THE COMPOSITION AND STRUCTURE OF MINNESOTAITE, A COMMON IRON SILICATE IN IRON FORMATIONS*

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ABSTRACT

The identity of a very abundant iron silicate in the iron formations of Minnesota has been established as an iron talc. Its structure and properties have been investigated and compared with its two associated silicates, stilpnomelane and greenalite.

INTRODUCTION

Ever since the discovery of the productive portion of the Mesabi range —the part west of the railroad from Two Harbors to Tower—petrographers have observed a mineral in this part of the Biwabik iron formation which they called an amphibole (1 and 2). This mineral, sometimes designated more specifically as grunerite, is *not* an amphibole but a talc. Grunerite and other amphiboles are found *only* on the East Mesabi range, that is, east of the railroad mentioned above. The mineral under consideration is very abundant in certain horizons of the Biwabik formation. These horizons have been mapped as "Slaty Divisions" by Wolff and Gruner (3). The mineral occurs, however, also in the "Cherty Divisions." In either case the rocks containing it in abundance have been called in the past, for the sake of classification, greenalite taconite and slaty taconite, and sometimes just greenalite rock.

It is proposed that this mineral be called *minnesotaite* because it was discovered in Minnesota and probably is more abundant in this state than anywhere else. It is also found on the Cuyuna range in central Minnesota. The minerals most commonly associated with minnesotaite are quartz, siderite, stilpnomelane, greenalite, and magnetite. Any two or three, or all five, may be found together. Stilpnomelane has not previously been reported in thin sections from the Mesabi range. It was discovered in x-ray powder photographs and then found under the microscope. Although abundant, it is very fine grained and hidden in the dense dark portions of the slaty taconite. Greenalite, in small amounts, is often found with minnesotaite. In a few places the two may be equally abundant. Siderite may be present in considerable quantities as the rock contains from 5% to as much as 15% of CO_2. Quartz, usually called chert, varies from practically nothing to 90% in volume.

Minnesotaite occurs only in microscopic plates or needles, the latter radiated or in sheaves. Sometimes it is so abundant that an inch of a drill

core may contain up to 90% of it, the rest being the other minerals mentioned.

The first investigator who positively stated that this "amphibole" was not an amphibole was Richarz (4, p. 701). He showed that the mineral had parallel extinction in all positions and, therefore, being an iron silicate, could not be an amphibole. He mentioned its similarity to mica and for want of a better name suggested "crystallized greenalite."

In 1935 Jolliffe (5) described the optical properties and even made a partial chemical analysis of it, though, as will be shown below, he did not have the choicest material. He called the material "mineral X." As Jolliffe did not employ x-rays in his studies he was unaware of the fact that he was dealing with three distinctly different silicates; namely, greenalite, stilpnomelane, and minnesotatite. He called them greenalite, metagreenalite (supposedly like greenalite in composition), and mineral X. The formula he proposed for greenalite is similar to that of minnesotaite and is quite different from true greenalite, which is an iron serpentine as shown by the writer (6) in 1936.

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OPTICAL DATA

It is not intended to give a detailed description of the occurrence of minnesotaite at this time, since it occurs not only on the Mesabi but also on the Cuyuna range and probably will be found in other iron formations. Neither will its derivation from any of the other minerals be discussed at present. Such a study has not been completed. The descriptions of earlier mineralogists agree as to its occurrence and relationship to the associated minerals (1, 2, 4, and 5). It is fibrous, rarely platy, in appearance and reminds one of sericite or pyrophyllite in thin sections. In the hand specimen it has a greenish-gray color. Usually, though not always, it is lighter than greenalite, which is a dark olive green. It is so soft that it is easily scratched by a mounted steel needle drawn across it under the weight of the metallic needle mounting. The coarsest grained material looks greasy to waxy under binoculars. The finer grained material is waxy to dull in luster. The optical properties would not be expected to be very constant for a mineral in which the amounts Fe'', Fe''', and Mg are somewhat variable.

The mineral has parallel extinction, a small optic angle with the acute bisectrix normal to the basal cleavage, and fairly high birefringence. Jolliffe's figures (5, p. 412) have been confirmed for the colorless variety and

differ little from those of Richarz (4, p. 701). $N_\gamma - N_\alpha = 1.615 - 1.580$ $= 0.035$. Positive elongation. Many specimens show practically no pleochroism but it may become noticeable and then Z and Y = pale green, X = colorless, or very pale yellow. In some sections the larger colorless needles will grade into definitely light yellowish-green confused aggregates of very small fibers. It was thought at first that these aggregates might be a different mineral but the x-rays show that they are also minnesotaite. The fibers are noticeably pleochroic and form ill-defined areas resembling somewhat the shape and size of greenalite granules. Associated stilpnomelane was not recognized as such by former investigators, chiefly because it is in such fine-grained aggregates in most sections that its strong pleochroism and parallel extinction are difficult to see.

It is possible that Jolliffe included it under his "metagreenalite." Most of the material which he (5, p. 411) designated as such is minnesotaite. It is so fine grained that even with a magnification of 300 diameters the material appears as felt-like yellowish-green masses. When these aggregates occur as granules they differ from greenalite only by their mottled appearance between crossed nicols. They were definitely identified as minnesotaite by using x-rays. They seem to have somewhat higher indices of refraction than the lighter colored, coarser minnesotaite described above and may contain more ferric iron. Here we have the unusual situation of two apparently different substances being alike in structure and probably very similar, if not identical, in composition.

X-ray Data

When greenalite was first x-rayed by the writer in 1934 (6), it happened that the material contained neither minnesotaite nor stilpnomelane in sufficient amounts to give their characteristic patterns. When a new study of the iron formations of Minnesota was begun in 1941, almost the first x-ray powder photograph showed patterns of both these minerals in association with quartz and iron carbonate. It is relatively easy to remove the carbonate without injury to the silicates, since the carbonate is soluble in boiling HCl. The finely powdered specimen is heated in about 200 cc. of nearly boiling water and to it is added a little more HCl than is estimated to dissolve the carbonate. Effervescence is very vigorous for a short time. As soon as it stops the solution is diluted to twice its volume with cold water. The powder that settles is washed by repeated decantation. It is practically impossible to separate stilpnomelane from minnesotaite. They are so similar in densities and other properties that no known method will produce results. It is, however, feasible to extract greenalite dialectrically. Most quartz can be removed relatively easily by centrifug-

ing in bromoform, except in the presence of stilpnomelane. Magnetite is removed by a hand magnet. A powerful electromagnet will also attract minnesotaite, stilpnomelane, and greenalite.

The most suitable material for x-ray and chemical analysis was a piece of drill core from a depth of 240 feet (M 4450) which contained practically no quartz, very little carbonate, but some magnetite. A powder was prepared which showed no trace of quartz in the x-ray powder photographs.

Its x-ray spacings are given in Table 1 in comparison with those of talc (9, p. 416) and margarite. Of the latter two minerals only those lines are listed which could be correlated with minnesotaite. They are mostly basal

TABLE 1. COMPARISON OF X-RAY PHOTOGRAPHS UNFILTERED Fe RADIATION.
CAMERA RADIUS=57.3 MM.

No.	Minnesotaite[1] d	I	Talc (9, p. 416) d	I	Margarite[2] d	I	Indices
1	9.53	10+	9.26	5	9.47	1–2	002
2	4.77	1	4.63	3	4.72	0.5	004
3	3.50	1	3.39	2	3.51	3	006β
4	3.177	5	3.086	10	3.168	10	006
5	2.750	0.5b			2.769	2	
6	2.651	0.5	2.578	1	2.677	1	
7	2.524	2	2.462	5	2.522	2b	
8	2.397	1			2.402	2	
9			2.315	1			008
10	2.312	0.5					
11	2.215	1					
12	2.112	0.5	2.039	1	2.097	1	0010β
13	2.005	1					
14	1.917	1	1.852	3	1.902	5	0010
15	1.659	1					
16	1.598	1b	1.544	2	1.608	2	0012
17	1.567	1	1.517	4	?		060
18	1.514	0.5					
19	1.384	0.5b					
20	1.366	1	1.323	1	1.361	0.5	0014
21	1.352	1	1.294	2	1.294	1	
22	1.329	1					
23	1.198	faint					
24			1.160	0.5			0016
25	1.177	0.5					

[1] Mesabi Range, No. 4450, Depth—240 feet.
[2] Emery Mines, Chester, Mass.

reflections. It is doubtful if line No. 16 of minnesotaite, which is broad, originates from 0012, though part of the reflection may be caused by it. The same may be said of line No. 12.

The similarity of the three photographs except for the intensities of 002, 004, 006, 0010, and 0012 is unmistakable. On the assumption that minnesotaite has a talc structure the theoretical intensities of the basal

TABLE 2. THEORETICAL AND OBSERVED INTENSITIES OF BASAL PLANES OF MINNESOTAITE

Indices	002	004	006	008	0010	0012	0014	0016
Spacing	9.550	4.775	3.183	2.387	1.910	1.592	1.364	1.194
Observed Intensity	10+	1	5	0	1	?	1	?
Theoretical Intensity	120	0.5	22	0	0.7	0.2	1	0.1

reflections were computed and are compared with the observed ones in Table 2. The agreement may be called fair, considering the assumptions which must be made with regard to the scattering factors. The ratio of Fe to Mg ions in the octahedral layer of the structure was taken as 3 to 1 in the calculation of the scattering factors. Disregarding the angle β (provided the mineral is monoclinic) we have a unit cell with the following dimensions:

$$d_{001} = 19.10 \text{ Å}, \ b_0 = 9.40 \text{ Å}, \ a_0 = 5.4 \text{ Å}$$

The length of a_0 is based on the pseudo-hexagonal character of the structure.

The dimension 19.10 Å for 001 is somewhat larger than one would expect when compared with $18.58 \pm .03$ Å for magnesium talc from Harford County, Maryland. On the other hand, 001 for margarite is very similar to minnesotaite. One is tempted, therefore, to consider the possibility of a "brittle iron mica" structure in which Fe" takes the place of K or Ca, respectively. The writer is not thinking of such minerals as chloritoid or ottrelite, which do not belong here structurally, but of a regular mica structure. It is at once realized that the chemical composition given below does not fulfill the requirements for such a mica. The structure would have to be a defect structure with a considerable number of positions where Fe is missing. The ratio of vacancies to the filled positions between the layers would be nearly 7 to 1. There are other complications that would arise in such a scheme as, for example, density, hardness, and opti-

cal discrepancies. On the other hand, the theoretical reflections from the basal planes would agree somewhat better than those of Table 2.

CHEMICAL DATA

Jolliffe (5, p. 416) made an attempt in 1935 to analyze minnesotaite. He does not mention how large a sample he had but states that he corrected the analysis for impurities. His results recalculated by the writer are recorded in columns 6 and 7 of Table 3. Dr. R. B. Ellestad made an analysis of the purified mineral whose x-ray pattern is given in Table 1. About 7 grams of material for a regular mineral analysis were available. TiO_2 and P_2O_5 were not determined because from thousands of analyses we know that these constituents are present in very minor amounts in the iron formations. There is a little MnO present which is included in the

TABLE 3. ANALYSES, ATOMIC DISTRIBUTION, AND DENSITIES OF MINNESOTAITE

	Minnesotaite, R. B. Ellestad, *Analyst*					Jolliffe's Mineral "X"	
	1	2	3	4	5	6	7
		Mol. R.	+ ions	+ charges	Column 3 adjusted	+ ions adjusted for densities	
SiO_2	51.29	.8540	32.0	128.0	30.37	28.67	27.23
Al_2O_3	.64	.0063	.48	1.4	.46		
Fe_2O_3	2.00	.0125	.94	2.8	.89	5.12	4.85
FeO	33.66	.4684	17.55	35.1	16.66	11.38	10.80
MgO	6.36*	.1577	5.91	11.8	5.61	8.69	8.25
CaO	none						
Na_2O	.08	.0013	.10	.1	.09		
K_2O	.03	.0003					
H_2O+	5.54	.3074	23.04		21.90	26.34	25.02
H_2O-	.24	.0133	1.00				
	99.84			179.2			
Mol. W.			3740		3551	3535	3358
Observed Density					3.01		2.86
Theoretical Density			3.18		3.02	3.01	

* It has been possible to determine MnO and TiO_2. The table should read Al_2O_3 .61, TiO_2 .04, MgO 6.26, MnO .12; total 99.87.

MgO. Due to the present emergency it could not be determined at this time.*

Column 2 of Table 3 contains the molecular ratios of the oxides; column 3 the number of cations in the structure based on the assumption that 32 Si ions are present as in two unit cells of talc. Column 4 tabulates the + charges of these cations. The charges due to H are omitted because as will be seen below, H is present as OH, in which capacity it occupies anion positions in the structure. The results of dehydration experiments on the mineral show that less than 3% of the H_2O+ can be driven off around 250°C. within three days. Above this temperature the FeO of the sample begins to oxidize. It is, therefore, concluded that practically all H_2O+ is present as OH. The molecular weight of the contents of column 3 is 3740. If this is put in the cell of the dimensions given above the density would be 3.18. This figure is much higher than the one observed when centrifuging the powder in Thoulet solution, where the settling of particles extended over a range from 3.03 to 2.99. Jolliffe (5, p. 415) reported a density of only 2.86, which is probably too low, particularly for material of his analysis. Ordinary talc has a theoretical density of 2.82. Also, as shown in the next paragraph and in column 7, Table 3, for a density of 2.86 the structure would not be balanced electrostatically, unless two O ions were omitted. Such a balance can be reached, however, if a density between that of column 6 and column 7 is assumed.

Two unit cells of talc contain $(OH)_{16}Mg_{24}Si_{32}O_{80}$ ions. There are 176 negative charges in 96 positions. These positions are probably always completely occupied since they form the "framework" between which the cations fill the small interstices. We have in minnesotaite 22 (OH) instead of 16 (OH). That leaves room for only 74 O. The total negative charges are $74 \times 2 + 22 = 170$. In column 4 we have 179.2+charges. The number of ions in column 3 must be multiplied, therefore, by a factor of $\dfrac{170.0}{179.2}$.

Column 5 is the result. The molecular weight of this column is 3551, which gives a theoretical density for minnesotaite of 3.02. This is in almost perfect agreement with the observed value.

We may safely assume that all of the Al and most of the Fe''' substitutes for Si, which is slightly deficient in amount. The formula then becomes:

$$(OH)_{22}(Fe'', \ Mg)_{22.3}Si_{30.4}(Al, \ Fe''')_{1.4}O_{74};$$

or, reduced to one unit cell and slightly simplified:

* See footnote under Table 3.

$$(OH)_{11}(Fe'', Mg)_{11}(Si, Al, Fe''')_{16}O_{37}.$$
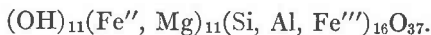
There is every reason to believe that minnesotaite varies in composition between considerable limits, particularly with regard to the ratio of Fe'' to Fe'''. For example, assuming a density of 3.01, the formula for Jolliffe's material (Table 3, column 6) would be:

$$(OH)_{26}(Fe, Mg'')_{20.7}(Fe''')_{1.8}(Si_{28.7}Fe_{3.3})O_{72}.$$
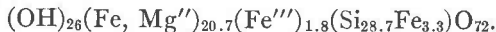
This formula contains, however, 98 O and (OH) anions instead of the permissible 96. This suggests that not all H_2O of his analysis is present as (OH).

The idea of the replacement of O by (OH) is, of course, not new. It has been reported in the structure of phosphates, and Hendricks (10, p. 531) refers to such an arrangement in the layer silicate cronstedtite from Kisbanya, whose formula is:

$$(Fe''', Al)_{1.10}(Fe'', Ca)_{4.65}(Si, Fe''')_4O_9(OH)_9.$$
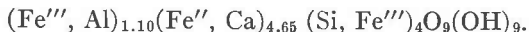
The formula in the original paper is incorrect. It contains too much (OH) and not enough O. Even in the corrected formula O_9 and $(OH)_9$, instead of O_{10} and $(OH)_8$, occupy the 18 available anion positions.

CONCLUSIONS

The identity of a mineral observed in thin sections for many years has been established as one with a talc structure but with about three-fourths of its Mg replaced by Fe. Talc analyses record a maximum of about 5% of Fe oxides. The name minnesotaite has been chosen for this mineral because it occurs in abundance in two of the three Minnesota iron ranges, the Mesabi and Cuyuna. In the Biwabik iron formation of the Mesabi range it is the most abundant of the three silicates with stilpnomelane and greenalite following in the order named. Richarz (4) and and Jolliffe (5) have determined the optical properties of the mineral which apply to the nearly colorless variety as seen in thin sections. $N_\gamma - N_\alpha = 1.615 - 1.580 = 0.035$, parallel extinction, positive elongation, small optic angle with acute bisectrix normal to the perfect basal cleavage. Pleochroism may become distinct in the yellowish-green varieties, Z and Y = pale green and Z = pale yellow. It can be proved by x-rays that much darker colored varieties exist which are probably considerably higher in indices and stronger in pleochroism though they are so fine grained that only the properties of aggregates can be observed under the microscope. Minnesotaite has been found only in microscopic needles and plates. Its hardness is less than 3, its density for chemically analyzed material = 3.01, though Jolliffe has reported a value of 2.86 which the

author considers somewhat too low. The structure of the mineral was deduced from x-ray powder photographs and the size of its unit cell determined. Based on this, the density, and the chemical analyses, the formula for a unit cell is:

$$(OH)_{22}(Fe'', Mg)_{22.3}Si_{30.4}(Al, Fe''')_{1.4}O_{74},$$
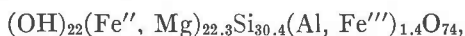
as compared with that of theoretically pure talc:

$$(OH)_{16}Mg_{24}Si_{32}O_{80}.$$

It is evident from these formulas that all 96 O and (OH) positions are filled but that minnesotaite has more (OH) and correspondingly less O, in order to balance the fewer + charges. As a matter of fact, if one is certain of the (OH) in the analysis he can calculate the chemical formula of the mineral without a knowledge of its density. This was done and an almost perfect agreement was obtained with the observed density.

Minnesotaite is associated with quartz (chert), siderite, magnetite, stilpnomelane, and greenalite. Many of the green granules which look exactly like greenalite in ordinary light, but are mottled, felt-like aggregates of greenish tints between crossed nicols, have been identified as minnesotaite by x-rays. Stilpnomelane, which had not been reported before from the Biwabik formation, occurs as very fine-grained needles and aggregates whose strong pleochroism is difficult to observe.

It is instructive to compare the three iron silicates with one another as to their structures and formulas:

Greenalite	$(OH)_{12}$	$(Fe'', Mg)_9 Fe'''_2$	Si_8	O_{22}	$\cdot 2$	H_2O
Stilpnomelane						
$(K, Na, Ca)_{0-1}$	$(OH)_4$	$(Fe'', Mg, Al, Fe''')_{7-8}$	Si_8	O_{23-24}	$\cdot 2-4H_2O$	
Minnesotaite	$(OH)_{5.5}$	$(Fe'', Mg)_{5.5}$	$(Si, Al, Fe''')_8$ $O_{18.5}$			

There is a decrease in total H_2O from greenalite to minnesotaite but an increase of SiO_2. All three contain MgO in appreciable quantities, but only stilpnomelane contains noteworthy amounts of Al_2O_3. The ratio of Fe'' to Fe''' varies considerably in all three. Greenalite has a serpentine structure (6). Stilpnomelane has a unique structure (8) which approximates that of mica or chlorite without, however, being a mixture of the two; while the structure of minnesotaite is similar to talc.

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