. As far as the author knows, this polytype of pectolite has not been observed before; it is tentatively called parapectolite.

Patterns like that shown in Fig. 1a were rarely observed in either sample of pectolite. Submicroscopically twinned crystals (Fig. 1c) were only found in the sample from Kinzigtal. Parapectolite (Fig. 1d) occurred only in the sample from Rauschermühle. Bright-field and

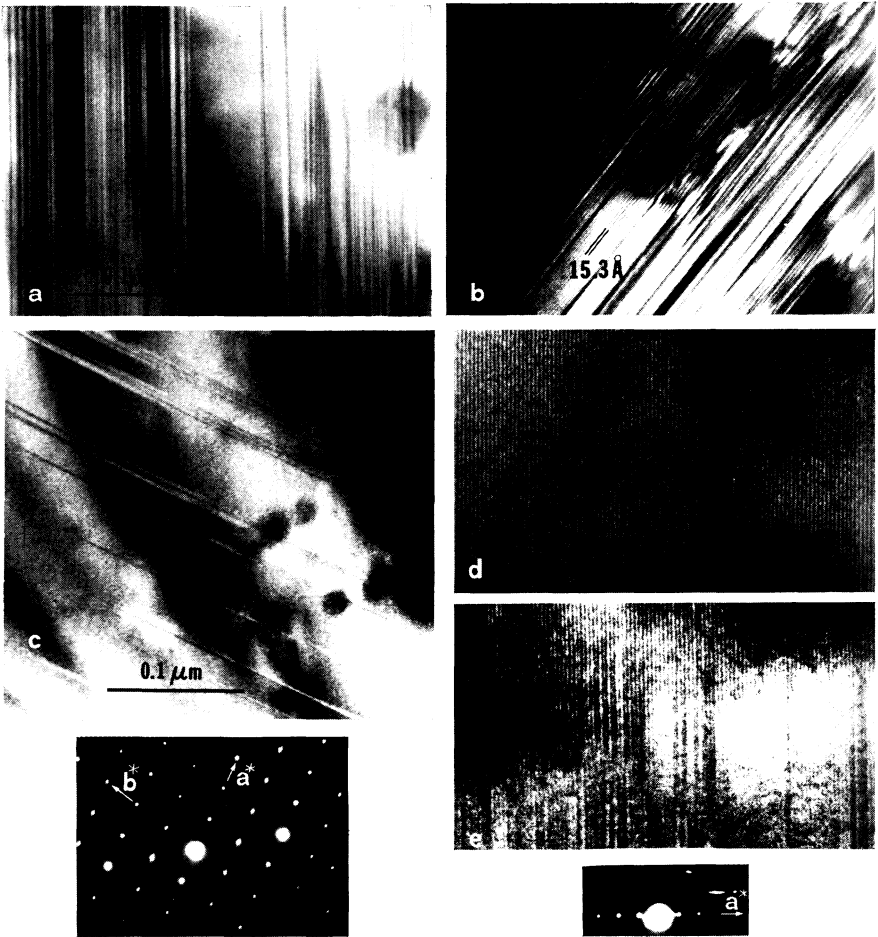


Fig. 2. Transmission electron micrographs of pectolite and serandite. (a) Pectolite. Stacking faults parallel to (100), bright field. (b) Parapectolite with characteristic 15.3 Å fringes parallel to (100) interrupted by faults. Lattice image in dark-field mode. (c) Serandite. Stacking faults parallel to (100), bright field. Below correspondingly oriented electron-diffraction pattern. (d) Serandite. (100) lattice fringes. (e) Same area as in (d) but different diffraction conditions. The faults on (100) become visible

dark-field images showed that most crystals display stacking disorder parallel to (100), (Fig. 2a). The stacking faults are in contrast for reflections of the type $k = 2n + 1$ and out of contrast for reflections $k = 2n$. Therefore, the displacement vector of the faults is $\frac{1}{2}b$.

Figure 2b shows characteristic 15.3 Å ($= 2 \cdot d_{100}$ of triclinic pectolite) lattice fringes of parapectolite. The sequence of fringes along \mathbf{a}^* is frequently interrupted by faults. The fringes also occasionally terminate in direction b . These and other crystal defects occurring in pectolite have not yet been studied in detail. The transmission electron-microscopic work was hampered by the fact that the crystals were destroyed by prolonged irradiation with the electron beam which is necessary for observation and focussing of images at high magnifications.

Serandite

Both serandite samples gave selected area electron-diffraction patterns having slightly diffuse diffraction maxima connected by streaks along \mathbf{a}^* in the $hk0$ layers with $k = 2n + 1$. The density of faults parallel to (100) in the Tanahita sample was relatively low in comparison with the pectolite samples and also with the other serandite sample. The displacement vector of the stacking faults is $\frac{1}{2}b$ as in wollastonite and pectolite. An electron-diffraction pattern with reflections from twins was obtained from only one small crystal from the Tanahota mine, but the intensity of the reflections from twins was much lower than the matrix reflections. In spite of careful searching, no crystal was found which gave a diffraction pattern analogous to parawollastonite and parapectolite. Electron micrographs of (100) faults are shown in Figs. 2c and 2e. Figure 2d displays lattice fringes parallel to (100) which are 7.5 Å apart. No faults parallel to (100) are visible because only diffracted beams with $k = 0$ were intense. Figure 2e is taken from the same area as Fig. 2d, but in this case faults parallel to (100) are revealed, because in addition to the beams ± 100 and 000 used for lattice imaging only $hk0$ beams with $k = 2n + 1$ are strong.

Discussion and conclusions

Pectolite and serandite display a submicroscopic lamellar texture on (100) like wollastonite. All three minerals contain stacking faults on (100) with a displacement vector of $\frac{1}{2}b$. The polytypic behavior of pectolite is similar to that of wollastonite: A polytype of pectolite, tentatively called parapectolite, was found which is analogous to parawollastonite regarding its diffraction maxima, extinctions and its 15 Å lattice fringes parallel to (100). Thus, the structural model for parawollastonite is proposed for parapectolite. In addition, submicroscopic twinning on (100) is frequent in pectolite, at least in

one sample. In contrast, no "paraserandite" polytype was found and submicroscopic twinning on (100) appears to be very rare in serandite.

If the observations obtained from only two serandite samples are accepted as typical for the behavior of that mineral, one may ask what is responsible for the difference between serandite and the other two minerals wollastonite and pectolite. One reason could be the degree of pseudosymmetry as expressed by the angle α and the relation $\cos\gamma = b/4a$ (cf.¹⁰, p. 101); α is very close to 90° while $\cos\gamma$ is nearly given by the wollastonite unit cell, but the deviations are significant for pectolite and even more for serandite. This does not explain, however, why a polytype analogous to parawollastonite exists for pectolite but not for serandite. In their recent paper⁸, TAKÉUCHI *et al.* discuss the questions of pseudosymmetry and polytypism of wollastonite, pectolite, and serandite, and give a structural explanation. They found in their crystal-structure refinement of serandite (which was not the pure end member) that the Ca which partially replaces the Mn is concentrated at one of the Mn sites. In such an ordered structure a periodic shift of structural units by $\frac{1}{2}b$ would mean a drastic change of the crystal structure which is energetically not favored. Therefore, according to these authors, polytypism should be limited to the pure end members of the pectolite-serandite series. Indeed, the results presented here support their view.

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