

NOTES ON VREDENBURGITE (WITH DEVADITE) AND ON SITAPARITE.

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I. INTRODUCTION.

Many years ago I published accounts of two new manganese-ore minerals under the names of vredenburgite and sitaparite respectively.¹ Vredenburgite

¹ 'Three new Manganese-bearing minerals :—Vredenburgite, Sitaparite and Juddite', *Rec. Geol. Surv. Ind.*, XXXVII, pp. 199–212, (1908).

'The Manganese-Ore Deposits of India', *Mem. Geol. Surv. Ind.*, XXXVII, pp. 42–49 (vredenburgite) and 49–52 (sitaparite), (1909).

was obtained from Beldongri in the Nagpur district, Central Provinces, and from Garividi in the Vizagapatam district, Madras; and for this mineral substance, of several possible formulæ, $3\text{Mn}_2\text{O}_4 \cdot 2\text{Fe}_2\text{O}_3$ was preferred. Sitaparite was obtained only from one locality, namely Sitapar in the Chhindwara district, Central Provinces, and for this mineral the somewhat complex formula $9\text{Mn}_2\text{O}_3 \cdot 4\text{Fe}_2\text{O}_3 \cdot \text{MnO}_2 \cdot 3\text{CaO}$ was adopted. The specific gravity of vredenburgite was determined as 4.74 (Beldongri) to 4.84 (Garividi) and that of sitaparite as 4.93 to 5.09. The hardnesses were determined as about 6.5 for vredenburgite and about 7 for sitaparite. In colour vredenburgite is dark steel-grey with a bronze tint, especially in the sun, whilst sitaparite is a dark bronze-grey, the bronze tint again being especially well seen in the sun. In each case it was the bronze tint that first drew my attention to the mineral. The streak of vredenburgite is a deep brownish black tending to a deep chocolate, whilst that of sitaparite is black. Each mineral shows a well-marked cleavage¹; but as no crystals of either mineral were found the directions of these cleavages were not definitely determined. It was suggested, however, that the cleavage of vredenburgite is parallel either to the isometric octahedron or the tetragonal pyramid, according as the mineral is isometric or tetragonal, and for sitaparite that the cleavage may be octahedral. Although these two mineral substances have somewhat similar bronze colours they are easily distinguished by the fact that vredenburgite is strongly magnetic, whilst sitaparite is only weakly so.

Although it seemed clear, in view of these properties, that we had to deal with two new mineral species, it was also clear that there was scope for further work on the chemical composition of both substances, as also for the discovery of crystals of each and the determination of their crystal constants. The opacity of these, as of other manganese-ore minerals, was, of course, a hindrance to the study of their composition and of the relationship of one mineral to another in complex ores; and that the method of the future for the study of manganese-ores was that already adopted for the study of alloys was suggested by my publication in the memoir cited above of a photomicrograph (Plate I) by reflected light of a polished and etched slice of manganese-ore (a mixture of braunite and psilomelane).

The study of opaque minerals in polished and etched slices by reflected light has since become a well-known branch of technique for the student of ore deposits, and much work has been done on Indian manganese-ores by several workers, in particular by Christie, Schneiderhöhn, and Ramdohr, Orzel and Pavlovitch, and lately by Dr. J. A. Dunn, amplifying, as one result of this work, our knowledge of vredenburgite and sitaparite. This work shows that vredenburgite in its present form is not a mineral species but a mixture of at least two minerals, whilst sitaparite is a definite species. In addition further

¹ As vredenburgite is now known to consist of a lamellar intergrowth the apparent cleavage may be better described as a parting plane.

chemical work has been done on vredenburgite not only in connection with Dr. Dunn's research, but also by Mr. M. R. Anantanarayana Iyer of Bangalore. Further, whilst vredenburgite has not yet been found outside India, except perhaps for the specimen from Jakobsberg in Sweden noticed on page 274, sitaparite has been found to occur abundantly in the manganese-ore deposits of Postmasburg in South Africa.

In view of these facts it seems suitable that I should contribute a note upon the additional knowledge acquired concerning these two mineral substances; and, as the author of the term, perhaps express an opinion on the use of the name vredenburgite in the future now that it has been shown that in its present form vredenburgite is a mixture of minerals.

II. VREDENBURGITE (WITH DEVADITE).

(a) *Researches mainly on polished surfaces.*

In 1928, whilst on study-leave, Dr. W. A. K. Christie, then Chemist to the Geological Survey of India, polished and etched with H_2O_2 and H_2SO_4 a specimen of vredenburgite from Kodur; the surface thus prepared recalled at once the Widmanstätten figures revealed on polishing and etching a section of a nickel-iron meteorite, this work thus showing that the specimen of vredenburgite examined must now be composite. It appeared in fact to be composed mainly of two substances, one forming the network and the other occupying the meshes of the net. Dr. Christie attempted to drill out and analyse separately under the microscope the two main constituents; but this proved impracticable. However, he succeeded in separating these two constituents by dissolving one of them in a mixture of H_2O_2 and H_2SO_4 ; but Dr. Christie was not satisfied with the analytical data thus obtained. This work was commenced in Professor Lacroix' laboratory at the Muséum d'Histoire Naturelle in Paris, where the first polished section of vredenburgite was prepared, and then continued first in Professor Hans Schneiderhöhn's laboratory at Freiburg in Breisgau, and later in the Geological Survey laboratory in Calcutta.

To me Dr. Christie's discovery was of extreme interest. For, on the analogy of the interpretation given by me to the crystalline structures of iron meteorites or siderites as revealed by the Widmanstätten figures¹ obtained on polishing and etching, in accordance with which I regarded the formation of these structures in meteorites as indicative of the release of pressure, it appeared that Dr. Christie's discovery provided evidence by analogy that the original vredenburgite had on release of pressure (or lowering of temperature), or both, broken down into two separate minerals, supporting my view that the Eastern Ghats Province of India was a special tract that had formerly been

¹ 'Preliminary Note on the Origin of Meteorites', *Jour. & Proc. As. Soc. Beng.* (New Series), VIII, pp. 320, 321, (1912).

subjected to much higher pressures and temperatures than normal, accounting for its very unusual petrographical and mineral facies.

Dr. Christie's visit to Paris and Freiburg appears to have stimulated research on manganese minerals, including vredenburgite and sitaparite, at both centres, namely in Paris by J. Orcel and St. Pavlovitch and at Freiburg i. Br. by Schneiderhöhn and P. Ramdohr.

The results of the studies at Freiburg have been incorporated in Volume II of Schneiderhöhn and Ramdohr's 'Lehrbuch der Erzmikroskopie' published in Berlin in 1931, and in two papers, one by Orcel alone¹ and the other by Orcel and Pavlovitch,² published in Paris in 1930 and 1931 respectively.

The data given in Schneiderhöhn and Ramdohr's volume³ were based on work by Christie and Schneiderhöhn on the microscopic aspects of vredenburgite. This study was made on a specimen from Kodur in the Vizagapatam district, Madras, a locality near Garividi, from which my type specimen from this area was derived. According to these authors (Schneiderhöhn and Ramdohr) vredenburgite in its present form consists of a lamellar network of hausmannite with the meshes occupied by jacobsite, the lamellæ of hausmannite being arranged parallel to the octahedron (111) of jacobsite. They write that the structure indicates that an originally homogeneous spinel mineral has broken down because the corresponding admixture was no longer stable with falling temperature. Further, as both components correspond to the formula R_3O_4 (Mn_3O_4 and $MnFe_2O_4$), the composition of the original vredenburgite can be easily determined by planimetric measurement. They remark further that the result so obtained agrees approximately with my formula for vredenburgite if one considers that I gave no valencies for the Mn and Fe.⁴ These authors remark that the strongly magnetic character of vredenburgite is due to the magnetism of the jacobsite. It is also noticed that with incipient weathering the hausmannite is often selectively altered before the jacobsite. An excellent photomicrograph brings out the resemblance to the Widmanstätten figures of an iron meteorite already noticed.

Orcel and Pavlovitch also give an account of a study⁵ of vredenburgite in polished surface, making use of reflecting power, and of chemical attack by a variety of reagents. Their work was done on a specimen from Kodur provided by Dr. Christie. They, also, recognise two constituents, referring to them as α for the constituent occupying the meshes of the network and β for the needles of the network itself. The constituent α is weakly but clearly anisotropic, whilst β

¹ *Bull. de la Soc. Franç. de Min.*, LIII, p. 347, (1930).

² *Op. cit.*, LIV, pp. 108-179, (1931).

³ *Loc. cit.*, pp. 602-604.

⁴ The distribution adopted by me of the Mn and Fe into sesquioxides and protoxides is based on the determination of available oxygen, which does not, of course, enable one to determine the distribution of Mn and Fe into sesquioxides and protoxides, but does enable one to decide on the proportion of R_3O_4 to R_2O_3 .

⁵ *Loc. cit.*, pp. 166-170.

is markedly polychroic. Judging from their optical characters and reactions to corrosive attack by various agents, the authors decide that neither of these constituents can be identified certainly with already known species. Constituent α is very similar in both optical and chemical properties to braunite, but as chemical treatment yielded a residue of only 1.02 per cent of SiO_2 the authors rightly rule out braunite.

They notice also that constituent α might be identified with jacobsite (as is done by Schneiderhöhn and Ramdohr), but for the fact that jacobsite is rigorously isotropic; and that before one could admit this identity it would be necessary to regard the anisotropy as provoked by internal tensions sufficiently regular to give rise to uniform extinctions throughout, which evidently appears to the authors improbable. In addition they find the reaction of α to hydrochloric acid different from that of jacobsite.

They consider the possibility of constituent β being hematite (*oligiste*), but reject this on both optical and chemical grounds, and conclude that vredenburgite may be an association of two new constituents, but that no definite conclusion can be drawn without a study by X-ray technique applied to material picked out under the microscope.

In addition to α and β they noticed, frequently bordering the needles of β , a fine band of a substance with the characters of polianite.

Concerning the relationship of the two constituents α and β to each other, the authors consider that the data suggest that constituent β separated in constituent α after the crystallisation of the latter; and that if this be the case it might be possible, at a certain temperature, to obtain a homogeneous compound. An experiment to test this possibility produced at points a partial fusion of the mineral; and after polishing it was found that at such points the 'needles' had disappeared completely, with replacement by an aggregate of anisotropic crystals with the optical properties of constituent α .

Whatever the nature of these two constituents it is clear that this experiment supports the suggestion of Schneiderhöhn and Ramdohr that vredenburgite is a composite substance resulting from the break up of an originally homogeneous mineral on fall of temperature.

In an appendix to their paper (*loc. cit.*, p. 177) Orzel and Pavlovitch mention that Volume I of the German authors' work had appeared during the printing of their own paper, and that the authors thereof had identified the two constituents of vredenburgite as jacobsite and hausmannite. They mention that they had not dared to identify constituent α as jacobsite for the reasons already given, principally its anisotropy. They agree that constituent β exhibits the majority of the characters of hausmannite, but it differs in not being attacked by a saturated solution of SnCl_2 , whilst hausmannite is so attacked. They suggest that this difference might be explained by the presence of foreign materials in the network of hausmannite, modifying its behaviour somewhat to attacking reagents. They reiterate the desirability of resolving the doubtful points by an X-ray study.

The next study to be noticed is that of Dr. J. A. Dunn¹ making use mainly of reflecting powers and etching tests. Whilst the authors noticed above had confined their research to material from Kodur in the Vizagapatam district, Dunn examines both my type material from Garividi in Vizagapatam and Beldongri in the Nagpur district, and also various specimens from Kodur and Beldongri, that, judging from their numbers, appear not to be a part of my original collection, but to be derived from the Geological Survey duplicate collection, and not necessarily examined by myself.

Concerning the Vizagapatam material Dunn notes that in the vredenburgite of Kodur, determined by Christie² and Schneiderhöhn as a mixture of jacobsite and hausmannite, the hausmannite is usually partly altered to psilomelane and pyrolusite, an alteration also noticed by Schneiderhöhn, although he does not name the alteration products. Dunn notes, however, that a polished piece of my type specimen from Garividi contains only a small proportion of such alteration products. Like Schneiderhöhn he finds the Vizagapatam jacobsite to be isotropic, not noticing the anisotropism detected by Orzel and Pavlovitch.

Dunn then examines the Beldongri material. My type specimen, which agrees so closely in chemical composition with the Garividi material, he finds to be a complex mixture of jacobsite, hausmannite, braunite, pyrolusite, and psilomelane, with some quartz. According to him the jacobsite and hausmannite in this specimen do not always show the intergrowth so typical of the Vizagapatam vredenburgite. One of his published photomicrographs (*loc. cit.*, Plate VI, fig. 6), however, shows the typical intergrowth, but also irregular patches of pyrolusite-psilomelane aggregates with what appears to be a reaction rim of braunite separating these aggregates from the vredenburgite, suggesting perhaps that the braunite has been formed from the vredenburgite mixture as an intermediate stage in the alteration into psilomelane and pyrolusite. The other figure in this Plate shows separate patches of hausmannite in jacobsite, the latter containing fine lamellæ, presumably of hausmannite; and the hausmannite patches, which Dunn regards as replacing, show twinning, retaining the direction of the original hausmannite lamellæ in jacobsite.

Combining the information given by Dunn's descriptions and photographs of the polished surfaces of my type material from Garividi and Beldongri, with the fact that on analysis these two specimens gave such very similar results³ for the principal constituents MnO_2 , MnO , and Fe_2O_3 , it seems logical to deduce that these mixtures have been formed by the break-down on change of physical conditions of a pre-existing homogeneous mineral and that the

¹ 'A study of some microscopical aspects of Indian manganese-ores', *Trans. Nat. Inst. Sci. Ind.*, I, pp. 103-124, (1936).

² Dr. Christie in private conversation informs me that he does not accept responsibility for this determination.

³ *Mem. Geol. Surv. Ind.*, XXXVII, p. 44, (1909).

composition of this mineral can be deduced from a study of these analyses. The Beldongri mineral has, judging from Dunn's account, evidently suffered a greater degree of surface alteration of the secondary metamorphic complex than the Garividi mineral, and this deduction agrees with the higher amount of combined water in the Beldongri specimen; whilst the presence of braunite in the Beldongri mineral, as detected by Dunn, is supported by the presence of 0.91 per cent of combined silica as against only 0.20 per cent in the Garividi specimen. It seems evident that we shall be able to secure a better idea of our primary mineral from a study of the Garividi analysis than from the Beldongri analysis.

Whereas the specimen for Beldongri selected by me as the type for analysis agrees so closely chemically with the Garividi mineral and contains a considerable proportion of the characteristic intergrowths of hausmannite and jacobsite, Dunn finds from a study of their polished surfaces that other specimens from Beldongri are much more nearly jacobsite, and he selects two of them for analysis. No. 779 (a) is estimated microscopically to contain a little more than 2 per cent of hematite and less than 0.5 per cent of psilomelane in minute cracks, and this specimen is regarded as the purest Indian jacobsite yet found. The other specimen, 779 (b), was less pure, but was subjected to analysis because the types of jacobsite in (a) and (b) show slight optical differences: (a) is of a darker brownish yellow than (b), and whilst (a) shows a barely perceptible anisotropism, (b) is slightly more anisotropic. The analyses were made by Mr. P. C. Roy.

That these specimens are not examples of vredenburgite is seen at once by comparing Mr. Roy's analyses (*loc. cit.*, p. 108) of specimens 779 (a) and (b) from Beldongri with the type analyses of vredenburgite from Beldongri and Garividi. The percentages of oxides of manganese and iron and of the two metals are compared below:—

Locality ..	Vredenburgite.		Jacobseite.			
	Garividi.	Beldongri.	Beldongri.	Beldongri.	Jakobsberg.	Långban.
No. of specimen.	A. 346 or 18/502.	1080 or 18/293.	779(a)	779(b)	Dana. 1.	Dana. 2.
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
MnO ₂ ..	24.94	23.37	4.82	11.35	4.03	6.96
MnO ..	35.53	38.24	34.61	33.31	20.72	29.93
Fe ₂ O ₃ ..	31.29	28.85	59.31	53.03	68.25	58.39
TOTAL ..	94.81	90.76	98.74	97.69	93.00	95.28
Mn ..	45.62	44.62	29.84	32.96	18.60	27.58
Fe ..	21.90	20.19	41.50	37.125	47.77	40.87
Sp. Gr. ..	4.84	4.74	4.90	4.82	4.75
MgO ..	1.20	0.99	0.12	0.59	6.41	1.68

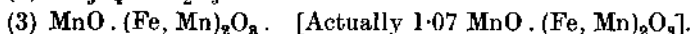
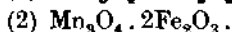
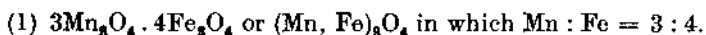
It will be seen that whereas in vredenburgite the percentage of manganese is about twice the percentage of iron, in jacobsite, as exemplified by the mineral from the original locality, namely Jakobsberg in Sweden, the reverse relation holds, whilst in both the purer Beldongri specimens 779 (a) and (b) the iron is substantially in excess of the manganese.

According to Dana magnesia is an important constituent of jacobsite ranging from 6.41 to 0.72 per cent in the analyses quoted.¹ In the Beldongri analyses Nos. 779 (a) and (b) the amounts of MgO are only 0.12 and 0.59 per cent respectively, and this might be thought to militate against this mineral being regarded as jacobsite. As, however, Dunn finds that the mineral agrees optically with jacobsite, it seems simpler to regard the MgO of jacobsite as a non-essential constituent replacing a portion of the MnO.

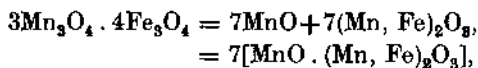
It is evident, therefore, from Dr. Dunn's studies, that some of the specimens from Beldongri registered in the collections of the Geological Survey of India as vredenburgite are jacobsite, and are chemically different from my type specimen from that locality.

As, according to Dana, jacobsite is a deep black mineral but magnetic, and hausmannite is brownish black and, presumably, not markedly magnetic, for this property is not mentioned, it appears that vredenburgite owes its magnetic character to the jacobsite and its bronze tint to the hausmannite. It should therefore be possible to distinguish vredenburgite from jacobsite by colour and from hausmannite by its magnetic property. The streak is not such a useful property, being blackish brown for jacobsite, deep brownish black tending to deep chocolate for vredenburgite, and chestnut-brown for hausmannite.

As there seems to be little doubt that specimen No. 779 is largely jacobsite, it is of interest to see if the analysis of 779 (a) supports this. Assuming 2 per cent of hematite (estimated from the polished surface) and that the combined water is present as H_4MnO_5 , Dr. Dunn calculates three possible formulæ according to three different assumptions:—



Formula (2) is clearly inadmissible, as the oxygen error involved is far too large, as Dr. Dunn recognises; whilst formulæ (1) and (3) are equivalent, for



the ratio of Mn : Fe in the sesquioxide portion being 1 : 6. The small quantity of MgO present could be included in the RO portion without upsetting the formula.

¹ 'System of Mineralogy', 6th Edit., p. 227, (1904).

Dana gives the formulæ of jacobsite and hausmannite as follows :—

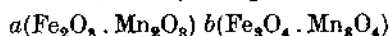
Jacobsite	(Mn, Mg)O . (Fe, Mn) ₂ O ₃ .
Hausmannite	MnO . Mn ₂ O ₃ .

There is thus no doubt that the Beldongri specimen No. 779 (*a*) analysed by P. C. Roy is jacobsite.

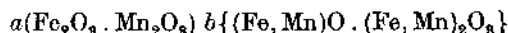
Dunn notes what he regards as the replacement of jacobsite by hausmannite (*loc. cit.*, p. 118). As hausmannite is relatively free from iron this should mean the liberation of iron oxide, which, however, is not described. He suggests that the slight anisotropism of the jacobsite is due to pressure and that the 'inversion' of jacobsite to hausmannite is also possibly a result of metamorphism under increased pressure.

(*b*) *Chemical researches.*

Vredenburgite has also been the subject of investigation by Mr. M. R. Anantanarayana Iyer of Bangalore. In a paper with the title 'An alternative formula for Vredenburgite',¹ read in abstract before the Geology Section of the Indian Science Congress at Bangalore in 1932, Mr. Iyer expressed the view that the formula



represented the composition of one specimen of the mineral, and that a more general form



represented the composition of four specimens including the two described on page 44 of my memoir on manganese, by which Mr. Iyer appears to mean four specimens analysed by him *plus* those of my two specimens. In the discussion on this paper at Bangalore I informed the author that recent work by Dr. Christie had shown that vredenburgite is a mixture of two or more minerals. This caused Mr. Iyer to make a further chemical examination of his four specimens, and the results of this work are given in a paper 'The Formula proposed for the mineral Vredenburgite', presented to the Geology Section of the Indian Science Congress held at Indore in 1936, and published in the *Records, Mysore Geol. Dept.*, XXXIV, pp. 75–84, (1936).² The object of this second investigation was to determine by chemical tests whether vredenburgite consisted of two minerals, as Dr. Christie had determined, or of only one, as proposed in Mr. Iyer's formula of 1932.

The material examined was supplied by the Geological Survey of India, and, besides specimens from Devada (No. 690) and Kodur (Nos. 691 and 692) in the Vizagapatam district, included No. 779 from Beldongri, also investigated by Dr. Dunn. The four analyses, with the two of No. 779 given in Dr. Dunn's paper, are shown below, as regards oxides of manganese and iron, the only constituents (with available oxygen) determined by Mr. Iyer :—

¹ *Proc. 19th Indian Sci. Cong.*, Bangalore, p. 373, (1932).

² For abstract, see *Proc. 23rd Ind. Sci. Cong.*, Indore, p. 247, (1936).

Analyst.	Roy.	Roy.	Iyer.	Iyer.	Iyer.	Iyer.
Locality.	Beldongri.	Beldongri.	Beldongri.	Devada.	Kodur.	Kodur.
No. of specimen.	779 (a).	779 (b).	779.	690.	691.	692.
MnO ₂ ..	4.82	11.35	15.11	25.73	26.26	52.86
MnO ..	34.61	33.31	33.11	30.84	32.06	12.76
Fe ₂ O ₃ ..	59.31	53.03	49.78	39.15	38.15	22.93
TOTAL ..	98.74	97.69	98.00	95.72	96.50	88.55
Mn ..	29.84	32.96	35.19	40.15	41.45	43.28
Fe ..	41.50	37.12	34.82	27.40	26.68	16.03
Molecular ratio						
$\frac{\text{Mn}}{\text{Fe}}$..	0.73	0.90	1.03	1.49	1.58	2.74
Molecular ratio						
$\frac{\text{MnO}_2}{\text{Fe} + \text{Mn}}$..	0.043	0.103	0.137	0.242	0.245	0.566

The molecular ratios Mn : Fe and MnO₂ : Fe + Mn shown above are utilised by Mr. Iyer in his paper, and to help the reader to understand their significance I give below these ratios for the various mineral substances under discussions :—

	Mol. $\frac{\text{Mn}}{\text{Fe}}$	Mol. $\frac{\text{MnO}_2}{\text{Fe} + \text{Mn}}$
Jacobsite, if MnO . Fe ₂ O ₃	0.50	0
Jacobsite, if 3MnO . Mn ₂ O ₃ . 2Fe ₂ O ₃	1.25	0.11
Vredenburgite, if MnO . Fe ₂ O ₃ + Mn ₃ O ₄	2	0.167
Vredenburgite, if $a(\text{Fe}_2\text{O}_3 . \text{Mn}_2\text{O}_3) . b(\text{Mn}_3\text{O}_4 . \text{Fe}_3\text{O}_4)$	1	0.2 (if $a=b$)
Vredenburgite, if 3Mn ₃ O ₄ . 2Fe ₂ O ₃	2.25	0.231
Bixbyite, Fe ₂ O ₃ .Mn ₃ O ₃	1	0.392
Hauemannite, MnO . Mn ₂ O ₃	0.33
My Beldongri specimen	2.25	0.232
My Garividi specimen	2.12	0.235

The method of investigation adopted by Mr. Iyer is to treat each specimen with sodium oxalate and dilute sulphuric acid, twice in the cold and once in a water bath, using different times for the various experiments, and making three experiments on each specimen except his No. 4 (692 above), on which, on account of its greater solubility, only two tests were made. His analytical results show that in each specimen, except his No. 1 (779), there is a selective solution of manganese and of MnO₂ leaving residues with lower Mn/Fe and MnO₂/Fe + Mn ratios than in the original specimen, that is residues with higher iron contents. The author deduces from his data that there is free MnO₂ in all the specimens and consequently that the specimens are not homogeneous

chemically. In fact, he considers that his experimental evidence shows that each of his specimens contains free MnO_2 —ranging from about 2 per cent in No. 1 to about 40 per cent in No. 4—as an impurity present with the characteristic mineral of each specimen, which he considers is represented by the composition of the residue in each case. This latter is a mineral composed of oxides of manganese and iron, exhibiting strong magnetism. This is the mineral vredenburchite according to Mr. Iyer. The proportions of free MnO_2 and of 'vredenburchite' in each specimen is, on this basis, calculated by Mr. Iyer to be as follows:—

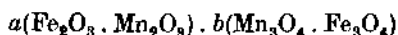
		Free MnO_2 .	'Vredenburchite.'	Total.
		Per cent.	Per cent.	Per cent.
No. 1	..	2.13	96.40	98.53
No. 2	..	4.0	91.90	95.90
No. 3	..	16.40	80.33	96.73
No. 4	..	39.60	48.91	88.51

The difference between the total and 100 represents minor constituents that were not determined.

The ratios Mn/Fe and $\text{MnO}_2/\text{Fe} + \text{Mn}$ in these four residues, regarded as the real vredenburchite, vary between wide limits as is shown by the following figures:—

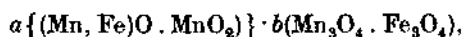
		$\frac{\text{Mn}}{\text{Fe}}$	$\frac{\text{MnO}_2}{\text{Fe} + \text{Mn}}$
No. 1	..	0.98	0.114
No. 2	..	1.41	0.187
No. 3	..	1.18	0.123
No. 4	..	1.16	0.246

For specimen No. 1 (779 from Beldongri), which is the lowest in free MnO_2 , and therefore the purest, according to Mr. Iyer's methods, the author deduces the formula to be



with a Mn/Fe ratio of 1, the ratio $a : b$ being such as to give available manganese peroxide as 13.47 per cent.¹ He also deduces that the two groups of the formula are chemically combined and not a mixture of bixbyite and a spinel.

The 'vredenburchite' of the other specimens, in which the Mn/Fe ratio exceeds unity, can also be made to conform to the above formula by adapting it as follows:—



with the ratios $a : b$ depending on the actual composition.

¹ On Mr. Iyer's data (*l.c.*, p. 78) $a = 22.48$ and $b = 77.52$, or roughly 2 and 7.

Finally, Mr. Iyer suggests that the earlier type formula given above may be taken as the type formula for 'the mineral vredenburgite'.

(c) *Discussion of results.*

This general formula does not, however, cover my original vredenburgite with its empirical formula of $3\text{Mn}_3\text{O}_4 \cdot 2\text{Fe}_2\text{O}_3$. This is not surprising, however, for my formula represents the specimen as a whole, and not a residue after partial solution.

Discussion of Iyer's analyses.

In fact, if one compares the Mn/Fe and $\text{MnO}_2/\text{Fe} + \text{Mn}$ ratios of Mr. Iyer's residual substances from his specimens Nos. 1 to 4 as shown in the tables in his paper with the corresponding ratios for my vredenburgite, shown with the ratios for jacobsite and hausmannite in the table on page 262 it is clear that the residues for which Mr. Iyer has devised his formula cannot be regarded as vredenburgite. The molecular ratio Mn/Fe determined on my Garividi and Beldongri type specimens is 2.12 and 2.25, whilst in Mr. Iyer's four residues the value of this ratio ranges from 0.98 to 1.41, and in his formula the value of this ratio is 1.

The molecular ratio $\text{MnO}_2/\text{Fe} + \text{Mn}$ as determined on my two specimens is 0.235 and 0.232, and for the formula adopted by me is 0.231; whilst the value of this ratio in Mr. Iyer's four residues ranges from 0.114 to 0.246, the last value being on his most impure specimen. Excluding the last value they range from 0.114 to 0.187. The question then arises—if these residues are not vredenburgite, then what are they? The answer appears to be that they are largely jacobsite. This mineral, if free from Mn_2O_3 , and corresponding to the formula $\text{MnO} \cdot \text{Fe}_2\text{O}_3$, would show the following molecular ratios:—

Mn/Fe	0.50
$\text{MnO}_2/\text{Fe} + \text{Mn}$	0

In practice, however, Mn_2O_3 is always present and for the four analyses of jacobsite given on page 259 the ratios are as follows:—

	$\text{MnO} \cdot \text{Fe}_2\text{O}_3$	$\text{MnO} \cdot (\text{Fe}, \text{Mn})_2\text{O}_3$			
		Beldongri 779 (b).	Beldongri 779 (b).	Jakobsberg Dana 1.	Långban Dana 2.
Mn/Fe ..	0.50	0.73	0.90	0.40	0.69
$\text{MnO}_2/\text{Fe} + \text{Mn}$..	0	0.043	0.103	0.039	0.065

The most homogeneous of Mr. Iyer's specimens was that represented by analysis No. 1 of 779 from Beldongri, and this specimen as a whole before treatment, and in residue after treatment, gave the following ratios:—

	As a whole.	Residue.
Mn/Fe ..	1.03	0.98
MnO ₂ /Fe + Mn ..	0.137	0.114

and is evidently very similar to Dr. Dunn's 779 (*b*), which he has shown to be impure jacobsite.

Of Mr. Iyer's other three specimens, the fourth, No. 692 from Kodur, may be omitted from the discussion, as it is admitted to be very impure.

In contrast with specimen No. 1 the remaining specimens, Nos. 2 and 3 from Devada and Kodur respectively, on treatment by Mr. Iyer yielded Mn/Fe and MnO₂/Fe + Mn ratios for residue and solutions that differ considerably from the corresponding ratios for the original specimens, as is illustrated by the following data for No. 3, showing the changes with successive stages of solution :—

	Period of treatment.	Mn.	Fe.	MnO ₂ .	Mn/Fe.	MnO ₂ /Fe + Mn.
Complete specimen.	Before treatment ..	41.45	26.68	26.26	1.58	0.245
Residue ..	5½ hrs. at ordy. temp.	23.78	20.54	9.98	1.18	0.143
Do. ..	20 hrs. at ordy. temp.	18.04	15.46	7.02	1.18	0.133
Do. ..	40 mins. on water-bath ..	7.35	6.31	2.64	1.18	0.123
Complete specimen.	Before treatment ..	41.45	26.68	26.26	1.58	0.245
Solution ..	5½ hrs. at ordy. temp.	17.48	6.20	16.48	2.87	0.442
Do. ..	20 hrs. at ordy. temp.	24.14	11.12	18.80	2.21	0.339
Do. ..	40 mins. on water-bath ..	34.63	20.26	23.40	1.74	0.271

These figures indicate that the original specimen of No. 3 was a mixture of two principal constituents, and that nearly the whole of the more soluble constituent was dissolved relatively quickly leaving a residue with an Mn/Fe ratio of 1.18; and that thereafter, as further portions of the residue were dissolved, the Mn/Fe ratio of the solution was reduced owing to the dilution of material with a Mn/Fe ration of 2.87 by material with a Mn/Fe ratio of 1.18. The explanation of the fall in the MnO₂/Fe + Mn ratio of the solution is of course similar.¹

¹ The variations in the value of this ratio in the residues may lie within the limits of experimental error, as the Mn/Fe ratio is constant. Judging from the corresponding figures for specimen No. 2, however, where the sequence of the MnO₂/Fe + Mn ratio is 0.200, 0.185, 0.187 and that of the Mn/Fe ratio is 1.35, 1.35, 1.41, the more probable interpretation

Mr. Iyer recognises that his specimens are composite, but regards them as mixtures of MnO_2 , as an impurity, and 'vredenburgite'. But it is clear that the solutions contain portions of both substances and also that the residues are not vredenburgite, if my original material is to remain the type. And it also seems clear that the figures after the greatest amount of dissolution give the nearest approach to the composition of the residue, whilst those after the least amount of dissolution give the nearest approach to the composition of the more soluble constituents. For specimens 1, 2, and 3 these values are as follows :—

Number of specimen.	..	Mn.	Fe.	MnO_2 .	Mn/Fe.	$MnO_2/Fe + Mn$.	Probable mineral.
1 (779)—Beldongri	Residue Solution	11.67 17.21	12.11 16.08	4.27 8.34	0.98 1.09	0.114 0.159	Jacobsite Do.
2 (690)—Devada	Residue Solution	10.69 9.37	7.68 4.92	5.39 9.26	1.41 1.94	0.187 0.412	Jacobsite. Hausmannite + MnO_2 .
3 (691)—Kodur ..	Residue Solution	7.35 17.48	6.31 6.20	2.64 16.48	1.18 2.87	0.123 0.442	Jacobsite. Hausmannite + MnO_2 .

The Mn/Fe ratios of the residues in the above table are all possible figures for jacobsite containing a considerable or large amount of Mn_2O_3 replacing Fe_2O_3 (with some surplus MnO_2); whilst in Nos. 2 and 3 the values of the $MnO_2/Fe + Mn$ ratio are possible figures for mixtures of hausmannite with some pyrolusite (see table on page 262) plus some dissolved jacobsite (to account for the iron).

The change of these ratios in the residues and solutions in comparison with those of the original specimens is consistent with the more ready solution of substances higher in manganese than the original substance (*e.g.* hausmannite and pyrolusite), and with the slower solution of a substance lower in manganese and higher in iron (*e.g.* jacobsite).¹ It does not appear, therefore, that Mr. Iyer's analytical results conflict with the view, based on microscopic study, that vredenburgite in its present condition is a mixture of minerals rather than a homogeneous substance.

Recognising, however, that the residues, even after the most prolonged dissolution, still contain an excess of MnO_2 compared with the quantity

is that a small but decreasing proportion of the more soluble, more highly peroxidised, substance remains with the residue until a late stage.

¹ I do not know if the relative rates of solution of pyrolusite, hausmannite, and jacobsite in various solvents have been determined, but Mr. Iyer's work seems to show that with the solvent used jacobsite dissolves the slowest.

appropriate to the jacobsite formula $\text{MnO} \cdot (\text{Fe}, \text{Mn})_2\text{O}_3$ it is desirable to see what is the extent of this departure. The formulæ of jacobsite and hausmannite, accepted as $\text{MnO} \cdot (\text{Fe}, \text{Mn})_2\text{O}_3$ and $\text{MnO} \cdot \text{Mn}_2\text{O}_3$ respectively, are of course of the same type and can be generalised as R_3O_4 . The extent to which Mr. Iyer's specimens depart either in original or after treatment from this general formula can be judged from the following data, in which the empirical formulæ are arranged to show the surplus of RO_2 over R_3O_4 :—

	ORIGINAL SPECIMEN.		AFTER TREATMENT.			
	Composition in terms of R_3O_4 & R_2O_3 .	Composition in terms of R_3O_4 & RO_2 .	Duration of treatment.	Residue.	Duration of treatment.	Solution.
No. 1 (779)— Beldongri.	$3\text{R}_3\text{O}_4 \cdot 2\text{R}_2\text{O}_3$	$4\text{R}_3\text{O}_4 \cdot \text{RO}_2$	48 hrs. at ord. temp.	$5\text{R}_3\text{O}_4 \cdot \text{RO}_2$	24 hrs. at ord. temp.	$15\text{R}_3\text{O}_4 \cdot 5\text{RO}_2$
No. 2 (690)— Devada.	$\text{R}_3\text{O}_4 \cdot 3\text{R}_2\text{O}_3$	$5\text{R}_3\text{O}_4 \cdot 3\text{RO}_2$	40 mins. on water-bath.	$3\text{R}_3\text{O}_4 \cdot \text{RO}_2$	$3\frac{1}{2}$ hrs. at ord. temp.	$5\text{R}_3\text{O}_4 \cdot 2\text{RO}_2$
No. 3 (691)— Kodur.	$5\text{R}_3\text{O}_4 \cdot 13\text{R}_2\text{O}_3$	$23\text{R}_3\text{O}_4 \cdot 13\text{RO}_2$	do.	$11\text{R}_3\text{O}_4 \cdot \text{RO}_2$	$5\frac{1}{2}$ hrs. at ord. temp.	$3\text{R}_3\text{O}_4 \cdot 5\text{RO}_2$
Garividi type	$8\text{R}_3\text{O}_4 \cdot 7\text{R}_2\text{O}_3$	$23\text{R}_3\text{O}_4 \cdot 7\text{RO}_2$				
Beldongri type.	$3\text{R}_3\text{O}_4 \cdot 2\text{R}_2\text{O}_3$	$4\text{R}_3\text{O}_4 \cdot \text{RO}_2$				

These data show that the original specimen, in each case, contains the RO_2 group in excess of the R_3O_4 formula. This may be due to the alteration (or replacement) of hausmannite to psilomelane and pyrolusite as detected by Dunn in both the Beldongri and Kodur specimens studied by Iyer (Dunn did not examine the Devada material). As shown above, Mr. Iyer's experiments show a selective solution of the RO_2 group and a reduction of this in the residue, which could on this interpretation be entirely jacobsite, or jacobsite with some hausmannite.

Now that we have good reason for regarding vredenburgite in its present form as an association of jacobsite and hausmannite with a certain proportion of other minerals in much smaller proportions, such as psilomelane, pyrolusite, braunite, and, in the material from Beldongri, hematite, it seems desirable to reinvestigate the mineralogical composition of the type-specimens as represented by the analyses given on page 44 of my Memoir already referred to. In each case we will assume that the magnesia is in the jacobsite, that the combined silica is due to the presence of braunite, and that the alumina, baryta, surplus lime (after allowing for apatite and calcite), alkalis, and combined water are present in psilomelane, and also, based on Dunn's work, that there is 2 per cent of hematite in the Beldongri mineral. On these assumptions the mineral composition of the two specimens is :—

Discussion of my type analyses.

		Beldongri. 1080 or 18/293.	Garividi. A. 346 or 18/502.
		Per cent.	Per cent.
' Vredenburgite '	75.33	89.13
Braunite	9.12	2.00
Psilomelane	10.16	8.60
Hematite	2.00
Quartz	0.86
Apatite	2.48	0.07
Calcite	0.20
TiO ₂	0.14
S	0.03
As ₂ O ₅	0.01
Moisture	0.18	0.20
		<u>100.34</u>	<u>100.17</u>

I have placed inverted commas about the first item because it has still to be determined whether the term vredenburgite should be applied to the whole of each of these specimens or restricted to the hausmannite-jacobsite intergrowths. If the above mineralogical interpretations are sound, then the composition of the 'vredenburgite' should be susceptible of interpretation in terms of $Mn_3O_4 + MnO \cdot Fe_2O_3$, without knowledge of what proportion of the Mn_3O_4 is hausmannite and what proportion is in the jacobsite. The composition of the 'vredenburgite' in the two analyses corresponds fairly closely to the following:—

Beldongri	3MnO . 2Mn ₃ O ₄ . 3(MnO . Fe ₂ O ₃).
Garividi	3MnO . 12Mn ₃ O ₄ . 13(MnO . Fe ₂ O ₃).

In each case there is a notable surplus of MnO, amounting to 12.97 per cent (on the total analysis) and 3.69 per cent respectively.

A recalculation of the mineral composition on the assumption that psilomelane is absent, and that the Al₂O₃, BaO, and other oxides are present as impurities, shows then a surplus of 5.17 per cent of MnO₂ in the Beldongri specimen, and of 8.27 per cent in the Garividi specimen. Treating this surplus as pyrolusite, the mineral compositions can then be shown as follows:—

		Beldongri. 1080 or 18/293.	Garividi. A. 346 or 18/502.
		Per cent.	Per cent.
' Vredenburgite '	76.37	85.89
Braunite	9.12	2.00
Pyrolusite	5.17	8.27
Hematite	2.00
Quartz	0.86
Apatite	2.48	0.07
Calcite	0.20
Impurities	3.96	3.74
Moisture	0.18	0.20
		<u>100.34</u>	<u>100.17</u>

The composition of the 'vredenburgite', as thus separated from the other constituents of the specimen, is then as follows :—

		Beldongri.	Garividi.
		Per cent.	Per cent.
(Mn, Mg)O . Fe ₂ O ₃	..	38.01	44.28
MnO . Mn ₂ O ₃	..	38.36	41.46
		76.37	85.80

It is, of course, impossible from these data to determine what proportion of the MnO . Mn₂O₃ is associated with the (Mn, Mg)O . Mn₂O₃ as jacobsite, and what proportion is in the form of the mineral hausmannite. If half the MnO . Mn₂O₃ were in the jacobsite then the ratio of jacobsite to hausmannite in the 'vredenburgite' would be roughly 3 : 1 ; any other proportion could of course be selected to suit actual proportions as determined by measurement on a polished surface under the microscope.

It will be seen that the second interpretation of these analyses gives a more satisfactory composition for the 'vredenburgite', in that there is no surplus MnO over the R₃O₄ formula. On the other hand, psilomelane has been shown to be present in these minerals under the microscope. This does not really cause any difficulty, for



so that it would be simple to represent this MnO₂ as psilomelane by utilising sufficient of the 'impurities' in accordance with the general formula R₂MnO₅ adopted for psilomelane in my Memoir on the manganese-ore deposits of India. On the other hand, if the view be adopted that psilomelane is merely a colloidal mixture of oxides of manganese and other substances, there is again no difficulty in regarding a portion or all of the MnO₂, with the 'impurities', as forming psilomelane. Consequently, in the second interpretation the pyrolusite and 'impurities' may be regarded as representing such mixture of psilomelane and pyrolusite as the facts require.

As my pair of type specimens from Beldongri and Garividi respectively yield on the foregoing interpretation such closely concordant analyses and compositions for the 'vredenburgite' portions thereof, it is of interest to submit to similar treatment Mr. Iyer's pair of analyses of specimens Nos. 2 and 3 from the two closely adjoining mines of Devada and Kodur in the Vizagapatam district.

As Mr. Iyer's analyses are only partial, it is not known if any allowance should be made for the presence of braunite, as would be revealed by the presence of combined silica ; but, assuming that all the undetermined constituents can be regarded as 'impurities', mainly available, with surplus MnO₂, to enter into the composition of psilomelane, we can show the mineral composition of the Devada and Kodur specimens as follows :—

	Devada. No. 2 or 690 Per cent.	Kodur. No. 3 or 691. Per cent.
'Vredenburgite':—		
MnO . Fe ₂ O ₃ ..	56.55	55.10
MnO . Mn ₂ O ₃ ..	21.69	24.42
Pyrolusite or surplus MnO ₂	17.48	16.98
'Impurities' ..	4.28	3.50
	100.00	100.00

It will be seen that although the Devada-Kodur pair of specimens, on this interpretation, are as similar mineralogically to each other as are the Beldongri-Garividi pair, yet there are marked differences between the two pairs. The differences and similarities are brought out in the following table:—

	3Mn ₃ O ₄ . 2Fe ₂ O ₃ .	Beldongri.	Garividi.	Devada specimen.	Kodur specimen.	Devada residue.	Kodur residue.
R ₃ O ₄ ..	91.36	74.47	85.89	78.24	79.52	89.87	96.88
Surplus MnO ₂ ..	8.64	5.17	8.27	17.48	16.98	10.13	3.12
	100.00	81.54	85.89	95.72	95.50	100.00(a)	100.00(b)
A. R ₃ O ₄ /surplus MnO ₂ ..	10.57	14.77	10.39	4.47	4.68	8.86	31.06
Molecular:— B. MnO . Fe ₂ O ₃ .	1.00	0.998	1.064	2.61	2.25	2.16	2.43
C. MnO . Mn ₂ O ₃	2.00	1.997	1.893	1.08	1.17	1.20	1.125
D. MnO ₂ /Fe+Mn in R ₃ O ₄ ..	0.167	0.167	0.176	0.093	0.103	0.106	0.098

(a) 25.75 per cent of the original specimen.

(b) 18.96 of the original specimen.

The figures for the residues from the treatment of the Devada and Kodur specimens are also given, from which it is seen that the only important result of the treatment is the reduction in the proportion of MnO₂ surplus to the R₃O₄ formula. Whether we consider either the original specimens of the Devada-Kodur pair or the residues from their treatment, we see that in all the three molecular ratios given in the above table this pair is persistently different from the Beldongri-Kodur pair. In the Devada-Kodur pair the MnO . Fe₂O₃/MnO . Mn₂O₃ ratio is over double, the Mn/Fe ratio is nearly half, and the MnO₂/Fe+Mn ratio is about two-thirds of the corresponding ratios for the Beldongri-Garividi pair.¹

¹ These differences are not due to the fact that in the Beldongri-Garividi pair a certain proportion of the oxides of manganese and iron have been excluded and treated as present in braunite and hematite. If no allowance is made for braunite and hematite, ratios A, B, C, D above become 1.022, 1.007, 1.990, and 0.166, respectively for the Beldongri specimen; and 8.62, 1.127, 1.831, and 0.156 respectively for the Garividi specimen.

That this difference should exist is surprising, for Garividi is close to Kodur and Devada¹ in the Vizagapatam District, whilst Beldongri is some 300 miles away in the Central Provinces.

When the Devada and Kodur specimens were originally named vredenburgite they had not been analysed; now that they have been analysed it is clear that they can no longer be regarded as examples of this mineral substance, if chemical analysis is to be taken as the criterion. It so happens, however, that one of these two specimens, namely that from Kodur, has also been examined microscopically by Dr. Dunn, and found to contain a hausmannite-jacobsite intergrowth similar to that characterising the Garividi specimen,² so that if the name is to be applied to hausmannite-jacobsite intergrowths irrespective of the proportion in which these two minerals are present in the intergrowth, and of the proportion of $\text{MnO} \cdot \text{Fe}_2\text{O}_3$ to $\text{MnO} \cdot \text{Mn}_2\text{O}_3$ in the jacobsite, then chemical composition has to give precedence to structure.

Whether chemical composition or structure is to be the deciding factor in the nomenclature really depends upon the significance of this intergrowth of hausmannite and jacobsite. It is agreed by all who have worked on vredenburgite that this intergrowth must represent the result of the break-down of a once homogeneous mineral, due probably to a change in the physical environment of the primary mineral; for example a fall of temperature, with or without a concurrent fall of pressure, presumably at a time when the mineral and its associated rocks were deeply buried and subject to physical conditions much more severe than those experienced at the surface.

If we can assume that when this break-down of the primary homogeneous mineral took place conditions were such that no removal or addition of constituents occurred, particularly of oxygen, then, allowing for the possibilities of subsequent modifications at or near the surface, such as hydration and oxidation, with formation of such a mineral as psilomelane, we ought to be able to deduce from the present composition of the purest material available the composition of the primary vredenburgite.

Of the two specimens originally investigated by me that from Garividi was undoubtedly the purer, consisting as it did of large crystal units with a noticeable cleavage (or parting) and marked polarity. The greater purity is also indicated by the analyses. Assuming that in both specimens the iron was present as Fe_2O_3 and the manganese as Mn_3O_4 , and assuming trivial errors in the determination of available oxygen, it was found that both the Beldongri and the Garividi analyses corresponded closely to the formula $3\text{Mn}_3\text{O}_4 \cdot 2\text{Fe}_2\text{O}_3$.

¹ See map, *Mem. Geol. Surv. Ind.*, XXXVII, p. 1051.

² *Loc. cit.*, p. 116.

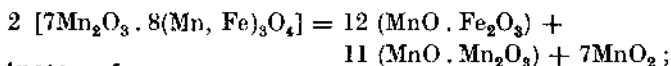
But if the oxygen, manganese, and iron as actually determined be utilised, then the formulæ approximate to—



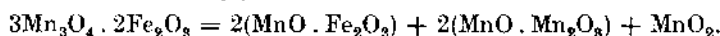
with Mn : Fe in the $(\text{Mn, Fe})_3\text{O}_4$ approximately 1 : 1.²

If one assumes that the primary vredenburgite was a compound including not only the constituents of the hausmannite and the jacobsite, but also the surplus MnO_2 now represented by pyrolusite and psilomelane, then some such formula as those just given may represent the primary mineral, with the sesquioxide group nearly as important as the protosesequioxide group.

The break-down of the Garividi formula would then give some such result as the following :—



Products of break-down of primary vreden-burgite. or if the simplest formula for vredenburgite used in my Memoir be adopted, then the break-down can be shown more simply as follows :—



The composition of a mineral of formula $3\text{Mn}_3\text{O}_4 \cdot 2\text{Fe}_2\text{O}_3$ would be :—

					Per cent.
MnO ₂	25.92
MnO	42.30
Fe ₂ O ₃	31.78
					100.00

and this rearranged to show the composition after break-down in accordance with the foregoing equation gives :—

					Per cent.
MnO . Fe ₂ O ₃	45.88
MnO . Mn ₂ O ₃	45.48
MnO ₂	8.64
					100.00

It is unknown what decides the distribution of $\text{MnO} \cdot \text{Mn}_2\text{O}_3$ between hausmannite and jacobsite, but if half goes to each then the composition of the intergrowth formed by the break-down of $3\text{Mn}_3\text{O}_4 \cdot 2\text{Fe}_2\text{O}_3$ would be :—

¹ There is an error in the Beldongri calculations on page 48 of *Mem. Geol. Surv. Ind.*, XXXVII. The figures for Mn_2O_3 and Mn_3O_4 should read 27.89 instead of 28.23, and 33.54 instead of 34.64.

² 1.218 and 0.957 respectively.

				Per cent.
Jacobsite	MnO . Fe ₂ O ₃ —45.88	}	..	68.62
	MnO . Mn ₂ O ₃ —22.74			
Hausmannite	22.74
Pyrolusite	8.64
				100.00

The composition of jacobsite of the composition shown above would be :—

				Per cent.	Långban.
				Per cent.	Per cent.
MnO	30.82	}	54.80
Mn ₂ O ₃	22.87		
Fe ₂ O ₃	46.31		43.85
MgO		0.94
SiO ₂ and CaO		1.15
				100.00	100.74

The composition of the second Långban analysis in Dana is placed alongside for comparison.

It seems clear from the evidence of the microscope that vredenburgite in its present form is characteristically and mainly an intergrowth of hausmannite and jacobsite, with the latter mineral predominating. It seems equally clear from the chemical side that both my original vredenburgite and also the material examined by Mr. Iyer, together with the residues from their chemical treatment, contain MnO₂ in excess of that required for the hausmannite-jacobsite intergrowths, which should conform to the general formula RO . R₂O₃ or R₃O₄. Such surplus MnO₂ is at least in part present in the form of visible psilomelane and pyrolusite, of which the former may be held to be due to later oxidation (Dunn, *e.g.* describes the replacement of hausmannite by psilomelane). Orzel and Pavlovitch have recorded, however, that in addition to the α and β constituents of vredenburgite there is also frequently a fine band of a substance with the characters of polianite bordering the needles of β (*i.e.* of hausmannite). There appears to be no evidence that this supposed polianite is later in age than the two principal constituents of the intergrowth; and we seem here to have evidence of the existence of the surplus MnO₂ required by the break-down equation given above. As, however, such surplus MnO₂ is not always observed as an apparently original constituent of the intergrowth, and as the amount of surplus MnO₂ required for a mineral of original composition 3Mn₃O₄ . 2Fe₂O₃ is only 8.6 per cent, it is also possible that within small but unknown limits such surplus MnO₂ may remain latent in solid solution in the hausmannite-jacobsite intergrowth. This possibility might account for the fact that even after the most severe treatment Mr. Iyer's residues still contain a surplus of MnO₂ over the R₃O₄ formula. It might also account for

anisotropism in some of the jacobsite. In the Beldongri material there is clear evidence of the presence of other minerals than hausmannite and jacobsite, e.g. pyrolusite-psilomelane aggregates in figure 6 of Dr. Dunn's Plate VI.

The evidence is admittedly incomplete, but on the whole it seems necessary to adopt the view that the primary vredenburchite, before the assumed break-down with change of conditions, had not the simple R_3O_4 formula, but in addition contained surplus R_2O_3 ,¹ as is shown by the simplest formula adopted by me for the type material. In fact, on this interpretation, the primary mineral was not a plain spinellid. Had it been so there seems to be no reason why, on change of physical conditions, the primary mineral should have separated into hausmannite and jacobsite, unless the different crystal symmetry at ordinary temperatures, one being tetragonal and the other cubic, should be sufficient cause. It seems necessary in any case to assume that the association of this surplus R_2O_3 with R_3O_4 was only stable at a relatively high temperature (and/or pressure), and that on fall of temperature (and/or pressure), the Mn_2O_3 separated into MnO_2 , and Mn_3O_4 , with the occasional separation of surplus Fe_2O_3 as hematite (cf. Dunn's Plate VI, figure 4).

On this basis we may accept the primary vredenburchite of Beldongri and Garividi as a mineral of the formula $3Mn_3O_4 \cdot 2Fe_2O_3 (=4R_3O_4 \cdot RO_2)$, which has, on lowering of temperature (and/or pressure), split up into a secondary vredenburchite consisting of a predominant hausmannite-jacobsite intergrowth, with some surplus MnO_2 , now represented by visible pyrolusite and psilomelane, or by surplus MnO_2 in solid solution in the intergrowth.

Attention must be drawn, however, to an analogous substance from Jakobsberg, Sweden,² which gave an analysis closely resembling my vredenburchite analyses, but in which the proportions of oxides can be interpreted as agreeing closely with the ratio $RO : R_2O_3$, so that no surplus MnO_2 is present. This Jakobsberg mineral also shows a lamellar intergrowth assumed to be a spinel and hausmannite. The proportions of MnO , MnO_2 , Fe_2O_3 , Mn , and Fe may be compared with those for my Beldongri and Garividi specimens as below:—

			Beldongri.	Garividi.	Jakobsberg.
MnO_2	23·67	24·94	23·17
MnO	38·24	38·53	42·65
Fe_2O_3	28·85	31·29	30·68
			90·76	94·86	96·50
Mn	44·62	45·62	48·20
Fe	20·19	21·90	21·48

The Jakobsberg mineral has a Mn/Fe ratio of 2·24, and a molecular ratio of $MnO_2/Fe+Mn$ of 0·211, both close to those for vredenburchite of formula

¹ $R_3O_4 + RO_2 = 2R_2O_3$.

² K. Johansen, *Zeit. f. Krist.*, Vol. 68, p. 116, (1928).

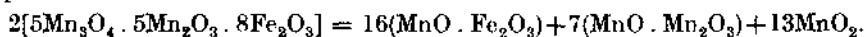
$3\text{Mn}_3\text{O}_4 \cdot 2\text{Fe}_2\text{O}_3$. The second ratio is lower than for my two specimens due to the substantially higher MnO in the Jakobsberg mineral.

On referring to the table on page 270 it seems, at first, that we cannot admit the Devada and Kodur specimens to be vredenburgite because of the great departure of the molecular ratios B, C, and D, from those of the type vredenburgite of Beldongri and Garividi. The reason for these differences is the much higher proportion of MnO . Fe_2O_3 in the Devada-Kodur pair than in the type mineral, affecting ratio B, and consequently ratios C and D, which depend on B. It is evident that the primary mineral of Devada and Kodur before break-down could not have had a formula even approximating to $3\text{Mn}_3\text{O}_4 \cdot 2\text{Fe}_2\text{O}_3$, owing to the much higher percentage of iron; and that if we were dealing with the pure minerals in a form that we could handle we should require different names for the two forms (the Devada-Kodur pair and the Beldongri-Garividi pair), in the same way as the various members of the spinellid group of minerals have different names to indicate their different compositions, e.g. magnetite, manganomagnetite, and jacobsite. In fact it seems necessary to propose a name for the mineral represented by the two specimens from Devada and Kodur analysed by Mr. Iyer. The name of the village Kodur has already been used for the rock series with which the manganese-ore deposits of this part of India are associated; it seems suitable therefore to use the name of the other locality and to call this mineral *devadite*.

To obtain an approximate idea of the composition of the primary devadite we must assume that the constituents not estimated in Mr. Iyer's analyses Nos. 2 and 3 represent impurities, and as the two analyses are so closely similar we may take an average of the two:—

	Devada.	Kodur.	Mean.	Molecular ratios.
	Per cent.	Per cent.	Per cent.	
MnO ₂ ..	25.73	26.26	26.00	$\text{Mn}_3\text{O}_4 = 1.442 = 5 \times .0284$
MnO ..	30.84	32.09	31.46	$\text{Mn}_2\text{O}_3 = 1.547 = 5 \times .0309$
Fe ₂ O ₃ ..	39.15	38.15	38.65	$\text{Fe}_2\text{O}_3 = 2.416 = 8 \times .0302$

This gives an approximate formula of $5\text{Mn}_3\text{O}_4 \cdot 5\text{Mn}_2\text{O}_3 \cdot 8\text{Fe}_2\text{O}_3$. The break-down of this primary devadite into the secondary intergrowth can be represented as follows:—



This corresponds to the following composition after break-down:—

	Per cent.
MnO . Fe_2O_3	57.48
MnO . Mn_2O_3	24.93
MnO ₂	17.59
	<u>100.00</u>

Since we have found it necessary to introduce a separate name for the Devada-Kodur pair of specimens it is desirable to set out side by side the available data for vredenburgite and devadite in order to display the similarities and differences. This is done herewith:—

	Vredenburgite.	Devadite.
Formula (primary mineral) ..	$3\text{Mn}_3\text{O}_4 \cdot 2\text{Fe}_2\text{O}_3$	$5\text{Mn}_3\text{O}_4 \cdot 5\text{Mn}_2\text{O}_3 \cdot 8\text{Fe}_2\text{O}_3$
Formula (secondary aggregate) ..	$4\text{R}_3\text{O}_4 + \text{MnO}_2$	$23\text{R}_3\text{O}_4 + 13\text{MnO}_2$
Chemical analysis (formula) :—	Per cent.	Per cent.
MnO ₂	25.92	27.06
MnO	42.30	33.13
Fe ₂ O ₃	31.78	39.81
	100.00	100.00
Mn	49.16	42.77
Fe	22.24	27.87
Mineral analysis (formula) :—		
MnO . Fe ₂ O ₃	45.88	57.48
MnO . Mn ₂ O ₃	45.48	24.93
MnO ₂	8.64	17.59
	100.00	100.00
R ₃ O ₄ /MnO ₂	10.57	4.68
	Molecular.	Molecular.
MnO . Fe ₂ O ₃ /MnO . Mn ₂ O ₃	1.00	2.29
Mn/Fe in primary mineral	2.25	1.56
Mn/Fe in R ₃ O ₄	2.00	1.09
MnO ₂ /Fe + Mn in primary mineral	0.231	0.244
MnO ₂ /Fe + Mn in R ₃ O ₄	0.167	0.101

It is evident from a study of these figures that the chief difference between vredenburgite and devadite is the great difference between the ratio of MnO . Fe₂O₃ to MnO . Mn₂O₃, this being unity for vredenburgite and about 2½ for devadite. It is also evident that future research may lead to the discovery of material with intermediate values for this ratio and that it will then be necessary to decide whether to introduce still another name or preferably to partition the intervening field between vredenburgite and devadite.

Although chemical facts appear to require two names as proposed, yet without chemical examination it is not on present data possible to distinguish devadite from vredenburgite. Consequently it will be necessary to continue to use the term vredenburgite in a general sense as the name of a group of substances, recognising that on closer examination

The vreden-
burgite group of
mineral sub-
stances.

some of the substances so named will prove to be different from the original vredenburgite, *i.e.* from vredenburgite in its restricted sense.¹ We shall also be able to continue to speak of the vredenburgite type of structure or inter-growth irrespective of the actual proportions of the constituent hausmannite and jacobsite.

Whilst I have given above special formulæ for the original vredenburgite and for devadite, a general formula can be devised to cover them both, and also related substances. This formula is



a formula, which is obviously related to the general formula proposed by Mr. Iyer (see page 263).

The formulæ of vredenburgite and devadite have been discussed on the assumption that the MnO_2 (or a portion of it) must be regarded as one of the products of break-down of the primary mineral. This is based on the inherent assumption either that the MnO_2 was a part of the primary mineral or that the surplus oxygen was in some way occluded in the primary mineral, and in the latter case participated in the break-down of the primary mineral with production of free MnO_2 . Such a case would be analogous to those discussed by me some years ago in connection with the formation in the Central Provinces of deep-seated manganese-oxide ores from manganiferous silicates and of deep-seated calcite from calc-silicate minerals.² Should, however, later research show that all the surplus MnO_2 in these secondary vredenburgitic aggregates is to be attributed to surface oxidation, without selective attack upon either of the principal minerals of the assemblage, then taking the figures from the table on page 276) and excluding the surplus MnO_2 , and taking also the analysis of the substance from Jakobsberg, Sweden, referred to on page 274, we may compare the ratios of $\text{MnO} \cdot \text{Fe}_2\text{O}_3$ and $\text{MnO} \cdot \text{Mn}_2\text{O}_3$ as follows:—

		Jakobsberg 'mineral'	Vredenburgite.	Devadite.
$(\text{Mn}, \text{Mg})\text{O} \cdot \text{Fe}_2\text{O}_3$..	43.35	45.88	57.48
$\text{MnO} \cdot \text{Mn}_2\text{O}_3$..	51.52	45.48	24.93
Ratio $\frac{\text{Fe}_2\text{O}_3}{\text{Mn}_2\text{O}_3}$..	0.85	1.00	2.29

The formula for the primary mineral is then in each case $\text{MnO} \cdot (\text{Fe}, \text{Mn})_2\text{O}_3$, the differences lying in the ratio of Fe_2O_3 to Mn_2O_3 . The ratio for the Jakobsberg substance is sufficiently close to that for vredenburgite for the primary Jakobsberg mineral to be included under vredenburgite.

¹ If these minerals were commoner and the matter, therefore, of more importance it would be easy to remove the ambiguity arising from the use of the term vredenburgite in both an extended and a restricted sense, by retaining the term in the extended sense that it has acquired and proposing a special term for the original mineral; *garividite* would then be appropriate. This refinement seems unnecessary, however, at present.

² 'On the Formation in Depth of Oxidized Ores and of Secondary Limestones', *Comptes Rendus, XII, Congrès géol. intern. Toronto*, pp. 271-274, (1913).

The essential difference between jacobsite and the vredenburgitic minerals then lies in the low Mn_2O_3 contents of jacobsite.

Postscript to Section II.

Since this paper was written, I have received from Mr. M. R. Anantanarayana Iyer a copy of a later paper entitled 'A Graphical Representation of the Composition of some Manganese minerals including a discussion of the nature of Vredenburgite', *Rec. Mys. Geol. Dept.*, XXXV, pp. 73-85, (1937). Some additional analytical results are given, reinforcing the author's previous work. Taking account of the microscopical demonstration of other authors that vredenburgite contains hausmannite lamellæ, Mr. Iyer treats this as an intergrowth not with jacobsite, but with an assumed definite compound vredenburgite, and in his covering letter to me Mr. Iyer writes that from the results discussed in the two papers published he finds it difficult to believe that some specimens of vredenburgite do not contain a compound whose molecule contains more oxygen in it than is present in a spinel mineral containing manganese and iron.

As seen above I have accepted the surplus MnO_2 as having probably been an inherent part of the presumed primary vredenburgite, and treat the secondary vredenburgite (and devadite) as intergrowths of jacobsite and hausmannite, with the surplus MnO_2 not required by the spinel formula now appearing as pyrolusite or psilomelane, or possibly sometimes concealed in solid solution.

Mr. Iyer gives an ingenious graph showing the position of various manganese and iron oxide minerals. My two vredenburgite analyses fall on the line ON in his group representing the formula $aFe_2O_3 \cdot bMn_3O_4$, and his two analyses of what I now call devadite fall on the line MP representing the formula $aFe_3O_4 \cdot bMn_2O_3$. Using the general formula $aMn_3O_4 \cdot b(Mn,Fe)_2O_3$ for the vredenburgite group adopted by me, it is not surprising to find that the spots representing these four analyses in Mr. Iyer's diagram fall roughly on a straight line with bixbyite, $Fe_2O_3 \cdot Mn_2O_3$, which might then be regarded as the end member of the vredenburgite series in which $a = \text{zero}$.

III. SITAPARITE.

Sitaparite has also been studied in polished and etched surfaces by Christie, Schneiderhöhn, and their results confirmed by Ramdohr, and an account of this research, based in a study both of material from Sitapar, the original Indian locality, and on specimens from Postmasburg in South Africa, is given in the work already cited.¹ According to Schneiderhöhn and Ramdohr sitaparite shows close resemblances both to braunite and to jacobsite, being closer to the former. Under the ore-microscope sitaparite is distinguished from braunite by its somewhat yellower tint and slightly greater

Christie, Schneiderhöhn, and Ramdohr.

¹ 'Lehrbuch der Erzmikroskopie', pp. 572-574, (1931).

brightness, and greater degree of etching with hydrofluoric acid. Both sitaparite and braunite are found to be weakly anisotropic. No cleavages are seen. The chief difference is the complicated lamellar twinning seen in both Indian and South African sitaparite. From jacobsonite, which, like sitaparite, is olive-yellow towards braunite and also magnetic¹, sitaparite is distinguished by anisotropism and somewhat greater hardness. Although the crystal system of sitaparite is unknown, it is regarded as probably tetragonal like braunite, and with the same lattice.

The authors point out that as the occurrences of sitaparite are in manganese-ore deposits formed by the regional or contact metamorphism of sedimentary manganese-ore deposits the mineral is probably more widely spread than is at present known. It is also suggested that the somewhat complicated formula for sitaparite adopted by me may be interpreted as representing an original psilomelane gel that on metamorphism has crystallised in the braunite lattice. This is, of course, only surmise, as it is not known that sitaparite and braunite do possess the same lattice.

Professor Schneiderhöhn also discusses sitaparite in a paper on the manganese-ores of Postmasburg in South Africa.² In these ores, based on his microscope studies, he recognises various stages of past metamorphic history, as shown in the following statement (retaining only the ore minerals):—

		Manganese and iron minerals.
Diaphthoretic and sub-recent to recent weathering products.		Psilomelane. Pyrolusite. Limonite. Polianite II.
Metamorphic paragenesis	Second stage First stage	Sitaparite. Braunite-hematite.
Pre-metamorphic remains	Archo-metamorphic ³ minerals and diagenesis.	Polianite II. Manganite.
	Primary minerals.	Not received (probably pyrolusite psilomelane, limonite).

¹ I find sitaparite to be much less strongly magnetic than vredenburghite, and therefore presumably than jacobsonite to which vredenburghite appears to owe its strongly magnetic property. Also braunite is weakly but distinctly magnetic. See *Mem. Geol. Surv. Ind.*, XXXVII, p. 63, (1909).

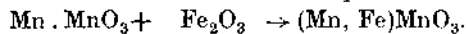
² 'Mineralbestand und Gefüge der Manganerze von Postmasburg, Griqualand West, Südafrika', *Neues Jahrb. f. Mineralogie, etc.*, Beilage-Band 64, Abt. A (Brauns-Festbuch), pp. 701-726, (1931).

³ F. Rinne's term to describe the commencement of metamorphic alteration and its resultant minerals, *loc. cit.*, p. 704.

From the study of the sitaparite of this locality it is often seen that a large idiomorphically bounded crystal has broken down into a number of irregularly bounded units of varied orientation with lamellar structures recalling the twinning lamellæ of leucite: and the conclusion is drawn that sitaparite represents the product of enantiomorphic alteration of a cubic or tetragonal mineral stable at a higher temperature into a tetragonal or rhombic mineral stable at a lower temperature. Crystals with zonal structure are also found, and the shells are probably not all of the same composition. An outer shell of braunite is not uncommon. Inclusions of hematite are also present, often as relict structures cutting through the crystals. On the other hand lamellæ of sitaparite occur in braunite and are regarded not as the result of the breaking down of a pre-existing mineral, but as due to parallel growth. The braunite also contains specular hematite zonally arranged. The hematite of these ores is regarded as contemporaneous with the braunite.

Concerning the relationship of sitaparite to braunite and hematite Schneiderhöhn finds that in the Postmasburg ores sitaparite is younger than braunite and grows idiomorphically therein, the hematite included in the braunite largely disappearing in the process. The author concludes, therefore, that sitaparite represents a higher stage in the metamorphism of braunite, rendered possible at higher temperatures and pressures in the presence of hematite, thus:—

Braunite + Hematite \rightarrow Sitaparite.



Orcel and Pavlovitch (*loc. cit.*, p. 158) have also studied sitaparite, and their results are given in the paper already cited. The material used was that of Sitapar only. The only difference between the results of their work and that of

**Orcel and
Pavlovitch.**

Schneiderhöhn and Ramdohr is that they find sitaparite to be isotropic and therefore to belong to the cubic system, whilst cleavages were detected. The anisotropy noticed by Schneiderhöhn and Ramdohr may be due to strain; and it may be recalled that the α constituent of vredenburgite was found to be anisotropic by Orcel and Pavlovitch and, as jacobsite, isotropic by Schneiderhöhn and Ramdohr.

Dunn (*loc. cit.*, p. 111) finds the sitaparite of Sitapar to be so weakly anisotropic as to be regarded as isotropic at times. He also discusses (*loc. cit.*, pp. 114, 115) the mutual relationships of the sitaparite-braunite ores of Sitapar. He finds that the braunite veins and replaces the sitaparite; in ore from Gowari Warhona in the same district, the braunite may be replacing the sitaparite, but the relation is more akin to that of simultaneous intergrowth. Dunn considers (p. 121) that at least a portion of the braunite in these Chhindwara ores is later than the sitaparite (and hollandite), and that the formation of this later braunite must be regarded as due to regressive metamorphism. As the direction of change noticed in the Indian ores is the reverse of that observed by Schneiderhöhn

J. A. Dunn.

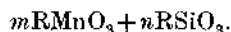
in the Postmasburg ores, Dunn looked for evidence of the reversal of Schneiderhöhn's equation given above. No hematite was found, but, as Dunn remarks, the Fe_2O_3 might possibly have been absorbed by the hollandite.

Perhaps I may contribute to this discussion on the relationship of braunite to sitaparite.

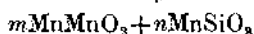
Two comments may be made on the simplified formula assigned by Schneiderhöhn to sitaparite. It is true that by neglecting about 13 per cent of its constituents my formula for sitaparite (see page 254) can be simplified to $9\text{Mn}_2\text{O}_3 \cdot 4\text{Fe}_2\text{O}_3$

and the latter rearranged as $(\text{Mn}_5\text{Fe}_8)(\text{MnO}_3)_{13}$ or $(\text{Mn, Fe})\text{MnO}_3$. But this involves regarding the whole of the very considerable amount of iron (19.32 per cent in the specimen analysed) as present in the ferrous condition in the presence of peroxidised manganese.

The other comment applies to the formula assigned to braunite. Many years ago I went very carefully into the composition of braunite and in particular into the point whether silica is an essential constituent.¹ One conclusion was that whilst it seems necessary to recognise the possible existence in Nature of a mineral with a composition corresponding to the formula Mn_2O_3 , such mineral must be extremely rare (*loc. cit.*, p. 64). A second conclusion was that braunite is probably an isomorphous mixture of manganites of the general formula RMnO_3 and of metasilicates of the general formula RSiO_3 , giving the formula



Further, as in all the analyses considered the ratio of $m : n$ lies between the limits of 3 : 1 and 4 : 1, and as manganese is the predominant basic constituent, the formula may be stated more definitely as



with the ratio $m : n$ usually between the limits of 3 : 1 and 4 : 1 (*loc. cit.*, p. 67).

As the original braunite of Elgersburg in Thuringia and of St. Marcel in Piedmont each contain high silica (8.63 and 7.70 per cent respectively corresponding to ratios of $m : n = 7 : 2$ and $4 : 1$) it must be emphasised that the correct formula for braunite must be one allowing for the presence of a substantial amount of silica. Mn_2O_3 is an exceptional mineral and should its existence be satisfactorily proved it should be given a separate name.

Further, in the Memoir cited, an analysis is given of braunite from Sitapar, showing 8.52 per cent of SiO_2 , giving $m : n = 15 : 4$. It seems clear then that Schneiderhöhn's equation, if applied to Sitapar minerals, would have to show a liberation of free silica in one direction and an absorption in the other. As no analysis appears to have been published it is not known whether the braunite of Postmasburg contains silica or not, and consequently whether Schneiderhöhn's equation in its present form applies even there. Judging from the analyses

¹ *Mem. Geol. Surv. Ind.*, XXXVII, pp. 63-77, (1909).

of the ores as exported, which show percentages of silica comparable with those of Indian ores, it seems likely that the South African braunite is a normal one with substantial amounts of silica.

As Dr. Dunn has found that some of the Sitapar braunite has been formed by the replacement of sitaparite, it is of interest that both minerals contain notably high amounts of lime: 4.28 per cent in the braunite and 6.14 per cent in the sitaparite.

When in South Africa in 1929 I met Dr. Schneiderhöhn at Kimberley during one of the excursions of the International Geological Congress, and he informed me then that he had found sitaparite in the ores of Postmasburg. At the end of the Congress excursions I returned to Kimberley specially to visit Postmasburg, and was able to verify for myself the presence of sitaparite in this field and to collect specimens. At the time it appeared to me that the tint of the sitaparite of Postmasburg was less bronze-like than that of Sitapar, though showing a distinct yellowish cast as compared with the other minerals in the ores. This indicated some variation from the composition of the Indian sitaparite; but as my collection of manganese-ores was unfortunately lost in transit, I was not able to test this point.

As Dr. Schneiderhöhn's micro-photographs appear to justify his conclusion that at Postmasburg braunite and hematite have together yielded sitaparite, and as the liberation of SiO_2 has not been noticed as accompanying this process, we must assume that the liberated silica has been removed in solution from the scene of reaction, or less probably (see above) that the braunite of Postmasburg is one of those rare examples of braunite corresponding to the formula Mn_2O_3 without MnSiO_3 in isomorphous admixture.

It appears therefore that careful chemical analysis of both the braunite and the sitaparite of Postmasburg is desirable.

It will be seen from the above that there is doubt about the crystal system of sitaparite. When originally described by me no crystals had been found, but I suggested that the almost perfect cleavage planes might be octahedral (*loc. cit.*, p. 49). Schneiderhöhn and Ramdohr consider that the mineral was originally either tetragonal or cubic, more probably the former on account of its anisotropism; whilst Orceel and Pavlovitch regard it as cubic on account of its isotropism. Specimens from Sitapar were later obtained by me showing crystal faces suggesting the octahedron: but these faces were not sharp enough for crystallographic study.

At Postmasburg also I collected specimens showing octahedral crystals in cavities, but these were in the lost collection. So it still remains unknown whether these faces belong to the cubic octahedron or to the tetragonal pyramid.

IV. SUMMARY.

(a) *Vredenburgite and devadite.*

In this paper an account is given of the micrographic work on vredenburgite done of recent years by Christie, Schneiderhöhn and Ramdohr, Orceel and

Pavlovitch, and Dunn, and the chemical work by Anantanarayana Iyer. By combining these results with those originally obtained by myself, it proves possible to make suggestions concerning the composition and nomenclature of vredenburgite.

2. Vredenburgite in its present form is a composite substance, characterised chiefly by a microscopically visible intergrowth of hausmannite and jacobsite, the latter predominating. In addition there is usually, associated with this intergrowth, pyrolusite or psilomelane, or both. In any case chemical analysis always reveals the existence of a surplus of MnO_2 over the general formula R_3O_4 of the hausmannite-jacobsite intergrowth, so that when such surplus MnO_2 is not recognisable as a separate mineral it may be assumed to be included, possibly in solid solution, in the visible minerals of the intergrowth.

3. It is probable that vredenburgite in its present form is the result of the breakdown, on amelioration of metamorphic conditions (*e.g.* falling temperature and/or pressure), of an original homogeneous mineral, to which the term *primary vredenburgite* may be applied.

4. Assuming that the surplus MnO_2 in the *secondary vredenburgite* of our collections has, at least in part, been liberated on the breakdown of the primary vredenburgite, it seems correct to utilise the results of the chemical analysis of our secondary vredenburgites, after allowing for impurities and surplus minerals to deduce the composition of the primary vredenburgite. On this basis slightly differing formulæ result for the type specimens from Beldongri and Garividi, but they are sufficiently close to the simplest formula already proposed in my Memoir on the manganese-ore deposits of India, namely $3\text{Mn}_3\text{O}_4 \cdot 2\text{Fe}_2\text{O}_3$, for the latter to be adopted.

5. From this primary vredenburgite the secondary vredenburgite of our specimens is assumed to have been formed according to the following equation:—



the right-hand side of the equation corresponding to the following composition:—

				Per cent.
$\text{MnO} \cdot \text{Fe}_2\text{O}_3$	45.88
$\text{MnO} \cdot \text{Mn}_2\text{O}_3$	45.44
MnO_2	8.64
				100.00

6. Taking $\text{MnO} \cdot (\text{Fe}, \text{Mn})_2\text{O}_3$ as the formula of jacobsite and $\text{MnO} \cdot \text{Mn}_2\text{O}_3$ as that of hausmannite, it is obviously impossible to allocate the $\text{MnO} \cdot \text{Mn}_2\text{O}_3$ between the jacobsite and the hausmannite, except on the basis of actual measurement of the areas occupied by the two minerals as shown on polished

surfaces. These surfaces show that the jacobsite is always largely predominant over the hausmannite. If we allocate the $\text{MnO} \cdot \text{Mn}_2\text{O}_3$ equally between the two minerals, then we have a ratio of jacobsite to hausmannite of about 3 to 1, and the jacobsite has a composition agreeing roughly with that of one of the Långban analyses. Actually, judging from the published figures, the proportion of jacobsite is usually greater than this.

7. If we are correct in treating surplus MnO_2 as a part of the primary vredenburgerite, then the latter was not a plain spinellid, and the breakdown, on lowering of the metamorphic conditions, may be due to the rejection of this surplus; and the separation of the remaining R_2O_4 into jacobsite and hausmannite may be due to the existence of a limit to which $\text{MnO} \cdot \text{Fe}_2\text{O}_3$, the fundamental jacobsite, can retain $\text{MnO} \cdot \text{Mn}_2\text{O}_3$ in isomorphous association at lower temperatures and pressures, and to the fact that under ordinary conditions $\text{MnO} \cdot \text{Mn}_2\text{O}_3$ as hausmannite possesses tetragonal symmetry as opposed to the cubic symmetry of jacobsite.

8. Should evidence ever be forthcoming to show that the surplus MnO_2 of secondary vredenburgerite is all of later origin, so that the primary mineral was a spinellid in composition, then the breakdown on amelioration of conditions can be interpreted as due to the separation of tetragonal hausmannite from cubic jacobsite, due to immiscibility under these lower conditions.

9. The purest available specimen of vredenburgerite is my type material from Garividi, which shows large crystal units with well-developed 'cleavage' planes, these being presumed to be pseudomorphs after the crystal units of the primary mineral, and not units of the present intergrowth.

10. The cause of the magnetic properties of the secondary vredenburgerite is, of course, the jacobsite. The deep brownish black to deep chocolate streak of vredenburgerite is derived from the blackish brown streak of jacobsite and the chestnut-brown streak of hausmannite.

11. Of the specimens investigated chemically by Mr. Iyer, two, from Devada and Kodur respectively, gave analytical results closely concordant with each other, but differing widely in composition from the Beldongri-Garividi type pair. The principal difference lies in the ratio of $\text{MnO} \cdot \text{Fe}_2\text{O}_3$ to $\text{MnO} \cdot \text{Mn}_2\text{O}_3$, which is 2.29 in the Devada-Kodur pair against 1.00 in vredenburgerite of composition $3\text{Mn}_3\text{O}_4 \cdot 2\text{Fe}_2\text{O}_3$. This difference affects also Mn/Fe ratios and the ratio of MnO_2 to $\text{Fe} + \text{Mn}$. On the other hand the specimens exhibit the physical properties of vredenburgerite, and the one microscopically examined (Kodur) shows the hausmannite-jacobsite intergrowth.

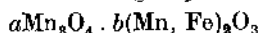
Whilst, therefore, the Devada-Kodur pair must be accepted as belonging to the vredenburgerite group, yet a separate name seems necessary to prevent confusion. The name *devadite* is proposed.

12. The principal chemical differences between vredenburgerite and devadite are shown on page 276. They may be summarised in the following formulæ and ratios:—

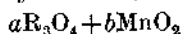
	Vredenburgite.	Devadite.
Primary mineral	$3\text{Mn}_3\text{O}_4 \cdot 2\text{Fe}_2\text{O}_3$	$5\text{Mn}_3\text{O}_4 \cdot 5\text{Mn}_2\text{O}_3 \cdot 8\text{Fe}_2\text{O}_3$
Secondary aggregate	$4\text{R}_3\text{O}_4 + \text{MnO}_2$	$23\text{R}_3\text{O}_4 + 13\text{MnO}_2$
Mn/Fe of R_3O_4	2.00	1.09

Roughly speaking vredenburgite is the high-manganese member of the series and devadite the high-iron member. Should intermediate members of the series be subsequently found they should be termed vredenburgite or devadite according to their chemical affinity.

13. As a general formula for the group, we may adopt



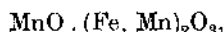
if we are referring to the primary mineral; or



if referring to the secondary aggregate.

14. The structure of both secondary aggregates may be appropriately referred to as the *vredenburgite structure*.

15. Should subsequent research show that the MnO_2 of the secondary aggregates is additional and not proper thereto, then the formulæ of primary vredenburgite and devadite both become

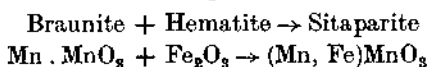


with the ratio of Fe_2O_3 to Mn_2O_3 ranging from unity for primary vredenburgite to $2\frac{1}{2}$ for primary devadite, the ratios for hausmannite being zero and for jacobsite much higher than for devadite (16.7 per Damour's type specimen).

(b) *Sitaparite*.

16. An account is also given of the micrographic work by the same authors, upon sitaparite, both from its original locality Sitapar in the Chhindwara district in India, and from the Postmasburg field in South Africa.

17. Schneiderhöhn's work shows a passage of braunite plus hematite into sitaparite, and the following is suggested as the type of reaction:—



As normal braunite contains from 8 to 10 per cent of SiO_2 as MnSiO_3 , silica should appear on the right side of the above equation. In its absence it must be presumed either that the Postmasburg braunite is of abnormal composition, or that silica has been removed in solution from the scene of action. The formula for sitaparite given in the above equation is a simplification of mine and has not been justified by chemical analysis.

18. Dunn in studying the Chhindwara sitaparite finds braunite later than sitaparite, and regards the formation of braunite as here due to regressive metamorphism, but he did not find any evidence of the reversal of

Schneiderhöhn's equation. It is evident that the micrographic work on the South African mineral requires amplification by the separation and analysis of both sitaparite and braunite.

19. Under the microscope sitaparite from South Africa shows lamellar structures recalling those of leucite, and Schneiderhöhn concludes that sitaparite represents the product of enantiomorphic alteration of a cubic or tetragonal mineral stable at a higher temperature to a tetragonal or rhombic mineral stable at a lower temperature.

20. It is still unknown whether sitaparite is a cubic or tetragonal mineral, though crystals showing apparent octahedral faces have been found.

(c) *General.*

21. Both vredenburgerite and sitaparite show under the microscope structural evidence of a change of one form of a mineral into another, thought to be due to a amelioration in metamorphic conditions, that is to say to falling temperature and perhaps falling pressure. There is no evidence, but only analogy, to guide us in choosing between these two factors; both may have played their part.

DISCUSSION ON L. L. FERMOR'S PAPER 'NOTES ON VERDENBURGITE (WITH DEVADITE) AND ON SITAPARITE'.

The author discusses the recent research of several workers on 'vredenburgerite' and sitaparite which were found by him some 30 years ago. I have a few comments to offer from my own knowledge of these minerals and of the significance of recent methods of attack.

Sir Lewis' discussion makes me regret that I have not had the pleasure of illustrating to him some features of these minerals which are so clear under the reflecting microscope. I feel sure that had he such microscopic acquaintance with these minerals his discussion would have been other than it is and reduced to a few salient points.

It should first be remembered that 'vredenburgerite' is *not* a mineral but a mixture or intergrowth of two minerals jacobsite and hausmannite, and should always be written either in italics or in inverted commas. Such regular intergrowths are quite abundant in mineralogy, it is not customary to give them special names, and I, personally, in this particular case, see no real necessity now for the term 'vredenburgerite,' much less Sir Lewis' new term 'devadite'. The structure of the intergrowth is exactly comparable to that of magnetite and ilmenite, and other mineral groups, intergrowths which have been known long before that of 'vredenburgerite' and to each of which a special name has not been found necessary; hence again, I find no necessity for the term 'vredenburgerite structure'.

The typical intergrowth is of jacobsite and hausmannite, but in a large number of specimens there has been definite alteration, due to weathering,

of the hausmannite to pyrolusite and psilomelane, that is, oxygen has been *added*. The author leaves it to subsequent research to 'show that the MnO_2 of the secondary aggregates is additional'—I can assure Sir Lewis that in every case I have yet examined there is not the slightest evidence other than that this added oxygen *is* due to later alteration. There is no alternative to the reading of the evidence of the pyrolusite and psilomelane. If additional MnO_2 could be proved in the *jacobsite* the case would be different, but I maintain, in the absence of chemical analyses done on material which has been examined under the microscope and proved to be free of alteration, that not one of the analyses discussed by Sir Lewis supplies evidence on which a reliable discussion could be based. It is not correct to say that analyses of 'vredenburgite' *always* reveal the existence of surplus MnO_2 —the so-called 'vredenburgite' which I found to be almost pure *jacobsite* in my paper, showed no such excess. Hence, the known unaltered *jacobsite* contains no excess MnO_2 whilst the obviously altered 'vredenburgite' does. The inference is obvious.

This does not mean to say I do not believe that excess oxygen might *not* originally have been present. In magnetite—related to *jacobsite*—excess of oxygen in the crystal lattice is well-known and, by analogy, there is the possibility of it being present in some *jacobsite*. This is no reason why separate formulæ should be given for mixtures of the type discussed. Well-known gradations of magnetite—mangan-magnetite—*jacobsite* occur according to the proportion of Fe:Mn present, and there are dozens of other similar graded mineral groups, so that it does not appear necessary to find a term 'devadite' merely for an Fe-rich hypothetical 'vredenburgite' which, as a mineral, could only have existed at a high temperature. In fact both may be regarded as high temperature Mn-rich *jacobsites* from which, on cooling, hausmannite separated. In any case there is no need for this additional nomenclature; it is an unusual practice in mineralogy for hypothetical minerals which do not now exist to be named in this way.

Most previous workers regarded the intergrowth as due to falling temperature. Sir Lewis would add the possibility of falling pressure—I know of no similar mineral intergrowth from which the analogy of falling pressure could be drawn.

I would like to say a few words about the formulæ of braunite and sitaparite. Microscopic examinations of these minerals show the unlikelihood that the analyses were done on perfectly pure material. The relatively constant SiO_2 content of the few braunite analyses have no more significance, say, than the commonly constant SiO_2 content of a granite; the latter is a mixture so may be the former. Until reliable analyses are done on *known* pure minerals I would favour Schneiderhöhn's simplified formulæ for both braunite and sitaparite.

J. A. DUNN.

REPLY TO DISCUSSION.

I must thank Dr. Dunn for his contribution to this discussion. I have not, of course, attempted in this paper to produce new evidence, but merely to discuss the work that has been done on vredenburgite and sitaparite by several workers, of whom Dr. Dunn is one.

Whilst it is clear that there is secondary psilomelane and pyrolusite in specimens of vredenburgite, the evidence as to the source of the *whole* of the surplus MnO_2 , referred to with such certainty by Dr. Dunn in paragraph 4 of his contribution to the discussion, has not appeared to me conclusive, and consequently I have allowed for the possibility of the presence in the primary mineral of MnO_2 surplus to the spinellid formula. [The unaltered jacobsite to which Dr. Dunn refers at the end of the same paragraph is not regarded by me as a form of vredenburgite, on account of its very different Mn/Fe ratio, apart from the absence of hausmannite.] I have, however, in paragraph 8 of my summary, provided for the possibility, supported by Dr. Dunn, that all the MnO_2 in vredenburgite may be of secondary origin, in which case the primary mineral was a spinellid.

Concerning nomenclature, no one who disapproves of my terms need use them, and instead he can speak of hausmannite-jacobsite intergrowths or mixtures.

I did not in this paper intend to embark on a discussion on the formula of braunite. The relatively constant amount of silica in braunite from several different localities abroad was thought by Dana to be of sufficient importance to justify representation of this constituent in the formula of the mineral. Subsequent work in India has added strong support to Dana's view, and it seems unlikely that the silica present in braunite is of fortuitous origin. An X-ray study of braunite would be of great interest as showing whether this silica enters into the space lattice or not.

L. L. FERMOR.