GAMAGARITE, A NEW VANADIUM MINERAL FROM THE POSTMASBURG MANGANESE DEPOSITS

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ABSTRACT

Gamagarite, a new mineral with a composition corresponding to the formula $Ba_4(Fe, Mn)_2V_4O_{15}(OH)_2$ has been found in the manganese ores of the Postmasburg district, Cape Province. It has the following properties: Colour, very dark brown. Habit, prismatic. $H. = 4\frac{1}{2} - 5$. Sp. gr. 4.62. Monoclinic, elongated parallel to b, $b = Y$. $\beta = 62°40'$. $X \wedge c = \pm 41°$ in the acute angle β. $\alpha = 2.016$, $\beta = 2.040$, $\gamma = 2.130$. $2V_z = 46° - 62°$. $r < v$ fairly strong. Pleochroism, red-brown to light salmon-buff.

GENERAL

While engaged upon a study of the manganese ores of the Postmasburg district, the writer found a mineral differing in composition and properties from previously described species. This mineral was found only in specimens collected at one locality on the farm Gloucester, situated about sixteen miles north of the village of Postmasburg. It takes its name from the Gamagara ridge, a prominent line of hills running from north to south across the western part of the farm.

The sample of manganese ore in which the gamagarite occurs is of variable texture and in a hand specimen presents a streaked or rudely banded appearance, due to an irregular concentration of the associated minerals. It is composed chiefly of dark iron-gray sitaparite with rose-coloured "books" of ephesite (1), and brown flakes of diaspore (2). In this ore gamagarite is present as aggregates of needles, a centimetre or more in length, and also as somewhat flattened prisms. A more detailed description of the ore specimens follows on a later page.

PHYSICAL PROPERTIES

The colour is dark brown to nearly black; the luster, adamantine. Its streak is reddish-brown. The mineral is moderately magnetic to the electromagnet. $H. = 4\frac{1}{2}-5$. Specific gravity $= 4.62$. This value is the mean of two determinations made on two portions of the crushed and cleaned mineral. Each portion of about 700 milligrams was weighed in a small pan, first in air and then in water. The values obtained were 4.616 and 4.624. Three cleavages were noted in the prismatic zone; two distinct and a third difficult. Under the microscope, gamagarite is clear but strongly coloured. It is pleochroic in colours varying from light salmon-buff to deep red-brown, and is for the most part crowded with minute opaque inclusions.

CRYSTALLOGRAPHIC AND OPTICAL PROPERTIES

Crystal faces are present on the prisms but these are of poor quality and in part epimorphic. The two cleavage planes are paralleled by crystal faces and gave fair reflections on the goniometer. The third difficult cleavage was observed in one instance on the goniometer and in numerous cases on the universal stage.

Measurements indicate that gamagarite is monoclinic with the prisms elongated parallel to b; $b = Y$. Extinction angles were impossible to measure with accuracy owing to the imperfect nature of the cleavages. In a number of thin sections, indeed, no cleavage directions could be seen. The two best cleavages were considered as {001} and {100}, and the third as {$\bar{1}$01}. In the case of flattened crystals it was observed that the largest face is always the base.

The angle between {001} and {100} is 62°40′ ($\pm$30′) and that between {001} and {$\bar{1}$01}, 65°($\pm$5°). The axial elements, as far as these could be determined are thus as follows:

$$\beta = 62°40'. \quad c/a = \frac{\sin (001 \wedge \bar{1}01)}{\sin (\bar{1}00 \wedge \bar{1}01)} = 1.15.$$

Figure 1 shows the positions of the various optical and crystallographic directions.
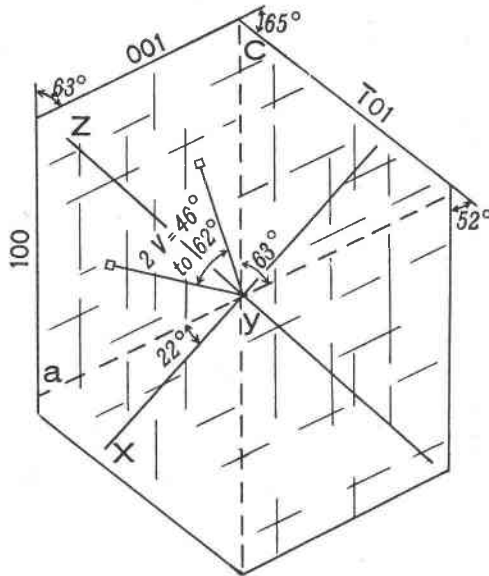
Optic orientation of gamagarite.

FIG. 1

The extinction angle $X \wedge c$ in the acute angle β probably varies somewhat, but in view of the indistinctness of the cleavages a study of this variation was not attempted. Out of 11 sections measured, 8 gave values between 43° and 39°. One gave 37° while for the remaining two sections the angle was 33°.

Gamagarite has the following optical properties:

$\alpha = 2.016$, $\beta = 2.040$, $\gamma = 2.130$ (all $\pm .01$).

$2V_x = 46° - 62°$. $r < v$, fairly strong.

Pleochroism, X = red-brown.

Y = very deep red-brown.

Z = light salmon-buff.

Absorption, $Y > X > Z$.

Alpha was measured by immersion of the crushed mineral in liquids of high index prepared according to the method described by West (3). Gamma was measured by embedding in sulphur-selenium melts in the manner previously noted by the writer (4). The following are actual values obtained during the measurement of γ: 2.136, considerably above γ; 2.132, very near but slightly above; 2.130, very near but slightly above; 2.125, considerably below γ. These figures show that the method yields results of good accuracy within the range in which observations were made. Where necessary, sodium light was used for accurate matching.

2V was measured on the universal stage and the results are considered accurate to about 4°. Variations in indices were not observed. One or more of the indices must, however, vary with 2V and small variations of α and γ are probable. Since the highest and lowest indices in a crush were measured, the true birefringence may be slightly lower than the value obtained experimentally.

CHEMICAL DATA AND DISCUSSION

Only a small proportion of the gamagarite in the rock was pure enough to be suitable for chemical analysis; the mineral for the most part being crowded with inclusions of hematite, cubes of sitaparite, etc. Clean material was obtained from the coarsely crushed rock by selecting the purest fragments. Each fragment was separately powdered and its purity judged by the colour of the powder and by occasional microscopic examination. The amount of impurities in the resultant material was difficult to estimate but probably did not amount to more than 2%. Dr. C. F. J. van der Walt of the Division of Chemical Services kindly undertook the quantitative analysis and his report is given below.

"0.5 gram of the mineral was fused with 6 grams sodium carbonate and the melt taken up with hot water and a little alcohol, to destroy any manganate present. The insoluble mat-

ter was filtered off and washed with a hot, dilute solution of sodium carbonate. The residue contained the barium, iron and manganese, while the filtrate contained the vanadium.

"The filtrate was acidified with sulphuric acid, reduced according to the sulphurous acid method, and the vanadium titrated with decinormal permanganate. The residue was dissolved in hydrochloric acid, carbon dioxide boiled off, and the iron precipitated with ammonia. The precipitate was filtered off, washed with a hot dilute solution of ammonium chloride, dissolved in hydrochloric acid and reprecipitated, etc. The combined filtrates contained the barium and manganese. The ferric hydroxide was dissolved in hydrochloric acid and the iron determined by titration with permanganate after reduction according to the stannous chloride method.

"The barium was precipitated from the filtrate with sulphuric acid and weighed as $BaSO_4$. The manganese was precipitated from the filtrate of the $BaSO_4$ according to the phosphate method and weighed as $Mn_2P_2O_7$.

"The water was determined according to the Penfield method. The available oxygen was determined by boiling the sample with hydrochloric acid, and the liberated chlorine passed through a solution of potassium iodide. The liberated iodine was titrated with decinormal sodium thiosulphate."

ANALYTICAL DATA

	1	2	3	4
BaO	52.4	.342	1.95	53.89
FeO	7.6	.106⎱	1.05	7.32
MnO	5.5	.078⎰		5.24
Al_2O_3	nil			
V_2O_4	29.1	.351	2.0	29.16
H_2O+	1.06	.118	.67	1.58
O	3.55	.222	1.27	2.81
	99.21			100.00

1. Analysis by C. F. J. van der Walt.
2. Atomic ratios.
3. Atomic ratios on the bais of $V_2O_4=2$.
4. Analysis recalculated from the formula $Ba_4(Fe, Mn)_2V_4O_{15}(OH)_2$ with Fe/Mn $=.58/.42$.

Qualitative tests by the writer showed the presence of a trace of calcium, but no lead, copper or arsenic was detected.

In connection with the above table the following observations may be made: (a) a simple ratio exists between the barium and vanadium atoms and the sum of the iron and manganese atoms; (b) the iron and manganese atoms are thus likely to be in a similar state of oxidation and structurally equivalent; (c) since the states of oxidation of the various metal atoms could not be determined, doubt as to the distribution of the available oxygen remains. In the present case it is assumed that vanadium would be in the vanadate condition rather than that vanadyl would exist in the presence of peroxidized manganese.

The available oxygen is sufficient for all the vanadium to be present as vanadate and for about one-half of the sum of the iron and manganese to be in the ferric and manganic states. The weight of the excess oxygen beyond the requirements of the proposed formula is actually small ($\pm 0.8\%$) and may result from a certain amount of weathering which was unnoticed because of the partial opacity and high relief of the mineral.

In order to obtain as accurate a figure as possible for the percentage of available oxygen, Dr. van der Walt carried out determinations on two different samples. In calculating the results (3.46% and 3.65% O), allowance was made for the fact that after boiling with hydrochloric acid the iron was in the ferric state whilst in the analysis it is given as ferrous oxide.

The water in the analysis has been considered as constitutional but there is no proof that it is not either wholly or in part adsorbed. If it were possible that part of the iron and manganese in the mineral is present in the trivalent state then the following alternative formula may be deduced:

$$Ba_2(Fe'', Mn'', Fe''', Mn''')V_2O_7OH(O, OH).$$

A structural investigation with the aid of x-rays would be of great value in reaching finality with respect to the composition of gamagarite.

The closest relative of gamagarite appears to be the rare and imperfectly known mineral, brackebuschite. In Dana's *System of Mineralogy* the following properties are given for this mineral: composition, perhaps $R_3V_2O_8 + H_2O$, with R chiefly Pb, also Fe and Mn. Occurs in groups of small prismatic crystals, flattened and vertically striated. Monoclinic? Optically negative? Axial plane perpendicular to striations. Axial angle large. Larsen and Berman (5) state that the mineral is optically positive and give the indices as $\alpha = 2.28$, $\beta = 2.36$, $\gamma = 2.48$ (all for lithium light).

Precise information on the composition and structure of brackebuschite is still lacking and its relationship to gamagarite cannot therefore be said to be proved.

MICROSCOPIC CHARACTERISTICS OF THE ORE SAMPLE

Sitaparite, the chief constituent of the ore, has a crystalline appearance, the individual crystals varying from a few tenths of a millimetre to a few millimetres in diameter. It is idioblastic towards all the other minerals and has a cubic habit. Between crossed nicols it is very weakly anisotropic and shows the typical twinning lamellae described by Schneiderhöhn (6). Lamellar inclusions of diaspore, oriented parallel to the cube faces are sparingly present and minute, rounded grains of hematite are scattered in patches throughout the sitaparite as well as through all the other minerals.
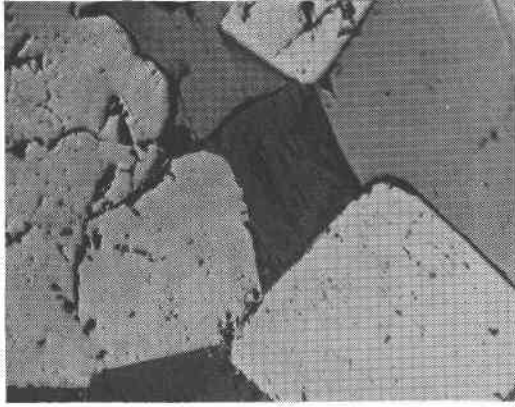
FIG. 2. Polished section showing white sitaparite, gray gamagarite and dark gray ephesite. Mineral in bottom, left-hand corner is diaspore. ×92.

FIG. 3. Thin section showing black sitaparite, gray diaspore and white ephesite. ×34.

FIG. 4. Thin section of gamagarite with inclusions of hematite showing relict oolitic texture. ×32.

Ephesite is present as rose-coloured idioblasts about 0.5 centimeters in diameter and as fine-grained aggregates, while diaspore forms small, lustrous brown plates. The latter mineral is pleochroic in pink and brownish-green and is usually interstitial to ephesite. Gamagarite is also interstitial to ephesite and may be either idioblastic or interstitial to diaspore.

Finally, small, hexagonal rods of amesite, a fraction of a millimetre in diameter and a few millimetres in length, are very sparingly present in the rock. It should be mentioned here that a small amount of nickel has been found in a different sample of amesite from the same locality.

The hematite inclusions referred to above, occur in patches and streaks and it is significant that their distribution in part indicates an original oolitic texture. It would thus appear that the ore is a replaced oolitic shale, of which a highly ferruginous variety is common in the vicinity. The conditions under which replacement took place and the source of the replacing solutions are problems intimately connected with the mode of origin of the manganese deposits as a whole. These problems are still being studied.

REFERENCES

(1) PHILLIPS, F. C., Ephesite (soda-margarite) from the Postmasburg district, South Africa: *Mineral. Mag.*, **22**, 482–485 (1931).

(2) CHUDOBA, K., Über "Mangandiaspor" und Manganophyll von Postmasburg (Griqualand-West, Südafrika): *Centralbl. Min.*, etc., Abt. A, 11–18 **(1929)**.

(3) WEST, C. D., Immersion liquids of high refractive index: *Am. Mineral.*, **21**, 245–249 (1936).

(4) DE VILLIERS, J. E., Columbomicrolite from Eshowe, Natal: *Am. Mineral.*, **26**, 501–506 (1941).

(5) LARSEN, E. S., AND BERMAN, H., The Microscopic Determination of the Nonopaque Minerals: *U. S. Geol. Surv., Bull.* **848** (1934).

(6) SCHNEIDERHÖHN, H., Mineralbestand und Gefüge der Manganertze von Potsmasburg, Griqualand-West, Südafrika: *Neues Jahrb. Min.* etc., Beil-Bd. **64**, Abt. A, 701–726 (1931).