

# GRIPHITE, A HYDROPHOSPHATE GARNETOID

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## ABSTRACT

Griphite is cubic and its structure is similar to that of garnets. The unit cell contains  $8[(\text{Na, Al, Ca, Fe})_3\text{Mn}_2(\text{PO}_4)_{2.5}(\text{OH})_2]$  and this formula represents a complex example of  $X_3Y_2(\text{ZO}_4)_{3-m}(\text{OH})_{4m}$ . The latter is a variation of  $X_3Y_2(\text{ZO}_4)_3$  which is necessary to accommodate the hydrogarnets and plazolite. An alternate formula is suggested and cannot be eliminated as a possibility, namely,  $8[(\text{Na, Ca, Fe, Mn})_3(\text{Al, Mn})_2(\text{PO}_4)_{2.5}(\text{OH})_2]$ . The space group could not be determined but appears to have lower symmetry than that of garnet ( $O_h^{10} = Ia3d$ ). Griphite and other substances with structures similar to garnet are classified as garnetoids.

## INTRODUCTION

The name griphite was proposed in 1891 by W. P. Headden (1) for a hydrated phosphate of manganese, aluminum, sodium, calcium, and iron. Griphite ( $\gamma\rho\iota\phi\omicron\varsigma =$  an enigma) seemed an appropriate name because of the chemical complexity of this mineral and the apparent absence of a simple relation to any other known mineral.

The present investigation will demonstrate that the chemical composition, physical properties and x-ray diffraction data for griphite permit its classification as a garnetoid.<sup>1</sup> Several interesting implications are to be attached to the fact that a sodium-calcium-manganese-aluminum hydrophosphate with garnet-like structure exists. Its existence suggests the possible replacement of calcium and silicon by sodium and phosphorus in garnets and garnetoids. Of particular interest is the possible entry of these constituents into the lattice of cubic tricalcium aluminate hexahydrate, one of the well established hydration products of portland cement, because both sodium and phosphorus are considered objectionable constituents in cement clinker, if they exceed certain limits.

Ionic substitutions involving sodium and phosphorus are relatively uncommon among garnets, or their occurrence has been overlooked as only a few analyses report  $\text{Na}_2\text{O}$  (about 2 per cent being the maximum amount), and the analyses that indicate  $\text{P}_2\text{O}_5$  are extremely rare (the amount of  $\text{P}_2\text{O}_5$  being less than 1 per cent). Although the writer (2) has demonstrated in ellestadite almost complete replacement of  $\text{PO}_4$ -groups by  $\text{SO}_4$ - and  $\text{SiO}_4$ -groups in the structure of apatite, nothing conversely similar has been previously shown among the garnets. Thus the rather

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<sup>1</sup> The term "garnetoid" is introduced to designate those substances which are not primarily silicates but have structures similar to that of true garnets. Examples are the various hydrogarnets, berzeliite, plazolite, and griphite.

complete substitution of  $\text{PO}_4$ -groups for  $\text{SiO}_4$ -groups encountered in griphite is noteworthy.

Cubic tricalcium aluminate hexahydrate has recently been investigated thoroughly by E. P. Flint, H. F. McMurdie, and L. S. Wells (3). These investigators likewise demonstrated the existence of a hydrogarnet corresponding to andradite and having the composition  $3\text{CaO} \cdot \text{Fe}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$ . The structural data presented by these authors, the data obtained for berzeliite by W. Bubeck and F. Machatschki (4), and the complete structural investigation of plazolite presented by A. Pabst (5), are invaluable in the establishment of the relationship of griphite to other garnetoids.

#### PHYSICAL PROPERTIES OF GRIPHITE

Headden (1) described griphite as "amorphous" because it is isotropic on microscopic examination and no crystal forms were observed. However, the relationships among the properties of griphite, plazolite,<sup>2</sup> and grossularite are quite apparent when tabulated.

	<i>Griphite</i>	<i>Plazolite</i>	<i>Grossularite</i>
Hardness	5½	6½(?)	6
Specific gravity	3.40	3.13	3.58 ca.
Refractive index	1.64-1.66	1.675	1.735
Fusibility	Easily fused	Fusible	3

Griphite apparently lacks the ability to form euhedral crystals, differing from garnets in this respect. However, it is not amorphous but exhibits discontinuous vectorial properties, as is demonstrated by the  $x$ -ray diffraction pattern which it produces. Both griphite and plazolite are soluble in HCl, whereas true garnets (except schorlomite) are difficultly soluble or insoluble in ordinary acids. Absence of cleavage is characteristic of the garnetoids as well as the garnets.

#### X-RAY DIFFRACTION DATA

Powder diffraction patterns were obtained for griphite (near Harney City, Pennington County, South Dakota; U.S.N.M. No. R-5315, obtained from Headden), grossularite (6), schorlomite (Magnet Cove, Arkansas), uvarovite (Washington, Nevada County, California) and andradite (near Randsburg, California) through the use of unfiltered iron radiation and precision cameras (M. J. Buerger's model) with  $r=57.3$  mm. The cell dimensions of these are as follows, omitting andradite:

	<i>Griphite</i>	<i>Schorlomite</i>	<i>Uvarovite</i>	<i>Grossularite</i>
$a_0$	12.26	12.09	11.97	11.87
		(all $\pm 0.01 \text{ \AA}$ )		

<sup>2</sup> D. S. Belyankin and V. P. Petrov (*Am. Mineral.*, **26**, 450-453, 1941) have recently shown through reexamination of hibschite that this substance is similar to plazolite.

TABLE 1. COMPARISON OF POWDER DIFFRACTION DIAGRAMS  
 (Unfiltered Fe Radiation— $r=57.3$  mm.)

No.	Indices*	Schorlomite**		Graphite			Hausmannite†		Mn-berzelite‡	
		$d_{\text{expt.}}$	$I$	$d_{\text{calc.}}$	$d_{\text{expt.}}$	$I$	$d$	$I$	$I_{\text{calc.}}$	$I_{\text{expt.}}$
1	220	4.31	<1		—				$\approx 0$	—
2	320	—		3.401	} 3.39	1			—	
3	$\beta$ 400	3.34	<1	(3.37)						
4	321	—		3.277	} 2.97	$\frac{1}{2}$			5.1	3
5	400	3.026	5	3.066			3.066	4	3.08	m
6	$\beta$ 420	2.975	2	(3.01)	} 2.97	4			—	
7	410, 322	—		2.974						
8	411, 330	—		2.890	2.884	1			—	
9	420	2.702	8	2.742	2.743	10	2.755	s	42	>20
10	332	2.584	<1	—	—				8.3	7
11	422	2.468	6	2.503	2.498	4	2.478	s	21.2	12
12	431	2.366	1	2.404	2.408	1			3.2	3
13	—	—		—	2.362	1	2.345	m	—	
14	520, 432	—		2.279	2.281	3			—	
15	521	2.205	1	—	—				$\approx 0$	—
16	610	—		2.015	2.018	3	2.032	m	—	
17	611, 532	1.964	2	—	—				0.4	—
18	620	1.909	<1	—	—				0.4	—
19	541, $\beta$ 640	1.845	<1	—	—				0.1	—
20	630, 542	—		1.828	1.832	2			—	
21	631	1.781	2	—	—		1.789	m	2.3	3
22	444	1.743	1	1.770	1.770	2			8	8
23	640	1.679	7	1.700	1.700	3			20.3	20
24	642	1.614	>10	1.638	1.637	6			34.3	>20
25	730	—		1.610	1.604	1			—	
26	732, 651	—		1.557	1.563	1	1.574	m	2.2	1-2
27	800	1.512	3	1.533	1.536	1	1.538	s	8.5	8
28	820, 644	—		1.487	1.478	2			0.05	—
29	822, 660	1.424	<1	—	—		1.437	m	0.2	—
30	840	1.351	5	—	—				9.7	10
31	842	1.319	5	1.338	1.344	1			17.2	15
32	921, 761, 655	—		1.322	1.325	1			3.1	2
33	664	1.290	4	1.307	1.303	1			7.2	8

\* The indices do not pertain to hausmannite.

\*\* Several of the weaker  $\beta$ -lines are omitted.

† Only the more intense lines are listed. Data from G. Aminoff: *Zeits. Krist.*, **64**, 475 (1926).

‡ Data from W. Bubeck and F. Machatschki: *op. cit.* Reflection from 211 was not observed by these authors although the calculated intensity is 6. Planes 653 and 752 gave observed intensities 2 and 1, respectively.

The cell edges of schorlomite and uvarovite are given, although analyses of these specimens are not available, because published measurements for these garnets are very rare in the literature. In addition it was observed that the diffraction pattern of schorlomite is not significantly different from those of other garnets. Therefore schorlomite is more closely related to the garnets than the garnetoids.

The similarities of the powder diffraction patterns of schorlomite and griphite are shown in Fig. 1 and the measurements obtained from these are given in Table 1. With one exception (line No. 13, Table 1) all of the lines obtained from the sample of griphite yield cubic indices. This line, presumably extraneous, may have been contributed by hausmannite. It was not feasible to completely eliminate one of the contaminating substances, a mineral which appears deep red-brown to opaque in thin section and resembles hausmannite in other respects.

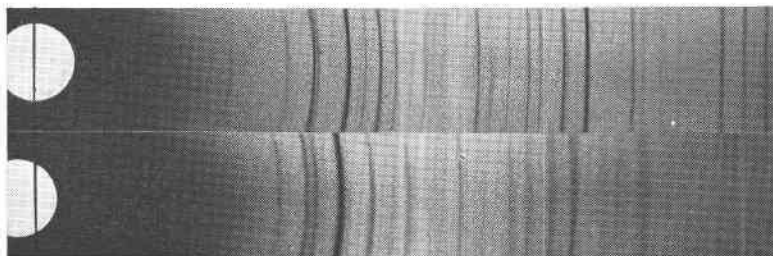


FIG. 1. Powder diffraction patterns of schorlomite (above) and griphite.  
Unfiltered Fe radiation.

If hausmannite is to be assumed as a contaminating substance, the diffraction pattern must be interpreted through consideration of all of the intense lines of this mineral, and these are shown in Table 1 for comparison. However, this assumption does not explain the occurrence of reflections from 320, 411, 730, 630 or 542, and 520 or 432, although the first two of these are similar in spacing to  $\beta$ -lines. Of significance are the similarities in intensities between the corresponding lines of griphite and Mn-berzeliite. The experimental and calculated intensities for Mn-berzeliite obtained by Bubeck and Machatschki (4) are given for comparison (Table 1).

Notwithstanding the similarities, there are certain differences among the patterns of schorlomite, griphite, and Mn-berzeliite, the most noticeable being the occurrence in the griphite pattern of reflections prohibited by the space group  $O_h^{10}$ . Otherwise, it is quite apparent that the more intense lines are those characteristic of garnet. X-ray data must be

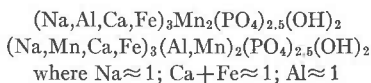
considered with caution when powder diffraction methods are employed to the exclusion of other methods and, particularly, when contamination of the sample is probable. Thus it is not possible to decide the space group of griphite but there is every indication that the structure closely simulates one based upon a body-centered cubic lattice. The true symmetry appears to be lower than that of garnet ( $O_h^{10} = Ia\bar{3}d$ ).

Were it not for several additional factors the conclusion that griphite is a garnetoid might seem unjustifiable. These factors are:

1. The composition indicated by Headden's analysis conforms with the type formula of garnets and garnetoids.
2. The calculated density is virtually identical with the experimental value.
3. The refractive index is similar to what would be expected for a substance with the structure of garnet and the chemical composition of griphite.

#### CHEMICAL DATA

The mean of Headden's analyses is used as a basis for calculating the cell contents (Table 2), assuming that all of the cations present enter and completely fill the 64 cationic positions of normal garnet and that the lattice contains 96 oxygens. This permits the correlation of griphite and the type formula  $X_3Y_2(ZO_4)_3$ , or the derived formula  $X_3Y_2(ZO_4)_{3-m}(OH)_{4m}$ , in one or the other or a combination of the following ways:



Of these possibilities, the former seems more probable, but nothing definite can be decided without a detailed structural investigation. The x-ray and chemical data available at present are not sufficiently complete for this purpose and several factors impede more accurate determinations.

The density calculated from the molecular weight ( $8 \times 474.5$ ) and the cell edge (12.26 Å) is 3.399. This compares most favorably with the density determined by Headden (3.401) which was confirmed by the writer as 3.40.

The calculations of the cell contents and density have been based on the assumption that all cationic positions of the lattice are filled, but the simultaneous assumption of 96 oxygen positions yields a slight discrepancy between the positive and negative charges. This is not serious, however, and probably is to be explained by the presence of one or more of the impurities mentioned below. An alternate explanation can be obtained by assuming that there are vacancies in the lattice. If it is assumed

TABLE 2. CHEMICAL ANALYSIS AND CELL CONTENTS OF GRIPHITE

Oxides*	Weight per cents	Molecular ratios	Ionic ratios	Contents of $\frac{1}{8}$ unit cell	
				Positive ions	Weights of ions
Li <sub>2</sub> O	trace	—			
Na <sub>2</sub> O	5.52	.089	.178	.86	19.8
K <sub>2</sub> O	0.30	.003	.006	.03	1.1
CaO	7.47	.133	.133	.64	25.7
MgO	0.15	.004	.004	.02	0.5
FeO	4.00	.056	.056	.27	15.1
MnO	29.64	.418	.418	2.02	110.9
Al <sub>2</sub> O <sub>3</sub>	10.13	.099	.198	.96	25.9
P <sub>2</sub> O <sub>5</sub>	38.52	.271	.542	2.62	81.2
Cl	0.11	.003			
F	trace	—			
H <sub>2</sub> O	4.29	.238	4 × .119	4 × 0.58†	2.3
Insol.	0.16	—		12 oxygens	192.0
	100.29			8.00	474.5

\* W. P. Headden, analyst. Mean of 2 complete and 3 partial analyses.

† Since  $\text{SiO}_2 \rightleftharpoons 2\text{H}_2\text{O}$ , the sum of all positive ions should be 8 when 4H are considered equivalent to Si, provided no vacancies occur.

that  $\frac{1}{8}$  unit cell has 24 negative charges (12 oxygens) and the cationic charges are balanced in their proper ratios, 7.64 cations are indicated rather than 8. There is no good reason for assuming vacancies in the lattice, however, and it is fully as reasonable to believe that the ratios of the cations would be slightly modified by deduction of impurities, if these could be determined quantitatively.

Spectroscopic observations failed to indicate the presence of prominent lines of Si, As or V in the range 2250–3600 Å, indicating that these elements are not more abundant than traces. With the possible exception of CC<sub>2</sub>, Headden's analysis seems to be complete and little improvement could be expected in terms of a new analysis because it is not feasible to separate the minor impurities mentioned below.

#### ASSOCIATED MINERALS

Graphite resembles most garnets in the number and diversity of the included minerals. The following substances were observed as inclusions:

Hausmannite (?)—Deep red-brown to opaque in thin section. Some of the diffraction lines (Table 1) correspond with the more intense lines of hausmannite.

Pseudowavellite—Colorless; uniaxial (+);  $\epsilon > n$  of griphite,  $\omega \approx n$  of griphite; medium-low birefringence. Identification made certain by microchemical tests and comparison of *x*-ray pattern made from concentrated material with patterns of pseudowavellite from Fairfield, Utah, and from Bavaria (U.S.N.M. No. R4271).

Apatite or mangan-apatite (?)—Colorless; low relief in griphite; low birefringence; uniaxial (−). Similar material occurs as spherulites. Possibly accounts for F and/or Cl of Headden's analysis. Identified by optical methods only.

Quartz (?)—Colorless; high negative relief in griphite; low birefringence; uniaxial (+). Identified by optical methods only.

Amblygonite or montebbrasite (?)—Colorless; low negative relief in griphite; moderate birefringence; occasionally with polysynthetic twinning. Possibly accounts for  $\text{Li}_2\text{O}$  reported in Headden's analysis. Identified by optical methods only.

All of these minerals are present in very small amounts except hausmannite which is frequently abundant. Two other substances occur as traces but these could not be identified. Diffraction lines of the identified substances, except hausmannite, were not found on the patterns prepared from selected samples of griphite.

In addition to the minerals occurring as inclusions, two specimens furnished by Dr. John C. Haff show considerable amounts of albite, quartz, and a white mica in association with the griphite. One of the unidentified substances occurring as inclusions resembles mica although its identification could not be confirmed.

It is noticeable that three of the contaminating substances are phosphates of one or more of the principal cations of griphite, and this suggests that the cationic ratios of Headden's analysis cannot be strictly representative of griphite. However, there is every reason to believe that they very closely approach the true ratios because the impurities apparently occur in very small amounts, if considerable care is taken to exclude the dark-colored material containing hausmannite. Headden's samples probably did not contain more than a few per cent of this material because they were carefully selected in this respect.

#### DISCUSSION

The *x*-ray, chemical, physical, and optical data for griphite are all contributory to the conclusion that this mineral has a structure similar to that of garnets. There seem to be no theoretical objections to this and, consequently, griphite has been classified as one of the garnetoids. The properties of the garnetoids are summarized in Table 3.

The occurrence of isomorphous mixtures of the Ca-Fe- and Ca-Al-hydrogarnets with corresponding true garnets has been shown (3); plazolite (7) represents such an intermediate isomorphous compound. Manganese- and magnesium-berzeliite probably form a complete series of isomorphous mixtures but these "molecules" are not known to occur

TABLE 3. SUMMARY OF THE PROPERTIES OF GARNETOIDS

	Composition	<i>n</i>	G	H	F	Solubility	Cell edge
Griphite	(Na, Al, Ca, Fe) <sub>3</sub> Mn <sub>2</sub> (PO <sub>4</sub> ) <sub>2.5</sub> (OH) <sub>2</sub>	1.64-1.66	3.40	5 $\frac{1}{2}$ <sup>a</sup>	easy <sup>a</sup>	sol. HCl	12.26 Å
Plazolite	Ca <sub>3</sub> Al <sub>2</sub> (SiO <sub>4</sub> ) <sub>2</sub> (OH) <sub>4</sub>	1.675 <sup>b</sup>	3.13 <sup>c</sup>	6 $\frac{1}{2}$ <sup>b</sup>	fusible <sup>d</sup>	sol. HCl <sup>b</sup>	12.14 <sup>c</sup>
Ca-Al-hydrogarnet*	Ca <sub>3</sub> Al <sub>2</sub> (OH) <sub>12</sub>	1.605 <sup>e</sup>	2.52 <sup>f</sup>	—	—	—	12.56 <sup>e</sup>
Sr-Al-hydrogarnet*	Sr <sub>3</sub> Al <sub>2</sub> (OH) <sub>12</sub>	—	3.12 <sup>g</sup>	—	—	—	13.02 <sup>h</sup>
Ca-Fe-hydrogarnet*	Ca <sub>3</sub> Fe <sub>2</sub> (OH) <sub>12</sub>	1.710 <sup>e</sup>	2.78 <sup>g</sup>	—	—	—	12.74 <sup>e</sup>
Mn-berzeliite	(Ca <sub>2</sub> Na)Mn <sub>2</sub> (AsO <sub>4</sub> ) <sub>2</sub>	1.78 <sup>j</sup>	4.45 <sup>j</sup>	5 <sup>j</sup>	3 <sup>j</sup>	sol. acid	12.46 <sup>k</sup>
Mg-berzeliite	(Ca <sub>2</sub> Na)Mg <sub>2</sub> (AsO <sub>4</sub> ) <sub>2</sub>	1.71 <sup>j</sup>	3.95 <sup>j</sup>	5 <sup>j</sup>	3 <sup>j</sup>	sol. acid	12.35 <sup>k</sup>

\* Compounds produced by synthesis, not known to occur naturally.

<sup>a</sup> W. P. HEADEN: *op. cit.* <sup>b</sup> W. F. FOSHAG: *op. cit.* <sup>c</sup> A. PABST: *op. cit.* <sup>d</sup> A. PABST: *Minerals of California*, p. 294. <sup>e</sup> E. P. FLINT, H. F. MCMURDIE and L. S. WELLS: *op. cit.* <sup>f</sup> T. THORVALDSON, N. S. GRACE and V. A. VIGFUSSON: *Canadian Jour. Research*, **1**, 201 (1929). <sup>g</sup> Calculated from cell edge. <sup>h</sup> E. BRANDENBERGER: *Schweiz. mineral. petrogr. Mitt.*, **13**, 570 (1933). <sup>i</sup> E. S. LARSEN and H. BERMAN: *U.S.G.S. Bull.* **848** (1934). <sup>k</sup> W. BUBECK and F. MACHATSCHIKI: *op. cit.*



isomorphously mixed with any other garnetoid or garnet. Nothing is known regarding the miscibility of griphite with garnets and other garnetoids. However, analyses of garnets occasionally indicate the presence of small amounts of  $\text{Na}_2\text{O}$  and, rarely, very small amounts of  $\text{P}_2\text{O}_5$ .

A similar compound, originally described as triplite but later referred to griphite, from near Rapid City, South Dakota, was analyzed by L. G. Eakins (8). The analysis shows a slightly higher value for  $\text{P}_2\text{O}_5$ , slightly less water, considerably more fluorine and 2.36 per cent of  $\text{Fe}_2\text{O}_3$ . In general, however, this analysis is conformable with Headden's results and confirms the composition assigned to griphite.

Eakins' analysis reports about  $\frac{1}{4}$  of 1 per cent of  $\text{CO}_2$ . The fact that specimens studied in the present investigation were observed to liberate gas when treated with acid suggests that a small amount of  $\text{CO}_2$  was overlooked by Headden.

Carbon dioxide is known to enter the lattice of apatite (9) and there is no theoretical reason which prohibits its occurrence in the structure of griphite. In the present investigation observations made with the microscope revealed the liberation of gas during treatment with dilute  $\text{H}_2\text{SO}_4$  from portions of the griphite that were completely isotropic. It can be said with certainty that neither calcite nor aragonite was present.

#### SUMMARY

Griphite is cubic and its structure is similar to that of garnets, i.e., it closely simulates a structure based on a body-centered cubic lattice, although the true symmetry is probably lower than that of garnets.

The structural formula of griphite is  $8[(\text{Na}, \text{Al}, \text{Ca}, \text{Fe})_3\text{Mn}_2(\text{PO}_4)_{2.5}(\text{OH})_2]$ , which correlates with the type formula  $\text{X}_3\text{Y}_2(\text{ZO}_4)_{3-m}(\text{OH})_{4m}$ , the latter being a variation of the formula  $\text{X}_3\text{Y}_2(\text{ZO}_4)_3$ .

The properties of the garnetoids (substances other than simple silicates having a structure similar to garnets) have been assembled and compared.

Pseudowavellite is reported from a second American locality. Its identification was confirmed by  $x$ -ray and microchemical methods.

Schorlomite is classified as a true garnet rather than a garnetoid because the substitution encountered here does not produce any significant changes in the powder diffraction pattern. Lattice dimensions are given for schorlomite (12.09 Å) and for uvarovite (11.97 Å) in addition to griphite (12.26 Å).

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Most of the specimens, including griphite, were furnished by the U. S. National Museum through the kindness of Drs. W. F. Foshag and E. P. Henderson.

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