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THE SUPERLATTICE OF MINNESOTAITE

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Abstract

Minnesotaite may be described by a *C*-centred triclinic subcell of dimensions a_o 5.623(2), b_o 9.419(2), c_o 9.624(3) Å, α 85.21(3)°, β 95.64(3)° and γ 90.00(2)°. Superlattice reflections extend the cell to $a=18a_o$, $b=6b_o$ and $c=12c_o$, although all crystals examined to date have been twinned, and the *c* periodicity should be considered tentative. The powder pattern has been indexed on the basis of the subcell and only one line is due to supercell reflections. The superlattice and the triclinic geometry indicate that minnesotaite is not the ferrous analogue of talc, but has a more complex structure involving regular modulations of both the octahedral and tetrahedral sheets of a 2:1 layer at periods of 57 to 115 Å along the three axes. These structural modulations are in response to the misfit of the lateral dimensions of the Fe-rich octahedral sheet with those of the Si-rich tetrahedral sheets.

Keywords: minnesotaite, talc, superlattice, X-ray diffraction.

Sommaire

La minnesotaïte peut être décrite par une maille triclinique à face *C* centrée: a_o 5.623(2), b_o 9.419(2), c_o 9.624(3) Å, α 85.21(3)°, β 95.64(3)°, γ 90.00(2)°. La maille du surréseau $a=18a_o$, $b=6b_o$ $c=12c_o$, permet de noter la seule réflexion du cliché de poudre à laquelle la maille sous-multiple $a_ob_oc_o$ ne donne pas d'indices entiers. Tous les cristaux étudiés sont maclés, et la période suivant *c* reste incertaine. Le surréseau et la géométrie triclinique montrent que la minnesotaïte n'est pas l'analogue ferreux du talc: sa structure, plus complexe, comporte la modulation des feuillets octaédrique et tétraédrique de la couche 2:1, le long des trois axes, à des périodes allant de 57 à 115 Å. Ces modulations proviennent de l'appariement imparfait des dimensions latérales des feuillets: l'octaédrique riche en Fe, d'une part, le tétraédrique riche en Si, d'autre part.

(Traduit par la Rédaction)

Mots-clés: minnesotaïte, talc, surréseau, diffraction X.

Introduction

Minnesotaite is a common constituent of iron formations that have been subjected to low-grade regional metamorphism. It usually occurs intermixed in fine particles with quartz, siderite, iron oxides, graphite, stilpnomelane and other iron silicates. This particle-size and intermixture problem has hindered previous investigations. In his original definition, Gruner (1944) suggested that minnesotaite is the ferrous analogue of talc. The X-ray powder patterns of minnesotaite and talc are only superficially similar, however, and we have been unable to index the minnesotaite pattern on the basis of either the 1*Tc* or 2*M* talc cells.

Blake (1965) was able to concentrate nearly pure minnesotaite from a fracture filling within the main iron-formation in the Cuyuna district of Minnesota. He reported data for the density, optical properties, differential thermal analysis, chemical analysis and X-ray powder pattern of this material. After the publication of these data, he located "single" crystals measuring up to several millimetres in diameter. X-ray studies of these crystals are reported here.

Octahedral sheets rich in ferrous iron provide an especially poor fit with the lateral dimensions of a silicon-rich tetrahedral sheet. As a result of this misfit, it would appear unlikely that minnesotaite would be structurally identical to talc even though the *d*(001) value of approximately 9.6 Å does suggest a 2:1 layer. Floran & Papike (1975) recognized this difficulty and suggested a series between minnesotaite and greenalite, the 1:1-layer iron serpentine, that involves an out-of-plane tilting or curling of the tetrahedral and octahedral sheets. Greenalite has since been shown to have a platy modification of the serpentine structure that does not involve such out-of-plane tilting (Guggenheim *et al.* 1982). In addition, it would be expected that significant

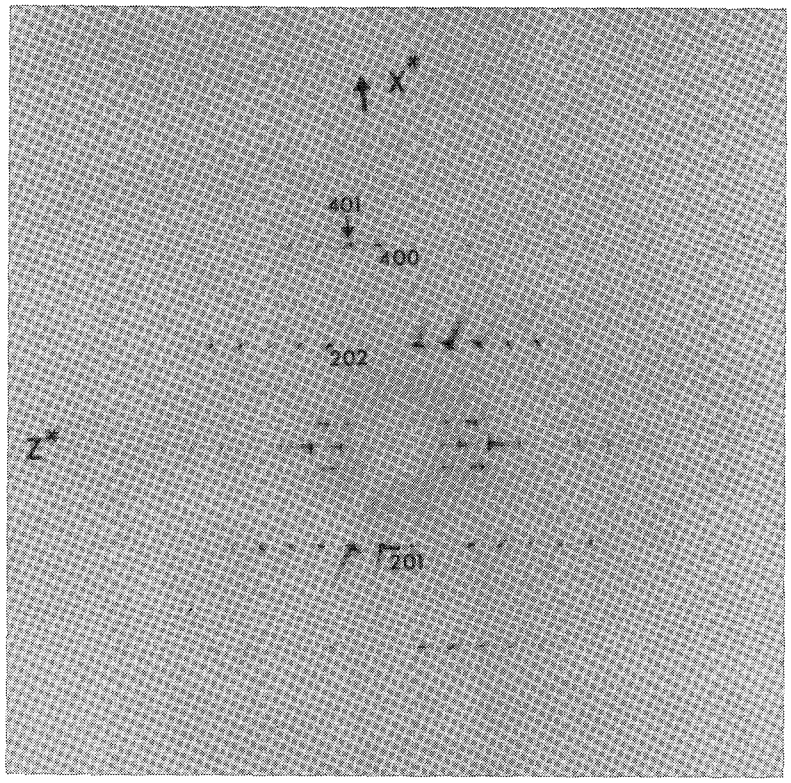

FIG. 1. The *h0l* X-ray precession net of minnesotaite (Mo radiation, Zr filter, 40 kV, 18 mA, 46 hours). A few reflections are indexed according to the subcell.

tilting as suggested by Floran & Papike should be minimal in minnesotaite because the octahedral sheet would be held under tension between the two opposing tetrahedral sheets. Some method of structural compensation other than curling can be anticipated as a result of the misfit in minnesotaite.

RESULTS AND DISCUSSION

X-ray precession photographs of minnesotaite crystals from the Cuyuna district in Minnesota show three types of reflections (Figs. 1–3). Weak reflections located predominantly in areas of low sin θ/λ are superlattice reflections indicating long periodicities. Superlattice reflections of index $k = 3n$ are sharp (Figs. 1, 3) and those of index $k \neq 3n$ are diffuse and elongate parallel to Z^* (Fig. 2). The strong subcell reflections may be divided into two groups based on intensity and degree of mosaic spread. The stronger subcell reflections (S1 type) in Figures 1 and 2 indicate a periodicity along the Z axis of approximately 9.6 Å. The second set (S2 type) of subcell reflections is located approximately on the same reciprocal lattice lines as the first set about midway between S1 reflections along Z^* (Fig. 2). Precise measurements show that these S2 reflections are not exactly halfway between the S1 reflections, and thus are twin reflections. Also, optical examination of the crystals reveals several individuals. Because of the fragile nature of the crystals and the sizes of the twin components, however, it has not been feasible to attempt to cut an untwinned portion. The S2 reflections have less mosaic spread than the S1 subcell reflections, which indicates that the latter are a composite of contributions from several individuals or twin components. In addition, the S2 reflections are weaker as a class than the S1 type, indicating that the twin components are not of equal volume.

Figure 3 shows the *hk*0 net of minnesotaite. This X-ray precession pattern is similar to electron-diffraction patterns obtained in our

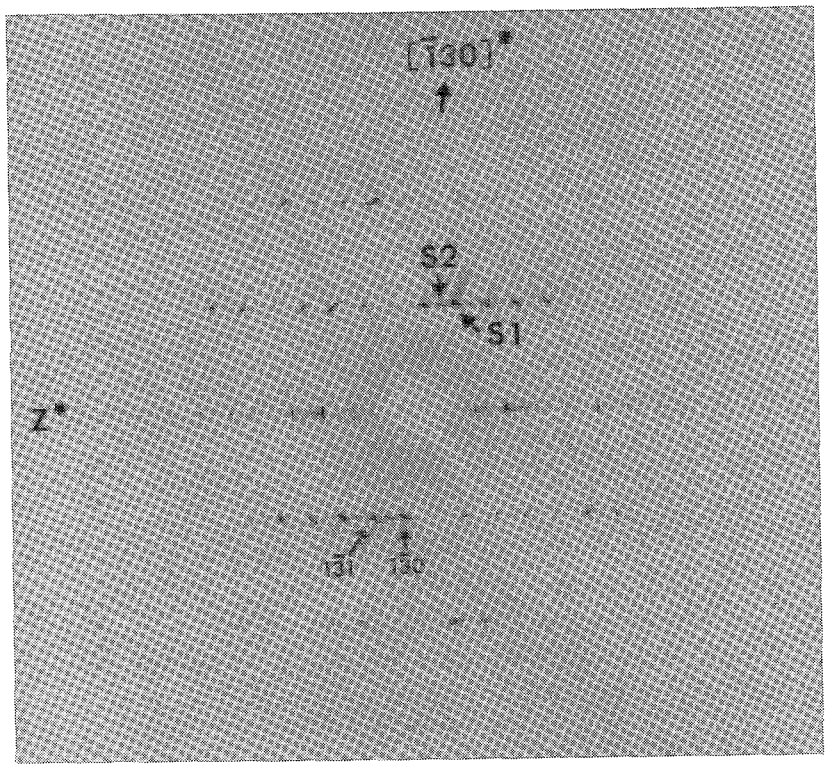

FIG. 2. The pseudohexagonal equivalent of *h0l* net (Mo radiation, Zr filter, 40 kV, 18 mA, 46 hours). The S2 subcell reflections are attributed to twinning. Note that the superlattice reflections are diffuse and elongate parallel to Z^*. Two reflections are indexed according to the subcell.

study and to one published by Champness *et al.* (1976), although the superlattice reflections are intensified in the electron-diffraction patterns. Comparison of these *hk*0 diffraction patterns with that of talc shows similar spacings of the subcell reflections in the two minerals, but an absence of the superlattice reflections in talc. In talc and other layer silicates, the *hk*0 net shows nearly hexagonal geometry. This is not the case in minnesotaite because the lattice geometry is triclinic and the pseudohexagonal lateral axes are not coplanar in reciprocal space. Hence, in the crystals we have examined by either X-ray or electron-diffraction techniques, slight angular errors from the true *hk*0 orientation produces significant variations in intensity of certain reflections, such as 060.

The observed superlattice and the measured triclinic interaxial angles show clearly that the structure of minnesotaite is much more complex than that of a normal layer-silicate, presumably in response to the anticipated tetrahedral–octahedral lateral misfit. The deviations from the normal phyllosilicate structure may account for the differences from the ideal ferrous talc composition that were observed by Floran & Papike (1975). Dark-field electron-optical photographs involving reflections from the *hk*0 net of minnesotaite from several localities are featureless; there are no bands suggestive of a wave-like structure.

The superlattice symmetry shown in Figures 1 and 3 indicates that the superlattice axes may be chosen parallel to the conventional axes of a layer silicate. Refined values of the subcell dimensions are a_o 5.623(2), b_o 9.419(2), c_o 9.624(3) Å, α 85.21(3)°, β 95.64(3)°, γ 90.00(2)°.

In evaluating the superlattice dimensions, it has been necessary to sort out the twin superlattice reflections. The superlattice repeats along X and Y are well defined owing to the presence of strong row-lines that do not appear to be affected by the twinning. For example, periodi-

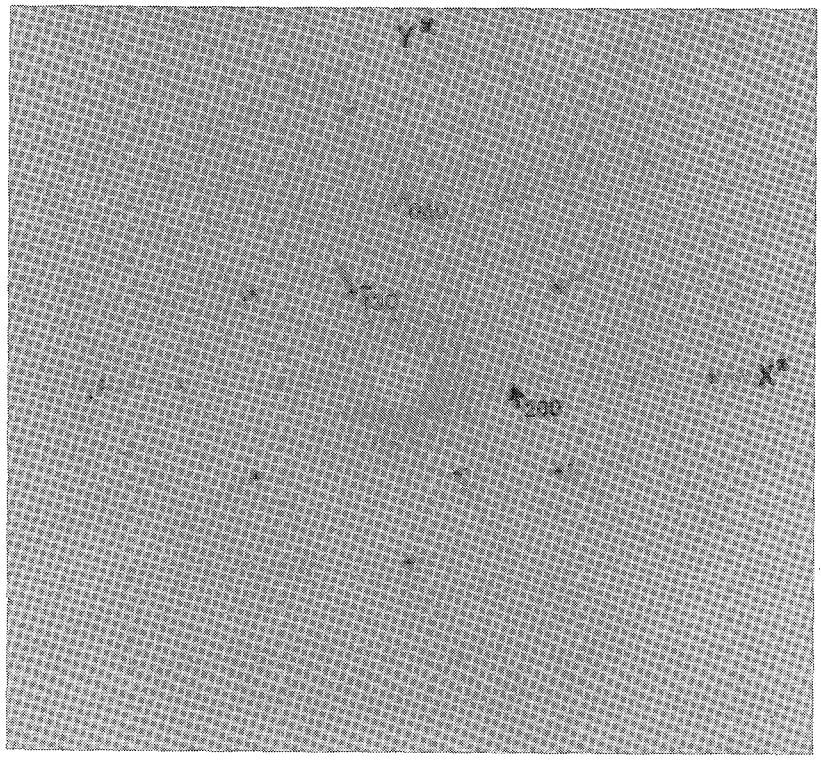

FIG. 3. An X-ray precession photograph of the $hk0$ net. Extra reflections occur in this photograph because of higher-level reflections passing through the layer-line screen owing to the long periodicity along Z and because of small unavoidable orientation errors. Indications of the effects of such errors, for example, are the appearance of superlattice reflections 44,0,$\bar{4}$, $\bar{4}\bar{4}$,0,4, 88,0,$\bar{4}$ and $\bar{8}\bar{8}$,0,4 and subcell reflections 60$\bar{1}$ as well as inconsistent relative intensities of the $h00$ reflections of this net as compared to Figure 1. A few reflections are indexed in the photograph according to the subcell (Mo radiation, Zr filter, 40 kV, 18 mA, 96 hours).

cities of $a = 9a_o$ and $c = 3c_o$ are evident in Figure 1 and of $a = 9a_o$ and $b = 1b_o$ on Figure 3. The lateral repeats must be increased to $a = 18a_o = 101.21$ Å and $b = 6b_o = 56.51$ Å as a result of superlattice row-lines on precession photographs (not illustrated) involving the subcell zones [110]* and [1$\bar{1}$0]*. The repeat along Z, however, depends on individual reflections, some of which are diffuse and elongate, on these row lines. In our best judgment, the latter superlattice-repeat is $c = 12c_o = 115.5$ Å, but this value should be considered tentative because of both the nature of the reflections and the possibility of inadvertently including some twin reflections.

In order to index the powder pattern of minnesotaite accurately, a crystal was placed on a FACS–1 single crystal diffractometer (Mo$K\alpha$ radiation) for acquisition of preliminary intensity-data. Subcell reflections were collected out to $2\theta = 40°$ in the omega scan mode with large scan-widths of 4.25°. In order to avoid unnecessary scan overlap of the closely spaced superlattice-reflections of the $k = 3n$ type, these were collected by keeping both counter and crystal stationary during the 40-second counting interval. No effort was made to measure the superlattice reflections of the $k \neq 3n$ type. Powder data were collected using a Gandolfi camera with a calibration ring (Donnay & Knoepfel 1980) to determine film shrinkage. The crystal used was reoriented nine times and exposed to graphite-monochromatized Fe$K\alpha$ radiation for 23 hours per orientation. Two photographs were made, and measured values were averaged. The relative intensities compare

TABLE 1. X-RAY POWDER DIFFRACTION DATA FOR MINNESOTAITE

hkl	[1] d_{calc}(Å)	[2] d_{obs}(Å)	[3] I/I_o	hkl	d_{calc}(Å)	d_{obs}(Å)	I/I_o
001	9.54	9.54	100(100)	$\bar{3}31$	1.597	1.597	6B(15)
002	4.78	4.78	15(20)	330	1.596		
		[4] 4.62	[5] 5B(10)	331	1.575	1.576	8
003	3.18	3.18	50(50)	061	1.565	1.565	13(20)
200	2.798	2.796	2	060	1.564		
$\bar{2}01$	2.759	2.759	25(22)	$\bar{1}35$	1.548		
$\bar{1}30$	2.721	2.721	15	$\bar{3}32$	1.543	1.541	2(10)
$\bar{1}31$	2.652	2.655	35(22)	331	1.543		
$\bar{1}31$	2.537	2.538	25 (70)	062	1.525	1.524	2(5)
$\bar{2}02$	2.525	2.528	45	$\bar{0}61$	1.523		
$\bar{1}32$	2.403	2.405	32(20)	205	1.509		
$\bar{1}32$	2.361	2.356	5	$\bar{3}33$	1.506	1.509	5B(10)
202	2.316	2.318	12(5)	332	1.505		
$\bar{1}32$	2.250	2.248	15(5)	$\bar{1}36$	1.452	1.450	2(10)
$\bar{2}03$	2.212	2.212	20(20)	$\bar{0}62$	1.451		
$\bar{1}33$	2.103	2.103	10(10)	401	1.365		
$\bar{1}33$	2.051	2.050	5	007	1.363	1.362	8B(15)
203	2.005	2.007	10(5)	064	1.362		
$\bar{1}33$	1.954	1.956	5(5)	$\bar{2}62$	1.352	1.351	8B(15)
$\bar{1}34$	1.912	1.913	10(10)	$\bar{2}61$	1.352		
$\bar{2}04$	1.911			206	1.328		
134	1.822	1.822	4(10)	$\bar{2}62$	1.326	1.325	8B(15)
$\bar{1}34$	1.695	1.695	5(5)	$\bar{2}61$	1.325		
$\bar{2}05$	1.655	1.656	5(10)	$\bar{3}34$	1.308		
$\bar{3}31$	1.608	1.609	15(20)	$\bar{2}62$	1.308	1.307	5B(10)
330	1.608			402	1.308		
				$\bar{1}36$	1.306		

1 calculated d values based on a 5.623(2), b 9.419(2), c 9.624(3) Å, α 85.21(3)°, β 95.64(3)°, γ 90.00(2)°.
2 d values obtained with 114.6-mm Gandolfi camera using monochromatic Fe$K\alpha$ radiation (λ = 1.9373 Å) and the calibration ring.
3 intensity data visually estimated from the Gandolfi photograph. Figures in parentheses are visually estimated from a Debye-Scherrer photograph using non-monochromatic Fe$K\alpha$ radiation as given in Blake (1965).
4 this reflection may be indexed on the supercell $a_S = 18a_o$, $b_S = 6b_o$, $c_S = 12c_o$, and has combined indices of 4,12,$\bar{2}$, $\bar{4}$,12,4, 4,12,0, 4,12,4 and $\bar{4}$,12,0 (see text).
5 B broad

well with those measured with the single crystal diffractometer, suggesting that twinning did not greatly affect the diffractometer measurements of subcell intensity and that the Debye–Scherrer data reported by Blake (1965) may involve the effects of preferred orientation. It appears likely that such preferred orientation may be unavoidable when the sample is prepared from ground material. The d value of 3.33 Å reported by Blake is due to the presence of graphite as an impurity.

The indexed powder-pattern (Table 1) contains mainly subcell reflections, and has been indexed on the basis of the subcell. The weights assigned to reflections in the least-squares cell-parameter refinement are based on an estimate of the quality of the d-value measurement as primarily determined by line intensity and sharpness. Only the line at 4.62 Å is due to superlattice reflections. Knowledge of the single-crystal-diffractometer intensities, indices and 2θ values was essential in the indexing. In view of the large standard errors of the supercell dimension, the indices of the 4.62 Å line are tentative. Reflections 4,12,0 and $\bar{4}$,12,0 are visible in Figure 3, and the other listed indices were recorded by the single crystal diffractometer. Because twinning does not affect a powder pattern, the absence of any S2 reflections on the powder pattern is further evidence for their twin origin.

The subcell is C-centred and has triclinic geometry. The supercell also is C-centered according to the data we have observed to date. The nets shown in Figures 1 and 3 exhibit a higher apparent symmetry than triclinic for the supercell. These superlattice reflections are all of index $k = 3n$, and must owe their origin to a regular modulation of the octahedral sheet where all atoms repeat at intervals of $b_o/3$. The tetrahedral atoms make only a minor contribution to these reflections. The octahedral modulation must influence the geometry of the attached tetrahedral sheet, however, and the modulation of the tetrahedral sheet shows up in the $k \neq 3n$ superlattice reflections. In other Fe-rich layer silicates, such as stilpnomelane, greenalite and zussmanite, the tetrahedral sheet is modified by the introduction of 3- or 4-member rings into the sheet or by inversion and relinkage of some tetrahedra (or by both mechanisms). These mechanisms enlarge the lateral dimensions of the tetrahedral sheet and permit articulation with the larger octahedral sheet. The diffuse and elongate nature of all $k \neq 3n$ reflections in minnesotaite indicates some irregularity in the stacking of adjacent layers along Z and in the domain size or degree of perfection of the tetrahedral modulation. Because of the large size of the supercell (volume 65,508 Å^3), triclinic symmetry and the lack of untwinned crystals to date, the elucidation of the nature of the modulations will be extremely difficult.

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