THE AMERICAN MINERALOGIST, VOL. 50, JANUARY–FEBRUARY, 1965

IRON PHYLLOSILICATES OF THE CUYUNA DISTRICT IN MINNESOTA

R. L. BLAKE, *Minneapolis Metallurgy Research Center, Bureau of Mines, U. S. Department of the Interior, Minneapolis, Minnesota.*

ABSTRACT

Petrographic examination of 96 thin sections of least oxidized, silicate-rich samples of the thin-bedded facies of the Trommald iron-formation in the Cuyuna district, Minnesota, showed the following minerals in order of decreasing abundance: Mn-Mg-siderite, stilpnomelane, minnesotaite, magnetite, quartz, two unidentified iron silicates, goethite, hematite, pyrite, amphibole and arsenopyrite. Much coarse nematoblastic minnesotaite is oriented along secondary rock cleavage traces. Reconstitution and recrystallization of minerals along certain beds is attested by the wavy or scalloped structures that have destroyed primary layering.

Three samples of stilpnomelane and one of minnesotaite were concentrated from fracture-fillings in iron-formation and subjected to chemical, optical, spectrographic, *x*-ray diffraction and differential thermal analyses. Stilpnomelane samples gave a distinct ammoniacal odor when heated at 70° C, and chemical analysis showed as much as 0.22 per cent ammonia. It is suggested that ammonia, from volcanic activity that produced lava flows and tuffs which overlie the iron-formation, entered the stilpnomelane structure as ammonium ions.

INTRODUCTION

One or more of the iron phyllosilicates, greenalite, minnesotaite, and stilpnomelane are found in most iron-formations of the Lake Superior region. Chemical and optical properties of greenalite from the Mesabi district were determined by Leith (1903) and Gruner (1936). Gruner concluded from *x*-ray powder diffraction study that it has a structure like serpentine with Fe substituting for Mg.

Chemical and optical properties of stilpnomelane from veins of the Mesabi district were presented by Grout and Thiel (1924). Gruner (1937, 1944a) presented chemical, thermal, density and *x*-ray data on stilpnomelane from various localities, and concluded that it has an unusual type of structure which is related to those of biotite and talc. Turner and Hutton (1935), and Hutton (1938, 1945, 1956) contributed much information on properties of stilpnomelane from New Zealand and California. USSR occurrences of the mineral were reported by Vernadski (1900), Eskola (1925), Svetalski (1932), Zavaretski (1950) and Lazarenko (1954). Lazarenko subjected stilpnomelane to chemical, DTA, weight loss on ignition, optical and thermal-optical, spectral absorption, and *x*-ray analyses.

Minnesotaite was mistaken for an amphibole until Richarz (1927) pointed out that optically this mineral was not an amphibole. Gruner

(1944b) determined that it has the structure of talc, named it minnesotaite, and presented chemical, optical and x-ray analyses.

Other iron phyllosilicates identified in iron-formations of the Lake Superior region are: nontronite reported by Ayres (1940) and Gruner (1946); chlorite reported by Gruner (1946); and chamosite described by Bailey and Tyler (1960) as a green clay which fills vugs in goethite ore. Recent publications on the Cuyuna district are those of Schmidt (1955, 1958, 1959, 1963) and Schmidt and Dutton (1952, 1957) on structure and stratigraphy; Grout and Wolff (1955) on general geology; and Blake (1964) on petrography and mineralogy. Properties, occurrence and literature of phyllosilicates are well summarized by Brown (1961) and by Deer *et al.* (1961).

Work reported here was conducted under a Bureau of Mines Fellowship in cooperation with the University of Minnesota to examine further the iron phyllosilicate minerals in less metamorphosed iron-formations of the Lake Superior region, especially in the Cuyuna district where fewer studies had been made on mineralogy and petrography. Samples were collected in 1955–57 from the central part of the Cuyuna district and represent the thin-bedded facies of the Trommald iron-formation (Schmidt, 1963) taken from open pit exposures and drill core.

Minerals were identified optically and by x-ray diffraction using Fe or Cu radiation in cameras of 57.3 mm radius. Diffractograms were made with filtered Fe or Cu radiation using a vertical circle unit with a Geiger counter and linear strip chart recorder. Pulverized samples were packed in aluminum holders. When determining intensities, precautions were taken to minimize preferential orientation as suggested by McCreery in Beatty's paper (1949) and by Yoder and Eugster (1954). Despite these precautions, considerable preferential orientation was observed in most patterns of the phyllosilicates. Four of the least altered samples were selected for mineral separation that consisted of initial hand-picking, followed by use of a Frantz magnetic separator and heavy liquids[1] in separatory funnels or a centrifuge. Attempts to separate minnesotaite and stilpnomelane from iron-formation were unsuccessful, but they were separated from coarse-grained fracture-fillings within iron-formation.

MAIN IRON-FORMATION

Petrography. The thin-bedded facies of the Trommald iron-formation is stratified with green, gray, brown, or black layers ranging from one inch thick to those just visible, with most less than one-quarter inch. Neither

---

[1] The non-polar heavy liquids, carbon tetrachloride, acetylene tetrabromide, and methylene iodide were chosen for the layered silicates, which have large surface electric charges and may have ion exchange capacity as does stilpnomelane (Gruner, 1937).

clastic layers nor the common granule texture of some Lake Superior region iron-formations were observed. Most rocks are gently folded, and show only bedding fissility; more highly folded rocks show secondary cleavage that may nearly obscure the bedding. Some undeformed rocks show another megascopic feature that obscures primary bedding: a group of thin parallel layers is interrupted by lenticular wavy zones, in which reconstitution and recrystallization of minerals has occurred. For example, beds composed predominantly of stilpnomelane and fine carbonate may be traced into reconstituted zones composed mostly of minnesotaite and coarse carbonate with some relics of stilpnomelane (Fig. 1).

Petrographic examination of 96 thin sections of least oxidized thin-bedded iron-formation shows the following minerals in order of decreasing abundance: Mn-Mg-siderite, stilpnomelane, minnesotaite, magnetite, quartz, two unidentified iron silicates, goethite, hematite, pyrite, amphibole, and arsenopyrite. The first three mentioned are far more abundant

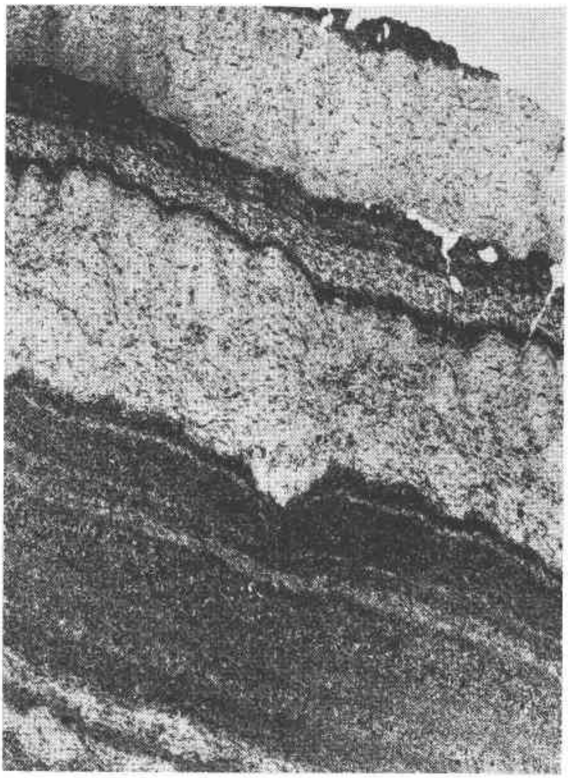

FIG. 1. Thin section showing dark stilpnomelane-rich layers and light reconstituted minnesotaite-rich layers with stilpnomelane relics. (BM 106, 4×).

than the remainder. For example, siderite comprises from 50 to 75 per cent of the rock in more than half of the sections, and was present in all but one thin section. Analysis of an impure carbonate concentrate indicates a composition $(Fe_{.7}\ Mn_{.2}\ Mg_{.1})CO_3$. One of the unidentified silicates had its principal reflection at a spacing of 14 Å; the other at 7 Å. No monomineralic layers were found, and any two, or as many as eight or nine of the minerals were observed in a given layer. Textures indicate that the greater part of the thin-bedded facies was deposited as a chemical precipitate, although occasional clastic quartz grains were observed. Textures of chemical sediments are similar to those of igneous and metamorphic rocks (Pettijohn, 1949), and the crystalloblastic terms apply to most of these rocks.

In thin sections from drill core, the ratio of green ferrous-rich stilpnomelane to the brown ferric-rich stilpnomelane increases with distance from iron ore deposits. The uninterrupted textures in samples containing both varieties indicate that the brown variety may form from green stilpnomelane by oxidation. This observation is supported by Hutton's (1938) microscopic evidence, and by Zen's (1960) interpretation of chemical data that all Fe^{3+} in stilpnomelane may be regarded as subsequently oxidized Fe^{2+}. However, Hutton (1956) suggested another possibility: that the change in the ratio between Fe^{2+} and Fe^{3+} in one sample of stilpnomelane may have occurred during crystallization of the mineral rather than from weathering processes.

Minnesotaite often shows two apparent generations: (1) an earlier network of very fine needles as long as 20 to 30 microns, and (2) later coarse plates, blades, or needles from 50 to several hundred microns in length that often cut across earlier minnesotaite and fine and coarse carbonate and stilpnomelane. Coarse nematoblastic minnesotaite is oriented along secondary rock cleavage traces.

Filled fractures in iron-formation generally strike north-northwest, are nearly vertical, and truncate bedding and east-northeast folds. Stilpnomelane is the predominant mineral in most filled fractures from 0.1 to 10 cm wide; in wider fractures milky quartz predominates, and stilpnomelane is concentrated adjacent to wall rock.

Petrology. The main iron-formation in the central part of the Cuyuna district has been subjected to low grade regional metamorphism, as shown by the gentle to tight folds with very little faulting, the conformable folding of stratigraphically older and younger rocks, some recrystallization and reconstitution of minerals, and the scattered development of secondary rock cleavage.

That most fracture openings have matching walls and generally undisturbed mineral filling indicates that opening and filling occurred after most folding had ceased. Minerals in fracture-fillings are the same as those in iron-formation. This fact, plus the lack of evidence of wall rock assimilation, suggests that minerals which fill fractures have formed from solutions originating within iron-formation, possibly by the process of metamorphic differentiation (Turner, 1948; Read 1933).

Mineral assemblages formed in equilibrium during metamorphism of iron-formation were discussed by Yoder (1957) and by Flaschen and Osborn (1952, 1957) based on hydrothermal experiments, and by Gundersen and Schwartz (1962) based on observed petrographic evidence. Some apparent mineral relations and interpretations of the thin-bedded facies of the Trommald iron-formation bearing on each of the above studies are discussed below. The present author is aware of the difficulty of interpreting sequence of mineralization from textural evidence of this primarily chemically-deposited rock.

Yoder deduced that, if the initial bulk composition of a sediment were greenalite+quartz+water+magnetite, then the successive index minerals to appear from reactions of progressive metamorphism would be: minnesotaite, grunerite, and fayalite (or hypersthene). If the sediment contained Al_2O_3, it might be represented by chamosite+quartz+water +magnetite. With progressive metamorphism of this rock, the minerals to appear (and mark isograds) would probably be stilpnomelane, chloritoid (Yoder explained that this mineral cannot form in stilpnomelane-bearing rocks), biotite, iron-rich garnet, staurolite, kyanite and finally cordierite. Yoder also revived Bowen's (1940) concept that, rather than consider the first appearance of an index mineral to mark an isograd, it may be more important to establish the disappearance of that mineral.

Yoder's mineral assemblage (and that of Flaschen and Osborn) did not include carbonate; yet the most abundant mineral observed in the thin-bedded facies of the Trommald iron-formation was an iron carbonate. Carbonate is also an important phase in mineral assemblages from other iron-formations in the Lake Superior region (Gruner, 1946; James, 1954). It is suggested that the abundance of carbonate and resulting partial pressure of CO_2 in these rocks might produce different metamorphic reactions from those deduced for an assemblage lacking carbonate.

In the Cuyuna rocks greenalite was not identified, and no granules (structures in which greenalite has usually been reported) were observed. The very fine-grained green silicate groundmass (represented by a 7-Å *x*-ray diffraction reflection) in some thin sections could represent this mineral, and if the groundmass contains a small amount of Al_2O_3, its composition probably falls between those of the 7-Å iron-rich chlorite end-members, greenalite and chamosite, of Nelson and Roy (1958, Fig. 8). An assemblage composed of this 7-Å mineral+quartz+water+magnetite could conceivably form stilpnomelane (usually containing from 4 to 7 per cent Al_2O_3) upon reconstitution, and textural evidence to support this reaction was observed in several thin sections. It is not known what effect the iron carbonate usually present would have on this reaction.

Stilpnomelane and minnesotaite have very similar compositions, the latter having less Al_2O_3 and H_2O. These two minerals were often observed intimately associated, usually with abundant iron carbonate, and occasionally the minnesotaite appeared to have formed at expense of stilpnomelane. It seems likely that both minerals could form from a sediment that contains a low—Al_2O_3 chamosite, thus not requiring that the primary silicate be greenalite for the formation of minnesotaite, or chamosite for the formation of stilpnomelane.

As predicted by Yoder, chloritoid was not found in the stilpnomelane-bearing rocks. The low degree of metamorphism precluded presence of higher metamorphic grade minerals listed by Yoder, except that a few needles of an amphibole (probably cummingtonite) were observed in one thin section of iron-formation and in two sheared fracture-fillings. Isograds might be defined by the disappearance of, first, chamosite; and, second, stilpnomelane. The next isograd to appear might be marked by disappearance of minnesotaite, although not enough evidence was found to suggest that minnesotaite usually forms at expense of stilpnomelane.

Flaschen and Osborn (1957) suggested temperature ranges in which certain mineral assemblages might be stable, based either on constant temperature and increasing partial pressure of oxygen, or on constant total oxygen and increasing temperature. They also indicated that relative oxygen partial pressures existing during metamorphism may be judged using Fe_2O_3:FeO ratios as a guide and comparing assemblages with similar Fe:SiO_2 ratios and similar temperature-pressure history. Some difficulty may be expected in deducing the ratio of Fe_2O_3:FeO existing during metamorphism because of possible subsequent oxidation. Oxidation of a mineral to form hematite or goethite can readily be determined microscopically, but it may be difficult to determine if an iron silicate has been slightly oxidized, say enough to change the Fe_2O_3:FeO ratio but not enough to form an iron oxide. If Zen's contention is true, that all Fe^{3+} in stilpnomelane is subsequent, and if this may be applied also to minnesotaite, there will be little difficulty in determining the Fe_2O_3:FeO ratio existing during metamorphism from the present mineral assemblage.

Gundersen and Schwartz (1962) made a comprehensive study of the mineralogy of the metamorphosed Biwabik iron-formation of the eastern Mesabi district. They also reviewed the work of Yoder and of Flaschen and Osborn, and concluded that in the eastern Mesabi district there was no evidence of the initial existence of the primary iron silicates, greenalite, stilpnomelane, and minnesotaite; that all evidence indicates the iron-formation to have consisted initially of quartz and magnetite; that metamorphism caused by the Duluth gabbro intrusion was initially thermal, resulting in recrystallization and formation of fayalite and other anhydrous minerals; and that a contemporaneous or slightly later metasomatic stage introduced enough water to form hydrous silicates, especially amphiboles, and also small amounts of stilpnomelane. They further suggest that there is no evidence from the entire Mesabi range that would invalidate the concept that the iron-formation originally consisted largely of chert and magnetite.

Gundersen and Schwartz's interpretation infers that most carbonates and hydrous silicates in the main and western Mesabi districts were formed at some later metasomatic stage rather than during diagenesis or in early stages of regional metamorphism. Presumably this interpretation might also apply to the Cuyuna iron-formation since its mineralogy, textures, and probable geologic history are rather similar to those of the main and western Mesabi iron-formations. The present author does not dispute Gundersen and Schwartz's interpretation of the petrologic history for the eastern Mesabi district which was based on very careful studies. However, in applying this interpretation to the main and western Mesabi range, and presumably also the Cuyuna iron-formation, one petrologic consideration has apparently been overlooked which supports the concept that the carbonate and hydrous silicates were formed during the imperceptibly merging sequential stages of deposition, diagenesis and low grade regional metamorphism. The environment of deposition of a water-laid clastic or chemical sediment insures that water is an abundant phase of the new deposit (Yoder, 1955). As diagenesis proceeds, some water is structurally incorporated in the formation of hydrous layered silicates with low degree of structural order, and by compaction excess water is expelled from the rock. As diagenesis continues and merges into low grade regional metamorphism, mineral reconstitution may form less hydrous and more highly ordered silicate minerals as water continues to be expelled. If carbonate formed initially, some CO_2 may have been expelled with water as mineral reconstitution and recrystallization proceeded. The inclusion of abundant water in a lithifying sediment agrees with the concepts of development of iron-formations as suggested by the work of Yoder and of Flaschen and Osborn. Therefore to the writer it seems incorrect to interpret the origin of hydrous iron silicates in the main and western Mesabi and in the Cuyuna iron-formations as primarily from late stage introduction of water to an anhydrous assemblage of quartz and magnetite.

RESULTS OF MINERAL STUDIES

Stilpnomelane. Stilpnomelane was concentrated from fracture-fillings within iron-formation from each of three open pits. Sample locations, all in T.46N., R.29W., are: BM 85—Portsmouth pit, SE$\frac{1}{4}$–SE$\frac{1}{4}$, Sec. 2, rock mass in middle of east-central part of pit; BM 95-Arko pit, NW $\frac{1}{4}$–NE $\frac{1}{4}$, Sec. 9, north wall in west part of pit; and BM 107—Alstead pit, SW $\frac{1}{4}$–NE $\frac{1}{4}$, Sec. 9, north wall at east end of pit. Quartz, carbonate, and iron oxides were removed by heavy liquid separations of fractions sized at minus 89- plus 38-microns, but the stilpnomelane was not separated into specific gravity fractions of small increments.

(*a*) Chemical analyses and optical properties. Chemical analyses and optical properties of each concentrated stilpnomelane are listed in Table 1. Each analysis was corrected for the following impurities determined by microscopic examination of a number of slides containing an estimated total of either 5,000 or 10,000 grains; BM 85—trace of quartz; BM 95—0.3 per cent quartz and 0.1 per cent hematite; BM 107—0.6 per cent quartz and 0.6 per cent carbonate assumed $(Fe_{2/3}\ Mn_{1/3})CO_3$. The small amounts of NH_3 and TiO_2 were considered as contamination and disregarded, although it will be shown later that NH_4^+ may occur in the structure. Using Hutton's (1938) nomenclature all three samples are ferrostilpnomelanes, with the following molecular proportions of

$$\frac{(Al, Fe^{3+})_2O_3}{(Al, Fe^{3+})_2O_3 + (Fe^{2+}, Mn, Mg)O} \times 100:$$

BM 85 = 18.6 per cent; BM 95 = 19.0 per cent; BM 107 = 33.1 per cent.

Optically all stilpnomelane plates in BM 85 have the same brownish-green color; those in BM 95 vary, but are mostly greenish-brown; and those in BM 107 also vary, but are primarily brown. The range and mean value of refractive indices are listed in Table 2.

The detection of ammonia in stilpnomelane samples reported here is the first such occurrence known to the writer. Ammonia odor was first detected in stilpnomelane samples that had been wet-screened in distilled water and were being dried at 70° C. At this temperature the odor was strongest from a dry sample, weaker from a slightly dampened one, and absent when water covered the sample. Seven samples of stilpnomelane from fracture-fillings in iron-formation and one sample (BM 129) of stilpnomelane iron-formation (all from the Cuyuna district) were analyzed for NH_3 (Table 2). Determinations were made on 0.5 gram samples dissolved in acid (HCl or HCl and HF) followed by distillation with NaOH and titration of the evolved ammonia with acid. No attempt was

Table 1. Chemical Analyses and Optical Properties of Three New Stilpnomelane Samples

<table>
<tr><th rowspan="3">Constituent</th><th colspan="6">Chemical analyses, weight per cent</th></tr>
<tr><th>BM 85</th><th>(R2252)[1]</th><th>BM 95</th><th>(R2191)[2]</th><th>BM 107</th><th>(R2253)[1]</th></tr>
<tr><th>As reported</th><th>Corrected, adjusted[4]</th><th>As reported</th><th>Corrected, adjusted[4]</th><th>As reported</th><th>Corrected, adjusted[4]</th></tr>
<tr><td>SiO_2</td><td>46.66</td><td>46.55</td><td>47.49</td><td>47.54</td><td>46.11</td><td>46.90</td></tr>
<tr><td>Al_2O_3</td><td>5.39</td><td>5.38</td><td>5.14</td><td>5.18</td><td>5.08</td><td>5.12</td></tr>
<tr><td>Fe_2O_3</td><td>8.01</td><td>8.00</td><td>8.69</td><td>8.61</td><td>17.75</td><td>17.90</td></tr>
<tr><td>TiO_2</td><td>.03</td><td>—</td><td>.00</td><td>—</td><td>.03</td><td>—</td></tr>
<tr><td>FeO</td><td>24.82</td><td>24.78</td><td>24.83</td><td>25.03</td><td>16.59</td><td>16.49</td></tr>
<tr><td>MnO</td><td>.58</td><td>.58</td><td>.84</td><td>.85</td><td>.57</td><td>.45</td></tr>
<tr><td>MgO</td><td>3.91</td><td>3.90</td><td>3.55</td><td>3.58</td><td>3.70</td><td>3.73</td></tr>
<tr><td>CaO</td><td>.46</td><td>.46</td><td>.33</td><td>.33</td><td>.29</td><td>.29</td></tr>
<tr><td>Na_2O</td><td>.14</td><td>.14</td><td>.00</td><td>.00</td><td>.06</td><td>.06</td></tr>
<tr><td>K_2O</td><td>1.84</td><td>1.84</td><td>1.31</td><td>1.32</td><td>1.47</td><td>1.48</td></tr>
<tr><td>H_2O+110° C.</td><td>5.86</td><td>5.84</td><td>5.74</td><td>5.79</td><td>5.66</td><td>5.71</td></tr>
<tr><td>H_2O–110° C.</td><td>2.54</td><td>2.53</td><td>1.76</td><td>1.77</td><td>2.84</td><td>2.86</td></tr>
<tr><td>P_2O_5</td><td>.00</td><td>—</td><td>—</td><td>—</td><td>.00</td><td>—</td></tr>
<tr><td>NH_3[3]</td><td>.02</td><td>—</td><td>.13</td><td>—</td><td>.22</td><td>—</td></tr>
<tr><td>F</td><td>—</td><td>—</td><td>.02</td><td>—</td><td>—</td><td>—</td></tr>
<tr><td></td><td>100.26</td><td>100.00</td><td>99.83
.01
99.82
Less O≡F</td><td>100.00</td><td>100.37</td><td>100.00</td></tr>
<tr><td></td><td colspan="6">Optical properties</td></tr>
<tr><td>α</td><td colspan="2">(Mean≅1.565; range 1.550–1.575 ± .005)</td><td colspan="2">(Mean≅1.565; range 1.552–1.585 ± .005)</td><td colspan="2">(Mean≅1.593; range 1.585–1.605 ± .005)</td></tr>
<tr><td>γ</td><td colspan="2">(Mean≅1.640; range 1.610–1.653 ± .005)</td><td colspan="2">(Mean≅1.635; range 1.615–1.640 ± .005)</td><td colspan="2">(Mean≅1.683; range 1.665–1.690 ± .005)</td></tr>
<tr><td>Mean $\gamma-\alpha$</td><td colspan="2">.075</td><td colspan="2">.070</td><td colspan="2">.090</td></tr>
<tr><td>2V</td><td colspan="2">(−) small</td><td colspan="2">(−) small</td><td colspan="2">(−) small</td></tr>
<tr><td>Elongation</td><td colspan="2">positive</td><td colspan="2">positive</td><td colspan="2">positive</td></tr>
<tr><td>Extinction</td><td colspan="2">parallel</td><td colspan="2">parallel</td><td colspan="2">parallel</td></tr>
<tr><td>Pleochroism:</td><td colspan="2"></td><td colspan="2"></td><td colspan="2"></td></tr>
<tr><td>X=</td><td colspan="2">pale greenish brown</td><td colspan="2">pale brown</td><td colspan="2">pale yellow</td></tr>
<tr><td>Y=Z=</td><td colspan="2">deep brown</td><td colspan="2">deep brown</td><td colspan="2">deep brown</td></tr>
</table>

[1] D. Thaemlitz, analyst, Rock Analysis Laboratory, Univ. of Minn.

[2] E. H. Oslund, analyst, Rock Analysis Laboratory, Univ. of Minn.

[3] NH_3 by C. O. Ingamells, Rock Analysis Laboratory, Univ. of Minn.

[4] Corrected, adjusted analysis is theoretical and its accuracy is limited by the accuracy of the chemical analysis and microscopic grain count.

TABLE 2. QUANTITY OF STILPNOMELANE AND AMMONIA IN SAMPLES FROM THE CUYUNA DISTRICT

Sample number	Per cent	
	Stilpnomelane (volume)	Ammonia[1]
BM- 1	77	0.01
16	97	.02
32	95	.13
85	98	.02
95	99	.13
107	98	.22
113	83	.13
129	25	.09

[1] Determinations (Anal. R. 2211) by C. O. Ingamells, Rock Analysis Laboratory, Univ. of Minn.

made to determine nitrate nitrogen. Ammonia in stilpnomelane might occur in three forms: (1) as an integral part of the lattice, *i.e.*, substitution by NH_4^+ for some cation, (2) as NH_3 or NH_4^+ in an interstitial position, or (3) as NH_3 or NH_4^+ absorbed on the mineral surface. The writer favors form (1) in view of the following information. Gruner (1944a) proposed channels in the hydrated layer of stilpnomelane in which potassium ions and water may be situated. The NH_4^+ ion probably could be accommodated in these channels because its ionic radius is close to that of K^+. The replacement of potassium in stilpnomelane by thallium was pointed out by Gruner (1937). Several other layered silicates have ion exchange properties, and the NH_4^+ ion can be fixed in their structures (Scott *et al.*, 1956). Stevenson (1959) found fixed ammonium within the lattice of silicate minerals, and he is of the opinion that "ammonium was present in the substrate at the time the minerals were synthesized and competed with potassium for the pockets formed by the hexagonal oxygen rings in the crystalline nuclei of the minerals." No ammonia odor was detected in two Mesabi district samples, both containing much stilpnomelane, from the diversion channel (Sec. 1, T. 58N., R. 16W.) and from the Gilbert pit.

Four samples of stilpnomelane iron-formation from three exploration drill holes in the Cuyuna district at some distance from open pits and underground mines were pulverized and tested. Because each sample had a strong ammonia odor, the source of the ammonia in stilpnomelane is not the ammonia dynamite used in blasting. It is suggested that ammonia, as NH_4^+ ion, entered the mineral structure at the time it was formed. A possible source of ammonia in stilpnomelane of the Cuyuna district is the volcanism that produced the lava flows and tuffs found by Schmidt and Dutton (1957) immediately overlying the main iron-formation.

The structure of stilpnomelane was proposed by Gruner (1937, 1944a) using powder *x*-ray data. Single crystal studies not yet published[1] have indicated a somewhat different structure than that proposed by Gruner. Some uncertainty therefore attends the calculation of its structural formula, particularly in accounting for H_2O^+ and H_2O^- in the structure. Several methods of calculating the formula are those of Gruner (1937, 1944a), Hutton (1956) and Stevens[2] (1946). Because the latter two methods ignore H_2O^-, and since the writer feels that there is, as yet, no justification for ignoring H_2O^- in the stilpnomelane structure, Gruner's method was chosen to calculate the formula of each analyzed stilpnomelane. Table 3 shows the number of cations per cell of 32 silicon ions, compares theoretical and measured densities, and lists formulas in the form Si_8O_{20}. Molecular weights and unit cell volumes used in calculating theoretical densities are also shown in Table 3. Unit cell volumes were calculated from *x*-ray cell parameters listed at the end of Table 4. The theoretical density of BM 85 is in good agreement with the measured value. It is not known why the measured densities of BM 95 and 107 are larger than their theoretical densities; measured densities are usually less than theoretical values because of voids within mineral fragments. The small amount of contaminating hematite in BM 95 and carbonate in BM 107 have increased their measured densities by only 0.002 and 0.007 g/cm^3 respectively.

(*b*) Spectrographic analysis. Qualitative emission spectrographic analyses of the three analyzed stilpnomelanes, and of one other, showed barium to be present. Strontium and titanium were found in two of these.

(*c*) *X*-ray diffraction. An *x*-ray powder diffractogram for one analyzed stilpnomelane is shown in Fig. 2. The characteristic 12.1 A spacing (001) is shown by the strong single[3] peak at about 9.2 degrees (2θ).

---

[1] *The Crystal Structure of Stilpnomelane*, by R. A. Eggleton, unpubl. Ph. D. thesis, University of Wisconsin, Madison, 1964.

[2] Yoder, H. S., Jr., of the Geophysical Laboratory, Wash., D. C., in a personal communication in Jan. 1958, suggested that Steven's method could be used for stilpnomelane by assuming a mica structure.

[3] Some stilpnomelane film patterns show two strong reflections close to 12 Å; they result from absorption of the center of the reflection by the sample mount (Klug and Alexander, 1954). This strong reflection was scanned at $\frac{1}{4}°$ (2θ) per minute with scale factor set so that the peak stayed on the chart; then only a single reflection occurred.

TABLE 3. ATOMIC DISTRIBUTION AND STRUCTURAL FORMULAS OF NEWLY ANALYZED STILPNOMELANE[1]

Cations	BM 85	BM 95	BM 107
Si	32.0	32.0	32.0
Al	4.4	4.1	4.1
Fe^{3+}	4.1	4.4	9.2
Fe^{2+}	14.2	14.1	9.4
Mn	0.3	0.5	0.3
Mg	4.0	3.6	3.8
Ca	0.3	0.2	0.2
Na	0.2	0.0	0.8
K	1.6	1.1	1.2
H^+	26.8	26.0	26.0
H^-	11.6	7.9	13.0
$Al+Fe^{3+}$	8.5	8.5	13.3
Al+Fe+Mg+Mn	27.0	26.7	26.8
Σ Cations without H and Si	29.1	28.0	29.0
Σ+charges without H	193	191	197
Mol. wt. (4 unit cells, 32 Si)	4129	4042	4139
Unit cell volume (A^3)[2]	615	621	615
Theoretical density (g/cm^3)	2.79	2.70	2.79
Measured density (g/cm^3)[3]	2.794 at 25.8° C.	2.833 at 24.8° C.	2.832 at 23.8° C.

Formulas in form Si_8O_{20}:

BM85 —$(OH, O)_{6.1}$ $(K, Na, Ca)_{0.5}$ $(Fe, Mg, Mn, Al)_{6.8}$ $Si_8O_{20}\cdot 2\cdot 8H_2O$

BM95 —$(OH, O)_{5.9}$ $(K, Ca)_{0.3}$ $(Fe, Mg, Mn, Al)_{6.7}$ $Si_8O_{20}\cdot 2\cdot 2H_2O$

BM107—$(OH, O)_{6.6}$ $(K, Na, Ca)_{0.4}$ $(Fe, Mg, Mn, Al)_{6.7}$ $Si_8O_{20}\cdot 2\cdot 9H_2O$

[1] Assuming 32 silicon ions, after Gruner (1944, Table 1, p. 293).

[2] Based on cell dimensions at end of Table 4.

[3] Determined by S. S. Goldich with fused silica pycnometer; density ±0.005.

Table 4 presents *x*-ray powder film data for the three analyzed stilpnomelanes. More accurate (001) spacings are shown at the end of the table as determined from (003) and (004) reflections.

One sample each of stilpnomelane and minnesotaite were dried at 100° C for 24 hours, then separately placed in ethylene glycol at room temperature for 48 hours. *X*-ray powder film patterns before and after treatment showed no expansion of their respective structures.

(*d*) Differential thermal analysis. DTA was carried out with a multiple chamber Inconel block and chromel-alumel thermocouples. The heating

Table 4. *X*-ray Powder Data for Cuyuna Samples of Stilpnomelane and Minnesotaite; Film, Radiation: Fe-Kα (Mn)

	Stilpnomelane[1]						Minnesotaite[2]		
Indices[3]	BM-85		BM-95		BM-107		BM-131		
	dÅ	I/I_1	dÅ	I/I_1	dÅ	I/I_1	Indices[4]	dÅ	I/I_1
(001)	12.1	100	12.2	100	12.2	100			
							(002)	9.6	100
	8.09	5							
	7.00	5			7.00	5			
(002)	6.06	10			6.14	10			
	5.39	15	5.38	5	5.43	10			
	4.71	20	4.68	5	4.69	15	(004)	4.78	20
	4.32	10			4.33	10		4.58	10
(003)	4.02	35	4.07	10	4.05	30			
	3.60	20	3.59	5	3.58	15			
	3.34	10	3.33	30	3.34	10		3.33	25
	3.14	10	3.12	10	3.14	10	(006)	3.17	50
(004)	3.03	25	3.03	15	3.04	20			
	2.71	35	2.71	30	2.83	35		2.75	22
								2.65	22
	2.56	50	2.56	40	2.56	40		2.52	70
	2.50	5			2.493	10			
	2.42	5						2.399	20
	2.342	25	2.346	30	2.343	30		2.310	5
								2.240	5
	2.178	5						2.204	20
	2.106	15	2.107	10	2.110	10		2.105	10
								2.003	5
	1.953	5						1.952	5
	1.883	10	1.884	5	1.883	5	(00, 10)	1.907	10
	1.811	5	1.819	5				1.818	10
	1.746	5			1.769	5			
	1.683	10			1.686	5		1.692	5
								1.651	10
								1.606	20
	1.578	20	1.580	10	1.576	20		1.592	15
(060)	1.564	20	1.566	10	1.561	20	(060)	1.563	20
								1.541	10
	1.527	10			1.525	10		1.524	5
	1.514	10						1.508	10
								1.450	10

[1] See also ASTM card 2-0036.

[2] See also ASTM card 6-0025.

[3] Indices from Gruner, except (002), (1937, Table 3, p. 919) are thought properly assigned to d-values.

[4] Indices from Gruner (1944, Table 1, p. 366).

TABLE 4—(*continued*)

	Stilpnomelane[1]						Minnesotaite[2]		
	BM-85		BM-95		BM-107		BM-131		
Indices[3]	Å	I/I_1	dÅ	I/I_1	dÅ	I/I_1	Indices[4]	dÅ	I/I_1
	1.415	10			1.418	5			
	1.399	10			1.398	5			
	1.362	10			1.359	5		1.362	15
	1.344	10			1.342	5		1.351	15
	1.323	10						1.325	15
								1.307	10
	1.284	15							
	1.229	5							
								1.176	20
								1.102	15
								1.051	15
	1.033	10			1.028	5			
	1.025	10			1.020	5		1.018	15
								.989	10
[5] d_{001}	12.09		12.16		12.14		[6] d_{002}	9.54	
[7] b	9.38		9.40		9.37			9.38	
[8] d_{100}	5.42		5.43		5.41			5.42	
Cell vol. in Å^3	615		621		615			970	

[5] $d_{(001)}$ average from (003 and (004) reflections.
[6] $d_{(002)}$ average from other basal reflections.
[7] From (060).
[8] Based on assumption of pseudo-hexagonal cell.

rate of about 11.5° C per minute was nearly linear above 200° C. DTA curves for the three analyzed stilpnomelanes were nearly identical, and only the curve of BM 85 is shown in Fig. 3. Endothermic reaction peaks point downward.

In an attempt to duplicate the phase or phases present at a given temperature during thermal analysis, small samples of stilpnomelane were wrapped in gold foil, heated to selected temperatures in the DTA apparatus, then air-quenched. The products were identified by *x*-ray diffraction, with results posted beside the DTA curve. No attempt was made during heating to keep air away from the samples, which were loosely covered by an Inconel disc. The following interpretation is offered for the DTA curve of stilpnomelane: The first endothermic reaction is caused by rapid loss of water, either adsorbed or in channels of the structure. The

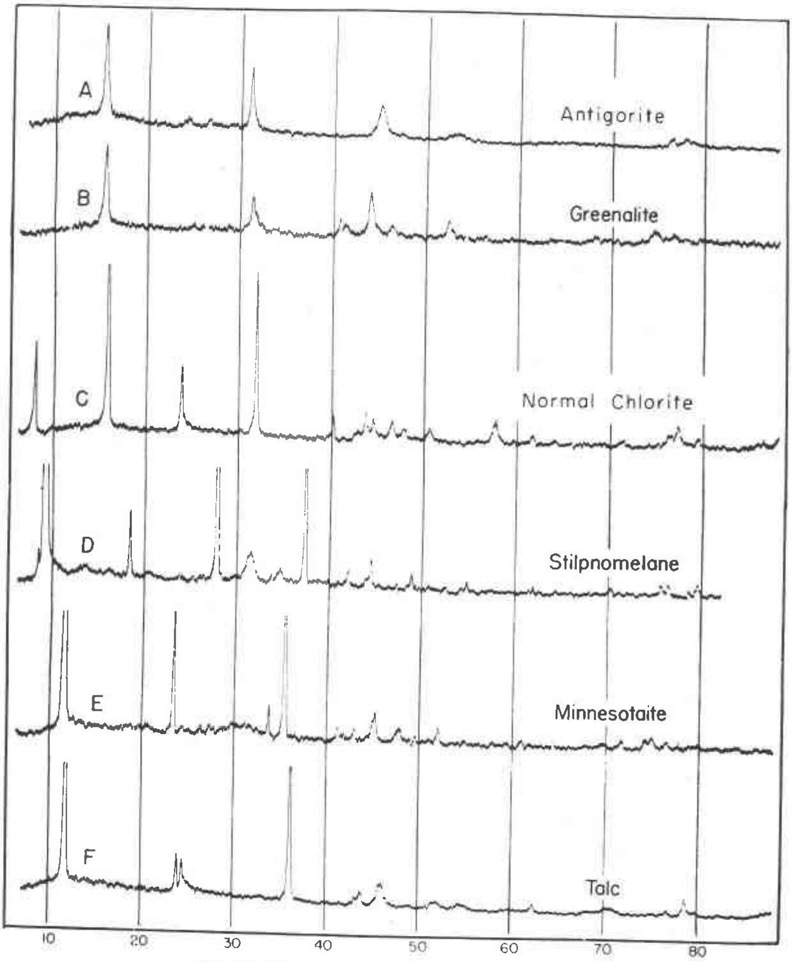

FIG. 2. *X*-ray powder diffractograms of some phyllosilicates.

apparent exothermic reaction at 200° to 400° C may be instrument rebound. The gradual return toward the endothermic direction starting about 400° C may represent increasing removal of lattice hydroxyl, so that at 700° C stilpnomelane is mostly dehydrated but its structure is intact. The strong exothermic reaction near 800° C may represent collapse of the structure and simultaneous formation of magnetite.

Minnesotaite. One sample (BM 131) of a fracture-filling in the main iron-formation of the Cuyuna district contained enough unaltered minne-

TABLE 5. CHEMICAL ANALYSIS, ATOMIC DISTRIBUTION, AND STRUCTURAL FORMULA FOR CUYUNA MINNESOTAITE SAMPLE BASED ON STEVENS' (1946) METHOD. ANALYSIS OF GRUNER'S MESABI MINNESOTAITE ALSO LISTED

Oxide	Gruner's Mesabi Sample[1]	Cuyuna Sample BM-131, Analysis R2474[2]				
		Analysis		Relative equivalents		Atomic distribution
		Weight per cent	Corrected, adjusted[3]	e[4]	e' = f · e[5]	
						Tetrahedral:
SiO_2	51.29	51.79	51.26	3.415	15.82	Si...... 3.95
Al_2O_3	.61	1.46	1.52	.089	.41	Al....... .05
TiO_2	.04	.08				
P_2O_5		.08				Total.. 4.00
						Octahedral:
						Al....... .09
Fe_2O_3	2.00	.61	.52	.020	.09	Fe^{3+}..... .03
FeO	33.66	35.65	37.23	1.036	4.80	Fe^{2+}..... 2.40
MnO	.12	.78	.77	.022	.10	Mn...... .05
MgO	6.26	3.21	3.38	.168	.78	Mg...... 39
CaO	.00	.10				
Na_2O	.08	.06		4.750 =	22.00 =	Total.. 2.96
K_2O	.03	.44		Σe_m	$\Sigma e'_m$	OH........ 2.72
H_2O^+	5.54	5.03	5.29	.587	2.72	
H_2O^-	.24	.03	.03			
F	—	.02				
CO_2	—	.14				
	99.87	99.43	100.00			
O≡F		.01				
		99.42				

Structural formula:

$$(Fe^{2+}_{2.40}Mg_{0.39}Mn_{0.05})(Al_{0.09}F^{3+}e_{0.03})(si_{3.95}Al_{0.05})O_{10}(OH)_{2.72}$$

---

[1] Gruner (1944b) Table 3, p. 368.

[2] Rock Analysis Laboratory, Univ. of Minn., E. H. Oslund, Analyst.

[3] See text for explanation.

[4] (e) from dividing weight per cent of each constituent by its equivalent weight (Stevens, 1946, p. 109). Example: Mol. wt. $Al_2O_3 = 101.94 \div 6$ cation charges $= 16.99$ (eq wt); $1.52 \div 16.99 = 0.089 = e$ for Al_2O_3.

[5] $f = 22/\Sigma e_m = 22/4.750 = 4.632$, a factor to make the total of cation equivalents equal 22 for talc $[R_3^{2+}Si_4\,O_{10}\,(OH)_2]$.

sotaite for concentration, but it was necessary to use a 5–15 micron fraction to obtain liberation. The sample location is: Sagamore pit, SE ¼–

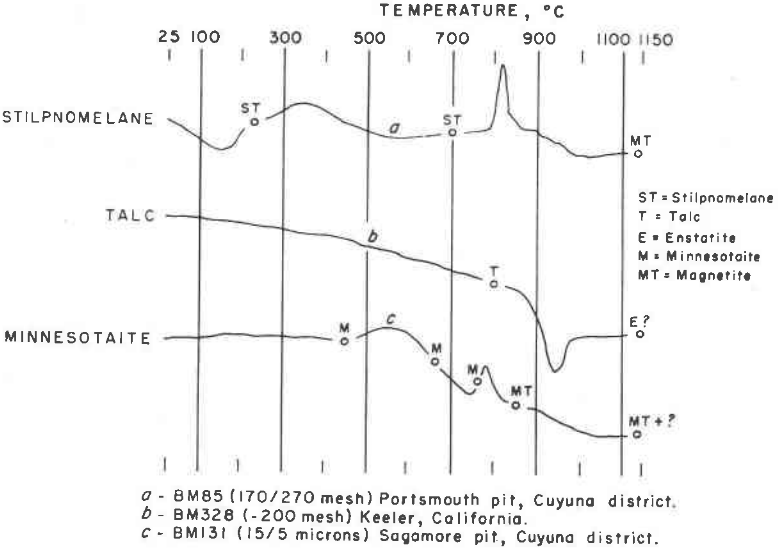

FIG. 3. Differential thermal curves showing phases identified at various temperatures by *x*-ray diffraction.

NW $\frac{1}{4}$, Sec. 19, T.46N.—R. 29W., north limb of anticlinal rock mass in central part of pit, approximately 500 feet NW. of center, Sec. 19.

(*a*) Chemical and optical properties. Repeated washing of concentrated minnesotaite with CCl_4 failed to remove all odor of heavy liquid. Some heavy liquid remaining in the concentrate may have contributed to the low total of the Cuyuna sample analysis in Table 5. Comparison with Gruner's analysis for minnesotaite concentrated from the Biwabik iron-formation of the Mesabi district shows that the Cuyuna sample contains more Al_2O_3, FeO and MnO; less Fe_2O_3, and only half as much MgO.

Optical examination of slides containing a total of about 10,000 grains indicated the following approximate contamination of the Cuyuna minnesotaite concentrate: stilpnomelane 0.2 per cent; opaques 0.2 per cent; other 0.1 per cent. The analysis was corrected for stilpnomelane based on the analysis of BM 107 (a brown stilpnomelane); for 0.37 per cent carbonate contamination based on 0.14 per cent CO_2 from analysis, and assuming a carbonate of composition $(Fe_{.7}Mn_{.2}Mg_{.1})CO_3$ determined from a carbonate-rich heavy liquid fraction; for opaques judged to be equal amounts of pyrite and hematite; and for 3 per cent quartz estimated from film and diffractogram patterns although none was recognized optically. Small amounts of P_2O_5 and TiO_2 were treated as contamination. Alkalies were treated as impurities because theoretically there are no known positions for these ions in the talc structure of minnesotaite proposed by Gruner (1944b). The small amounts of CaO and Na_2O are more readily interpreted as impurities than the large amount (0.44 per cent) of K_2O. Assuming that 0.2 per cent stilpnomelane is present, and that it contains as much as 3.3 per cent K_2O (maximum of 30 analyses of this mineral), the stilpnomelane would contribute less than 0.01 per cent K_2O, with the balance from another source of contamination or within the minnesotaite structure itself.

The Cuyuna minnesotaite concentrate contained 1.73 per cent Al_2O_3 as determined by difference from Al+Fe+Ti+P; direct determination gave 1.46 per cent. The writer considers this large amount of Al_2O_3 significant, especially because the minnesotaite in this sample is thought to have partly replaced stilpnomelane, which usually contains from 4 to 7 per cent Al_2O_3. Only 0.01 per cent Al_2O_3 could be furnished by the 0.2 per cent stilpnomelane contaminant if the stilpnomelane contained 7 per cent Al_2O_3.

No ammonia odor was detected from either wet or dry minnesotaite at 70° C.

Calculation of the structural formula for the Cuyuna minnesotaite is also shown in Table 5. Stevens' (1946) method was used since there was no problem with H_2O^-. In Table 6 the theoretical density of the Cuyuna minnesotaite (3.21 g/cm^3), calculated from its molecular weight and from its cell volume based on *x*-ray parameters listed at the end of Table 4, is

TABLE 6. COMPARISON OF MOLECULAR WEIGHTS, CELL VOLUMES, AND DENSITIES OF CUYUNA AND MESABI MINNESOTAITE SAMPLES

	Cuyuna minnesotaite sample-BM 131	Mesabi minnesotaite sample[1]
Molecular weight, for one unit cell with $(Si, Al)_{16}$	[2] 1,875	$\frac{3,740}{2}=1,870$
Unit cell volume Å^3	[3] 970	970
Theoretical density		
Unadjusted g/cm^3	3.21	3.18
Adjusted[4] g/cm^3	3.08	3.02
Measured density g/cm^3	[5] 3.032	3.01

[1] Gruner (1944b), Table 3, p. 368, and pages 367, 369.

[2] Based on structural formula of Table 5.

[3] Based on cell volume given at end of Table 4.

[4] See text for explanation.

[5] Determined by S. S. Goldich with fused silica pycnometer; density ±0.005 at 24.2° C.

considerably greater than the observed density (3.032 g/cm^3). A similar situation was reported by Gruner (1944b) who found a theoretical density of 3.18 g/cm^3 and a measured value of 3.01 g/cm^3. Gruner adjusted his atomic distribution by balancing positive and negative charges to obtain a smaller molecular weight which gave an adjusted theoretical density of 3.02 g/cm^3 which was almost identical to the measured one. When Gruner's method is used on the Cuyuna minnesotaite, the adjusted theoretical density is 3.08 g/cm^3, which is considerably closer to the measured value than is the unadjusted theoretical density.

Theoretical density may also be determined by using a cell volume calculated from the following parameters: $d_{(001)}$ from *x*-ray data, *b* calculated from chemical analysis using some formula such as proposed by Radoslovich (1962), and *a* from the relation $a=b/\sqrt{3}$ as usual for a pseudo-hexagonal cell. Using Radoslovich's kaolin formula recommended for minnesotaite, a density of 3.11 g/cm^3 results for the Cuyuna sample by this method.

Radoslovich suggests that in determining *b* from *x*-ray data, possibly Gruner's reflection 1.514 Å should be assigned index (060) rather than his 1.567 Å reflection. Applying this idea to minnesotaite of Table 4, the following calculated densities result for each of the three reflections nearest 1.563 Å, each considered separately as (060): $d_{(060)}=1.541$ Å, density $=3.30$ g/cm^3; $d_{(060)}=1.524$ Å, density $=3.38$ g/cm^3; $d_{(060)}=1.508$ Å, density $=3.45$ g/cm^3. Therefore density considerations suggest that the 1.563 Å reflection is more correctly assigned to (060) as in Table 4. However, more structural information is needed on this mineral, as pointed out by Radoslovich.

Optical properties of the Cuyuna minnesotaite sample are: $\alpha=1.592\pm0.003$ (Na), $\gamma=1.632\pm0.003$ (Na), $\gamma-\alpha=0.040\pm0.006$ (Na); 2V $=(-)$ small, positive elongation, parallel extinction; pleochroism, X = pale green, Y = Z = colorless to pale greenish-yellow.

(*b*) Spectrographic analysis. Concentrated Cuyuna minnesotaite was analyzed spectrographically in the visible region. Elements found were Al, Ca, Fe, Mg, Mn, Si and Zr (trace). No contaminating zircon was observed.

(*c*) *X*-ray diffraction. An *x*-ray diffractogram of minnesotaite is compared with one of talc in Fig. 2, showing their similarity and the strong 9.4 Å basal (002) spacing at about 11.6 degrees (2θ). Table 4 lists *x*-ray data from a film pattern for this minnesotaite.

(*d*) Differential thermal analysis. In Fig. 3 the DTA curves show that reactions begin at lower temperatures in the iron talc, minnesotaite, than in iron-free talc, probably because of both the iron and the larger amount of water in minnesotaite. Phases at indicated temperatures were determined by *x*-ray analysis as described above for stilpnomelane. The curve for minnesotaite suggests that little or no water was lost from below 500° to 600° C; that water was lost from 600° to 750° C; that the strong exothermic reaction beginning at 750° C was the breakdown of minnesotaite; and that some magnetite apparently had formed by 760° C, for the material was moderately magnetic. The talc DTA curve published by Grim (1953, Fig. 76G) shows no endothermic reaction starting below 800° C, hence the apparent reaction below this temperature in Fig. 3 is due to instrument drift. Flaschen and Osborn (1952, Fig. 3) show a nitrogen atmosphere DTA curve for synthetic minnesotaite with a single endothermic reaction starting at about 525° C with a maximum at 665° C, and practically no drift.

ACKNOWLEDGMENTS

The Minneapolis Research Center of the Bureau of Mines generously supported this work under a Fellowship in cooperation with the University of Minnesota. The writer wishes to thank Professors J. W. Gruner for guidance in all phases; S. R. B. Cooke for mineral separation suggestions; and S. S. Goldich for density determinations and suggestions on petrography and chemical analyses. Special thanks are due personnel of iron mining companies for many courtesies in furnishing samples and analyses; Dr. H. S. Yoder, Jr., Geophysical Laboratory, Washington, D. C., for suggestions and discussion; Drs. R. G. Schmidt and C. E. Dutton, U. S. Geological Survey, for stratigraphic information; and Dr. J. N. Gundersen, Dept. of Geol., Los Angeles State College, for obtaining emission spectrograms.

REFERENCES

AYERS, V. L. (1940) Mineral notes from the Michigan iron country. *Am. Mineral,* **25,** 432–434.

BAILEY, S. W. AND S. A. TYLER (1960) Clay minerals associated with the Lake Superior iron ores. *Econ. Geol.* **55,** 150–175.

BEATTY, S. V. (1949) *X*-ray spectrometer study of mica powders. *Am. Mineral,* **34,** 74–82.

BLAKE, R. L. (1964) Some iron phyllosilicates of the Cuyuna and Mesabi districts in Minnesota. *U.S. Bur. Mines Rept. Invest.* **6394.**

BOWEN, N. L. (1940) Progressive metamorphism of siliceous limestone and dolomite. *Jour. Geol.* **48,** 225–274.

BROWN, G. (1961) *X-ray Identification and Crystal Structure of Clay Minerals.* Mineral. Soc London, Sec. Ed.

DEER, W. A., R. A. HOWIE AND J. ZUSSMAN (1961) *Rock Forming Minerals.* J. Wiley & Sons, Inc., N. Y., v. 3.

ESKOLA, P. (1925) The mineral development of basic rocks in the Karelian formations. *Fennia* **45,** No. 19.

FLASCHEN, S. S. AND E. F. OSBORN (1952) A hydrothermal study of the system FeO-SiO_2-H_2O. *Penn. State College, School Mineral Ind.*

——— (1957) Studies of the system iron oxide-silica-water at low oxygen partial pressures. *Econ. Geol.* **52,** 923–943.

GRIM, R. E. (1953) *Clay Mineralogy.* McGraw-Hill Book Co., Inc., New York.

GROUT, F. F. AND G. A. THIEL (1924) Notes on stilpnomelane. *Am. Mineral.* **9,** 228–131.

——— AND J. F. WOLFF (1955) The geology of the Cuyuna district, Minnesota: A progress Report. *Minn. Geol. Survey Bull.* **36.**

GRUNER, J. W. (1936) The structure and chemical composition of greenalite. *Am. Mineral.* **21,** 449–455.

——— (1937) Composition and structure of stilpnomelane. *Am. Mineral.* **22,** 912–925.

——— (1944a) The structure of stilpnomelane reexamined. *Am. Mineral.* **29,** 291–298.

——— (1944b) The composition and structure of minnesotaite, a common iron silicate in iron formations. *Am. Mineral.* **29,** 363–372.

——— (1946) Mineralogy and geology of the Mesabi range. *Office Comm. Iron Range Resources and Rehabilitation. St. Paul, Minn.*

GUNDERSEN, J. N. AND G. M. SCHWARTZ (1962) The geology of the metamorphosed Biwabik iron-formation, eastern Mesabi district, Minnesota. *Minn. Geol. Survey Bull.* **43.**

HUTTON, C. O. (1938) The stilpnomelane group of minerals. *Mineral. Mag.* **25,** 172–206.

——— (1945) Additional optical and chemical data on the stilpnomelane group of minerals. *Am. Mineral.* **30,** 714–718.

——— (1956) Further data on the stilpnomelane mineral group. *Am. Mineral.* **41,** 608–615.

JAMES, H. L. (1954) Sedimentary facies of iron formation. *Econ. Geol.* **49,** 235–293.

KLUG, H. P. AND L. E. ALEXANDER (1954) *X-ray Diffraction Procedures for Polycrystalline and Amorphous Materials.* John Wiley & Sons, Inc., N.Y.

LAZARENKO, E. K. (1954) On stilpnomelane. *Mineral. Coll. Lvov Geol. Soc.* **8,** 119–144.

LEITH, C. K. (1903) The Mesabi iron-bearing district of Minnesota. *U. S. Geol. Surv. Mono.* **43.**

NELSON, B. W. AND R. ROY (1958) Synthesis of the chlorites and their structural and chemical constitution. *Am. Mineral.* **43,** 707–725.

PETTIJOHN, F. J. (1949) *Sedimentary Rocks.* Harper & Brothers, New York.

RADOSLOVICH, E. W. (1962) The cell dimensions and symmetry of layer-lattice silicates, II. regression relations. *Am. Mineral.* **47,** 617–636.

READ, H. H. (1933) On quartz-kyanite rocks in Unst, Shetland Island, and their bearing on metamorphic differentiation. *Mineral. Mag.* **23,** 317–328.

RICHARZ, S. (1927) Grunerite rocks of the Lake Superior region and their origin. *Jour. Geol.* **35,** 690–708.

SCHMIDT, R. G. (1955) Stratigraphy in the central part of the Cuyuna district, Minnesota. Paper, *Inst. Lake Superior Geol.*, Minneapolis, Minn., April 1–2.

——— (1958) Bedrock geology of the southwestern part of the North range, Cuyuna district, Minnesota. *U. S. Geol. Survey, Mineral Invest. Field Studies Map,* **MF181.**

——— (1959) Bedrock geology of the northern and eastern parts of the North range, Cuyuna district, Minnesota. *U. S. Geol. Survey, Mineral Invest. Field Studies Map,* **MF182.**

——— (1963) Geology and ore deposits of the Cuyuna North range, Minnesota. *U. S. Geol. Survey Prof. Paper* **407.**

——— AND C. E. DUTTON (1952) Progress report on geologic study of Crosby and Ironton area of the Cuyuna range, Crow Wing County, Minnesota. *U. S. Geol. Survey Open File Rept.*

——— AND C. E. DUTTON (1957) Bedrock geology of the south-central part of the North range, Cuyuna District, Minnesota. *U. S. Geol. Survey, Mineral Invest. Field Studies Map.* **MF99.**

SCOTT, A. D., J. J. HANWAY AND G. STANFORD (1956) Thermal studies of ammonium fixation and release in certain clay minerals. *Am. Mineral.* **41,** 701–721.

STEVENS, R. E. (1946) A system for calculating analyses of mica and related minerals to end members. *U. S. Geol. Survey Bull.* **950,** 101–113.

STEVENSON, F. J. (1959) On the presence of fixed ammonium in rocks. *Science,* **130,** 221–222.

SVETALSKI, N. E. (1932) Iron ore deposits of Krivoi Rog. *Works All Soviet Geo-Explor. Soc.* **153.**

TURNER, F. J. (1948) Mineralogical and structural evolution of the metamorphic rocks. *Geol. Soc. Am. Mem.* **30.**

——— AND C. O. HUTTON (1935) Stilpnomelane and related minerals as constituents of schists from Western Otago, New Zealand. *Geol. Mag.* **72,** 1–8.

VERNADSKI, V. E. (1900) Concerning thuringite and stilpnomelane of Russian deposits. *Bull. Moscow Soc. Nat. Exper.,* **14.**

WINCHELL, A. N. (1951) *Elements of Optical Mineralogy.* Part II. John Wiley & Sons, Inc., New York.

YODER, H. S., JR. (1955) Role of water in metamorphism. *Geol. Soc. Am. Spec. Paper* **62,** 505–524.

——— (1957) Isograd problems in metamorphosed iron-rich sediments. *Ann. Rept.* (1956–1957), *Geophys. Lab., Carnegie Inst., Washington, D. C.,* 232–237.

——— AND H. P. EUGSTER (1954) Phlogopite synthesis and stability range. *Geochim. Cosmochim. Acta* **6,** 157–185.

ZAVARETSKI, V. A. (1950) Metamorphism of greenstones connected with pyritiferous deposits of the Third International in the central Urals. Collection of Pyrite Deposits of the Urals. Academy of Science, U.S.S.R.

ZEN, E. (1960) Metamorphism of lower Paleozoic rocks in the vicinity of the Taconic range in west-central Vermont. *Am. Mineral.* **45,** 129–175.

Manuscript received, January 15, 1962; accepted for publication, May 16, 1964.