

THE STRUCTURE AND CHEMICAL COMPOSITION OF GREENALITE

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INTRODUCTION

More than two years ago the writer made an *x*-ray examination of greenalite from the iron formation of the Mesabi Range in Minnesota. It was noticed that the powder of greenalite gave a definite pattern on which that of quartz was superimposed. The pattern did not resemble chlorite (or thüringite which is definitely a chlorite), nor biotite, nor glauconite or stilpnomelane. Neither was any resemblance observed between greenalite and chamosite, which gives a pattern different from any mentioned above. About a year ago the writer, when investigating serpentine, noticed a striking similarity in the powder photographs of it and greenalite. About this time Jolliffe¹ published a paper containing microscopic and chemical data on greenalite with which the present findings could not be reconciled.

One of the great difficulties is the securing of specimens of greenalite rock from which greenalite granules² can be separated. Three drill cores were finally found that answered the purpose. Also material identical with that used by Jolliffe was obtained through the kindness of Dr. C. K. Leith from the collection at Madison, Wisconsin. Three drill cores came from the following localities and depths:

No. 13156A, Depth about 550 ft. Section 24, T. 58 N., R. 17 W., near Gilbert.

No. 13156B, from the same drill hole but different, though unknown depth. Catalog No. M. 315S.

No. 11053, Depth about 905 ft. Section 35, T. 58 N., R. 18 W., near Virginia.

Dr. Leith's specimen came from a test pit near Biwabik. Generous grants from the Graduate School of the University of Minnesota have made this study possible. The writer is also indebted to Mr. Russel Wayland and Mr. Samuel Goldich for valuable assistance.

PHYSICAL AND CHEMICAL DATA

Microscopic examination of the drill cores confirmed largely the findings of Jolliffe in his single specimen. His "pure" isotropic greenalite has an index near 1.670, though many grains may be found which are below 1.655. Such differences may be due to sub-microscopic admixtures

¹ Jolliffe, Fred., A study of greenalite: *Am. Mineral.*, vol. 20, pp. 405-425, 1935.

² For the occurrence of greenalite and greenalite rock, the reader is referred to Jolliffe's paper. In thin sections of a single specimen of greenalite rock he found three significant minerals besides quartz. He named them greenalite, metagreenalite, and mineral X. The weight per cent. of these minerals based on micrometric analyses of six thin sections are 12.9, 34.6, and 44.2, respectively. These figures include matrix as well as granules.

of quartz. The writer is still of the same opinion, expressed ten years ago,³ that this greenalite is not isotropic when viewed with a very strong source of light. Jolliffe calls the material which is definitely anisotropic, metagreenalite, formed "through incipient crystallization" of greenalite. Obviously this distinction is one of degree of crystallization only. The finer grained the "metagreenalite" the more closely it would resemble "isotropic" greenalite.

Jolliffe's "mineral X" is of great interest. It has been mistaken for sericite, also for one of the amphiboles. It also resembles talc. Its optical properties do not fit any of these minerals completely, as Jolliffe has already pointed out. It might possibly be an iron serpentine, as will appear later. At any rate, its percentage in the different greenalite rock specimens is not as great as in that from Biwabik, described by Jolliffe. For example, in thin section No. 13156B, it is present in only very minor amounts, not exceeding 10 per cent. of the total volume. In No. 13156A it is practically absent. This is a very important fact for *x*-ray powder photographs of these samples are identical with those of other greenalite concentrates eliminating, therefore, mineral X as a source of the *x*-ray pattern recorded in Table 1.

The amount of quartz in greenalite rock can be estimated only very roughly, for some of it is extremely fine grained and only visible under high magnifications. Jolliffe seems to have greatly underestimated the quartz in his thin sections for he gives an average of only 5.7 per cent. by weight while his analysis shows 19.53 per cent. of "insoluble" SiO₂.⁴ *X*-ray powder photographs show complete strong quartz patterns even after a bromoform separation.

To free greenalite from quartz the material was crushed to 100 or 150 mesh and placed in bromoform. More quartz was eliminated by running the material through a three stage magnetic separator. But the best method seems to be the dielectric one which also proved so successful with glauconite.⁵ All three methods were used in succession, but only in the sample furnished by Dr. Leith could the quartz be eliminated to such an extent that even its strongest *x*-ray diffraction lines did not show in the films. But about 5 per cent. of this sample was "mineral X," even after this treatment.

In Table 1 the *x*-ray pattern of greenalite is compared with those of antigorite, picrolite and precious serpentine. A striking resemblance is noted which is even more pronounced in the actual negatives. The in-

³ Gruner, J. W., Contributions to the geology of the Mesabi Range; *Minnesota Geol. Surv.*, Bull. 19, p. 57, 1924.

⁴ *Op. cit.* Table 3 and p. 416.

⁵ Gruner, J. W., *Am. Mineral.*, vol. 20, p. 699, 1935.

dices which are given in the last column of the table are based on those published for chrysotile by Warren and Bragg.⁶ They agree closely. No other indices could be definitely identified, so far, for either serpentine or greenalite, but the writer believes that line No. 29 has the indices 0120 which would make the unit cell of greenalite slightly greater than that of serpentine along the *b*-axis.

No corrections were applied to the readings in Table 1. Therefore, the interplanar distances *d* are a trifle too small in the upper part of the table. Not all lines have the same sharpness of definition. For example, Nos. 12 and 17 are broad and especially No. 17 is difficult to define. Lines sharp in serpentines are also relatively sharp in greenalite. The intensities also show good agreement when one considers that the serpentines *x*-rayed are very low in iron as compared with greenalite. This difference also explains the discrepancies in *d* values which are not any greater than those encountered, for example, in different members of the garnet group. Whether the β angle of the unit cell is also affected is impossible to tell. It may be assumed that the lines under the same number in Table 1 originate from corresponding planes, though this may not be true for all of them.

When Leith published his analyses of greenalite⁷ he assumed that the portion of the rock which was insoluble in HCl and in a 5 per cent. solution of Na₂CO₃ was quartz. This was more or less substantiated by microscopic examination of the residue. The analyses, exclusive of the insoluble SiO₂ and recalculated by Clark to 100 per cent., are given in Table 2. Jolliffe proceeded differently. He analyzed the rock⁸ and instead of subtracting his 19.53 per cent. insoluble SiO₂, deducted only 5.7 per cent. of quartz which he saw under the microscope. In other words, most of his insoluble SiO₂ was averaged in with his three iron silicates. The writer recalculated Jolliffe's analysis on the assumption that the insoluble SiO₂ was quartz and obtained the figures given in column 4 of Table 2.

Jolliffe made an analysis of his mineral X without stating, however, how he was able to separate this extremely fine grained fibrous mineral from the rest, after he admitted⁹ "that so many finely divided inclusions of other minerals are contained in the greenalite that its separation for chemical analysis is impossible." It seems to the writer the same statement applies to mineral X. Since nothing is said about soluble or insol-

⁶ Warren, B. E., and Bragg, W. L., The structure of chrysotile H₄Mg₃Si₂O₉: *Zeit. Krist.*, vol. 76, p. 201, 1931.

⁷ Leith, C. K., *U. S. Geol. Survey, Monograph* 43, p. 108, 1903.

⁸ *Op. cit.*, pp. 416 and 417.

⁹ *Op. cit.*, p. 408.

uble SiO_2 in this analysis¹⁰ it is difficult to accept his analysis as that of mineral X.

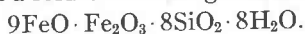
In order to ascertain whether greenalite contains about the same amount of Fe_2O_3 at depth as at the surface, Dr. R. Ellestad analyzed the iron in two of the drill cores for the writer with the following results.

	No. 13156A	No. 11053
FeO	24.35	31.08
Fe_2O_3	5.39	11.70

No. 11053 had been treated with bromoform. Therefore, the total percentage of iron is higher in it. Practically no iron oxides could be detected in these samples. Comparison with the analysis in Table 2 will show that the ratio of Fe_2O_3 to FeO in test pit material and deep drill cores is not materially different. Of great importance is the fact that No. 13156A, as seen in thin section, contains practically no "mineral X." Therefore, the Fe_2O_3 which Jolliffe¹¹ assigns to mineral X must be in the greenalite, in this specimen at least. Though no analysis was made for MgO in No. 13156A its presence in amounts proportional to those in other greenalite rocks is likely. Obviously, it would have to be in the greenalite and not in mineral X as Jolliffe proposes for greenalite rock in general.

DISCUSSION

The chemical evidence presented favors a composition for greenalite (including "metagreenalite") which is very similar to that proposed by Leith and Clark in 1903. The molecular ratios presented in Table 2 seem to agree well with a formula which given in oxide form is:¹²



The theoretical composition and molecular ratios of such a formula are recorded in the last column of Table 2. A serpentine whose magnesium was replaced by iron would correspond to this formula. Ordinarily iron in serpentine is largely ferrous but Doelter's *Handbuch der Mineralchemie*¹³ contains a number of reliable analyses in which Fe_2O_3 may be as high as 8 per cent.

The outstanding fact in the present investigation is that greenalite, when properly concentrated, gives an x-ray powder diagram which indicates that it is like serpentine in structure. Its unit cell when compared with serpentine gives almost the same dimensions for a_0 and b_0 , namely 14.5 Å and 18.6 Å, respectively. If c_0 corresponds to that of chrysotile,

¹⁰ *Op. cit.*, p. 416.

¹¹ *Op. cit.*, p. 423.

¹² The very high Fe_2O_3 content in the first two analyses of Table 2 seems to be partly due to iron oxide minerals in the two samples judging from Leith's description. *Op. cit.*, p. 109.

¹³ Vol. 2, 2nd Hälft., p. 385.

the theoretical density of greenalite is 3.25, on the assumption that 2 molecules of $(\text{OH})_{12}\text{Fe}_9^{11}\text{Fe}_2^{11}\text{Si}_3\text{O}_{22}\cdot 2\text{H}_2\text{O}$ are contained in it. Since probably a few per cent. of magnesium always replace Fe^{11} the actual density would be less. The specific gravity of greenalite rock varies between 2.7 and 3.0, while the density of the granules lies between 2.85 and 3.15, according to Jolliffe. Since most of the impurities in the granules are considerably lower in gravity than greenalite itself the theoretical and measured densities seem to be in fair agreement.

The occurrence of greenalite is almost entirely confined to the Biwabik formation of the Mesabi Range in Minnesota. Such restriction cannot be accidental but must be due to very special conditions. The almost total absence of Ca, Al and alkalis in the solutions from which greenalite was precipitated colloiddally may have been a factor. Possibly relatively low concentration of CO_2 caused greenalite to form in certain layers in preference to iron carbonates and chert, which are preponderant in the iron formations of Michigan.

A serpentine structure with such an abundance of iron might be rather metastable, especially in its early stages of deposition. Slight changes in conditions might cause it to break down into iron oxides (mostly magnetite), siderite and quartz (usually called chert). The preservation of the granule texture of such layers might be the only remaining witness of the former existence of greenalite. The often described ferruginous cherts are of exactly such a nature. They are far more abundant than the greenalite layers which are interstratified with them, but are of the same granule texture.¹⁴

SUMMARY

Four samples of greenalite rock from the iron formation of the Mesabi Range were investigated microscopically, by x -rays and partly chemically. It was possible to separate greenalite from quartz, siderite and Jolliffe's mineral X by the combined applications of three methods, namely, bromoform solution, magnetic separation, and dielectric separation.

Greenalite is a distinct mineral species which has the crystal structure of such serpentines as antigorite and precious serpentine. These, however, are somewhat different in structure from the fibrous varieties. The chemical formula of greenalite approaches $9\text{FeO}\cdot\text{Fe}_2\text{O}_3\cdot 8\text{SiO}_2\cdot 8\text{H}_2\text{O}$, which structurally is $(\text{OH})_{12}\text{Fe}_9^{11}\text{Fe}_2^{11}\text{Si}_3\text{O}_{22}\cdot 2\text{H}_2\text{O}$. The ratio of Fe_2O_3 : FeO varies considerably, of course. Also, several per cent. of MgO usually replaces FeO . The theoretical density of an iron serpentine of this compo-

¹⁴ Gruner, J. W., Contribution to the geology of the Mesabi Range: *Minnesota Geol. Surv., Bull.* 19, pp. 10-17, 1924.

sition is 3.25. It is believed that greenalite appears to be isotropic because it is extremely fine grained and dark in color. Actually it is anisotropic like the metagreenalite of Jolliffe which is simply coarser grained greenalite. Jolliffe's formula $2\text{H}_2\text{O} \cdot 3\text{FeO} \cdot 4\text{SiO}_2$ for greenalite is too high in SiO_2 , because he based his SiO_2 ratio on the "soluble" and "insoluble" percentages of SiO_2 instead of discarding the insoluble portion as quartz as was done by Leith.

TABLE 1. COMPARISON OF POWDER PHOTOGRAPHS OF GREENALITE AND VARIOUS SERPENTINES. Fe RADIATION. RADIUS 57.3 MM.

Line No.	Greenalite ¹		Antigorite ²		Picrolite ³		Precious Serpentine ⁴		Indices
	<i>d</i>	<i>I</i>	<i>d</i>	<i>I</i>	<i>d</i>	<i>I</i>	<i>d</i>	<i>I</i>	
1	7.12	4	7.16	6	7.16	8	7.12	6	200
2			4.66	0.5	4.68	0.5	4.61	1	
3					4.22	0.5			
4	3.95	0.5	3.96	2	3.98	2	3.95	2	β400
5					3.85	0.5	3.81	0.5	
6	3.559	4	3.588	7	3.592	9	3.592	7	400
7			3.48	0.5	3.462	0.5	3.490	0.5	
8	3.169	0.5							
9	3.010	0.5							
10	2.849	1	2.798	1	2.802	1	2.784	1	β of 12
11	2.737	1			2.671	0.5	2.677	0.5	
12	2.571	5	2.521	4	2.535	5	2.514	4	
13	2.457	1					2.450	0.5	
14	2.407	0.5	2.402	1	2.418	2	2.411	2	600
15					2.364	0.5	2.370	0.5	
16	2.334	0.5					2.210	0.5	β of 17
17	2.184	2	2.152	1	2.165	1	2.150	2	
18	2.058	0.5					2.012	0.5	
19	1.989	0.5	1.986	0.5	1.991	0.5	1.962	0.5	
20	1.928	0.5							
21	1.887	0.5					1.880	0.5	
22			1.848	0.5			1.831	1	
23	1.809	1	1.808	1	1.812	2	1.808	1	800
24					1.778	0.5	1.778	1	
25	1.759	0.5	1.723	0.5	1.729	1	1.722	1	β of 28
26	1.713	0.5	1.695	0.5	1.699	0.5	1.693	0.5	
27	1.647	0.5			1.592	0.5	1.584	0.5	β of 29
28	1.593	3	1.562	3	1.567	3	1.560	3	
29	1.553	2	1.538	2	1.540	2	1.536	2	
30			1.529	1	1.527	1	1.522	1	
31	1.509	1	1.509	1	1.509	1	1.503	1	
32							1.494	1	
33			1.478	0.5	1.471	0.5	1.472	0.5	
34	1.458	0.5	1.454	0.5			1.459	0.5	

TABLE 1. (Cont.)

Line No.	Greenalite ¹		Antigorite ²		Picrolite ³		Precious Serpentine ⁴		Indices	
	<i>d</i>	<i>I</i>	<i>d</i>	<i>I</i>	<i>d</i>	<i>I</i>	<i>d</i>	<i>I</i>		
35			1.442	1	1.447	2	1.446	1	1000	
36	1.428	0.5	1.417	0.5	1.416	0.5	1.410	0.5		
37	1.377	0.5					1.381	0.5		
38	1.354	0.5					1.358	0.5		
39			1.342	0.5			1.341	0.5		
40							1.328	0.5		
41	1.324	0.5	1.315	1	1.316	1	1.312	2		
42			1.298	0.5	1.296	0.5	1.295	0.5		
43	1.288	1					1.284	0.5		
44							1.273	0.5		
45			1.259	0.5			1.258	0.5		
46	1.246	0.5					1.244	0.5		
47	1.194	0.5	1.201	1	1.205	2	1.206	1		1200

¹ Dr. Leith's specimen.

² Antigorio Valley, Italy.

³ Chester, Mass.

⁴ Montville, N. J.

TABLE 2. ANALYSES OF GREENALITE ROCK EXCLUSIVE OF INSOLUBLE SiO₂

	45758*		45765*		45766*		Jolliffe†		Iron Serpentine	
		Ratio		Ratio		Ratio		Ratio		Ratio
SiO ₂	30.08	.501	30.49	.508	38.00	.633	35.92	.598	33.58	.559
Fe ₂ O ₃	34.85	.218	23.52	.147	8.40	.052	9.80	.061	11.16	.070
FeO	25.72	.357	36.92	.513	46.56	.648	46.16	.643	45.19	.629
H ₂ O	9.35	.519	9.07	.503	7.04	.391	8.11	.450	10.07	.559
Total	100.00		100.00		100.00		99.99		100.00	

* Leith, C. K., *Op. cit.*, p. 246.

† CO₂ was combined with a corresponding amount of FeO and deducted. MnO, MgO, and CaO were recalculated into their equivalents of FeO. Therefore, the treatment of this analysis corresponds to those of Leith's.