

# THE AMERICAN MINERALOGIST

JOURNAL OF THE MINERALOGICAL SOCIETY OF AMERICA

Vol. 20

JUNE, 1935

No. 6

## A STUDY OF GREENALITE\*

FRED JOLLIFFE, *Queen's University, Kingston, Canada.*

### TABLE OF CONTENTS

I. INTRODUCTION.....	405
Summary of Properties of Greenalite.....	406
Occurrence and Distribution of Greenalite.....	406
Summary of Literature.....	407
Acknowledgments.....	408
II. EXPERIMENTAL WORK.....	408
Microscopic Study.....	409
Specific Gravity.....	413
Chemical Composition.....	414
III. DISCUSSION OF RESULTS.....	418
Origin of Greenalite.....	419
Alteration of Greenalite.....	422
IV. CONCLUSIONS.....	424

### I. INTRODUCTION

The mineral greenalite occurs in the Biwabik iron formation of Minnesota. It is an iron silicate and possesses a granular structure akin to that of the cherty iron formations which make up the greater part of the Biwabik. Both composition and structure have suggested that greenalite is a primary mineral from which many of the cherty iron formations or jaspilites were formed. These in turn, by leaching of the silica, have yielded the rich iron deposits of Minnesota.

In the present work it has been found possible to examine in detail only the typical greenalite rock from the Mesabi range containing the original greenalite mineral. The experimental work involved a study of the microscopic, physical, and chemical properties of the type material and also of the important associated minerals. The results tend to confirm Leith's<sup>1</sup> view that greenalite is a definite mineral, distinct from other known mineral species.

\* Published by permission of the National Research Council of Canada.

<sup>1</sup> Leith, C. K., The Mesabi Iron-bearing District of Minnesota: Monograph 43, *U. S. Geol. Survey*, p. 115, 1903.

## SUMMARY OF PROPERTIES OF GREENALITE

Greenalite is a pure hydrous ferrous silicate occurring as small greenish rounded granules having a specific gravity of 3.0. It is isotropic and probably amorphous, and is associated with very similar material (herein called metagreenalite) slightly mottled in appearance, occurring as a felt of fine anisotropic green needles. The isotropic mineral has an index of refraction of about 1.675 and a fairly high dispersion. It is moderately magnetic and on heating loses water readily, becoming opaque black and strongly magnetic. Three types of alteration were observed; one to iron oxides on the surface of the specimen, due to ordinary weathering; the second to metagreenalite, apparently through incipient crystallization; and the third to a light colored fibrous mineral by the agency of magnesian waters. This fibrous mineral (herein called mineral X) occurs in the rock to the extent of about 40% and is a hydrous metasilicate of ferrous iron, magnesium, and ferric iron. It possesses properties which indicate that it is a new or little known species, and will be reported on in a later paper.

## OCCURRENCE AND DISTRIBUTION OF GREENALITE

Greenalite occurs as a primary mineral in some of the iron ranges of the Lake Superior region. This district still remains the only one in which the mineral has been positively identified, although other occurrences of greenalite-like material<sup>2</sup> have been described.

The Biwabik iron-bearing formation of the Mesabi range, in which the mineral greenalite is most extensively developed, is the largest of the Lake Superior iron formations. Its original extent is believed by Gruner<sup>3</sup> to have been from 5,000 to 10,000 square miles in area with an average thickness of 330 feet. This tremendous volume of rock consisted largely of chert. The next most abundant constituents were the iron minerals—greenalite, siderite, and iron oxides. Geologists who have studied the Mesabi range are not entirely in accord with regard to the relative amounts of each of these iron minerals in the original rock. An earlier theory held that greenalite was the only one of importance. More recently, emphasis has been placed on the other iron minerals.

<sup>2</sup> Moore, E. S., The Iron Formation on Belcher Islands, Hudson Bay, etc.: *Jour. Geol.*, vol. 26, p. 415, 1918.

<sup>3</sup> Gruner, J. W., Origin of Sedimentary Iron Formations: *Econ. Geol.*, vol. 17, p. 412, 1922.

At present greenalite is found only in the least altered portions of the Biwabik formation, and as these contain no iron ores they have received little geological examination. The mineral is characteristically associated with slate layers which apparently have acted as protective coatings. Dr. F. F. Grout\* states that it is now almost impossible to obtain good samples in place as the pits from which samples were taken some years ago, near Biwabik, Minnesota, are largely filled in.

#### SUMMARY OF LITERATURE

The composition and properties of greenalite have been studied by Spurr<sup>4</sup> and Leith.<sup>5</sup> The former, though identifying the mineral as glauconite, was the first to point it out as a source mineral for the other iron-bearing rocks of the Mesabi. Leith showed later that the mineral approaches a pure hydrous ferrous silicate in composition unlike any known species, and suggested the name "greenalite." In both of these studies, neither the composition nor the properties of the mineral were determined exactly due to the difficulties of separating pure greenalite. Such values as were obtained differ somewhat from those arrived at in this investigation.

The origin of greenalite was studied experimentally by Leith.<sup>6</sup> He found that alkaline silicates and ferrous salts react to produce a precipitate similar to greenalite in composition and in globular habit. He concluded that natural greenalite might be formed by similar reagents resulting from the action of sea-water on hot submarine basalts. Other conjectures as to the origin of greenalite are: (1) that greenalite represents clastic fragments of a volcanic glass, proposed by N. H. Winchell;<sup>7</sup> (2) that greenalite is an organic precipitate, proposed by Spurr;<sup>8</sup> and (3) that greenalite is a precipitate, deposited from solutions deriving their iron from normal

\* Personal Communication to J. E. Hawley.

<sup>4</sup> Spurr, J. E., The Iron-bearing Rocks of the Mesabi Range: *Bull. Geol. Nat. Hist. Survey, Minnesota*, **X**, 1894.

<sup>5</sup> Leith, C. K., *op. cit.* (Monograph **43**), pp. 102-116, 1903.

<sup>6</sup> Leith, C. K. (Van Hise, C. R., and), The Geology of the Lake Superior Region: *U. S. Geol. Survey, Monograph 52*, pp. 521-529, 1911.

<sup>7</sup> Winchell, N. H., *Geol. Nat. Hist. Survey, Minnesota*, vol. **V**, 1900.

Sketch of the Iron Ores of Minnesota: *Am. Geol.*, vol. **XXIX**, p. 160, 1902.

Saponite, Thalite, Greenalite, Greenstone: *Bull. Geol. Soc. Am.*, vol. **23**, p. 330, 1912.

<sup>8</sup> Spurr, J. E., *op. cit.*, p. 242.

weathering with or without organic materials assisting in the solution and precipitation of iron, and in the diagenetic reduction of ferric compounds, proposed by Leith<sup>9</sup> (but later abandoned by him), and followed by Moore,<sup>10</sup> Gruner,<sup>11</sup> and Gill.<sup>12</sup>

#### ACKNOWLEDGMENTS

This investigation was carried out at Queen's University, Ontario, with the aid of a studentship from the National Research Council of Canada, on specimens obtained through the courtesy of Dr. C. K. Leith from the Geological Museum of the University of Wisconsin. Drs. J. E. Hawley, and E. L. Bruce of Queen's University supervised the work and the writer is greatly indebted to them for suggestions and criticism. For the spectrographic examination of greenalite rock he is indebted to G. A. Harcourt. To members of the Geology Department of Princeton University thanks are due for helpful advice.

#### II. EXPERIMENTAL WORK

The experimental work consisted of a study of the habit, properties, and associations of the mineral greenalite in a specimen of greenalite rock from the Mesabi iron range (from the eastern outskirts of the town of Biwabik, Minnesota, Sec. 2, T. 58 N, R. 16 W). This may be considered a type locality.

A general microscopic examination of greenalite rock served to indicate the minerals present, their modes of occurrence, and some of their optic properties. A complete chemical analysis of the rock was supplemented by a spectrographic examination, the latter indicating the presence or absence of various minor oxides.

The microscopic examination showed that so many finely divided inclusions of other minerals are contained in the greenalite that its separation for chemical analysis is impossible. Hence its composition was determined indirectly, but by a somewhat more accurate method than any used previously.

<sup>9</sup> Leith, C. K., *op. cit.* (Monograph 43), p. 255, 1903.

The Genesis of the Lake Superior Iron Ores: *Econ. Geol.*, vol. I, p. 47, 1905.

<sup>10</sup> Moore, E. S., The Iron Formation on Belcher Islands, Hudson Bay, etc.: *Jour. Geol.*, vol. 26, 435, 1918.

<sup>11</sup> Gruner, J. W., The Origin of Sedimentary Iron Formations; the Biwabik Formation of the Mesabi Range: *Econ. Geol.*, vol. 17, p. 459, 1922.

Contributions to the Geology of the Mesabi Range: *Bull. Minn. Geol. Surv.*, vol. 19, p. 63, 1924.

<sup>12</sup> Gill, J. E., Origin of the Gunflint Iron-bearing Formation: *Econ. Geol.*, vol. 22, pp. 726, 727, 1927.

MICROSCOPIC STUDY

The most characteristic and conspicuous feature of Mesabi greenalite rock under the microscope is the presence of numerous small rounded granules which make up over 70% of the rock volume. Some of these are homogeneous—composed entirely of either green isotropic material, mottled green anisotropic material, or a colourless to pale yellow fibrous mineral aggregate; whereas others consist of various combinations of these. The materials present in minor quantities are iron oxides and quartz. In the specimens examined all the various types of granules seem to have been derived from granules composed originally of pure green isotropic material. Steps in this alteration are illustrated in figures 1 and 2.

The matrix surrounding the granules is composed of quartz and a fibrous mineral. The latter is somewhat lighter in colour than the fibrous aggregates noted above as occurring in altered granules. On close inspection the deeper colour of the fibrous mineral in the granules is seen to be due to brown iron oxides and remnants of unchanged green material. The quartz of the matrix is rather finely crystalline though in places it shows evidences of later recrystallization into larger units. Where the matrix is predominantly quartz the granules are composed mainly of green isotropic and anisotropic material. Where the fibrous mineral predominates in the matrix, the granules are largely altered to the same fibrous mineral. This is illustrated in the following micrometric analyses giving areal percentages:

TABLE 1

Minerals in granules			Minerals in matrix	
Isotropic green material	Anisotropic green material	Fibrous mineral	Fibrous mineral	Quartz
1. 28.4%	21.1%	9.9%	15.7%	24.9%
2. 2.1	27.3	36.6	30.6	3.4
3. 6.0	46.2	12.7	14.7	20.4
4. 0.0	53.1	25.2	19.5	2.2

Analyses 3 and 4 illustrate further that the nature of the matrix bears no relation to the amount of isotropic green material altered to mottled anisotropic green aggregates.

Besides the above minerals or aggregates present in the granules and matrix, there are numerous small veinlets carrying quartz with minor amounts of carbonates and iron oxides. These veinlets cut both the granules and matrix except where the latter is composed of more coarsely crystalline quartz. The latter appears to have been derived from an originally finely-crystalline quartz or chert matrix by later recrystallization.

These various minerals and aggregates making up the bulk of the greenalite rock are:

1. ISOTROPIC GREEN MATERIAL. This consists of an apparently homogenous mineral, transparent to translucent in thin section,

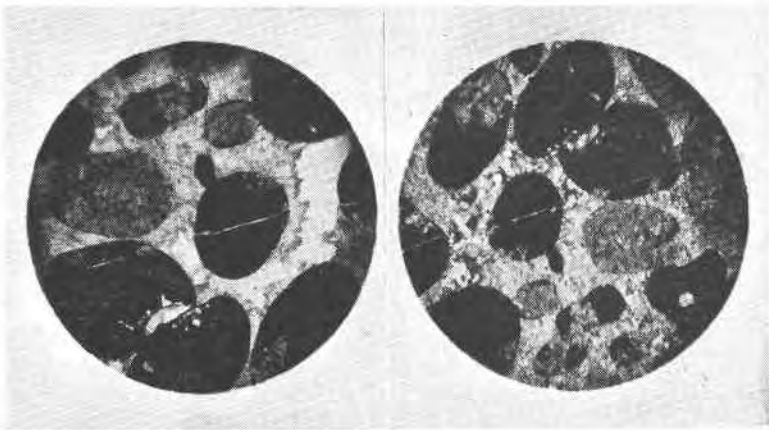


FIG. 1.  $\times 31$  (1 nicol)

FIG. 2.  $\times 26$  (crossed nicols)

Greenalite and metagreenalite granules (black) in various stages of alteration to mineral *X* (grey, mottled by iron oxides and remnants of greenalite). The matrix is quartz and mineral *X*.

and yellow-green to blue-green in colour. It is completely isotropic under crossed nicols, and possesses a refractive index of about 1.675. In some cases such material shows a network of small cracks similar to shrinkage cracks formed in gels, and the absence of any definite orientation to these indicates that true cleavage is wanting. This material would seem to be identical with that to which Leith<sup>13</sup> originally gave the name "greenalite," a name retained in this paper for only the pure isotropic green material.

<sup>13</sup> Leith, C. K., *op. cit.* (Monograph 43), p. 101.

2. MOTTLED ANISOTROPIC GREEN MATERIAL. Granules composed of this material appear exactly similar to the isotropic greenalite granules except that small, nearly opaque, dark green, indefinitely bounded spots are scattered through parts of them. Under crossed nicols minute pin-points of light are seen which under the highest magnification are resolved into extremely fine needles showing sensibly parallel extinction. Leith<sup>14</sup> describes very similar granules as follows: "Here and there incipient alteration to chert, grünerite, cummingtonite, or actinolite, scarcely discernible in ordinary light, give low polarization colors in minute spots and make the term aggregate polarization applicable." In the present investigation it was not found possible to obtain sufficient data on these fine aggregates to determine definitely the mineral present. Such aggregates have a slightly lower mean index of refraction than the pure isotropic greenalite, while the mean index for the semi-opaque spots is somewhat higher. All gradations between pure isotropic granules and mottled anisotropic granules were observed. The amorphous character of the former as contrasted with the microcrystalline character of the latter, suggests that the greenalite is the primary mineral; the other an alteration product. There is no indication of any marked change in volume, any alteration of matrix, or any subtraction or addition of material taking place during this alteration. In other words, the evidence indicates that the amorphous greenalite, through incipient crystallization, has formed the anisotropic green aggregates. Because of this possible relationship and the general similarity in appearance and structure to greenalite, it is suggested that the mineral (or minerals) making up these mottled green anisotropic aggregates be called "meta-greenalite" until further data are obtained.

3. LIGHT-COLORED FIBROUS MINERAL (MINERAL X). This mineral occurs in both granules and matrix. Its distribution in these is characteristic; where granules are largely altered to the fibrous mineral, the surrounding matrix is composed of the same material; and where it is not present in the granules, it is similarly lacking in the immediately surrounding matrix. This association is illustrated in figures 1 and 2, and in table 1. The fibrous mineral definitely replaces greenalite and probably was formed at the expense of both it and the quartz of the matrix. It shows parallel extinction, a small optic angle (normal to the most perfect cleavage), and a fairly

<sup>14</sup> Leith, C. K., *op. cit.* (Monograph 43), p. 102.

high birefringence ( $N_g - N_p = 1.615 - 1.580 = 0.035$ ). It has positive elongation and is very slightly pleochroic ( $Z$  and  $Y$  = pale blue green,  $X$  = colorless to pale yellow). In its mode of development, as seen under crossed nicols, it resembles the formation of sericite in feldspathic rocks. It would appear that this mineral is the same as that assumed to be an amphibole by N. H. Winchell<sup>15</sup> and Leith.<sup>16</sup> More recently Richarz<sup>17</sup> has suggested that it be called "crystal-

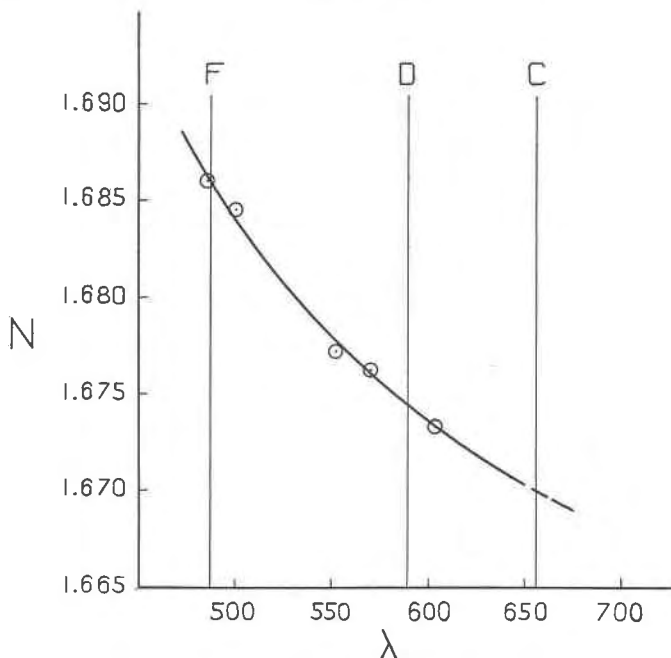


FIG. 3. Dispersion of Greenalite

lized greenalite." However, the analyses made during this investigation indicate a marked difference between the composition of greenalite and that of the fibrous mineral, and indicate that the latter is a new or little known species.\* In this paper it will be called mineral X.

<sup>15</sup> Winchell, N. H., *Geology of Minnesota*, vol. V, pp. 927-929, 1900.

<sup>16</sup> Leith, C. K., *op. cit.* (Monograph 43), p. 107.

<sup>17</sup> Richarz, S., *Grünerite Rocks of the Lake Superior Region and Their Origin: Jour. Geol.*, vol. 35, pp. 690-708, 1927.

\* Further study of this mineral is being carried on, the results to be published shortly.



4. QUARTZ. This mineral occurs chiefly as a fine mosaic in the matrix surrounding granules of greenalite and metagreenalite. It is usually absent where these granules show much alteration to mineral X. It occurs also, though in very minor amounts, as irregular patches in some of the granules and in veinlets along with carbonates and iron oxides.

5. IRON OXIDES. Small particles of black and brown iron oxides occur scattered through the altered granules and matrix of the greenalite rock. By far the major concentration of these minerals occurs around the outside of the specimens where the latter have obviously undergone weathering.

The above five constituents—greenalite, metagreenalite, mineral X, quartz, and iron oxides—make up more than 99% of the greenalite rock. The relative amounts of these were determined by means of a series of micrometric analyses using a grid eyepiece. These analyses were made on six thin sections cut at various orientations from the same greenalite rock specimen as was used for the chemical analysis. The results are shown in table 2, the average representing closely the mineral composition (by volume) of the greenalite rock.

TABLE 2

Granules				Matrix	
Greenalite (isotropic)	Metagreen- alite (anisotropic)	Mineral X	Fe oxides	Quartz	Mineral X
1. 5.26	33.49	36.68	4.10	1.62	18.85
2. 19.15	26.70	21.63	1.27	8.65	22.60
3. 13.27	37.57	23.62	0.84	6.55	18.15
4. 17.05	36.05	16.73	0.37	9.00	20.80
5. 7.52	41.55	24.93	1.00	1.65	23.35
6. 14.11	28.82	22.36	1.13	11.00	22.58
Av. 12.72%	34.03%	24.33%	1.45%	6.41%	21.06%

SPECIFIC GRAVITY

Due to the difficulty of separating pure greenalite from its alteration products and other associated minerals, both Spurr<sup>18</sup> and Leith<sup>19</sup> used indirect methods to obtain its specific gravity. The

<sup>18</sup> Spurr, J. E., *op. cit.* p. 238.

<sup>19</sup> Leith C. K., *op. cit.* (Monograph 43), p. 108.

values arrived at from their calculations were 2.8 and 2.75, respectively.

In this investigation it was found possible to separate a few grains of nearly pure greenalite. These were freed from air bubbles and suspended in Thoulet solutions of different densities. The specific gravities of these grains were found to vary between 2.85 and 3.15, the majority lying close to the mean value of 3.00.

#### CHEMICAL COMPOSITION

On account of the difficulty of separating a sufficient amount of pure greenalite for a chemical analysis, its composition has always been determined indirectly. It has been suggested that it has the composition of glauconite,<sup>20</sup> a distinct species,<sup>21</sup> a garnet,<sup>22</sup> and a chlorite.<sup>23</sup>

In the present study an indirect method was again used but it is believed the result arrived at represents the composition of greenalite almost as closely as if obtained by a direct chemical analysis. The method is as follows:

1. The composition of each mineral in the rock with the exception of greenalite and metagreenalite is obtained.
2. The percentage of each of these minerals in the rock is determined by means of micrometric analyses.
3. From 1 and 2 the total composition of all the minerals present in the rock with the exception of greenalite and metagreenalite is calculated.
4. The values for the different oxides obtained in 3 are subtracted from the total oxide percentages appearing in the chemical analysis of the rock, the remainder giving the sum composition of greenalite and metagreenalite.

The microscopic examination indicated that metagreenalite is crystallized greenalite and both probably have the same composition, hence the value obtained in 4 will represent the composition of pure greenalite.

The weight-percentages of the minerals present in the greenalite rock are obtained from the micrometric analyses (table 2) by multiplying the volume percentage of each mineral by its specific

<sup>20</sup> Spurr, J. E., *op. cit.*, p. 235.

<sup>21</sup> Leith, C. K., *op. cit.* (Monograph 43), p. 115.

<sup>22</sup> Clarke, F. W., Data of Geochemistry, Bull. 770, U. S. Geol. Survey, p. 584, 1924.

<sup>23</sup> Lindgren, W., *Mineral Deposits*, p. 269, 1933.

gravity and recalculating to 100%. The results are shown in table 3.

TABLE 3

	Volume per cent	Specific gravity	Weight	Weight per cent
Greenalite	12.72%	3.00	38.2	12.9%
Metagreenalite	34.03	3.00	102.1	34.6
Iron oxides	1.45	5.20	7.5	2.6
Quartz	6.41	2.65	17.0	5.7
Mineral X	45.39	2.86	129.8	44.2
	100.00%		294.7	100.0%

TABLE 4

Mineral		Iron oxides	Quartz	Mineral X	Totals
% in rock		2.6	5.7	44.2	52.5
SiO <sub>2</sub>	% in mineral		100.0	48.7	
	% in mineral x % of mineral		5.7	21.5	27.2
Fe <sub>2</sub> O <sub>3</sub>	% in mineral	81.6		11.6	
	% in mineral x % of mineral	2.1		5.1	7.2
FeO	% in mineral	18.4		23.1	
	% in mineral x % of mineral	0.5		10.2	10.7
MgO	% in mineral			9.9	
	% in mineral x % of mineral			4.4	4.4
H <sub>2</sub> O	% in mineral			6.7	
	% in mineral x % of mineral			3.0	3.0

Of the constituents in table 3, the compositions of the last three were obtainable directly. The iron oxides are assumed to consist of equal amounts of hematite and magnetite. This is in accord with such experimental observations as were made, and even if this assumption were entirely incorrect the results would be only very slightly different due to the small percentage of this material in the rock. The composition of mineral X was determined directly by analyzing a small amount of the purified material. This gave the following result (after correcting for impurities and recalculating to 100%):

SiO <sub>2</sub>	48.7%
Fe <sub>2</sub> O <sub>3</sub>	11.6
FeO	23.1
MgO	9.9
H <sub>2</sub> O	6.7

From the above data the amounts of the various oxides included in all the minerals excepting greenalite (and metagreenalite) in 100 grams of greenalite rock can be calculated;—as in table 4.

The total composition of the greenalite rock was obtained by means of a chemical analysis checked by a spectrographic examination:

SiO <sub>2</sub>	49.43%
("soluble" = 29.90)	
("insoluble" = 19.53)	
TiO <sub>2</sub>	none
Al <sub>2</sub> O <sub>3</sub>	none
Fe <sub>2</sub> O <sub>3</sub>	8.16
FeO	30.52
MnO	0.17
MgO	4.77
CaO	0.18
Na <sub>2</sub> O	none
K <sub>2</sub> O	none
P <sub>2</sub> O <sub>5</sub>	none
H <sub>2</sub> O+ (above 110°)	6.24
H <sub>2</sub> O- (below 110°)	0.51
CO <sub>2</sub>	0.43
Cl, S, SO <sub>3</sub>	trace
	100.41

Specific Gravity = 2.87

The spectrographic examination confirmed the above analysis in every respect. The relatively small amounts of CaO and MnO,

and the absence of  $\text{TiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{Na}_2\text{O}$ ,  $\text{K}_2\text{O}$ ,  $\text{P}_2\text{O}_5$ ,  $\text{Cr}_2\text{O}_3$ ,  $\text{V}_2\text{O}_3$ ,  $\text{NiO}$ ,  $\text{CoO}$ ,  $\text{BaO}$ ,  $\text{SrO}$ ,  $\text{B}_2\text{O}_3$ ,  $\text{SnO}$ ,  $\text{PbO}$ , and  $\text{Ag}_2\text{O}$  were indicated.

The sum composition of greenalite and metagreenalite is obtained by subtracting the values in the last column of table 4 (representing the amounts of the various oxides in all the minerals except greenalite and metagreenalite) from the total amounts of these oxides appearing in the rock analysis. The results recalculated to 100% represent the chemical composition of greenalite and metagreenalite. This is shown in table 5.

TABLE 5

	% in rock	% in iron oxides quartz and mineral X	% in greenalite and meta- greenalite	Calculated to 100%
$\text{SiO}_2$	49.4	27.2	22.2	46.8
$\text{Fe}_2\text{O}_3$	8.2	7.2	1.0	2.1
$\text{FeO}$	30.5	10.7	19.8	41.7
$\text{MnO}$	0.2		0.2	0.4
$\text{MgO}$	4.8	4.4	0.4	0.9
$\text{CaO}$	0.2		0.2	0.4
$\text{H}_2\text{O}+$	6.2	3.0	3.2	6.8
$\text{CO}_2$	0.4		0.4	0.9
Total	99.9*	52.5%	47.4%	100.0%

\* Neglecting  $\text{H}_2\text{O}$ —(0.5%), and figures in second decimal place.

From the above table it is seen that greenalite and metagreenalite (with various amounts of other minerals too finely divided to appear in the micrometric analyses) compose 47.4% of the rock. Over 95% of the total composition of all these materials is made up of  $\text{SiO}_2$ ,  $\text{FeO}$ , and  $\text{H}_2\text{O}$ . The oxides in the remaining 4.7% ( $\text{Fe}_2\text{O}_3$ ,  $\text{MgO}$ ,  $\text{CO}_2$ ,  $\text{CaO}$ , and  $\text{MnO}$ ) probably belong to the finely divided mineral impurities present. Thus, greenalite and metagreenalite appear to be pure hydrous ferrous silicates.

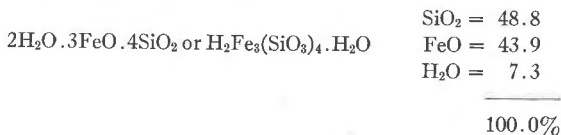
The microscopic examination of thin sections of greenalite rock suggests strongly that the amorphous greenalite altered to metagreenalite by simple crystallization without the addition or subtraction of any material. On this assumption, the total composition of the two minerals should represent the composition of the original

pure greenalite. The molecular ratios of the oxides in greenalite on this basis are calculated as follows:

TABLE 6. MOLECULAR RATIOS IN GREENALITE

		Divided by molec- ular weight	Molecular ratios
SiO <sub>2</sub>	46.8%	0.779	4.02
FeO	41.7	0.582	3.00
H <sub>2</sub> O	6.8	0.376	1.94
	95.3%		

The close approximation of these molecular ratios to simple whole numbers lends further support to the assumption stated above and suggests the following formula and composition for greenalite:



However, despite the weight of evidence justifying the assumption that greenalite and metagreenalite have the same composition, it is possible to state definitely only that greenalite is a hydrous ferrous silicate near  $2\text{H}_2\text{O} \cdot 3\text{FeO} \cdot 4\text{SiO}_2$ .

### III. DISCUSSION OF RESULTS

The foregoing experimental work has established certain new data regarding the composition, properties, association, and alteration of the mineral greenalite. These are discussed below as well as their bearing upon two major problems connected with greenalite: (1) origin of greenalite; and (2) the origin of the Mesabi iron ores. The results obtained in this investigation support Leith's<sup>24</sup> original contention that greenalite is a definite mineral species distinct from other iron silicates and thus worthy of a mineral name. The accurate determination of refractive index in a number of granules of greenalite has shown that this is a fairly definite quantity. Furthermore, its composition as obtained in this inves-

<sup>24</sup> Leith, C. K., *op. cit.*, (Monograph 43), p. 115, 1903.

tigation is that of a hydrous ferrous silicate probably possessing a definite formula ( $2\text{H}_2\text{O} \cdot 3\text{FeO} \cdot 4\text{SiO}_2$ ).

On the other hand, the habit of greenalite, its association, and its amorphous character (as shown by isotropism and the absence of all characters indicative of a regular internal arrangement—cleavage, crystal outline, etc.) strongly suggest that it is of colloidal origin. Such minerals do not generally possess a definite composition or formula. Thus, it may be that the whole-number ratio of the oxides in greenalite, as determined in this investigation, is merely fortuitous. However, even if the composition of the mineral be found by later work to vary somewhat, it would still seem to deserve being called a mineral species quite as much as any gel mineral—opal, for example. The crystalline mineral called meta-greenalite in this paper must be a definite mineral species. Further study of it involving x-ray examination is planned.

#### ORIGIN OF GREENALITE

The origin of greenalite has been the subject of considerable speculation and experimental study.<sup>25</sup> In the present investigation no further experiments on the synthesis of the mineral were performed but the more accurate determination of the composition of greenalite justifies a brief consideration of theories of its formation. The theories considered here are the two most generally followed:

1. Greenalite is a precipitate deposited from solutions deriving their iron from normal weathering, with or without organic materials assisting in the solution and deposition of iron and in the diagenetic reduction of ferric compounds.
2. Greenalite is a chemical precipitate formed from waters which have received their iron and silica largely by direct contribution from a magma or by the interaction of sea water and hot submarine lavas.

The two properties of greenalite which are most pertinent to any consideration of its origin are habit (texture) and composition.

The granule forms assumed by greenalite are characteristic of the mineral. In the present investigation nothing was observed to indicate that greenalite is a secondary mineral owing its form to replacement of granules of primary material. In all cases the greenalite granules are completely homogeneous except for minor

<sup>25</sup> Leith, C. K., *op. cit.*, (Monograph 52), pp. 518–529.

amounts of obvious impurities and alteration products. This strongly suggests that the greenalite represents an original precipitate whose characteristic forms were assumed during the precipitation and were not the results of later diagenetic action. The amorphous character of greenalite and its association with meta-colloidal chert indicate that it is a gel mineral. All the greenalite forms observed in the present study could have been produced by purely physical means (surface tension, etc.) if the precipitate were of this gel nature. This is not purely hypothetical since in Leith's<sup>26</sup> synthesis of greenalite such simple granule forms were produced, and even the more complex "tail" structures can be developed by physical (osmotic) processes.<sup>27</sup> Thus, from the textural standpoint, the present investigation supports Leith's thesis that greenalite was precipitated as such in a gel form which physical forces modified during precipitation into the various shapes assumed by the granules.

With regard to composition, the present study has shown that greenalite is a pure hydrous ferrous silicate. In any theory of origin it is necessary to account not only for the source of the iron (and silica), but also for its occurrence in the ferrous state. The experimental work of Gruner<sup>28</sup> and Moore and Maynard<sup>29</sup> has shown that although large amounts of iron (and silica) may be brought to the sea through normal weathering aided by abundant vegetation, this iron will all be in the ferric state (ferric hydrosol). Consequently, if weathering processes have been the source of the iron in greenalite, reduction must have occurred on a tremendous scale between the time the ferric hydrosol was brought to the sea by surface waters and the time of its precipitation as a ferrous silicate. The suggestion of Van Hise that the iron was precipitated as a ferric compound, buried with organic matter, reduced, and still later combined with the silica present, is not borne out by the microscopic examination of greenalite rock. Everything—the granule texture, the absence of any indication of the tremendous shrinkage the above process would necessitate, the common occurrence at the

<sup>26</sup> Leith, C. K., *op. cit.*, (Monograph 52), p. 525.

<sup>27</sup> Hawley, J. E., An Evaluation of the Evidence of Life in the Archean: *Jour. Geol.*, vol. 34, p. 354, 1926.

<sup>28</sup> Gruner, J. W., The Origin of Sedimentary Iron Formations: *Econ. Geol.*, vol. 17, pp. 407-460, 1922.

<sup>29</sup> Moore, E. S., and Maynard, J. E., The Solution, Transportation, and Deposition of Iron and Silica: *Econ. Geol.*, vol. 24, pp. 272-303; 365-402; 506-527; 1929.



present time of ferric hydroxides in bogs with organic matter but showing no evidence of reduction, the low carbon and phosphorus content of the greenalite rock (evidence of little organic material)—seems to indicate that the greenalite was precipitated as such and that diagenetic processes did not assist in its formation. Another possibility is that reduction of the ferric hydrosols took place in the sea before or during the precipitation of greenalite. Such a process might occur through the agency of iron-secreting organisms capable of reducing iron during their life processes. This is, however, entirely hypothetical and is opposed by the general scarcity in the greenalite rock of those elements regarded as indicative of organic agencies—uncombined carbon, and phosphorus. One further possibility has been suggested which has a bearing on this question—that the pre-Cambrian atmosphere was deficient or lacking in oxygen.<sup>30</sup> In this case surface waters could carry and contribute to the sea ferrous salts. From such ferrous solutions, alkaline silicate solutions (likewise of weathering origin) would readily precipitate greenalite. However, the existence of an anaerobic atmosphere in late pre-Cambrian times is hypothetical and has been questioned.<sup>31</sup> Furthermore, Gruner<sup>32</sup> has shown the possibility of an extensive land flora at this time, in which case there would be appreciable amounts of oxygen in the atmosphere—sufficient, at least, to prevent the transportation of ferrous iron in surface waters.

On the other hand, recent work by Fenner<sup>33</sup> has indicated a concentration of iron (including ferrous iron) in liquids given off by basic magmas. Furthermore, Leith<sup>34</sup> has shown that alkaline silicate solutions are produced by the reaction of a hot igneous rock with water, and that such solutions combine readily with ferrous salts to form a hydrous ferrous silicate similar in appearance and properties to greenalite, and, like it, possessing a slight excess of silica over the metasilicate ratio.

<sup>30</sup> Macgregor, A. M., The Problem of the pre-Cambrian Atmosphere: *South African Journal of Science*, vol. 24, pp. 155–172, 1927.

<sup>31</sup> Quirke, T. T., Discussion on "Origin of Sedimentary Iron Ores": *Econ. Geol.*, vol. 20, pp. 770–771, 1925.

<sup>32</sup> Gruner, J. W., The Origin of Sedimentary Iron Formations: *Econ. Geol.*, vol. 17, p. 459, 1922.

<sup>33</sup> Fenner, C. N., The Crystallization of Basalts: *Am. Jour. Sci.* (5), vol. 18, p. 245, 1929.

<sup>34</sup> Leith, C. K., *op. cit.*, (Monograph 52), p. 525.

Thus, in summary, most geologists are agreed that the compounds deposited in important amounts in the original Biwabik formation were chert, ferrous silicate, ferrous carbonate, and iron oxides. Of these materials only chert and the ferric oxides could have been deposited from solutions derived from surface weathering. Ferrous carbonate also could have been formed from such solutions provided that an abundance of organic matter was associated with it (cf. the occurrence of siderite in coal seams). On the other hand, without enlisting the aid of organic matter, it is possible for all these materials—chert, ferrous compounds, and iron oxides—to have been precipitated from sea waters which had received direct contributions from an igneous source. Consequently when this consideration is joined with the evidence afforded by the greenalite textures, it strongly favors a direct igneous source for the iron in the greenalite and opposes an origin dependent on weathering processes.

#### ALTERATION OF GREENALITE

The alteration processes by which iron ores were formed from the original Mesabi rocks have been the subject of recent controversy. The classical theory (developed by Spurr,<sup>35</sup> Van Hise and Leith<sup>36</sup> holds that these ores were formed by the leaching and oxidizing action of cold surface or near-surface waters on the source minerals (chert, greenalite, siderite, and iron oxides). A later view, advanced by Gruner,<sup>37</sup> is that hot waters of igneous origin have been more effective in this alteration.

The present investigation throws little light on this question. Two types of alteration were observed taking place within the greenalite rock:

- (1) alteration of greenalite to metagreenalite.
- (2) alteration of greenalite to mineral X.

Of these, the first has already been discussed, the conclusion having been reached that the change represents simple crystallization involving possibly a slight segregation or redistribution of certain constituents of the mineral.

<sup>35</sup> Spurr, J. E., *op. cit.*, p. 253.

<sup>36</sup> Van Hise, C. R., and Leith, C. K., *op. cit.*, pp. 529-546.

<sup>37</sup> Gruner, J. W., Hydrothermal Oxidation and Leaching Experiments; Their Bearing on the Origin of Lake Superior Hematite-Limonite Ores: *Econ. Geol.*, vol. 25, pp. 697-719; 837-867, 1930.

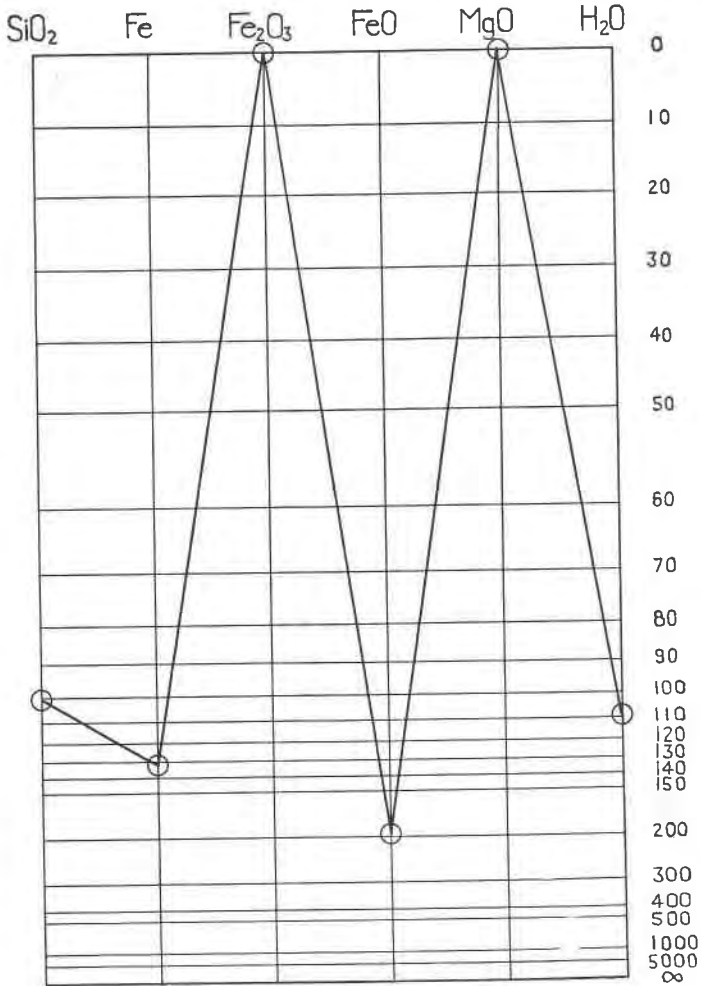


FIG. 4. Alteration of Greenalite to Mineral X.

TABLE 7

	Greenalite	Mineral X	$\frac{\% \text{ in greenalite}}{\% \text{ in mineral X}} \times 100$
SiO <sub>2</sub>	48.8%	48.7%	100.3
Fe	34.2	26.1	131.0
Fe <sub>2</sub> O <sub>3</sub>	—	11.6	0.0
FeO	43.9	23.1	190.3
MgO	—	9.9	0.0
H <sub>2</sub> O	7.3	6.7	109.0

The chemical changes involved in the alteration of greenalite to mineral *X* are shown in table 7 together with their comparison in a straight-line diagram.

In this alteration (relative to total iron) ferrous oxide has been lost, silica and water increased slightly, ferric oxide has been developed, and a relatively large proportion of magnesia introduced. The relations of the minerals as seen in the thin sections suggest that the gain in silica involved in the change from greenalite to mineral *X* has resulted from attack on the quartz matrix. The loss in ferrous iron is accounted for by partial oxidation. The gain in magnesia suggests that the solutions effecting the alteration were high in this constituent. Since only part of the ferrous iron has been oxidized and since considerable magnesia has been introduced, it is probable that this alteration of greenalite was affected by other than surface waters (i.e., either deeper ground waters or hydrothermal solutions). However, the temperature of these waters was probably only moderate, as under even slight heating mineral *X* loses water and forms magnetite by union of the constituent ferrous and ferric oxides.

Thus, both the types of alteration noted within the greenalite rock studied (the crystallization to metagreenalite, and the alteration to mineral *X*) are not due to surface waters. This, however, is not to be interpreted as evidence favoring a hydrothermal origin for the iron ores. In neither of the above types of alteration is any appreciable amount of iron oxides being formed. The only place in the material examined where these oxides are being extensively developed is on the surface where ordinary weathering processes have produced limonite and hematite.

#### IV. CONCLUSIONS

The conclusions drawn from the results of this investigation may be summarized as follows:

The typical greenalite from the Mesabi iron range is a hydrous ferrous silicate possessing the following properties:

Habit: in rounded granules usually between 0.1 and 1 mm. in diameter, possessing no cleavage or crystal outline.

Color: green (light yellow-green to blue-green) in transmitted light, dark green to black in reflected light.

Specific gravity: 3.0 (varying from 2.85 to 3.15 depending on nature and extent of alteration or crystallization).

Optically isotropic.

Indices of refraction:	$N_F$	$N_D$	$N_C$
	1.686	1.674	1.670
	$\pm 0.001$	$\pm 0.001$	$\pm 0.002$

Dispersion:  $F - C = 0.016$ .

Moderately magnetic.

On heating loses water readily, becomes opaque black in color and strongly magnetic.

The above results rest wholly on the basis of experimental observation. Consequently they are kept separate from the following conclusions which depend on one or two minor assumptions. Thus, it is highly probable:

1. That greenalite is a definite mineral varying only slightly in composition and properties because of its probable colloidal origin.
2. That its composition is most closely represented by the formula  $2\text{H}_2\text{O} \cdot 3\text{FeO} \cdot 4\text{SiO}_2$ , corresponding to 48.8%  $\text{SiO}_2$ , 43.9%  $\text{FeO}$ , and 7.3%  $\text{H}_2\text{O}$ .
3. That its alteration proceeds as follows:
  - (A) To iron oxides and hydroxides by the oxidizing and leaching action of surface waters.
  - (B) To an aggregate of minute green crystals associated with small opaque green masses (herein called metagreenalite) by simple crystallization.
  - (C) To a light-colored fibrous mineral (herein called mineral X) through the agency of magnesium-bearing waters not of surface origin.
  - (D) To an intergrowth of magnetite and amphiboles in the vicinity of heated igneous bodies.
4. That its habit and properties show it to be of colloidal origin.
5. That it was deposited as a chemical precipitate from waters which received their iron and silica directly from igneous sources.
6. That it owes its granule form to purely physical processes (surface tension, osmotic pressure) acting on the semi-fluid gel precipitate.
7. That the above conclusions apply to all greenalite throughout the Mesabi range.