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DISTINCTION BETWEEN TWO MEMBERS OF THE BRAUNITE GROUP[1]

P. R. de Villiers[2] *Geological Survey, Pretoria, South Africa*

AND

F. H. Herbstein[3] *Chemical Physics Group, Council for Scientific and Industrial Research, Pretoria, South Africa.*

Abstract

Braunite from the Northern Transvaal has cell dimensions $a=9.44$, $c=18.76$ Å, space group $D_{4h}^{20}-I4_1/acd$. A related manganese mineral (with 16.3% Fe_2O_3, 4.3% CaO and 4.4% SiO_2) from the Black Rock manganese mine, northwestern Cape Province has been found to have $a=9.44$, $c=37.76$ Å, space group $D_{4h}^{20}-I4_1/acd$. This is considered to be an ordered version of ordinary braunite and is provisionally called braunite-II.

Introduction

Problems of classification are often encountered among certain manganese minerals. The trio partridgeite, bixbyite, and sitaparite, where varieties from different localities differ in chemical composition but not (as far as is known) in crystallography, constitute a well-known example of this nature (Mason, 1942, 1944). A similar situation exists in the braunite group of minerals: the ideal composition of ordinary braunite is $3Mn_2O_3 \cdot MnSiO_3$ and most analyses conform reasonably well to this formula. However J. E. de Villiers (1945) has reported the occurrence of a so-called ferrian braunite with less than half the silica content required by the ideal formula and containing in addition appreciable amounts of iron and alkaline earths (see Table I for details). In the present investigation we have used single-crystal X-ray diffraction techniques to study the difference between J. E. de Villiers' mineral and ordinary braunite. Our work suggests that J. E. de Villiers' mineral is an ordered version of ordinary braunite. The detailed nature of the differences between the two species will only become clear after the crystal structures of both have been determined. We have therefore decided to give J. E. de Villiers' mineral the provisional and noncommittal label braunite-II.

Geological and Mineralogical Background

Geology. The ordinary braunite studied in this investigation is from the arenaceous beds of the Loskop System on the farm Weenen, some 80

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[2] Present address: Research Laboratories, South African Iron and Steel Corporation, Pretoria.

[3] Present address: Department of Chemistry, Technion—Israel Institute of Technology, Haifa.

TABLE 1. CHEMICAL ANALYSES OF VARIOUS BRAUNITES

	3 Mn_2O_3 $MnSiO_3$	Kalahari braunite		N. Transaal braunite	Långban braunite	Mason County ferrian braunite	Kajlidongri braunite	Sitapar braunite	Kalahari braunite-II	Otjosondu ferrian braunite
		1	2							
MnO		40.10	42.3	39.9			37.98	41.10	31.5	
or MnO	82.13				78.91	66.89				59.04
MnO_2		46.50	43.6	39.6			40.93	37.10	43.3	
O	7.94				7.35	6.27				5.31
Fe_2O_3 (incl. Al_2O_3)	—	1.44	2.1	7.4	—	15.39	1.59	8.84	16.3	23.59
FeO	—				3.81	—	—	—	—	—
CaO	—	1.40	2.2	1.3	0.34	0.06	3.85	4.28	4.3	0.00
BaO	—	0.13	—	—	—	—	0.09	—	0.2	
MgO	—			0.1	0.15	0.19	4.36	0.94	—	0.31
SiO_2	9.93	9.32	9.6	9.9	9.98	9.90	10.26	8.52	4.4	9.94
B_2O_3										0.20
Rem.						1.40 (H_2O 0.73; insol. gangue 0.67)	1.57 (H_2O at 100°C)	0.10 (H_2O at 100°C)		
Total	100.00	98.89	98.8	98.3	100.45	100.10	100.63	100.88	100.00	100.14
Sp. Gr.	4.67		4.76	—	4.72	4.73	4.704	4.798	4.727	—
Ref.		J. E. de Villiers (1945)		This paper	Palache, Berman and Frondel (1951)	Hewett and Schaller (1937)	Fermor (1909)	Fermor (1909)	J. E. de Villiers (1945)	J. E. de Villiers (1951)

miles northwest of Potgietersrust, Northern Transvaal. Manganese is present in the low-grade ore as braunite, psilomelane, and pyrolusite. The ore is of a sedimentary origin with supergene enrichment. This sample was selected because of its granular nature and chemical purity; however no well-formed crystals were found.

The braunite-II sample was obtained by one of us (P. R. de V.,) from the Black Rock mine which is situated at the extreme north of the Kalahari manganese field. This field extends over a distance of about 40 miles north of Sishen in the Kalahari, northwestern Cape Province, Republic of South Africa. The manganese ore of the Black Rock mine consists mainly of braunite, bixbyite, cryptomelane, hematite, and pyrolusite. J. E. de Villiers (1945) obtained his braunite-II samples from the same locality and indeed we were fortunate to have access to some of his specimens which are now in the Museum of the Geological Survey, Pretoria.

The Black Rock manganese mine is situated on the only outcrop of banded ironstone of the Upper Griquatown Stage of the Pretoria Series, Transvaal System (Precambrian) in this area. The outcrop of banded ironstone protrudes approximately 90 feet above the nearly flat surface of Kalahari sand, is almost oval in outline and measures 1,560 feet in length and 600 feet in width across the widest part. The banded ironstone which extends below the sand cover contains three consistent intercalated bands of manganese ore each of which is 20 feet thick. The general but varying dip is 35° to the west.

There is no agreement regarding the origin of the ore from Black Rock although most investigators favour the supergene theory, possibly involving replacement of contemporaneous manganese carbonate. The manganese may have resulted in the first instance from volcanic exhalations related to the underlying Ongeluk Lava or possibly from interformational erosion of the dolomite of the Transvaal system which outcrops five miles to the east. The banded ironstone and the intercalated carbonate layers were later subjected to post-Matsap orogenic movements and became susceptible to percolating solutions.

Mineralogy of braunite-II

(a) Physical characteristics: hardness 6; nonmagnetic. The crystals are tetragonal with length of 0.5 to 20 mm (Fig. 1). Interpenetration twins (Fig. 2) and contact twins are also present.

(b) Optical characteristics: color in reflected light is yellow-brown; bireflection is difficult to observe; anisotropism is like that of braunite. Sometimes intergrown with ordinary braunite along certain crystallographic directions.

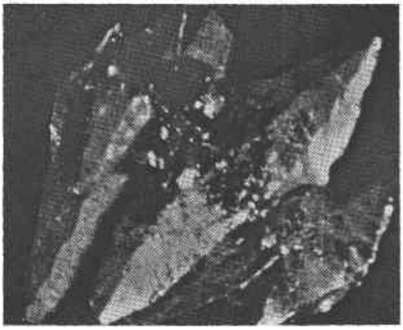

FIG. 1. Crystals of braunite-II showing pyramid faces, 65×.

(c) Occurrence: braunite-II has only been found in the Black Rock Mine, usually in vuggy ore and often associated with andradite. The crystals are generally rimmed and replaced by cryptomelane (Fig. 3). J. E. de Villiers (1945) reported pyrolusite as an impurity but our X-ray photographs of his sample show that this impurity is in fact cryptomelane.

(d) Diagnosis: braunite-II is very similar to ordinary braunite and, particularly, bixbyite; however the color in reflected light is intermediate between that of these two minerals.

(e) Minor elements: semiquantitative spectrochemical analysis shows that the braunite-II samples contain 0.05 percent Al and 0.005 percent of each Cr, Co, Ti, Ag, Cu, and Sn.

Preliminary comparison of ordinary braunite and braunite-II. Braunite has been found in many localities since its discovery by Haidinger in

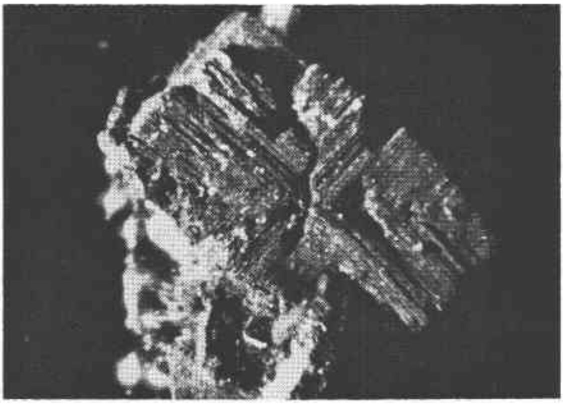

FIG. 2. Interpenetrating twins of braunite-II, 75×.

1826. Most analysed specimens have SiO_2 contents close to the 9.98 weight percent required by the ideal formula; some of the divergent values are discussed below. Results for specimens from India are given by Fermor (1909) and a general summary of the older analyses by Koechlin (1926); more recent results are given by Palache, Berman and Frondel (1951). Goniometric measurements show braunite to be tretagonal and c/a was given as 0.99. However Aminoff's X-ray diffraction measurements (1931) indicate that $a=9.5$, $c=18.9$ Å and hence the true axial ratio is 1.99. The space group is a matter of dispute. Previous results for cell dimensions and space group are discussed below.

A few of the many chemical analyses reported for braunite are included

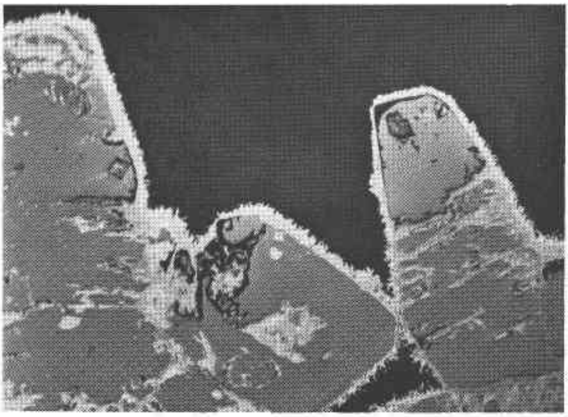

FIG. 3. Polished section of braunite-II rimmed and replaced by cryptomelane. The large black region is opal, 225×.

in Table 1 and at this stage we wish to compare only the results for standard braunite specimens, for example those from the Northern Transvaal, the Kalahari and Långban, with the Kalahari braunite-II of J. E. de Villiers. The most striking difference is the SiO_2-content of the latter which is 4.4. percent, a value less than half the standard value. The appreciable CaO and Fe_2O_3 contents are also noteworthy but not exceptional, as reference to the other specimens in Table 1 will show. Goniometric examination of crystals of braunite-II shows them to be tetragonal with c/a ratio similar to that of ordinary braunite but with a different face development. Powder photographs also reveal small but definite differences (J. E. de Villiers, 1945) which could, however, be due to impurities adhering to the fragments drilled out of the matrix. The results are suggestive of a real difference between the two varieties but are hardly conclusive. Thus we decided that a more intensive study of ordinary braunite and braunite-II was necessary and that single-crystal X-ray diffraction techniques would be most likely to show up any real differences.

X-Ray Study of Single Crystals of Ordinary Braunite and Braunite-II

Only small fragments of ordinary braunite, without recognisable faces, were available. They were oriented entirely by X-ray methods. Needle-shaped crystals of braunite-II were obtained from J. E. de Villiers' specimens and were mounted about the needle axis [001] for X-ray photography. Preliminary photographs, to determine cell dimensions, were taken by the oscillation and the Weissenberg techniques, but it soon became clear that, because of the size of the unit cells, the Buerger precession camera would give much more reliable results for the systematic absences. A combination of methods was therefore used. Despite a fairly high fluorescence background, Cu$K\alpha$ radiation was found suitable for the oscillation and the Weissenberg photographs, while Mo$K\alpha$ was used for the precession photographs.

Braunite (ordinary)

$$a = 9.44 \pm .005\ \text{Å}$$
$$c = 18.76 \pm .01\ \ \text{Å}$$

(Wavelengths used: Cu$K\alpha$ (mean) $= 1.5418$ Å, $K\alpha_1 = 1.54054$ Å, $K\alpha_2 = 1.54436$ Å).

Standard deviations were rather roughly estimated.
Systematic absences: hkl absent for $h+k+l \neq 2n$
$hk0$ absent for $h(k) \neq 2n$
$0kl$ absent for $l(k) \neq 2n$
hhl absent for $(l \neq 2n)$, $2h+l \neq 4n$

The space group is thus uniquely determined as $D_{4h}^{20}-I4_1/acd$

Cell-dimensions have been reported for a number of braunite specimens of different origins and a selection of these is given in Table 2. A detailed comparison is made difficult by uncertainty whether the earlier results are actually in kX units, although reported as Å units. The change from kX to Å units would be $+0.02$ Å for a and $+0.04$ Å for c.

Aminoff (1931) reported the space group as $D_{4h}{}^{20}-I4_1/acd$ but this was disputed by Byström and Mason (1943) on the grounds of the appearance of a (550) reflection on a Weissenberg photograph. On the basis of their structure analysis these authors chose $D_{2d}^{10}-I\bar{4}c2$. Mukherjee (1959) found a (130) reflection in his powder patterns of braunite and chose

$D_{4h}^{17}-I4/mmm$ as the space group. We have searched carefully for these reflections on our precession photographs but without success. Our results thus confirm Aminoff's original proposal.

The analytical figures given for the two specimens from the Kalahari in Table 1 were used to calculate the contents of the unit cell. These contain 8 formula units of composition $Mn_{6.66}Fe_{0.11}Ca_{0.15}Ba_{0.01}Si_{0.94}O_{12}$ for sample 1 and $Mn_{6.54}Fe_{0.04}Al_{0.18}Si_{0.95}O_{12}$ for sample 2. The calculated densities for the two specimens are respectively 4.769 and 4.742 $g \cdot cm^{-3}$ while the calculated density for the ideal composition Mn_7SiO_{12} is 4.812 $g \cdot cm^{-3}$. In these calculations the oxygen content of the unit cell has been normalized to 96 atoms, and the same cell dimensions (9.44, 18.76 Å) have been assumed for all three samples. The measured density of specimen 2 is 4.76 $g \cdot cm^{-3}$ which is in good agreement with the calculated values. If we assume that iron, aluminum, calcium and barium atoms are in the same sites as manganese atoms (thus ignoring any consideration of charge) then there are respectively 6.93 and 6.99 atoms for the 7 manganese atoms of the ideal formula. The apparent deficiency in silicon atoms in the formula is somewhat higher.

TABLE 2. CELL DIMENSIONS FOR BRAUNITE

Specimen	*a*	*c*	Units	Reference
Synthetic (from $MnSO_4$ and Na_2SiO_3)	9.41±0.01	18.64±0.02	Å ?	Byström and Mason (1943)
Långban	9.42	18.67	Å ?	Byström and Mason (1943)
Lohdongri (Nagpur, India)	9.42	18.72	Å ?	Byström and Mason (1943)
Nagpur	9.36	18.77	Å ?	Switzer (1938)
Kacharwahi, Nagpur	9.402	18.740	Å	Mukherjee (1959)
N. Transvaal	9.44±0.005	18.76±0.01	Å	This paper.

The crystal structure given for braunite by Byström and Mason (1943) cannot be entirely correct because they used the incorrect space group. The crystal structure is now being reanalyzed by one of us (F.H.H. with J. P. Roux) and the results will be reported elsewhere.

Braunite-II

$$a = 9.44 \pm 0.005 \text{ Å}$$
$$c = 37.76 \pm 0.01 \text{ Å}$$

The *a*-spacing agrees within the limits of error with that of braunite but the *c*-spacing is significantly greater than twice that of braunite, the difference being 0.24 ± 0.014 Å. The systematic absences lead to the unambiguous determination of the space group as $D_{4h}^{20}-I4_1/acd$.

The analyses for braunite-II given in Table 1 were used to calculate the contents of the unit cell, which contains sixteen formula units of composition: $Mn_{5.80}Fe_{1.25}Ca_{0.46}Ba_{0.008}Si_{0.45}O_{12}$ (the oxygen content of the unit cell has been normalized to 192 atoms). The calculated density is 4.834 $g \cdot cm^{-3}$ which is rather higher than the measured value of 4.727 $g \cdot cm^{-3}$. J.E. de Villiers (1945) has observed that the measured density of braunite-II is likely to be lower than the true value because of the "somewhat porous nature" of the material.

It is interesting to note that there are 7.2 Si atoms and 7.4 Ca atoms per unit cell; thus it seems probable that the Si and Ca atoms are ordered in two different sets of eightfold positions. The stronger reflections on comparable precession photographs of ordinary braunite and braunite-II show a resemblance both in arrangement and in relative intensity but there are appreciable differences for the weaker reflections. This is consistent with similar general arrangements of oxygen atoms and metal atoms in both structures, the differences probably arising from ordered arrangements of some of the metal atoms in braunite-II, together with some differences in the arrangement of oxygen atoms. A full structure analysis by means of X-ray methods, which is now in progress, will be required to check these suggestions; unfortunately X-rays are unlikely to give any indication of possible ordering of the iron atoms and recourse to neutron diffraction will be necessary to settle this point.

POWDER PATTERNS OF ORDINARY BRAUNITE AND BRAUNITE-II

Powder patterns of ordinary braunite have been given by Smitheringale (1929), Harcourt (1942), Lee (1955), Mukherjee (1959) and Roy (1962). We have also prepared a pattern of the ordinary braunite from Northern Transvaal described in this paper. The various results are in reasonably good agreement. The pattern given on ASTM Card No. 2-0895 is a somewhat modified composite of the results of Smitheringale and Harcourt. The best available pattern is probably that of Mukherjee (his Table 1) but some corrections are required. The most important correction is that the lines with $d=2.96$ Å ($I=10$) and 3.33 Å are not the (130) and (220) reflections but are due to impurities. Harcourt also gives these lines but they do not appear in patterns by Lee and Roy nor in our pattern. Mukherjee also lists some other indices which violate the space group, but these should be ignored.

We have also determined the powder pattern of braunite-II (114.6 mm camera, FeKα) and the results are given in Table 3. Some lines due to impurities have been eliminated by comparing the observed powder pattern with a calculated version based on the single-crystal results. Intensities of reflections from the single-crystal patterns are not yet available and thus multiple-index coincidences due to the large size of the unit cell cannot be eliminated. For this reason indices have been omitted in Table 3.

DISCUSSION

The difference found between ordinary braunite and braunite-II will be used as the basis for discussion of the significance of other reported deviations from ideal compositions in the braunite and bixbyite groups.

The silica contents of most specimens of braunite lie in the range 8–10 weight percent and thus agree reasonably well with the silica content based on the ideal composition. Braunite-II is the only established exception to this statement as the low values of silica reported for some specimens (see Koechlin (1926) for summary) generally come from older analyses of doubtful reliability. (We note that a value of 3.93 weight percent SiO_2 has been reported in a sample from Brazil (Ježek, 1910; analysis No. 32 of Koechlin's summary) and this may be worth following up.)

TABLE 3. X-RAY POWDER PATTERN OF BRAUNITE-II (FeKα RADIATION)

d_{obs} Å	I_{obs}	d_{obs} Å	I_{obs}
4.54	10	1.499	10
4.15	15	1.423	70
3.68	40	1.261	10
2.72	100	1.233	10
2.35	60	1.176	15
2.10	10	1.162	15
1.996	20	1.141	10
1.913	10	1.081	30
1.666	90	1.052	20
1.517	10		

Two specimens of braunite from India contain appreciable amounts of alkaline earths (see Table 1) and both Fermor (1909) and Byström and Mason (1943) have already pointed out that the composition of the Kajlidongri specimen can be written as $3Mn_2O_3\cdot(Mg,Ca)SiO_3$. If this specimen had an appropriate thermal history, then it is possible that the alkaline earth atoms are ordered. It is unlikely that the braunite from Sitapar, with only half an alkaline-earth atom per formula unit, has these atoms ordered. Diffraction effects resulting from ordering would be small and hence difficult to detect by qualitative examination of powder patterns; studies of single crystals, particularly of the specimen from Kajlidongri, may give interesting results.

Alkaline earths have also been considered as essential constituents of sitaparite (Mason, 1942) although this is not supported by analyses given by J.E. de Villiers (1945) for two samples of sitaparite from Postmasburg which contain virtually no alkaline earths. Fermor's (1909, p. 50) original analysis of sitaparite gave 6.14 weight percent CaO and 1.02 weight percent MgO but this only amounts to 3 atoms of alkaline earth per unit cell and it is therefore unlikely that these atoms are ordered. Both Mason (1942) and Mukherjee (1959) have obtained powder patterns of various samples of sitaparite and they were found to be identical to the powder patterns of bixbyite. Mukherjee has reported that the presence of the (310) and (510) lines in his photographs precludes sitaparite from having the same space group as bixbyite ($T_h^7 - Ia3$). The earlier results of Zachariasen (1928) and Pauling and Shappel (1931) for bixbyite have recently been confirmed for a synthetic sample of Mn_2O_3 (Swanson, Cook, Isaacs and Evans, 1960) and it seems possible that the additional lines in Mukherjee's pattern were due to impurities. Confirmatory photographs on single crystals would be desirable but we note that the available evidence for differences between bixbyite and sitaparite is much weaker than for ordinary braunite and braunite-II, or even for ordinary braunite and braunite from Kajlidongri.

Iron is also an important substituting element in the braunite and bixbyite groups. Samples of bixbyite of varying iron content have been shown to correspond to the wide range of solid solution of Fe_2O_3 in Mn_2O_3, established experimentally, (Mason, 1942, 1944; Muan and Sōmiya, 1962). It is therefore reasonable to suppose that even the braunite from Otjosondu with 23.6 weight percent Fe_2O_3 and the braunite from Mason County, with 15.4 weight percent Fe_2O_3 (Table 1), have the same crystal structure as ordinary braunite and should be called ferrian braunite in terms of the nomenclature of Schaller (1930). More subtle effects, such as ordering of Fe and Mn atoms, could only be detected by neutron diffraction, or, perhaps, by suitable magnetic measurements.

CONCLUSION

We conclude that only in braunite-II is there experimental evidence for an ordered arrangement of substituting atoms. Ordering of alkaline-earth atoms is possible in braunite from Kajlidongri, but this is unlikely in other samples of braunite or in sitaparite. Ordering of atoms of iron and magnese also appears unlikely and could not have been observed by X-ray diffraction. Whether braunite-II should be considered a separate phase from ordinary braunite cannot be settled on the available evidence but must await the results of the analyses of the crystal structure of both species and perhaps also a study of their interconvertibility.

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