

*Manganese-iron garnet from Otjosondu, South-West Africa.*¹

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Introduction.

GARNETS rich in manganese and iron, associated with barium-felspars, have been reported by de Villiers² from the manganese ores of Otjosondu, South-West Africa, in which they occur as the most abundant silicate mineral. The farm Otjosondu is 80 miles NE. of Okahandja, a railway station on the line between Windhoek and Walvis.

One specimen (referred to as no. 1), of which de Villiers published a chemical analysis, is massive and of a somewhat dark-yellowish colour. The material is traversed by veinlets of hyalophane (Cn₉), about 0.5 mm. broad. The other specimen (referred to as no. 2) is medium to fine grained and of a dark-reddish colour. Grains of celsian (Cn₉₄) are evenly distributed throughout this sample. Under the microscope both garnets appear to be free from inclusions and other impurities.

Physical properties.

Both garnets are optically isotropic. Refractive indices were determined for sodium-light at room-temperature by the immersion method using phosphorus-bearing liquids as embedding media, and found to be: no. 1, n 1.872; no. 2, n 1.901 (± 0.003).

Specific gravities were determined by suspension in Clerici solution. The results obtained were: no. 1, D_4^{16} 4.081; no. 2, D_4^{16} 3.962 (± 0.005).

X-Ray examination.

X-ray powder diffraction patterns were obtained by using a 114.59 mm. diameter camera in which the film is mounted according to the Straumanis method.³ The centres of the entrance and exit holes in the film were determined by measuring the lines on either side of these

¹ Published by permission of the Honourable, the Minister of Mines of the Union of South Africa.

² J. E. de Villiers, The manganese ores of Otjosondu, South-West Africa. Trans. Geol. Soc. South Africa, 1951, vol. 54, pp. 89-98. [M.A. 11-553.]

³ M. E. Straumanis, Journ. Appl. Physics, 1949, vol. 20, p. 726.

holes in order to obtain check points from which a shrinkage correction factor was determined. The temperature during the exposure remained reasonably constant and did not vary more than 2° C. above room-temperature (22° C.). The films were allowed to dry for two weeks before measuring. The exposure time for both samples was 20 hours using cobalt radiation with an iron filter at 30 kV. and 10 mA. The samples were mounted in Lindemann glass capillary tubes of about 0.05 mm. diameter. Values for a were obtained according to the Bradley and Jay graphical extrapolation method, as described by Wasserstein of this Laboratory.¹

TABLE I. X-ray intensities and spacings of garnets nos. 1 and 2 in Å.

No.	(hkl) .	No. 1, a 11.819 (± 0.003) Å.			No. 2, a 12.000 (± 0.003) Å.		
		Int.	θ .	d (meas.)	Int.	θ	d (meas.)
1.	(400)	9	17.82°	2.92	9	17.52°	2.97
2.	(420)	10	19.94	2.62	10	19.68	2.66
3.	(422)	9	21.96	2.39	9	21.62	2.43
4.	$\left\{ \begin{matrix} (510) \\ (431) \end{matrix} \right\}$	6	22.87	2.30	6	22.50	2.34
5.	(521)	6	24.66	2.14	6	24.27	2.18
6.	$\left\{ \begin{matrix} (611) \\ (532) \end{matrix} \right\}$	8	28.00	1.906	8	27.55	1.934
7.	(444)	5	31.80	1.698	5	31.31	1.721
8.	(640)	9	33.23	1.632	9	32.73	1.654
9.	(642)	10	34.64	1.574	10	34.10	1.596
10.	(800)	7	37.37	1.474	7	36.83	1.492
11.	(840)	7	42.81	1.316	7	41.99	1.337
12.	(842)	7	44.05	1.288	7	43.31	1.304
13.	(644)	7	45.35	1.257	7	44.63	1.273
14.	(10.4.0)	6	54.76	1.095	$\left\{ \begin{matrix} 6(\alpha_1) \\ 4(\alpha_2) \end{matrix} \right\}$	$\left\{ \begin{matrix} 53.68 \\ 53.90 \end{matrix} \right\}$	1.110
15.	$\left\{ \begin{matrix} (10.4.2) \\ (873) \end{matrix} \right\}$	6	56.16	1.077	$\left\{ \begin{matrix} 6(\alpha_1) \\ 4(\alpha_2) \end{matrix} \right\}$	$\left\{ \begin{matrix} 55.02 \\ 55.24 \end{matrix} \right\}$	1.092
16.	(880)	6	59.07	1.043	$\left\{ \begin{matrix} 6(\alpha_1) \\ 4(\alpha_2) \end{matrix} \right\}$	$\left\{ \begin{matrix} 57.79 \\ 58.02 \end{matrix} \right\}$	1.057
17.	$\left\{ \begin{matrix} (12.0.0) \\ (884) \end{matrix} \right\}$	4	65.47	0.983	$4(\alpha_1)$	63.67	0.998
18.	(12.2.0)	4	67.11	0.971	$4(\alpha_1)$	65.26	0.985
19.	$\left\{ \begin{matrix} (12.2.2) \\ (10.6.4) \end{matrix} \right\}$	9	69.03	0.968	$\left\{ \begin{matrix} 9(\alpha_1) \\ 5(\alpha_2) \end{matrix} \right\}$	$\left\{ \begin{matrix} 67.01 \\ 67.31 \end{matrix} \right\}$	0.972

Chemical properties and unit-cell contents.

The chemical analyses of the garnets were carried out on material separated by a Frantz isodynamic separator. The final material submitted for analysis contained less than 1% impurities. The spectrographic analyses were done on selected fragments, which were examined

¹ B. Wasserstein, Precision lattice measurements of galena. Amer. Min., 1951, vol. 36, pp. 102-115. [M.A. 11-316.]

microscopically and found to be free from impurities, with the following results: No. 1—present, Si, Al, Fe, Mn, Ca, Mg; traces, Ba, Na, K; absent, Ti, Cr, Li, Rb, Cs, Be. No. 2—present, Si, Al, Fe, Mn, Ca, Mg; traces, Ba, Na; absent, Ti, Cr, K, Li, Rb, Cs, Be.

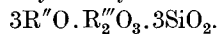
TABLE II. Chemical analysis of garnet no. 1.
(Analyst, C. F. J. van der Walt, in J. E. de Villiers, 1951.)

			Mol. ratios.		Atomic ratios.		Unit-cell contents.	
SiO ₂	...	34.56	0.0579	Si	...	0.5759	23.64	24
Al ₂ O ₃	...	4.72	0.0463	Al	...	0.0926	3.80	4
Fe ₂ O ₃	...	22.96	0.1435	Fe	...	0.2870	11.79	12
MnO	...	22.12	0.3116	Mn	...	0.3116	12.79	13
MgO	...	0.56	0.0140	Mg	...	0.0140	0.57	} 11
CaO	...	14.60	0.2607	Ca	...	0.2607	10.70	
BaO	...	0.00	—	O	...	2.3075	94.73	96
			99.52					

TABLE III. Chemical analysis of garnet no. 2. (Analyst, P. L. le Roux.)

			Mol. ratios.		Atomic ratios.		Unit-cell contents.	
SiO ₂	...	34.26	0.5710	Si	...	0.5710	23.89	24
Al ₂ O ₃	...	5.98	0.0586	Al	...	0.1172	4.90	5
Fe ₂ O ₃	...	22.20	0.1388	Fe	...	0.2776	11.61	12
MnO	...	13.29	0.1872	Mn	...	0.1872	7.83	8
MgO	...	0.67	0.0168	Mg	...	0.0168	0.70	} 18
CaO	...	22.74	0.4061	Ca	...	0.4061	16.98	
			99.14					

Garnet no. 1 conforms very closely to the ideal ratio of



It seems likely that in this case isomorphous replacement is restricted to atoms of the same valence. In the case of garnet no. 2 the ratio of 3:1:3 does not hold. Although it seems unlikely that any Al has replaced Si, it is obvious that there is an excess of 1R''', 2R'', and 2 oxygen atoms.

The specific gravity of garnet no. 1 calculated from the X-ray data and the molecular weight (4142.49/8) is 4.07. In garnet no. 2, if the excess of 1R''', 2R'', and 2 oxygen atoms in the unit cell did not occupy positions in the unit-cell it would not have had any influence on α , and consequently would not affect the calculated specific gravity, and there would be three possibilities of assembling the unit-cell contents, viz.:

	Mol. wt.	Sp. gr.
1. 24Si, 5Al, 11Fe, 17Ca, 7Mn, and 96O ...	4025.19/8	3.78
2. 24Si, 5Al, 11Fe, 18Ca, 6Mn, and 96O ...	4010.33/8	3.76
3. 24Si, 5Al, 11Fe, 16Ca, 8Mn, and 96O ...	4040/8	3.80

These calculated specific gravities are in very poor agreement with the measured value of 3.96. However, if the contents of the unit cell are taken as 24Si, 5Al, 12Fe, 18Ca, 8Mn, and 98O, yielding a molecular weight of 4208.07/8, the calculated specific gravity is 3.95, which agrees very well with the experimental value of 3.96. Therefore it seems reasonable to believe that the excess atoms occupy positions in the unit cell. The presence of excess atoms in the unit cell may also be regarded as a probable cause of the higher refractive index of garnet no. 2 as compared to no. 1, in spite of the fact that it contains less manganese.

If the packing indices of both garnets are determined according to the formula¹ $P.I. = (\text{volume of ions})/(\text{volume of unit cell}) \times 10$, it is found that both garnets have a P.I. of 6.3. Fairbairn lists the following: almandine 6.6, andradite 6.1, grossular 6.4, pyrope 6.5, spessartine 6.5. From a purely geometrical viewpoint there are cavities in the garnet structure which may provide accommodation for the above-mentioned excess atoms. For the determination of the volume of the ions in the unit cell the values of ionic volumes used are those listed by Fairbairn.

Norm calculations of the garnets.

In both garnets, with low alumina, the excess of manganese cannot be accounted as spessartine, and the presence of the molecule $3\text{MnO} \cdot \text{Fe}_2\text{O}_3 \cdot 3\text{SiO}_2$ is clearly indicated. To this garnet molecule Fermor² in 1909 applied the name *calderite*, a name that had been previously given by Piddington³ to a 'silico iron and manganese rock' from India. Piddington's unsatisfactory analysis (SiO_2 46.35, Al_2O_3 0.35, Fe_2O_3 30.18, MnO 21.00, CaO 1.00, As 0.20) was interpreted by Mallet⁴ as a massive Fe-Mn garnet with admixed quartz. Dana,⁵ who had evidently not seen this analysis, classified calderite as a variety of andradite.

The norms for each garnet can be calculated in many ways, depending upon the relative amounts of grossular and spessartine in each case. The presence of grossular increases the resulting amount of calderite at the expense of andradite, while the presence of spessartine decreases the calderite content and causes an increase in the amount of andradite.

¹ W. H. Fairbairn, Packing in ionic minerals. Bull. Geol. Soc. Amer., 1943 vol. 54, p. 1035. [M.A. 9-41.]

² L. L. Fermor, Mem. Geol. Surv. India, 1909, vol. 37, p. 182; Rec. Geol. Surv. India, 1926, vol. 59, p. 204. [Min. Mag. 21-558; M.A. 3-308.]

³ H. Piddington, Journ. Asiatic Soc. Bengal, 1851, vol. 19 (for 1850), p. 145.

⁴ F. R. Mallet, Geology of India, pt. 4, mineralogy, 1887, p. 90.

⁵ J. D. Dana, System of mineralogy. 5th edit., 1868, p. 443.

Only these extreme cases where the maximum quantities of grossular (norm A) and spessartine (norm B) are formed, will be considered.

TABLE IV. Norm A of garnet no. 1, calculated with all Mn as calderite.

	Mol. ratios.	Pyrope.	Grossular.	Andradite.	Calderite.	Residue.
SiO ₂ ...	0.5759	0.0140	0.1248	0.1359	0.2946	0.0066
Al ₂ O ₃ ...	0.0463	0.0047	0.0416	—	—	—
Fe ₂ O ₃ ...	0.1435	—	—	0.0453	0.0982	—
MnO ...	0.3116	—	—	—	0.2946	0.0170
MgO ...	0.0140	0.0140	—	—	—	—
CaO ...	0.2607	—	0.1248	0.1359	—	—
Weight %	...	1.89	18.72	23.02	54.30	= 97.93

TABLE V. Norm B of garnet no. 1, calculated with all Ca as andradite.

	Mol. ratios.	Pyrope.	Spessartine.	Andradite.	Calderite.	Residue.
SiO ₂ ...	0.5759	0.0140	0.1248	0.2607	0.1698	0.0066
Al ₂ O ₃ ...	0.0463	0.0047	0.0416	—	—	—
Fe ₂ O ₃ ...	0.1435	—	—	0.0869	0.0566	—
MnO ...	0.3116	—	0.1248	—	0.1698	0.0170
MgO ...	0.0140	0.0140	—	—	—	—
CaO ...	0.2607	—	—	0.2607	—	—
Weight %	...	1.89	20.59	44.14	31.31	= 97.93

TABLE VI. Norm A of garnet no. 2, calculated with all Mn as calderite.

	Mol. ratios.	Pyrope.	Grossular.	Andradite.	Calderite.	Residue.
SiO ₂ ...	0.5710	0.0168	0.1431	0.2292	0.1872	—0.0053
Al ₂ O ₃ ...	0.0586	0.0056	0.0477	—	—	0.0053
Fe ₂ O ₃ ...	0.1388	—	—	0.0764	0.0624	—
MnO ...	0.1872	—	—	—	0.1872	—
MgO ...	0.0168	0.0168	—	—	—	—
CaO ...	0.4061	—	0.1431	0.2292	—	0.0338
Weight %	...	2.25	21.47	38.81	34.50	= 97.03

TABLE VII. Norm B of garnet no. 2, calculated with all Ca as andradite.

	Mol. ratios.	Pyrope.	Spessartine.	Andradite.	Calderite.	Residue.
SiO ₂ ...	0.5710	0.0168	0.1432	0.4061	0.0102	—0.0053
Al ₂ O ₃ ...	0.0586	0.0056	0.0477	—	—	0.0053
Fe ₂ O ₃ ...	0.1388	—	—	0.1354	0.0034	—
MnO ...	0.1872	—	0.1432	—	0.0102	0.0338
MgO ...	0.0168	0.0168	—	—	—	—
CaO ...	0.4061	—	—	0.4061	—	—
Weight %	...	2.25	23.61	68.78	1.87	= 96.51

In deciding between these two possibilities guidance is provided by the specific gravities calculated from the cell dimensions as given by Bragg¹ (table VIII, with the addition of calderite).

¹ W. L. Bragg, Atomic structure of minerals. Cornell Univ., 1937. [M.A. 7-7.]

TABLE VIII. Garnet group.

Garnet.	Formula.	<i>a</i> .	Mol. wt.	Sp. gr.
Pyrope	$3\text{MgO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{SiO}_2$	11.51 Å.	403.1	3.43
Almandine	$3\text{FeO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{SiO}_2$	11.50	497.6	4.25
Spessartine	$3\text{MnO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{SiO}_2$	11.60	494.9	4.12
Grossular	$3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{SiO}_2$	11.83	450.4	3.53
Uvarovite	$3\text{CaO} \cdot \text{Cr}_2\text{O}_3 \cdot 3\text{SiO}_2$	11.95	500.2	3.81
Andradite	$3\text{CaO} \cdot \text{Fe}_2\text{O}_3 \cdot 3\text{SiO}_2$	12.02	508.1	3.80
Calderite	$3\text{MnO} \cdot \text{Fe}_2\text{O}_3 \cdot 3\text{SiO}_2$	11.82	552.7	4.42

By taking the specific gravity of garnet no. 1 as 4.08 and no. 2 as 3.96, and referring to the two norms A and B of each of the two garnets, the specific gravity of the calderite molecule can be calculated and from the values obtained it can be decided which one of the two norms is more likely to be correct. The results are given below:

	Sp. gr.
Garnet no. 1, Norm A	4.42
Norm B	4.49
Garnet no. 2, Norm A	4.44
Norm B	6.09

By comparing these values it seems reasonable to believe that the specific gravity of pure calderite is 4.42, and in the case of both garnets the norm A is therefore correct. The unit-cell dimension of pure calderite was calculated as 11.82 Å. (mol. weight of calderite being 552.7), which seems acceptable when the unit-cell dimensions and specific gravities of calderite and andradite are compared. The molecular weight of MnO is higher than that of CaO and the ionic radius of Mn (0.91 Å.) is smaller than that of Ca (1.06 Å.), so therefore one would expect a higher specific gravity and a smaller unit cell for calderite as compared with that of andradite. Taking the unit cell for pure calderite as a 11.82 Å., then its packing index can be calculated as 6.2.

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