THE MINERALOGY OF THE KALAHARI MANGANESE - FIELD NORTH OF SISHEN, CAPE PROVINCE

by

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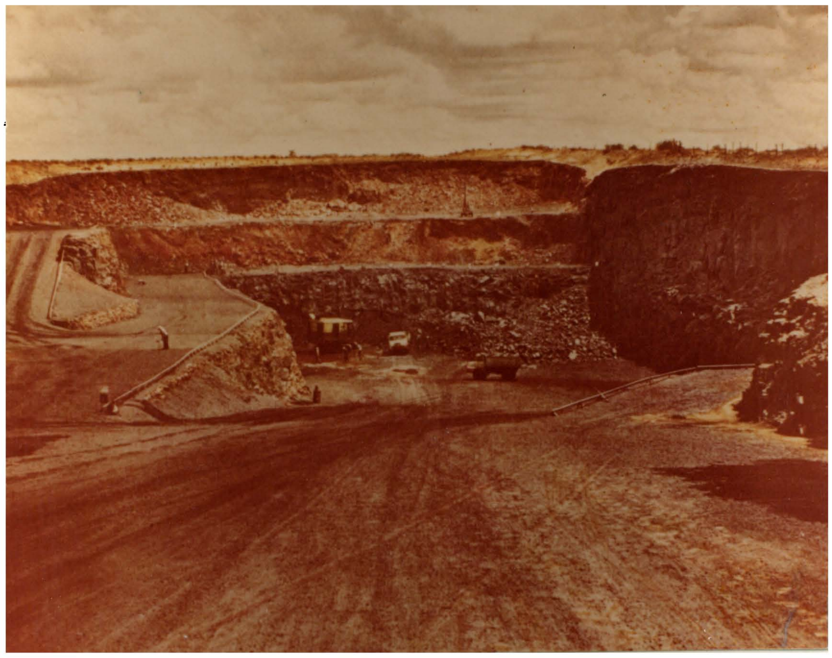
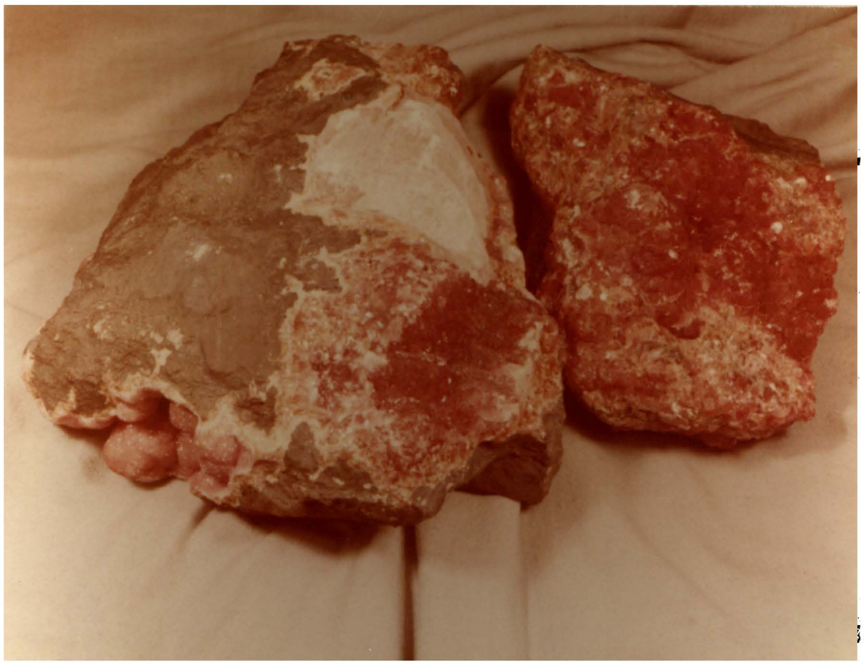


Devon Manganese Mine

(Photo L.G. Boardman)



Rhodochrosite (red) and selenite (white) in manganese ore. Actual size of large sample: approximately 14 inches high.
Hotazel.

CONTENTS

II. THE GEOLOGY AND THE STRUCTURE OF THE KALAHARI MANGANESE-FIELD

III. MINERALOGY OF THE ORE

THE MINERALS - continued

IV. DISTRIBUTION OF THE MINERALS IN THE ORE AND IN THE WALL-ROCK

V. THE GEOCHEMISTRY OF THE MANGANESE ORE

VI. THERMAL STUDIES

VII. THE ORIGIN OF THE ORE

ABSTRACT

The subject matter of this treatise is based on observations of the deposits of manganese ore at the mines Hotazel, Devon, Langdon, Smartt, Adams, Mamatwan and Black Rock which are all in the Kalahari. This area is referred to as the Kalahari Manganese-field and the investigation is devoted to the geology and the structure of this field, and in particular to the mineralogy and the geochemistry of the manganese ore and the associated rocks as well as to thermal data on the manganese minerals.

It is considered that the rocks of the Upper Griquatown Stage in the Kalahari Manganese-field were deposited in a basin in which the precipitation of manganese was greatly attenuated towards the Korannaberg, the Upper Griquatown Stage of which is correlated stratigraphically with that of the Langberg.

The geology of the mines of the Kalahari Manganese-field is described, two geological maps are provided, one for the Kalahari Manganese-field as a whole and one for Black Rock.

The mineralogical investigation comprises the main study of this treatise. Altogether 28 minerals are described, some of them in detail. The minerals nsutite, rhodochrosite, ankerite, acmite, cymrite, tremolite, talc and piedmontite have not previously been reported in the rocks of the Upper Griquatown Stage of the Kalahari Manganese-field. The mineral cymrite is known from only three other localities elsewhere in the world. According to the literature there appears to be a close relationship between cymrite and the barium feldspars. Todorokite does not seem to represent replaced asbestos fibre as postulated by many geologists.

In this treatise it is shown that the mineralogy of the various mines differs considerably, that there is an apparent relationship between the mineralogy and the geological structure, and that, in areas of more intensive deformation, thermal metamorphism of the rocks resulted in the presence of andradite. The contention that the minerals hausmannite and jacobsite formed at high temperature is upheld.

Chemical data are given which consist of detailed analyses of the manganese ore, the results of which are illustrated graphically, as well as semi-quantitative spectrochemical determinations of the trace-constituents of the manganese ore and the banded ironstone. The following minerals were analysed:- braunite (Northern Transvaal), andradite, todorokite, cymrite and acmite.

The thermal data comprise investigations by means of a Reichert high-temperature microscope, a Leitz heating microscope and a differential thermal apparatus.

The manganese ore is interbedded with the banded ironstone. The material for the original sediments is considered to have been derived from the Ongeluk lava and the Campbell Rand dolomite and was deposited in a marine basin as manganese-hydroxides and carbonate mostly in an oxidising environment. Evidence suggests that thermal metamorphism and to some extent load-metamorphism and metasomatism have modified a group of interbedded, highly manganiferous, well-laminated, calcareous sediments. The resultant rocks have subsequently been subjected to supergene enrichment. Hydrothermal action must have prevailed at some stage and accounts for the formation of acmite and the albitisation of the bostomite (intruded into the manganese ore and the banded ironstone). The formation of the manganese ore is in no way related to this hydrothermal action.

I. INTRODUCTION

Manganese is present in organic substances, in oceanic and inland waters, in most rocks but then mostly in minute quantities, and occassionally in deposits of economic importance. Manganese is less abundant than iron. Values determined during 1958 - 1959 for manganese in the water from the Orange River, which had an average flow of 9,000 cusecs during that period, show that the water contained 0.05 parts per million manganese and that the river would therefore deliver approximately 580 tons of manganese a year to the Atlantic Ocean. For iron the figure would be 31,000 tons (P.R. de Villiers, 1962, pp. 197 - 206).

Manganese occurs in many minerals (Dana-Ford, 1932, pp. 806 - 807, lists 128) of which bixbyite, braunite, hausmannite, jacobsite, psilomelane and pyrolusite are the most common. Amongst the oxides those which correspond to MnO_2 chemically and which are generally formed under supergene conditions are the important ones. Only during the last few decades has it been realised how complex the group of manganese ore-minerals are, and how the characteristics of even monomineralic material may vary and sometimes may correspond with those of others. Identification under the ore-microscope is reliable only with relatively coarse-grained material whereas in some samples it has to be supplemented by X-ray investigations.

Most manganese-bearing material normally consists of several minerals intimately intergrown and the importance of obtaining pure samples for X-ray identification cannot be over-emphasized. New minerals are continually being identified even in ores previously examined by older investigators, e.g. nsutite, a manganese oxide first described in 1960 in ore from Ghana, has now been found to be fairly common in South African ores. Furthermore, hydrohausmannite is now considered to be a mixture of hausmannite and beta-MnO(OH), (Feitknecht, Brunner and Oswald, 1962, pp. 154 - 160).

In 1962 a batch of ten samples representative of the ore of the Hotazel Mine was examined for South African Manganese Limited by the author, at that time mineralogist in the Geological Survey, Department of Mines. During the course of that investigation it was realised how little indeed was known about the mineralogy of the manganese ores of that area and it was decided to carry out a detailed mineralogical investigation.

The subject matter of this treatise is based on observations on the deposits of manganese ore at Hotazel, Devon, Langdon, Smartt, Adams, Mamatwan and Black Rock. The mines stretch over a distance of some 40 miles in the Kalahari, a sandy shrub-covered terrain north of Sishen and west of the Kuruman Hills (Fig.1). For this reason the area is referred to as the Kalahari Manganese-field.

The area is masked by a layer of sand. The main rivers, the Gamagara and the Kuruman, ultimately join the Molopo River. There is no surface-water and for most of the time these rivers are dry. The climate is semi-arid and with a summer rainfall of 15 inches per annum the area lends itself to cattle-farming only. The region is approximately 3,400 feet above sea-level. The only eminence in the immediate neighbourhood of the deposits is the Black Rock, an isolated 'hogback' some 90 feet above the surrounding country. From Black Rock to Kuruman is a distance of 56 miles and the rail-head is at Hotazel.

Previous Work

The Northern Cape was mapped by Rogers in 1904 - 1905. He correlated the isolated outcrop of banded ironstone of Black Rock with that of the Lower Griquatown Stage.

In 1922 the late captain T.L.H. Shone discorered manganese just north of Postmasburg in the northern part of the Cape. Consequently prospecting was carried out farther afield and the terrain was examined by Hall in 1926 and studied in greater detail by Dr. L.T. Nel in 1927 and 1928. The outcome of these investigations was that manganese deposits of primary importance were discovered in two parallel belts extending from Postmasburg northwards for some 38 miles to where they disappear under the Kalahari beds.

During 1936 members of the Government Geological Survey carried out mapping of the Northern Cape, including the southern portion of the Kuruman area. As a result of this investigation Sheet No. 173 (Olifants Hoek) was published in 1938.

Black Rock was examined by Boardman (1941, pp. 51 - 60) during the mapping of the Postmasburg manganese deposits. A noteworthy paper was published by J.E. de Villiers (1946) on the mineralogy of the manganese ores from South Africa. The ores from Hotazel and Smartt Mines were examined mineralogically by Frankel (1958). In Handbook 2, John de Villiers (1960) describes the geology of the manganese ore-deposits of the Kuruman manganese-field. Two papers on the manganese deposits of the Kalahari Manganese-field were also published by Boardman (1961 and 1964).

Boardman (1961, p. 208), who has made a thorough study of the geology of the Griqualand West area, summarises our knowledge on the stratigraphical occurrence of the manganese ore by stating that the deposits are located in four different geological formations of widely differing geological ages. Commencing with the youngest-formed rocks, ore is found, according to him, in the following stratigraphic positions:-

i) "Below and in the cataclastic rocks, fault gouges and breccias formed by the post-Matsap thrust faulting, where these rocks lie on the dolomite.

ii) "Along the base of the Gamagara beds (lower Matsap) of pre-thrusting age, where these lie on the dolomite.

iii) "Near the base of the upper Griquatown banded ironstones forming part of the top of the Transvaal System".
These comprise the deposits on which the subject-matter of this treatise is based.

iv) "In the shaly facies near the top of the lower Griquatown succession, about 1,000 stratigraphic ft. above the top of the dolomite and 3,000 stratigraphic ft. below the upper Griquatown manganese-bearing rocks".

Boardman continues:-

"Finally, must be added that along the middle portions of the Postmasburg western belt the manganese ore lies in deep solution channels in the dolomite exposed near the base of that succession. Similarly, solution channels in the dolomite underlying or abutting against the cataclastic gouges and breccias in the Postmasburg eastern belt are are also mineralised with manganese. Thus we have simultaneous manganese mineralisation in the younger two formations listed above, and in the oldest in the area, the dolomite.

"It is obvious therefore that we are not dealing with a sedimentary or series of sedimentary manganese ore-deposits, but a period or periods of manganese mineralisation by impregnation and replacement of a variety of formations of widely differing geological ages and origins where these happened to be suitably located to undergo such intense mineralisation. The age of this mineralisation is definitely post-thrust faulting and antedates the permo-carboniferous glaciation preceding the deposition of the permo-carboniferous Dwyka tillite. Drilling in the Kuruman region revealed completely unmineralised Dwyka tillite deposited on a smoothed floor of high-grade manganese ore.

"The manganese ore-deposits in category (i) above comprise essentially the Postmasburg eastern belt deposits; those in category (ii) above comprise essentially the Postmasburg western belt deposits; those in category (iii) comprise essentially the new and very large Kuruman region deposits, while those in category (iv) above comprise the smaller and somewhat ferruginous deposits 50 miles south of Postmasburg".

II. THE GEOLOGY AND THE STRUCTURE OF THE KALAHARI MANGANESE-FIELD

A. GENERAL

The rocks of the Pretoria Series of the Transvaal System are found in two large areas of deposition, i.e. one in the Transvaal, called the Bushveld Basin, and the other in the Northern Cape. The latter includes the Kalahari Manganese-field.

Stratigraphically there is an agreement between the basal rocks of the Pretoria Series in the Bechuanaland portion of the Northern Cape Basin and those of equivalent age in the Bushveld Basin, but there is a difference between the basal rocks of the northern portion (Bechuanaland) and the rocks of the southern portion of the basin in the Northern Cape. Boocock (1961, p. 78) states that the Pretoria Series is typically developed in the Segwagwa area, Bechuanaland Protectorate, where it comprises the usual alternation of shales and quartzites with an interbedded volcanic horizon. Cullen (1956, p. 457) has shown that the beds developed in this area are similar to those belonging to the Pretoria Series in the Bushveld Basin and quite different from the typical Griquatown Rocks in the southern portion of the basin in the Northern Cape. Furthermore, according to Cullen, some of the rocks outcropping near Segwagwa, which consists of a succession of quartzite, grit and shale, are identical with the rocks of the Timeball Hill Stage found near Lobatsi, i.e. at the western extremity of the Bushveld Basin, whereas the rocks present in the southern part of the basin in the Northern Cape, on the same stratigraphic stage, consist of banded ironstone and jaspilite, with quartzite and shale apparently absent.

The geological succession in the Griquatown area, as established by the Geological Survey (John de Villiers, 1960, p. 22) is given in Table 1. This classification differs from the previous one by Truter and his colleagues (1938) in this respect that the quartzite, shale and limestone formerly included in the Lower Matsap Stage is now correlated with the Gamagara Formation of the Loskop System. According to the classification of the Geological Survey (John de Villiers, 1960) the Gamagara Formation (Loskop System) is found in an Eastern Belt, known as the Gamagara Rand, and a Western Belt which flanks the Langberg on its eastern side.

Recent drilling by the South African Iron and Steel Industrial Corporation, Ltd., in the Sishen-Postmasburg area (Eastern Belt) revealed that a group of sediments similar to the Gamagara rocks lie unconformably on the Ongeluk lava and also that rocks lithologically similar to the rocks of the Gamagara Formation are persistently overlain along strike and down dip by the Ongeluk lava of the Middle Griquatown Stage.

As a result of the information gained from the drilling by ISCOR, the Geologist, Mr. J.T. Wessels, has proposed a new structural interpretation as well as a new stratigraphic classification (in press) but a discussion of this theory is beyond the scope of this treatise.

TABLE 1

CLASSIFICATION OF FORMATIONS OF THE GEOLOGICAL SURVEY (John de Villiers, 1960)

1.	Recent deposits			Sand, surface limestone, etc.
2.	Karroo System	Dwyka Series		Tillite and shale
3.	Waterberg System	Matsap Formation	Upper Matsap	Quartzite and grit
			Lower Matsap or Hartley Hill	Mainly andesitic lava
4.	Loskop System	Gamagara Formation	Quartzite, conglomerate and shale	
			Basal conglomerate and quartzite	
5.	Transvaal System	Pretoria Series	Upper Griquatown Stage	Banded jasper, chert, quartzite and lava
			Middle Griquatown or Ongeluk Stage	Andesitic lava with interbedded tuff, chert and jasper
			Lower Griquatown Stage	Banded ironstone and jaspilite, also subordinate shale and quartzite, limestone and tillite
		Dolomite Series		Dolomitic limestone and chert

Footnote by the author

To correspond with the classification of formations in the Transvaal basin, the banded ironstone, jaspilite and associated shale should be grouped with the Dolomite Series and the tillite, quartzite and limestone of the Lower Griquatown Stage with the Ongeluk lava.

B. GEOLOGY

The manganese deposits of the Kalahari Manganese-field have been the subject of geological investigation on various occasions in the past. In this treatise the mineralogy of the ores is emphasized, therefore only a brief description is given of the rocks shown on the geological map (Folder 1), compiled from data contained in publications of other investigators and information received from other sources. The location of the Upper Griquatown Stage indicated on Folder 1 is according to the positions of magnetic anomalies interpreted by the writer from magnetic surveys carried out by Messrs. S.A. Manganese Ltd.

The writer is indebted to Messrs. S.A. Manganese Ltd., for making available the records of the magnetic surveys, and also to members of the Geological Survey, Pretoria, and "Federale Mynbou Beperk" for information supplied for the compilation of the map.

For the sake of completeness the area of the Kuruman Hills, situated to the east, is included on the geological map.

The stratified rocks of the area may be divided into four groups, according to whether they belong to the Transvaal System, the Loskop System, the Karroo System or to deposits of recent origin.

THE TRANSVAAL SYSTEM

1. <u>The Dolomite Series</u> is composed of a succession of dolomitic limestone and irregular bands and lenses of interbedded chert.

2. The Pretoria Series

   a) The Lower Griquatown Stage - The normal rocks of the Lower Griquatown Stage are subdivided into a Banded Ironstone Zone, a Banded Jasper Zone and a Tillite Zone, of which only the last two are represented in the area of the Kuruman River.

b) The Middle Griquatown Stage consists of the Ongeluk lava which is andesitic. The lava is amygdaloidal in places, and the cavities are filled with quartz and calcite. Coarse- and fine-grained varieties of the lava are present.

c) The Upper Griquatown Stage - In the Kalahari Manganese-field this stage consists of banded ironstone in which are situated the ore-deposits that form the subject matter of this treatise.

Associated with the deposits of manganese ore are remnants of a manganiferous, ferruginous, siliceous, carbonate-rock.

No limestone or lava of the type present in the Upper Griquatown Stage south of and at Olifantshoek (Visser, 1958, p. 22) were found in the area of the Kalahari Manganese-field. Quartzite was located above the zone of banded ironstone in bore-holes (Dr. L.G. Boardman: personal communication).

THE LOSKOP SYSTEM

The Gamagara Formation

In the Kalahari Manganese-field a group of sediments, consisting of indurated mudstone, shale, quartzite and containing locally an odd, thin band of calcareous material and in places, at the base, a conglomeratic breccia, overlies rocks of the Upper Griquatown Stage. These rocks have been correlated with the Gamagara Formation of the Loskop System by Boardman (1961, p. 212) and by John de Villiers (1960, p. 140).

Some of these rocks were encountered in the following localities:

i) West of Black Rock, at the foot of the 'hogback', overlying banded ironstone of the Upper Griquatown Stage unconformably.

ii) In shaft No. 4 to the east of Black Rock Mine (Folder 2), quartzite was found in contact with the banded ironstone (John de Villiers, 1960, p. 140).

iii) In bore-holes, overlying the manganese bearing banded ironstone of the Adams-Kuruman River belt (Central Belt), presumably in an unconformable manner (Boardman, 1961, p. 212).

iv) In bore-holes northeast of the Black Rock Mine, on the farms Eersbegint and Grafton (Grafton is not shown on Folder 1), overlying the Ongeluk lava (personal communication: Mr. J.J. Taljaardt, S.A. Manganese Ltd.).

The following formations were intersected in a bore-hole drilled at Eersbegint:-

Depth in feet	
0 - 40	sand
- 810	Dwyka rocks (bedding of shale horizontal)
- 818	quartzite: grayish
841	shale (mudstone): reddish brown
846	calcareous-rock: light gray
849	breccia: fragments of chert and jasper
857	indurated mudstone: reddish brown
927	shale (arenaceous): dark brown
930	shale (arenaceous) light gray
937	mudstone: dark gray
944	breccia (arenaceous): angular fragments of jasper
947	sedimentary or conglomeratic breccia: angular and subangular pebbles and fragments of banded ironstone and manganese ore
948 - 967	as 944 to 947
982 -1028	Ongeluk lava: andesitic

(Information received from S.A. Manganese Ltd.)

A sample of the core from 947 feet was examined microscopically and it was concluded that the breccia is of a sedimentary origin. This deduction was made after observing the rounding of some of the pebbles. These pebbles and fragments of banded ironstone and manganese ore in all probability represent the eroded rocks of the Upper Griquatown Stage.

In open-cast working No. 3 (Folder 2) at Black Rock Mine the author observed a conglomerate dipping at 5° to the west which overlies folded rocks of the Upper Griquatown Stage unconformably (photo 1). In the immediate vicinity, the conglomeratic material is overlain by approximately 20 feet of Kalahari sand. In a bore-hole some 400 yards to the northwest of open-cast working No. 3, the conglomeratic material overlies the banded ironstone at a depth of 120 feet and overlying the conglomeratic material is 60 feet of indurated mudstone. The mudstone is not Kalahari mudstone as consolidated chips (¼") were present in the drilling sludge. Quartzite and mudstone were encountered in another bore-hole half a mile to the southwest (see drilling machine on photo 1 for location of bore-hole) where they lie directly on the Ongeluk lava. The conglomeratic horizon encountered in the bore-hole most probably represents the base of the Gamagara beds in this area. Similarly all the rocks encountered from 818 to 967 feet in the bore-hole at Eersbegint, and the equivalent rocks in the other bore-holes as well as those in shaft No. 4 and in open-cast working No. 3 are correlated with the Gamagara Formation.

It would seem as if there had been a lengthy break between the deposition of the Transvaal System and the Loskop System in this area, during which the rocks of the Transvaal System were folded and eroded. This is deduced from the geological conditions illustrated on photo 1 as well as from the absence of the Upper Griquatown Stage on the farms Eersbegint and Grafton. In the Olifantshoek area Truter and his co-workers (1938, p. 33) observed that the rocks of the Gamagara Formation follow to all appearance, without any unconformity, on the rocks of the Upper Griquatown Stage. Visser (1958, p. 23) also observed an unconformity in the Griquatown area although not a major one.

THE KARROO SYSTEM

As far as is known, the rocks of this System are not exposed and their extent has only been determined from intersections in bore-holes. Only the basal member, the Dwyka Series, which consists of horizontal shale and tillite, is represented.

SURFICIAL DEPOSITS

These deposits, which are of recent origin, comprise the Kalahari beds and consist mainly of wind-blown sand, unconsolidated mudstone and surface-limestone. The largest portion of the area of the Kalahari Manganese-field is covered by wind-blown sand.

INTRUSIVE ROCKS

Intrusive into the manganese-bearing formations of the Kalahari Manganese-field in the form of dykes and sills is a bostonite which is present fairly persistently. According to Boardman (1964, p. 432) the bostonite has not been found in any of the other formations in the area.

C. STRUCTURE

On Fig. 1 two pitching synclines are shown, the Dimoten Syncline and the Ongeluk-Witwater Syncline with the Maremane Anticline as the core of the structure. The trough of the Dimoten Syncline in which the Kalahari Manganese-field is situated, is occupied largely by andesitic lava of the Ongeluk Stage. The lava is sporadically but normally overlain by the banded ironstone. Banded ironstone outcrops at Black Rock and rises 90 feet above the surrounding country. These sediments dip gently to the west. By means of geophysical observations carried out by the various mining companies and tested by drilling, a belt of manganese-bearing banded ironstone present underneath the cover of sand was traced east of the outcrop at Black Rock from north of the Kuruman River to the Mamatwan Mine in the south. Two outliers of the banded ironstone were located on the farms Hotazel and Devon (Folder 1). According to Boardman (1961, p. 212) results of drilling along the belt of manganese bearing banded ironstones have disclosed that the banded ironstone rests with undisturbed conformity on the Ongeluk lava and therefore belongs to the Upper Griquatown succession. Previously this banded ironstone was correlated with the Lower Griquatown Stage by John de Villiers (1960, p. 156).

To the northeast of Black Rock drilling has disclosed a change of formations due to erosion. In this area the conglomeratic breccia near the base of the Gamagara Formation rests on the Ongeluk lava. This relationship has been encountered on five farms (Personal communication: Mr. J.J. Taljaardt, S.A. Manganese Ltd.).

Rocks of the Lower Griquatown Stage were encountered in the bed of the Kuruman River, five miles to the north of the Hotazel Mine. These rocks have come into this present position as a result of block-faulting which gave rise to a horst which extends north - south.(Folder 1).

Rocks of the Loskop System were encountered in belts to the east and to the west of the Black Rock Mine; they extend north - south. The Karroo beds are found in a glacial valley of which the probable course is approximately north - south, extending across the farms Wessels, Gloria, Botha and Smartt (John de Villiers, 1960, p. 128).

The formations of the Area display folding which is open in the east, but towards the west the formations have been strongly overfolded towards the east and faulting becomes more pronounced. The overfolding eastwards, as observed at Black Rock Mine (Folder 2) is an indication that strong compressional forces from the west had at some time prevailed in the area. Intense overfolding and slickensiding are observed at the Black Rock Mine. The Hotazel body is considered to be an outlier unaffected by strong folding (Folder 1). At the mines Smartt, Adams and Mamatwan the ore-body dips gently but regularly to the west.

In this treatise it will be shown that the mineralogy of the ores at the various mines differs considerably and that there is an apparent relationship between the mineralogy and the geological structure. It will be indicated that in the areas of more intensive folding, thermal metamorphism probably led to the formation of high-temperature minerals, for example andradite and to a lesser extent tremolite.

Faulting in the Area is closely associated with the folding. Moreover, as strong compressional forces from the west must have prevailed at some time and as the layers are overfolded towards the east, it follows that the faults are mainly high-angle or low-angle reverse-faults. The evidence obtained in the field indicates that the faults around Black Rock are intermediate between high-angle and low-angle types, whereas towards the eastern end of the Kalahari Manganese-field, where the folding is gentle and open, the faults are of the high-angle, tensional type.

Evidence for a number of faults have been found in the area and the faults are shown on Folder 1.

Fault f 1

The author has examined material from shaft No. 3, east of the Black Rock outcrop (Folder 2) and has found much brecciated banded ironstone. John de Villiers, who had access to shafts Nos. 3 and 4 while mining was still being carried out, shows in this area a quartzite faulted against manganiferous banded ironstone (1960, p. 140). According to the evidence found in these shafts the southward extension of this fault seems to be towards the south - west.

Fault f 2

The belt of westward-dipping manganiferous beds present at Mamatwan, Adams, Smartt and Wessels has not been encountered to the west although the rocks of this belt should again approach the surface. This suggests the termination against a fault as indicated by Boardman (1961, p. 207).

In the bed of the Kuruman River, on the farms Matlipani and Titanic, jaspilite has been faulted against Ongeluk lave (personal communication: Mr. P.J. Smit, Geological Survey).

Fault f 3

No Ongeluk Tillite is found between the Ongeluk lava and the jaspilite of the Lower Griquatown Stage, in the bed of the Kuruman River, although the tillite is present in the vicinity. This is suggestive of faulting. Northwards this fault would seem to extend west of the Ongeluk Tillite, which, on Pioneer, is duplicated by a small, local fault (information received from the Geological Survey). The extension of this fault to the south of the Kuruman River is difficult to determine but it would seem to pass east of the Langdon Mine as lava was encountered in a bore-hole drilled for water just east of the workings.

Fault f 4

In the bed of the Kuruman River where fault f 4 crosses it, the Ongeluk Tillite has evidently been faulted against the Ongeluk lava. Northwards the position of this fault can be found on the farms Venters Rust and Karlsruhe where Ongeluk lava is again faulted against the jaspilite (according to the Geological Survey).

Fault f 5

The Ongeluk Tillite outcropping on the farms Matlipani and Titanic, in the bed of the Kuruman River just to the east of the outcrop of jaspilite, may be due to folding. However, the Ongeluk lava normally does not lend itself to folding but rather to faulting. From bore-holes drilled for water it would appear that a fault extends along the boundary between Matlipani and Titanic (personal communication: Mr. P.J. Smit, Geological Survey).

Fault f 6

On the eastern rim of the workings of the Langdon Mine the ore-body is terminated, presumably against a fault, as Ongeluk lava was encountered in a bore-hole drilled for water farther to the east.

Fault f 7

The ore-body on Devon terminates rather abruptly to the west of the workings. For this reason faulting is suspected.

Transverse Fractures

Vertical fractures which extend east - west, have been observed in the Devon Mine (photo 6) and at the Black Rock Mine (Folder 2). These fractures are now filled with rubble near the surface whereas at depth, in the Black Rock Mine, the fracture is filled with material resembling a bostonite.

D. THE MANGANESE ORE-BODIES

The succession of manganese-bearing rocks varies from mine to mine. Generally the ore-bodies tend to follow the stratification but they may also be lenticular.

Stratigraphically the manganese ore-bodies are

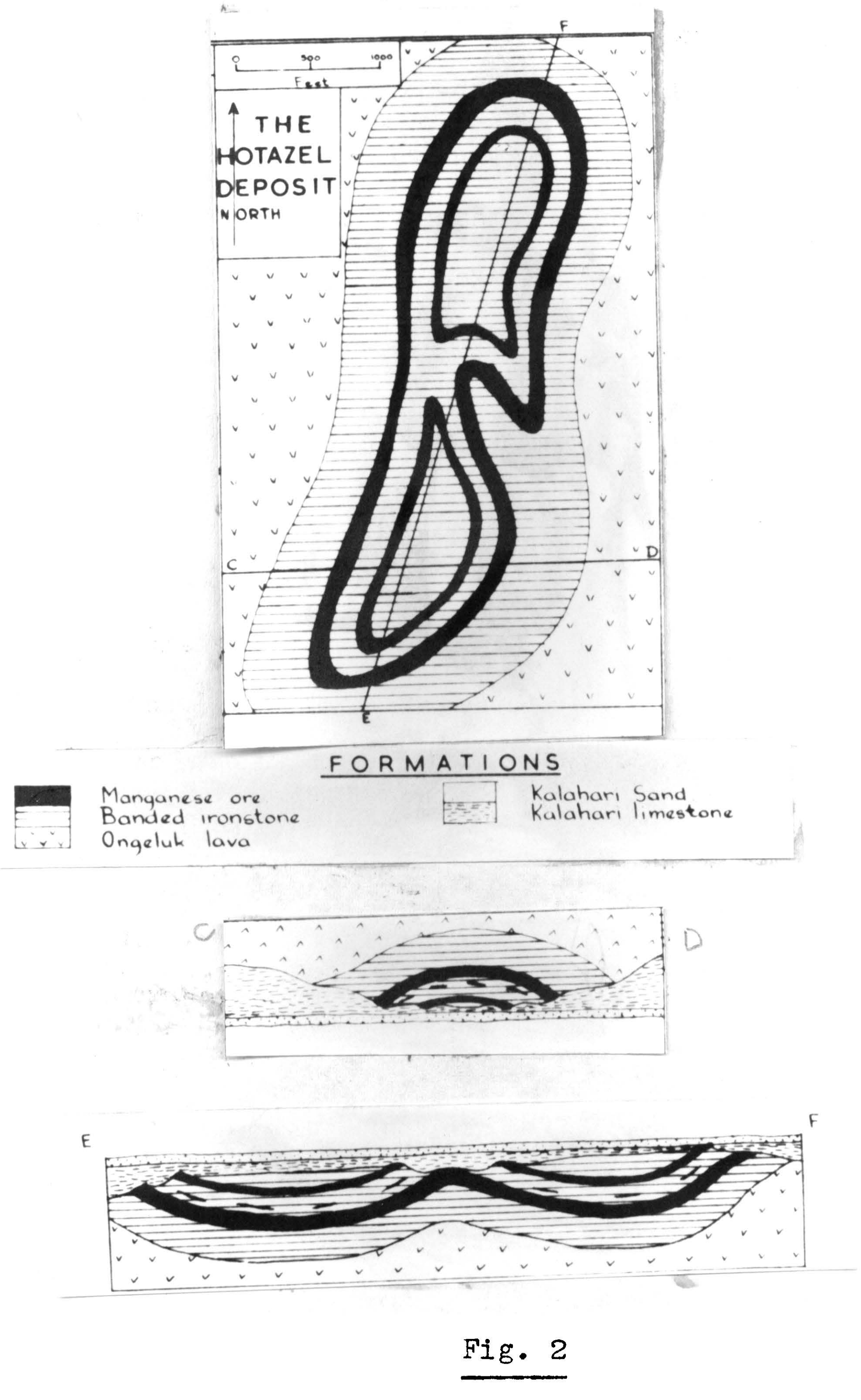


Fig. 2

'(After Boardman, 1964, modified by P.R. de Villiers) confined to the following areas:-

The Eastern Belt - Hotazel, Langdon and Devon
The Central Belt - Mamatwan, Adams and Smartt
The Western Belt - Black Rock

The location of ore-bodies other than those mined (Folder 1) were determined by means of magnetic surveys carried out by Messrs. S.A. Manganese Ltd.

THE EASTERN BELT

HOTAZEL MINE

The Hotazel ore-body under a cover of Kalahari limestone and sand consists of two oval basins joined together on a common axis by a saddle-anticline, as determined by drilling and by mining in the northern portion (Fig. 2). The succession of the strata at Hotazel is set out in Figure 3 (also photo 2) and is described from the lowermost banded ironstone upwards to the upper ore-body:-

Lowermost body of banded ironstone

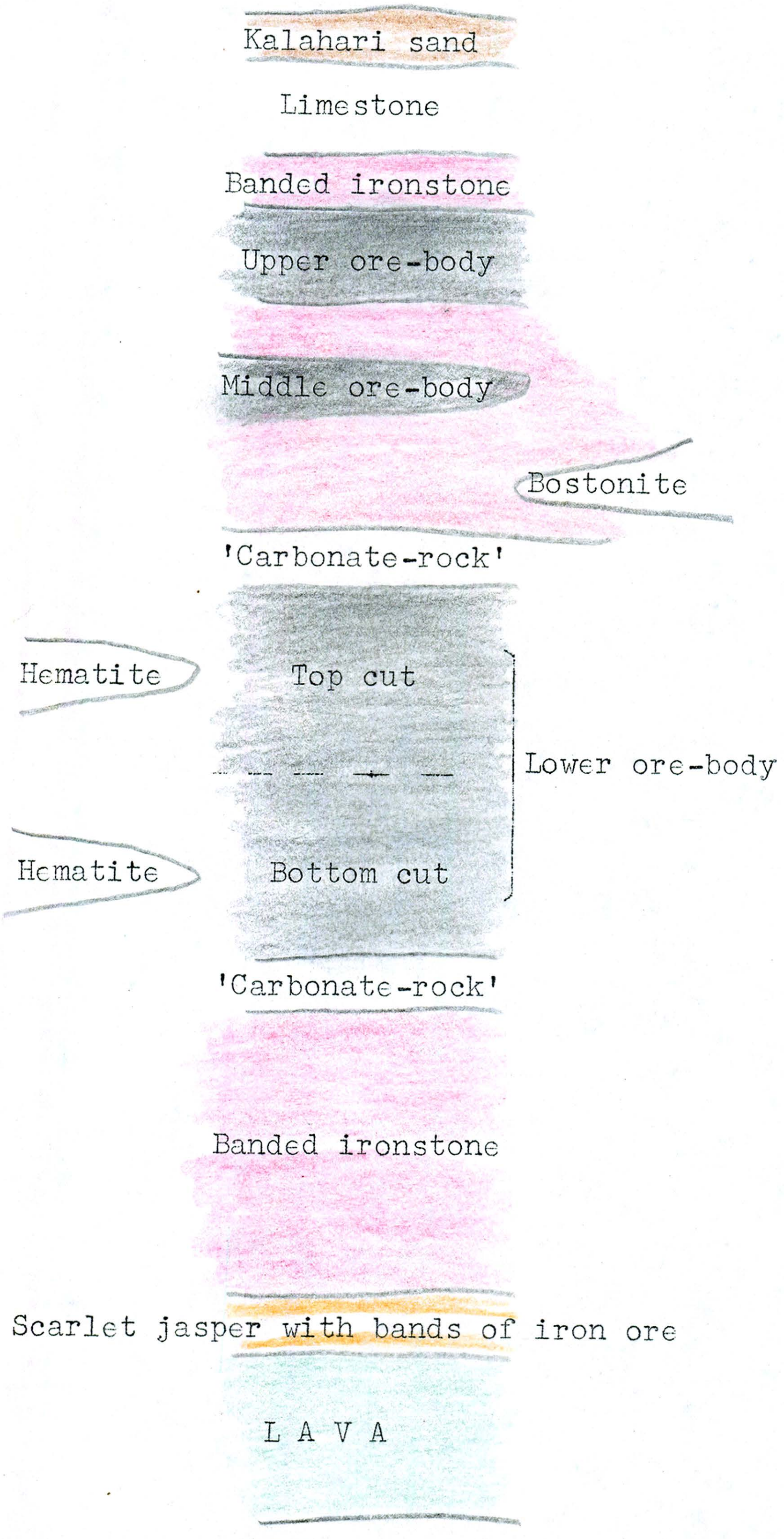
Approximately 95 feet of banded ironstone lies to all appearances conformably on the Ongeluk andesitic lava (Boardman, 1964, p. 429).

Lower ferruginous, siliceous, manganiferous, carbonate-rock

At the base of the lowermost manganese ore-body is a ferruginous, siliceous, manganiferous, carbonate-rock, which will hereafter be referred to as the 'carbonate-rock'. The thickness and the extent of this rock is not known (Fig. 3). At Hotazel the 'carbonate-rock' is much altered (ferruginised) and is closely associated with the ore-body. It is present in patches only and

Fig. 3

SUCCESSION OF STRATA AT HOTAZEL



(Not to scale)

in the following localities:-

1) In a bore-hole drilled horizontally into the foot-wall of the lower body along the western face of the mine, a shaly, banded, hard reddish-brown rock evidently represents the 'carbonate-rock'. The bands are thin and accentuated by an occasional band of red jasper (as in photo 7). No carbonate-minerals were found in this area.

2) In a hole, 10 feet deep, in the floor of the mine, a brown, ferruginous, jaspery rock with numerous streaks and blobs of yellow opal, as well as a little calcite and quartz, was encountered. This jaspery rock is laminated in places and is fairly soft, containing patches of red jasper. No primary carbonate-minerals were found in this area.

3) In a bore-hole drilled below the ore-body, this 'carbonate-rock' contains rhodochrosite and ankerite in certain places (as in photo 96).

The Lower Ore-body

Overlying the lowermost banded ironstone is the lower body of manganese ore which varies in thickness from 60 to 100 feet. This body is not always composed entirely of manganese minerals. In places, particularly in the lower half, patches of ferruginised material are common (photos 3a and b).

In order to facilitate mining operations the 'bench method' of quarrying is employed, i.e. the lower body is worked in a bottom cut and a top cut (photo 2).

(a) The Bottom Cut

This portion is approximately 25 to 30 feet in thickness and consists largely of a dull, black, well-layered manganese ore which resembles a black shale. In places the ore is more massive than in the rest of the mine. Secondary enrichment, as a result of the concentration of hausmannite, cryptomelane and braunite, has taken place along and across the laminations. In this way the manganese content of the ore was increased and the ore acquired a silvery, banded and streaky appearance. The laminated ore contains numerous inclusions of remnants of oolites[@] of grayish carbonate ranging in diameter from 0.5 to 2.0 mm. Calcite fills cracks and veins, particularly in the lower portion of the bottom cut where the silica content is also rather high.

(b) The Top Cut

The top cut is approximately 20 to 30 feet thick and the manganese ore is of a higher grade than that from the bottom cut. The ore is also layered but secondary enrichment is more common and massive ore consisting mainly of hausmannite is prevalent.

Ferruginisation and silicification of the manganese ore are closely related as seen in the eastern face of the bottom cut where an irregular body of earthy hematite (some 10 to 20 feet across), rimmed by a band of red-brown jasper, one foot wide, is present in layered manganese ore. The laminations of the manganese ore terminate against this irregular, ferruginous body which is in no way laminated (photo 3b). Furthermore, no signs of secondary enrichment of manganese were seen in any of the ferruginised or silicified patches except for microscopic

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[@] The term 'oolite' is used for the round to oval grains of mineral matter generally showing concentric bands, and only when a relationship with calcareous material is suspected.

veins (photo 47) although patches enriched in manganese are present near by. Considering the abrupt termination of the laminations against this ferruginous body it seems reasonable to conclude that slumping may be the cause.

During September, 1962, when mining operations had not yet reached the bottom of the basin, ferruginisation and silicification were limited to shrinkage-cracks, with the manganese ore along them altered to red-brown jasper over a distance of approximately one to three feet. In places the cracks are filled with Kalahari sand.

The upper 'carbonate rock'

Between the lower ore-body and the middle body of banded ironstone is a lenticular, shaly, transition-rock, approximately 2 feet in thickness. The contact with the ore-body is sharp whereas the contact with the banded ironstone proper is gradational. Along the contact with the ore is a strip of banded ironstone, 2 inches wide, which consists of hematite and bands of chert. The bands of chert contain minute, slender needles of amphibole. No minerals of the carbonate group were found in this rock. This transition-rock contains a little minnesotiate and it resembles the ferruginous, siliceous, manganiferous, carbonate-rock encountered below the lower ore-body.

The middle body of banded ironstone

Overlying the upper 'carbonate-rock' is some 70 feet of banded ironstone. The upper portion of this banded ironstone has been subjected to secondary ferruginisation, possibly prior to the formation of the manganese ore. The ferruginisation of this banded ironstone has resulted in closely spaced hematite specks which give the rock a metallic appearance (photo 4).

A sheet-like, lenticular body of bostonite is present in this banded ironstone (photo 2).

(a) The Bostonite

The bostonite is situated in the middle body of banded ironstone. It is sheet-like, lenticular, and tends to follow the planes of stratification although the contacts with the banded ironstone are irregular (photo 2). This body is some 10 to 20 feet thick in the west and thins out to almost a stringer in the eastern face where it deviates from the stratification to follow a fault-plane for a short distance. Drilling results indicate that the bostonite continues eastwards across the line of faulting. The indications are that the faulting antedates the intrusion of the bostonite.

Although no signs of any thermal effect were observed in the banded ironstone along the contact with the bostonite, a 'chill-zone' is present in the bostonite along the contacts of the hanging and the foot-wall. In these 'chill-zones' the bostonite is not altered to the same extent as towards the middle portion of the bostonite, where it is highly altered to a soft, green to white, soapy mass of nontronite. The relatively unweathered bostonite is brick-red to reddish-brown in colour, showing numerous laths of feldspar.

(b) The middle ore-body

This body of manganese ore is not mined at all owing to its lenticularity. It varies in thickness from a few feet to a mere stringer and it is not persistently present.

The Upper Ore-body

This manganese ore-body, some 20 feet thick, is situated between the middle and the upper banded ironstone (photo 2). The ore is hard and of a bright steel-gray colour with a conchoidal fracture and it is massive. In weathered portions large, hard, rounded boulders are found. The ore is of an unusually high quality although little sign of secondary enrichment has been observed.

The upper ore-body is overlain by slightly weathered banded ironstone which in turn is overlain by Kalahari limestone and sand (photo 5).

DEVON MINE

Devon Mine is situated approximately 2 miles due south of Hotazel Mine.

The manganese body of the Devon Mine is situated in the banded ironstone of the Upper Griquatown Stage and tends to follow the stratification. To facilitate mining operations the ore-body is worked according to the 'bench method'. The manganese ore-body is overlain by banded ironstone, with Kalahari sand on top (colour-photo on front page).

Only one ore-body is present and it is on the same stratigraphical horizon as the lower ore-body at Hotazel, although it is less laminated.

In places, at the base of the ore-body, a 'carbonate-rock' is located just as at Hotazel, with manganese oxide replacing it (photo 7). This 'carbonate-rock' is seen at the southern entrance to the mine and also in the northern part of the mine, on the contact between the underlying banded ironstone and the manganese ore-body. Along the northern part of the mine the manganese ore-body tends to cut for short distances across the laminations of the banded ironstone. This may be due to secondary replacement.

Extending east - west across the workings is a transverse fracture (photo 6), 12 to 15 feet in width, now filled with surface-rubble amongst which was found weathered material in which nontronite predominates. In the Kalahari Manganese-field nontronite appears to be one of the diagnostic products of weathering of the bostonite.

The ore-body is approximately 50 - 80 feet thick, dips at a shallow angle to the north and to all appearances terminates against a fault to the west (Folder 1, f 7). Towards the middle portion of the body the ore has a more shiny appearance than that of the lower portion. Towards the hanging wall side the ore becomes harder, with brighter bands appearing and in certain areas it resembles a completely manganised banded ironstone although no remnants of actual banded ironstone were found. Steel-gray nodules, mainly of secondary hausmannite, elongated parallel to the laminations, are common. Overlying the manganese ore-body is approximately 30 feet of monotonous banded ironstone which is in turn overlain by 5 to 10 feet of Kalahari sand.

LANGDON MINE

This mine is just across the fence and to the east of Devon Mine and on the same manganese ore-body under similar geological conditions except for a thin bed of laterite between the banded ironstone and the Kalahari sand. Mining operations are not being extension of the Mamatwan ore-body.

The ore-body is being mined in one cut, is approximately 45 - 50 feet thick and dips at 5° to 10° to the northwest. The ore is dull and laminated near the base. Higher up it becomes progressively enriched in respect of manganese as a result of the appearance of nodules and inconsistent, thin veins of hausmannite. The ore also contains nodules mainly of cryptomelane as replacement-material. Veins of todorokite, approximately ½ - 1 inch thick, are common in the ore-body, especially in the upper half and they tend to follow the bedding. One vein of todorokite was traced across nearly half of the mine.

Near the hanging wall the ore is riddled with horizontal joints along which calcite, originating from the overlying body of limestone, is emplaced. The overlying body of Kalahari limestone is approximately 40 feet thick and contains numerous inclusions of manganese ore as well as a few pebbles of 'jaspery' material and banded ironstone. Higher up the body of limestone becomes whiter in colour and quite hard whereas just below the sand cover the colour is a dirty brown.

SMARTT MINE

This is the only mine of the southernmost group in which banded ironstone of the Upper Griquatown Stage has been exposed during mining operations. Excavations across the strike exposed the banded ironstone which forms the hanging wall in contact with the ore-body. The banded ironstone of the foot-wall is not exposed. The ore-body is approximately 40 - 50 feet thick and tends to follow the stratification of the banded ironstone which dips at an angle of approximately 15° to

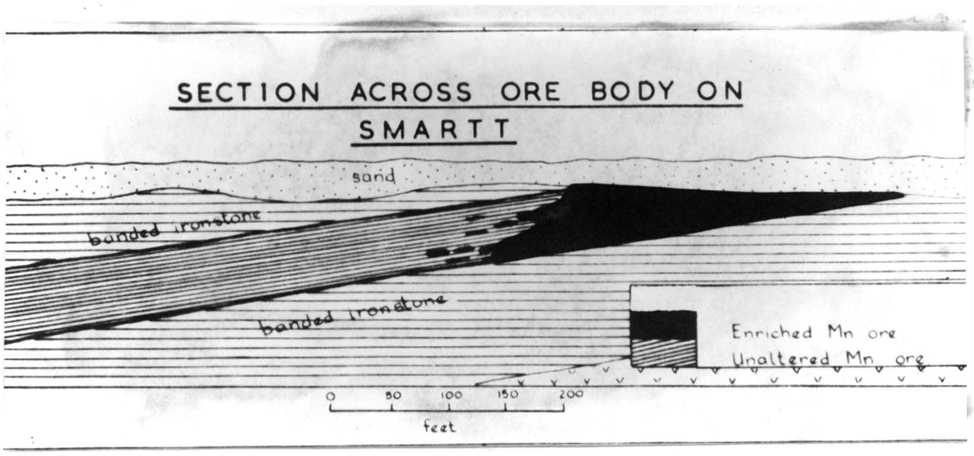


Fig. 4

(After Boardman, 1964, modified by P.R. de Villiers) the west. Down dip beneath the gradually thickening cover of banded ironstone, low-grade ore was encountered (Fig. 4). Mining operations had been carried out along the line of strike in open-cast workings for a distance of half a mile to a maximum depth of 40 feet and a width of 100 feet.

Near the base the ore is hard, siliceous and ferruginised, with a banded appearance accentuated by thin bands of jasper. This rock resembles the 'carbonate-rock'. Slightly higher up the ore has a dull appearance with numerous oolites and lenticular remnants of limestone which tend to be concentrated in layers (photo 8). Still higher up in the ore-body numerous nodules and elongated streaks of hausmannite and bixbyite appear. Near the top the ore is hard, bright and of a high grade. Veins of todorokite are common and they tend to follow the laminae in the ore-body. Near the hanging wall veins of calcite originating from the overlying body of limestone are common.

The banded ironstone has a yellow colour due to weathering and is overlain by approximately 5 to 10 feet of sand.

THE WESTERN BELT

The Black Rock Mine is situated near the extreme northwestern end of the Kalahari Manganese-field and is referred to as the Western Belt merely for the sake of distinguishing it from the rest.

BLACK ROCK MINE

Mining operations at Black Rock are carried out mainly underground although some open-cast mining is also applied.

Geology

At Black Rock Mine there are two areas in which banded ironstone is found with presumably Ongeluk lava in between:-

1) The 'hogback' of banded ironstone which protrudes approximately 90 feet above the nearly flat surface of Kalahari sand. It is roughly oval and measures 1,560 feet in length and 600 feet in width across the widest part. The strike of the major axis is roughly parallel to the trend of the Kuruman Hills to the east and to the Korannaberg to the west. In shafts and bore-holes this banded ironstone has been proved to extend farther northwards below the cover of sand, for a distance of approximately 700 feet.

2) A separate body of banded ironstone occurs to the east of the outcrop at Black Rock (Folder 2) below the sand-cover and it was found to contain several consistent bands of manganese ore and an igneous rock which is apparently conformable with the banded ironstone. Just farther east this banded ironstone and its associated rocks are terminated against a coarse, gritty, purplish quartzite, presumably of the Loskop System. At shaft No. 3 (Folder 2), which is no longer in use, much brecciated material was collected from the dump near by. The samples contain bright-red jasper and streaks of shiny hematite. Microscopic investigations showed that the hematite is idiomorphic but shattered and broken. The jasper is much more bright-red than the jaspery chert of the normal banded ironstone of the area.

John de Villiers (1961, p. 130) describes a coarse-grained diabasic rock which was encountered in a bore-hole situated in between the two areas of banded ironstone. It is possible that this material is in fact coarse-grained Ongeluk lava. Similar samples of Ongeluk lava examined microscopically give the impression of being a diabase.

The geology below the sand-cover immediately east of the Rock as shown on Folder 2 has been transferred from John de Villiers' publication (1960, p. 131).

Structure

On first appearances the outcrop at Black Rock seems to be an undisturbed succession of rocks dipping to the west. Along the western flank of the hill the ground drops gradually to the west, whereas the eastern flank is more precipitous and consists of a series of low, cliff-like steps and shelves in between. The cliffs are formed by bodies of manganese ore (photo 10) and the shelves by banded ironstone. Closer investigation has disclosed many irregularities in the structure. The general but varying dip of the banded ironstone is 35° to the west (photo 11) although dips to the east have been observed in areas of local disturbances (Folder 2). The banded ironstone is more reddish in colour in these areas of local disturbances than elsewhere and the transition to the normal banded ironstone is gradational. Further irregularities are observed in the form of puckering of the banded ironstone which in some places give way locally to brecciation and faulting. Slickensides in the manganese ore are common (photo 12) and irregularities typical of more intense deformation were observed in an example of asymmetrical and recumbent folding encountered in the open-cast workings No. 2 and

No. 4 (Folder 2). In the area of the asymmetrical fold the manganese ore-body dips at 40° to the west and within a short distance the dip is almost 90° (photo 14). During mining operations along the centre of the fold the banded ironstone of the foot-wall was encountered. In the area of the recumbent fold the manganese ore-body is found overlying the banded ironstone which in turn, owing to infolding, overlies the same manganese ore-body (photo 15). Mining operations underground have encountered a local thickening of the ore-body to as much as 80 feet in places. It is the opinion of the author that the ore-bodies of this thickness are the result of repeated folding, as shown in photos 13 to 15.

The apparent change in strike of the formations which has resulted in a curved structural pattern, concave to the west (Folder 2), is not altogether due to the topography but is in fact a true change of the strike and is in harmony with the broad structural trend farther to the east.

The structural relationship of the suite of rocks situated to the east of Black Rock and below the sand-cover is set out in the profile on Folder 2.

During the mapping of the area four faults were located on the surface and two zones of small-scale faulting were observed underground. The position of fault f 1 on the surface corresponds with the fault-zone encountered underground where the downthrow is on the eastern side. This agrees with indications on the surface. Along the same line of strike as fault f 2 clayey material representative of a highly weathered bostonite was encountered underground. The displacement along this fault is hardly noticeable; the downthrow is on the northern side. This fault is in actual fact more of a transverse fracture filled with rubble at the surface, similar to the fracture encountered in the Devon Mine.

Distribution of the manganese ore-bodies

The main rock-type at Black Rock is a banded ironstone similar to the banded ironstone of the other mines and the manganese ore-bodies are intercalated in it; their distribution is indicated on Folder 2. Two main groups of ore-bodies are observed:-

1) those forming the 'hogback' which are the only ones that have been worked extensively to date;
2) those located below the sand-cover to the east in shaft No. 3 (Folder 2).

At the Hotazel Mine the manganese ore-bodies are regularly intercalated in the banded ironstone. At Black Rock, however, the structure sometimes reveals greater intricacies, for instance in the portion on Santoy where the manganese ore-body bifurcates (Folder 2), with the most westerly branch of the fork cutting across the lamination of the banded ironstone. This may be due to a metasomatic process possibly resulting from severe and prolonged tectonic stress. In fact, Boardman (1964, p. 437) considers that the peculiar bifurcating and lenticular habit of the ore-body at Black Rock strengthens his supposition that the manganese ore originated directly from intercalated manganiferous limestone in the banded ironstone succession. He states: "It is a well known fact that under severe and prolonged tectonic stress limestones tend to 'flow' from their original bedded conformable habit to be virtually eliminated from part of their original position and to 'flow' into thickened lenses and even to twist back upon themselves to simulate a bifurcating habit". This could be exactly what happened at Black Rock.

The manganese ore-bodies tend to be lenticular and some are discontinuous, particularly the upper bodies. Towards the hanging-wall side the ore-bodies become more ferruginous and in some localities even grade into a hematite ore. The foot-wall side may also be ferruginous but to a much lesser extent. According to John de Villiers (1960, p. 137) ferruginisation of both hanging-wall and foot-wall sides is prevalent in the thick ore-body located in shaft No. 3.

The contact between the banded ironstone and the manganese ore-body is usually sharp (photo 10), particularly along the foot-wall where within inches from the ore-body the banded ironstone contains virtually no manganese oxide. At the end of the ore-body the transition is more gradational. The contact of the manganese ore-body may follow a single bedding-plane of the banded ironstone for as much as 40 feet. However, the manganese ore-body also transgresses across the laminations of the banded ironstone, particularly where the ore-body thickens. Yellow, ochreous material or weathered banded ironstone, only a few inches thick, is fairly common in the banded ironstone portion of the contact.

Numerous coarse slickensides were observed in the manganese ore (photo 12). They are probably related to the intense folding, the indications of which are seen at Black Rock.

At Black Rock there are only three consistent ore-bodies (Folder 2) although along section AB four are indicated.

The lower ore-body is the only one that has been worked underground. This body is 20 feet thick and shows little variation in thickness along the strike, as well as down the dip for some 500 feet, as seen in shaft No. 2 (Folder 2). Farther down dip to 900 feet it gradually thins out to approximately 8 feet.

Some 10 feet above the lower ore-body is an inconsistent seam of ore which is followed within a few feet by the middle ore-body, some 20 feet thick. The lower portions of the middle ore-body is of high grade, whereas near the hanging wall the ore is more ferruginous. This ore-body has been worked only near the surface.

The upper ore-body is the one indicated along section AB and is not considered to be the same as the ore-body in No. 1 open-cast working (Folder 2). This upper cro-body is markedly lenticular and inconsistent and transgresses across the laminations of the banded ironstone to the extent that in places it is in direct contact with the middle ore-body. It is also unpredictable as far as mining is concerned, as has already been proved in the extensive open-cast workings No. 1 and 2. The lower portion of the ore-body is of a dull steel-gray colour and of a low grade. It becomes markedly ferruginous nearer the hanging wall and in places it is virtually a manganiferous iron ore. This is the only area in the Kalahari Manganese-field where a major transgression of the ore-body across the laminations of the banded ironstone was observed.

The downthrow of fault f 2 is on the northern side and it is therefore considered that just below the ferruginous portion in No. 1 open-cast working a higher grade of ore should be encountered, presumably similar to that mined in No. 2 working.

Little is known about the distribution and the relationship of the ore-bodies situated to the east of Black Rock, below the sand-cover. The rocks encountered by mining in this area have not been examined by the author as the shafts are no longer accessible. However, for the sake of completeness the information supplied by John de Villiers (1960, p. 139) warrants a brief discussion. According to him, four zones of mineralisation can be traced within a thickness of 350 feet of banded ironstone. The four zones have given rise to four separate ore-bodies that vary in thickness and in manganese content. He numbered them 1 to 4 from west to east:-

<u>Ore-body No. 1</u> which is nearest to the outcrop of Black Rock is remarkably consistent in thickness and in quality along strike and down the dip. In the cross-cuts near the surface as well as in the bore-hole, it is approximately 20 feet thick where it was intersected at approximately 350 to 400 feet below the surface. Near the surface as well as at depth the grade of the ore is of the order of 40% Mn and 10% to 20% Fe.

This description corresponds with that of the lower ore-body of the 'hogback'.

<u>Ore-body No. 2</u> is ferruginous and never exceeds 4 feet in thickness.

<u>Ore-body No. 3</u> appears to represent the main development of ore in this area. It varies in thickness from 45 to 90 feet. The sides tend to be ferruginised and the over-all quality of the ore seems to be about 40% Mn and 15% Fe.

<u>Ore-body No. 4</u> is nearer the top of the succession of banded ironstone. It varies in thickness from 10 to 20

feet and is highly ferruginous.

From this description it would seem as if No. 1 ore-body may be correlated with the lower ore-body of the 'hogback', No. 2 ore-body with the inconsistent seam of ore, No. 3 ore-body with the middle ore-body and No. 4 with the upper ore-body. This correlation is suggestive of folding as also postulated by Boardman (1964, p. 430) and as shown in the profile AB of Folder 2.

III. MINERALOGY OF THE ORE

INTRODUCTION

The investigation of the ore from the Kalahari Manganese-field comprised the study of polished sections and, in rare instances, polished thin sections. The minerals were identified by means of X-ray diffraction techniques, supplemented by chemical analyses, spectrochemical determinations, X-ray fluorescence, differential thermal analyses and to a lesser degree by etching-tests and electron-diffraction methods. Individual samples normally contain at least four minerals usually intimately intergrown and the difficulty and importance of obtaining pure samples for X-ray indentification can scarcely be over-emphasized.

The material for X-ray identification was removed from polished sections by means of a micro-drill which contains a cut diamond sharply pointed and inserted in the microscope in the position of the objective (photo 16). Whilst observing the magnified image (20 x) under oblique illumination, drilling was carried out by rotating the stage and the fine powder obtained in this way was transferred to a small ball of rubber-solution which was prepared in advance between two glass slides. The rubber-ball, approximately 0.2 mm.in diameter, was mounted on the tip of a glass-fibre needle approximately 0.1 mm thick which was then placed in the X-ray camera. In rare instances where the unknown mineral was in a narrow vein (photo 17) too small to be drilled, an improvised micromanipulator was used, which consists of a sapphire stylus attached to a pin vice and fitted to the stage of a second microscope alongside it. Micro-scraping movements, continually observed under high magnification (100 x), were controlled from the second microscope by means of a mechanical stage holding the pin vice.

In many of the ores some of the minerals are so finely intergrown that in spite of the precautions mentioned, some of the material for X-ray diffraction still consisted of mixtures which complicated investigations. Furthermore, besides the difficulty of obtaining mono-mineralic material for X-ray diffraction, many of the patterns obtained from manganese minerals are diffuse. The reason for this may possibly be:-

1) Non-crystallinity of the material. Some of the manganese minerals, particularly those minerals from the psilomelane group, consist of small crystals or are even of colloidal size. As the size of the crystallite diminishes the width of the X-ray lines increases until the lines assume a diffuse character. According to Klug and Alexander (1954, p. 384) back-reflection lines disappear at sizes less than 0.01 micron and α1 and α 2 are not resolved. According to them crystallites of 0.1 micron and more should give sharp diffraction patterns.

2) Strain in the lattice which may be due to impurities and to randomness of the atomic arrangement in a layered structure.

Many of the X-ray diffraction patterns taken during the course of this investigation were too diffuse to be identified and consequently more than the normal number had to be taken. A Philips X-ray apparatus was used for this work with Fe-radiation for the manganese minerals and Co-radiation for the others.

THE MINERALS

The information on the properties of the minerals outlined in this chapter comprises the results of the investigation of samples from the Kalahari Manganese-field, but would also be applicable to minerals outside that area. Altogether 28 minerals are described and as far as possible according to the paragenetic sequence, from the early stage to the main stage.

1) Wad

This soft, black mineral is present in earthy masses and readily soils the fingers. It can be described as amorphous owing to the impossibility of obtaining an X-ray diffraction pattern. Dispersed through the amorphous material are minute hematite granules.

Wad occurs mainly at Devon, Langdon and Hotazel and is often altered to cryptomelane (photos 18, 19). Whether the wad present had formed owing to lithification or as a secondary product is not certain.

2) Rhodochrosite - $MnCO_3$

Physical characteristics: It is present as distinct crystals in beautiful clear rhombohedrons r(10$\bar{1}$1) and also in globular form when fine-grained. The cleavage (10$\bar{1}$1) is perfect and the colour varies from rose-red, yellowish pink, red-brown to gray. The red-brown to gray rhodochrosite is mostly fine-grained. The molecular percentage of $CaCO_3$ in rhodochrosite was determined from Goldsmith's graph (1957, p. 312) after calculating $\Delta d_{(104)}$ for pure calcite and rhodochrosite from the Kalahari Manganese-field. The $CaCO_3$ in the following samples of rhodochrosite were determined:

a) the rhodochrosite illustrated on the frontispiece - 2 mol. %

b) a sample of the material used for analysis 5 (Table 20) - 17 mol. %

Optical properties: $\epsilon' = 1.621$ (sodium light) for the sample shown on the frontispiece. This sample probably contains ~~calcite~~ $MnCO_3$ as for pure $MnCO_3$ $\epsilon' = 1.702$

Occurrence: The mineral occurs sparingly at Hotazel Mine and then in vugs. It is often associated with selenite (frontispiece). It is present at Mamatwan Mine in the 'carbonate-rock' as remnants (photo 9 - pol.secs. M7, 7a) where it is replaced by pyrolusite.

Diagnosis: The composition in the series $CaCO_3$-$MnCO_3$ was determined by means of X-ray diffraction techniques to be near to that of $MnCO_3$.

3) Calcite - $CaCO_3$

Calcite is found as a secondary product mainly in veins in all the mines of the Kalahari Manganese-field. In the mines of the Central Belt it also represents remnants of the original sedimentary carbonate (photo 8). At Adams this original material contains more magnesium than at Smartt.

4) Braunite

Problems of classification are often encountered among certain manganese minerals. A similar situation exists in the braunite group of minerals: the ideal composition of ordinary braunite is $3Mn_2O_3.MnSiO_3$ and most analyses conform reasonably well with this formula. However, J.E. de Villiers (1946, p. 7) has reported the occurrence of a so-called ferrian braunite from the mine at Black Rock with less than half the silica content required by the ideal formula and containing in addition an appreciable amount of iron and alkaline earths (Table 3).

Braunite has been found in many localities since its discovery by Haidinger in 1826. Most analysed specimens have a SiO_2 content close to the 9.98 weight per cent required by the ideal formula. Results for specimens from India are given by Fermor (1909, p. 75) and a general summary of the older analyses by Koechlin (1926). More recent results are given by Palache, Berman and Frondel (1951, p. 553).

Goniometric measurements show braunite to be tetragonal and c/a is given as 0.99. However, Aminoff's X-ray diffraction measurements indicate that $a \sim 9.5$, $c \sim 18.9$ Å and hence the true axial ratio is 1.99. The space group is a matter of dispute.

A few of the many chemical analyses reported for braunite are included in Table 3 and at this stage it is desirable to compare only the results for standard braunite specimens, for example those from the Northern Transvaal, the Kalahari and Långban, with the Kalahari braunite of J.E. de Villiers. The most striking difference between these analyses of braunite is the SiO_2 content of the braunite of J.E. de Villiers which is 4.4 per cent, a value less than half the standard value. The appreciable CaO and Fe_2O_3 contents are also noteworthy but not exceptional, as reference to the other specimens in Table 3 will show. Goniometric examination by J.E. de Villiers (1946, pp. 7 - 10) of crystals of the braunite from the Kalahari shows it to be tetragonal with the c/a ratio similar to that of ordinary braunite but with a different face development. X-ray powder photographs of this Kalahari braunite taken by the author also reveal small but definite differences. The results are suggestive of a real difference between the two varieties, but are hardly conclusive. Accordingly it was decided that a more intensive study of ordinary braunite and the braunite of J.E. de Villiers is necessary and that X-ray diffraction techniques, as applied to single crystals, would be most likely to show up any real difference.

X-ray study of single crystals

On the suggestion of the present author Dr. Herbstein at that time of the Council for Scientific and Industrial Research carried out the investigation of single crystals of braunite in order to obtain more information on the differences of two possible variations of this mineral as deduced from the evidence submitted above. The ordinary braunite studied is from the arenaceous beds of the Loskop System on the farm Weenen, some 80 miles northwest of Potgietersrust, Northern Transvaal. Manganese is present in the low-grade ore as braunite, psilomelane and pyrolusite (John de Villiers, 1960, p. 215). The ore is of a sedimentary origin with supergene enrichment. This sample was selected from the collection of the Geological Survey, Pretoria, because of its granular nature and chemical purity; however, no well-formed crystals were found. Only small fragments without recognisable faces were available and they were oriented entirely by X-ray methods.

Dr. Herbstein reported as follows:-

"Needle-shaped crystals of braunite were obtained from J.E. de Villiers' specimens and were mounted about the needle axis [001] for X-ray photography. As this mineral seems to be an ordered version of ordinary braunite it is given the provisional label braunite-II.

"Preliminary photographs to determine cell dimensions were taken by the oscillation and the Weissenberg techniques, but it soon became clear that, because of the size of the unit cells, the Buerger precession camera would give much more reliable results for the systematic absences. A combination of methods was therefore decided upon. Despite a fairly high fluorescence background, Cu $K\alpha$ radiation was found suitable for the oscilliation and the Weissenberg photographs, while Mo $K\alpha$ was used for the precession photographs.

"Braunite (ordinary)

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

(Wavelengths used: Cu K_{α} mean 1.5418, K_{α_1} 1.54054 Å, K_{α_2} 1.54436 Å))

The standard deviations are rather roughly estimated.

Systematic absences: $hk\ell$ absent for $h + k + \ell \neq 2n$
$hk0$ " " $h\ (k) \neq 2n$
$0k\ell$ " " $\ell\ (k) \neq 2n$
$hh\ell$ " " $(\ell \neq 2n)$, $2h + \ell \neq 4n$

The space group is thus uniquely determined as D_{4h}^{20}-14_1/acd (No. 142 of International Table 1952).

"Values of cell-dimensions have been reported for a number of specimens of braunite of different origins (Table 4). A detailed comparison is made difficult owing to the uncertainty whether the earlier results are actually in kX units, although reported as Å units. To change from kX to Å units would be by adding 0.02 Å for a and by adding 0.04 Å for c.

"Aminoff (1931, p. 15) reported the space group as $D^{20}_{4h} - 14_1acd$ but this was disputed by Byström and Mason (1943, p. 4) on the grounds of the appearance of a (550) reflection on a Weissenberg photograph. On the basis of their structure analysis these authors chose D^{10}_{2d} - 14c2. Mukherjee (1959, p. 334) found a (130) reflection in his powder patterns of braunite and chose D^{17}_{4h} - 14/mmm as the space group. A careful search has been made for these reflections on the precession photographs but without success, which confirms Aminoff's original proposal.

"The analytical figures (Table 3) for the two specimens from the Kalahari were used to calculate the contents of the unit cell. These contain 8 formula units of composition $Mn_{6.66}Fe_{0.11}Ca_{0.15}Ba_{0.01}Si_{0.94}O_{12}$ for sample 1 and $Mn_{6.54}Fe_{0.04}Al_{0.18}Si_{0.95}O_{12}$ for sample 2. The calculated densities for the two specimens are 4.769 and 4.742 gcm^{-3} respectively while the calculated density for the ideal composition Mn_7SiO_{12} is 4.812 $g.cm^{-3}$. In these calculations the oxygen content of the unit cell dimensions (9.55, 18.76 Å) have been assumed for all three samples. The measured density of specimen 2 is 4.76 $g.cm^{-3}$ which is in good agreement with the calculated values. The crystal structure given for braunite by Byström and Mason (1943) cannot be entirely correct because they used the incorrect space group."

The crystal structure is now being re-analysed by Dr. Herbstein and Mr. J.P. Roux and the results will be reported elsewhere.

The report by Dr. Herbstein continues as follows:

"<u>Braunite</u>-II

$\underline{a}$ = 9.44 ± 0.005 Å

$\underline{c}$ = 37.76 ± 0.01 Å

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

"The analytical figures for braunite-II were used to calculate the contents of the unit cell, which contains sixteen formula units of composition $Mn_{5.80}Fe_{1.25}Ca_{0.46}Ba_{0.008}Si_{0.45}O_{12}$ (the oxygen content of the unit cell has been normalized to 192 atoms). The calculated density is 4.834 $g.cm^{-3}$ which is rather higher than the measured value of 4.727 $g.cm^{-3}$. J.E. de Villiers (1946, p. 10) observed that the measured density of braunite-II is likely to be lower than the true value because of the 'somewhat porous nature' of the material.

"It is interesting to note that there are 7.2 Si-atoms per unit cell, and 7.4 Ca-atoms are ordered in two different sets of eightfold positions. The stronger reflections on comparable precession photographs of ordinary braunite and braunite-II show a resemblance both in arrangement and in relative intensity, but there are appreciable differences for the weaker reflections. This is consistent with similar general arrangements of oxygen atoms and metal atoms in both structures, the differences probably arising from ordered arrangements of some of the metal atoms in braunite II, together with some differences in the arrangement of oxygen atoms.

"A full structure analysis by means of X-ray methods, which is now in progress, will be required to check these suggestions; unfortunately X-rays are unlikely to give any indication of possible ordering of the iron atoms and recourse to neutron diffraction would be necessary to settle this point."

Powder patterns of ordinary braunite and braunite-II

Powder patterns of ordinary braunite have been given by Smitheringale (1929), Harcourt (1942) and Mukherjee (1959). A pattern of the ordinary braunite from the Northern Transvaal was also prepared. The various results are in reasonably good agreement. The pattern given on ASTM Card No. 8 - 78 is a somewhat modified composite of the results of Smitheringale and Harcourt. On this issue Dr. Herbstein remarked (unpublished report):

"The best available pattern is probably that of Mukherjee (his Table 1) but some corrections are required. The most important correction is that the line with d = 2.96 Å (I = 10) is not the (130) reflection but is due to an impurity. Harcourt also gives this line, but it does not appear in the pattern of braunite-II. Mukherjee also lists some other indices which violate the space group, but these should be ignored."

The powder pattern of braunite-II was determined (114.6 mm camera, Fe K_α radiation) and the results are given in Table 5. Some lines due to impurities have been eliminated by comparing the observed powder pattern with a calculated version based on the single-crystal results. As intensities of reflection from the single-crystal patterns were not yet available, multiple-index coincidences due to the large size of the unit cell could not be eliminated by Dr. Herbstein. For this reason indices have been omitted in Table 5.

Discussion

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

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

Dr. Herbstein observed (unpublished report):

"Two specimens of braunite from India contain appreciable amounts of alkaline earths and both Fermor (1909, p. 68 and 76) and Byström and Mason (1943) have already pointed out that the composition of the Kajlidongri specimen can be written as $3Mn_2O_3.(Mg,Ca)SiO_3$. It may be quite possible that the alkaline earth atoms of this sample were ordered, but it is unlikely that the braunite from Sitapar, with only half an atom of alkaline earth per formula unit, has these atoms ordered. Diffraction effects resulting from ordering would be small and hence difficult to detect by qualitative methods. Examination of the specimen from Kajlidongri may give interesting results.

"Alkaline earths have also been considered as essential constituents of sitaparite (Mason, 1942) although this is not supported by analyses given by J.E. de Villiers (1946, p. 11) for two samples of sitaparite from Postmasburg which contain virtually no alkaline earths. Fermor's (1909, p. 50) original analysis of sitaparite gave 6.14 weight per cent CaO and 1.02 weight per cent MgO, but this only amounts to 3 atoms of alkaline earth per unit cell and it is therefore unlikely that these atoms are ordered. Both Mason (1942) and Mukherjee (1959) have obtained powder patterns of various samples of sitaparite and they were found to be identical with the powder patterns of bixbyite. Mukherjee has reported that the presence of the (310) and (510) lines in his photographs precludes sitaparite from having the same space group as bixbyite (T_h^7 Ia3). The earlier results of Zachariasen (1928) and Pauling and Shappel (1931) for bixbyite have recently been confirmed for a synthetic sample of Mn_2O_3 (Swanson, Cook, Isaacs and Evans, 1960) and it seems possible that the additional lines in Mukherjee's pattern were due to impurities. Confirmatory photographs on single-crystals would be desirable, but it is noted that the available evidence for differences between bixbyite and sitaparite is much weaker than for ordinary braunite and braunite-II or even for ordinary braunite and braunite from Kajligongri.

"Iron is also an important substituting element in the braunite and bixbyite groups. Samples of bixbyite of varying iron content have been shown to correspond with the wide range of solid solution of Fe_2O_3 in Mn_2O_3 established experimentally (Mason, 1942 and 1944; Muan and Sōmiya, 1962, p. 239). It has also been shown that the cell dimension of Mn_2O_3 is little affected by Fe_2O_3 (Muan and Sōmiya, 1962, p. 239). It is therefore reasonable to suppose that even the braunite from Mason County, with 15.4 weight per cent Fe_2O_3 (Table 3), has the same crystal structure as ordinary braunite and should be called ferrian braunite in terms of the nomenclature of Schaller (1930). More subtle effects, such as ordering of Fe and Mn atoms, could only be detected by neutron diffraction or, perhaps, by suitable magnetic measurements.

"It is concluded that it is only in braunite-II that there is experimental evidence for atoms of alkaline earth occurring in an ordered arrangement as substitution. There is a possibility of ordering of atoms of alkaline earths in braunite from Kajlidongri, but it is unlikely that this occurs in other samples of braunite or in sitaparite. Ordering of the atoms of iron and manganese also appears unlikely, but could not have been observed by X-ray diffraction. Whether braunite-II should be considered a separate phase from ordinary braunite cannot be settled on the available evidence but must await the results of the analyses of the crystal structure of both species and perhaps also a study of their inter-convertibility."

TABLE 5

CHEMICAL COMPOSITION OF VARIOUS BRAUNITES

	$3Mn_2O_3$ $MnSiO_3$	KALAHARI BRAUNITE		N. TRANSVAAL BRAUNITE	LÅNGBAN BRAUNITE	MASON COUNTY FERRIAN BRAUNITE	KAJLIDONGRI BRAUNITE	SITAPAR BRAUNITE	KALAHARI BRAUNITE-II
		1	2						
MnO)) or MnO	82.13	40.10	42.3	39.9	78.91	66.89	37.98	41.10	31.5
MnO_2)		46.50	43.6	39.6			40.93	37.10	43.3
O	7.94				7.35	6.27			
Fe_2O_3 (incl. Al_2O_3)	-	1.44	2.1	7.4	-	15.39	1.59	8.84	16.3
FeO	-				3.81	-	-	-	-
CaO	-	1.40	2.2	1.3	0.34	0.06	3.85	4.28	4.3
BaO	-	0.13	-	-	-	-	0.09	-	0.2
MgO	-			0.1	0.15	0.19	4.36	0.94	-
SiO_2	9.93	9.32	9.6	9.9	9.98	9.90	10.26	8.52	4.4
Remainder						1.40 (H_2O 0.73; insol. gangue 0.67	1.57 (H_2O at 100°C)	0.10 (H_2O at 100°C)	
Total	100.00	98.89	99.8	98.3	100.45	100.10	100.63	100.88	100.0
Spec. Gravity	4.67		4.76	-	4.72	4.73	4.704	4.798	4.727
Reference		J.E. de Villiers (1946)		Sample Studied in this treatise	Dana and Dana (1944)	Hewett and Schaller (1937)	Fermor (1909)	Fermor (1909	J.E. de Villiers (1946)

TABLE 4.

Cell dimensions for various specimens of braunite

Specimen	a	c	Units	Ref.
Synthetic (from $MnSO_4$ and Na_2SiO_3)	9.41 ± .01	18.64 ±.02	Å ?	(a)
Långban	9.42	18.67	Å ?	(a)
Lohdongri (Nagpur, India)	9.42	18.72	Å ?	(a)
Nagpur	9.36	18.77	Å ?	(b)
Kacharwahi, Nagpur	9.402	18.740	Å	(c)
N.Transvaal	9.44 ± .005	18.76 ±.01	A	(d)

References:
(a) Byström and Mason 9 (1943)
(b) Switzer (1938)
(c) Mukherjee (1959)
(d) This treatise.

TABLE 5.

X-ray powder data (Fe K_α radiation)

Braunite (ordinary) (Mukherjee, 1959, p. 335)		Braunite-II (114 mm camera)	
I/Io	d Å	I obs	d obs (Å)
10	5.36		
20	4.65		
		10	4.54
		15	4.15
		40	3.68
30	3.47		
10	3.32		
10	2.96		
100	2.710	100	2.72
15	2.508		
5	2.405		
40	2.345	60	2.35
45	2.141	10	2.10
		20	1.996
10	1.915	10	1.913
20	1.871		
10	1.841		
15	1.803		
20	1.735		
5	1.681		
80	1.659	90	1.666
20	1.537		
		10	1.517
25	1.501	10	1.499
20	1.464		
60	1.418	70	1.423
30	1.412		
15	1.368		
25	1.355		
20	1.265	10	1.26
		10	1.23
20	1.175	10	1.176
20	1.164	15	1.162
10	1.146	10	1.141
50	1.078	30	1.081
	1.07		
40	1.051	20	1.052

4(a) Braunite (ordinary)

Physical characteristics: It is non-magnetic and its hardness is 6.

Optical properties: Its colour in reflected light is slightly brown. The bireflectance is difficult to observe and the anisotropism is only just noticeable in oil (photo 20). Braunite is replaced by cryptomelane along grain boundaries (photos 21, 22(a) and (b) - pol. sec. H2) and sometimes it is intergrown with bixbyite (photo 27 - pol. sec. BR 1c) and braunite-II along certain crystallographic directions.

Occurrence: The mineral is present in all the mines of the Kalahari Manganese-field as a major constituent of the ore, except at Hotazel where it forms only a minor constituent.

Diagnosis: Its similarity with bixbyite, braunite-II and hausmannite can be confusing. However, bixbyite is more yellow, braunite-II is lighter brown and hausmannite has internal reflections and strong anisotropism.

4(b) Braunite-II

Physical characteristics: Braunite-II is non-magnetic and the crystals observed vary in length from 0.5 to 20 mm (photo 23). Interpenetration-twins (photo 24) and contact-twins were observed. Semi-quantitative spectrochemical determinations show that braunite-II contains 0.05 per cent Al and 0.005 per cent each of Cr, Co, Ti, Ag, Cu and Sr.

Optical properties: The colour of braunite-II in reflected light is yellow-brown. The bireflectance is difficult to observe and anisotropism is weak like braunite, however slightly stronger. It is sometimes intergrown with ordinary braunite along certain crystallographic directions.

Occurrence: It is present only at Black Rock Mine, often in vuggy ore and associated with andradite. Some of the crystals are rimmed and replaced by cryptomelane (photo 25 - pol. secs. BR 1a, b, c).

Diagnosis: Braunite-II is very similar to ordinary braunite and bixbyite. Its colour in reflected light is intermediate between that of the last two minerals.

5) Bixbyite (Sitaparite, partridgeite) - $(Mn,Fe)_2O_3$

Mason (1943, pp. 117 - 125) found bixbyite and sitaparite to be structurally identical. He suggested that the name sitaparite be discarded. J.E. de Villiers (1943, pp. 336 - 338) disagreed with this scheme of Mason and suggested that the name sitaparite be retained. In addition he described a new species, partridgeite, natural Mn_2O_3 with only a small substitution of iron for manganese. His words are: "... I suggest that the name partridgeite be applied to those manganese-iron sesquioxides containing less than 10% Fe_2O_3, sitaparite to the sesquioxides containing between 10% and 30% Fe_2O_3 and bixbyite to the mineral with more than 30% Fe_2O_3". Fleischer (J.E. de Villiers and Fleischer, 1943, pp. 468 - 469) recommends that the name sitaparite be dropped and the other two be retained.

Mason (1944, pp. 66 - 69) commented on this classification and by means of a phase diagram showed that the homogeneous mineral $(Mn,Fe)_2O_3$ can be subdivided into two components of two composition ranges:-

a) Those of pneumatolytic or fumarolic origin, with a Fe_2O_3 content from 40 - 60%

b) Those occurring in metamorphosed manganese ores, with a Fe_2O_3 content from 0 - 30%.

Mason points out that he has a good case for subdivision but does not consider it necessary and recommends that the name bixbyite be retained to cover the $(Mn,Fe)_2O_3$ group. The status of partridgeite has been questioned in Dana's system of Mineralogy (7th edition, p. 551) where the mineral is considered to be identical with bixbyite.

A sample of 'partridgeite' taken from the collection of the Geological Survey, Pretoria, was examined by means of X-ray powder diffraction (Table 7) and the cell edge was determined.

TABLE 6.

Cell edge of members of the $(MnFe)_2O_3$ group.

Locality of sample		Cell edge (Å)
Partridgeite	(Synthetic ASTM card No. 10 - 69)	9.411
Partridgeite	(Museum, Geological Survey, Pretoria)	9.407
Bixbyite	(ASTM card No. 8 - 10)	9.384

It seems as if a series exists in the $(Mn,Fe)_2O_3$ group of minerals with Fe substituting for Mn. Whether this calls for a subdivision is a matter of opinion.

TABLE 7.

X-ray diffraction data.

(Fe-rad.)

Bixbyite (A.S.T.M.) (No. 8 - 10)			Partridgeite (114 mm camera) (Geological Survey, Pretoria)		
d (Å)	I/Io		d-(meas.)	I(obs)	
4.68	10				
4.21	10	x	4.058	10	
3.83	60		3.83	60	
3.35	10				
2.99	30	x			
2.72	100		2.715	100	
2.51	20		2.51	20	
2.35	40		2.34	40	
2.21	20		2.21	10	
2.11	10		2.09	10	
2.01	40		2.003	40	
1.924	10		1.91	10	
1.873	40	x	1.85	40	
1.719	25		1.71	10	
1.657	90		1.65	90	
1.617	20		1.61	10	
1.567	20		1.56	10	
1.530	30		1.52	20	
1.483	20		1.48	10	
1.454	30		1.45	20	
1.421	80		1.42	70	
1.388	40		1.38	20	
1.359	30		1.355	15	
1.330	10		1.325	5	
1.307	20		1.302	10	
1.282	30		1.278	30	
1.258	20		1.258	10	
1.177	40		1.177	30	
1.157	40		1.156	35	
1.141	30		1.139	30	
1.125	30		1.123	30	
1.107	30		1.106	10	
1.093	30				
1.079	70		1.078	30	x
1.077	40	x			
1.052	60		1.0496	40	

x lines not present on patterns by Zachariasen, (1928, p. 457).

Optical properties: The colour in reflected light is khaki-green. Twinning is occassionally seen (photo 26 - pol. secs. BR 1a, b, c). The mineral is often isotropic but is sometimes also weakly anisotropic.

Occurrence: Bixbyite is common in ore from Hotazel and Black Rock as veins, as intergrowths with braunite along certain crystallographic directions (photo 27 - pol. sec. BR 1c), as replacement residues in pyrolusite and goethite and as idioblasts from pyrolusite (photo 71).

Diagnosis: Optically there is a close resemblance with braunite-II and jacobsite. However, the reflectance of braunite-II is more brown and that of jacobsite more olive-green. Braunite-II is anisotropic and without twinning.

6) Hausmannite - Mn_3O_4

Physical characteristics: It is grayish black, has a submetallic lustre and a distinct cleavage. Hardness ≈ 5.

Optical properties: The colour in reflected light is dark-gray and is suppressed in oil. Its bireflection is distinct and its anisotropism is strong with the colours varying from gray to bluish- and dark purple-brown. In oil it has deep-red internal reflections and a clouded appearance like watered silk (moire sheen - Ramdohr, 1956, p. 54). Certain orientations have a finely scratched appearance which is diagnostic (photo 28 - pol. sec. H10).

Occurrence: Coarse- and fine-grained types are present in Hotazel (photo 29). Fine-grained hausmannite is rarely twinned but coarse-grained nearly always so (photo 30 - pol. sec. H10). It is replaced by many minerals and relic textures are common (photos 31, 32, 33 - pol secs. A4, D3, D6).

Diagnosis: The internal reflections, twinning, scratches and moire sheen colour are all features that make identification of hausmannite easy. Its twinning distinguishes it from the rather similar manganite.

7) Jacobsite - FeO,Mn_2O_3

Physical characteristics: Jacobsite forms an unlimited solid solution series with magnetite. The mineral is strongly magnetic like magnetite and takes a good polish.

Optical properties: The reflective colour is gray with a distinct olive tint and the reflectivity is strongly diminished in oil. Deep-red internal reflections are sometimes seen in oil.

Occurrence: It is present at Hotazel (photo 34 - pol. secs. H11), Langdon (N1) and Eersbegint (photos 35, 36 - pol. sec. E1). The mineral in some specimens contains minute inclusions of hematite (photos 37, 38, 28, pol. secs. H7, 9, 10), and is often intergrown with hausmannite as an exsolution product (photo 39). Sometimes it is formed from pyrolusite (photo 37).

Diagnosis: Jacobsite may be confused with magnetite, braunite and particularly bixbyite. However, the reflective colour of magnetite is more gray without the olive tint and bixbyite is more yellow. Jacobsite is decidedly negative to the polishing test to which most magnetites are positive, viz. the magnetite examined became blue-gray when given a brief final polish on a dry lead lap. Braunite never has internal reflections.

8) Magnetite - $FeO.Fe_2O_3$

Optical properties: The reflective colour of magnetite is gray with a brownish tint. When polished on a cloth the colour is pinkish but when given a brief final polish on a dry lead lap the colour of most magnetites is blue-gray.

Occurrence: The mineral is present as a mosaic of roundish grains (photo 40 - pol. sec. H9) and also as idiomorphic crystals and distorted veins (photo 41).

Diagnosis: Magnetite may be confused with jacobsite and braunite. The reader is accordingly referred to the diagnosis of jacobsite.

9) Hematite - Fe_2O_3

Optical properties: The reflective colour is gray-white.

Occurrence: Hematite is common in ore from the Kalahari Manganese-field

a) as minute inclusions in jacobsite (photos 28 and 38 - pol. secs. H7, 10), nsutite (photo 90 - pol. sec. H10) and goethite (photo 42 - pol. sec. H10)

b) as crystals either coarse- and fine-grained (photo 46 - pol. sec. BR 3E) or rimmed by jacobsite (photo 43 - pol. sec. H5) or with inclusions of bixbyite or jacobsite (photo 44 - pol. sec. D2)

and c) as veins relatively young in the paragenetic sequence.

Diagnosis: Coarse-grained crystals are more readily identified than fine-grained ones. Fine-grained hematite may be confused with cryptomelane. However, the relief of hematite is diagnostic.

10) Andradite - $Ca_3(Fe^3Ti)_2(Si_3O_{12})$

Physical characteristics: In rare cases andradite is found as distinct crystals, usually dodecahedrons. The colour is brown and the mineral has a weathered appearance. According to J.E. de Villiers (1946, p. 33) the S.G. for andradite from Black Rock is 3.81 (± 0.02).

Optical properties: It is slightly anisotropic and the refractive index is high. J.E. de Villiers reported 1.86 as the refractive index for the andradite from Black Rock.

Occurrence: The mineral is present only at Black Rock and Hotazel, and then in vugs. It is also dissemminated in the ore and in the banded ironstone. It occurs as follows:-

a) Associated with the manganese ore (photos 45, 46, 48, 49 - pol. secs. BR3E, Fol. a, b,c.d.e).

b) Encrusted by braunite-II which is itself encrusted by chalcedony (Sample B1).

c) In the 'carbonate-rock' at Hotazel.

d) In the micaceous rock (photo 50 - thin sec. TB 1) at Black Rock.

e) In the banded ironstone at Black Rock where it is associated with acmite and iron oxide (photo 51 - thin sec. TB 2).

f) Associated with jacobsite in a vein situated in the hematite ore from Hotazel (photo 47).

The relationship shown on photo 47 tends to indicate that the andradite may be younger than some of the manganese minerals.

Diagnosis: The mineral was identified by means of X-ray and chemical methods (Table 8). The cell edge (12.04 Å., 12.05 Å and 12.06 Å)

TABLE 8.

CHEMICAL ANALYSIS OF ANDRADITE

	1.	2.	3.
SiO_2	35.40	34.91	39.96
TiO_2	-	trace	trace
Al_2O_3	1.78	0.69	1.80
Fe_2O_3	28.71	30.40	24.70
FeO	-	-	0.14
MnO	0.48	-	trace
MgO	0.12	0.58	trace
CaO	31.36	33.20	34.84
Na_2O	-	-	-
K_2O	-	-	-
H_2O	2.16	0.19	-
P_2O_5	0.15	-	-
	100.16	99.97	101.44

CALCULATED TO 24 O-ATOMS

	1.		2.		3.	
Si	6.05	6.05	5.908	6.00	7.1	7.1
Al	-		0.092		-	
Al	0.36	4.03	0.046	3.92	0.37	3.66
Fe^3	3.67		3.873		3.29	
Ti	-		-		-	
Mg	0.03	5.83	0.146	6.17	-	7.6
Fe^2	-		-		0.02	
Mn	0.07		-		-	
Na	-		-		-	
Ca	5.73		6.02		7.58	
K	-		-		-	

1. Red-brown andradite garnet, Black Rock (analysed by Soils Research Institute, Pretoria).
2. Andradite garnet, Reškovic stream, Serbia (Deer, Howie and Zussman, 1963, p. 90).
3. Andradite garnet, Zeekoegat (279), Pretoria District. (Van Biljon, S. 1936, p. 64).

was also calculated and from this the species was established by means of the graphs of Sriramadas (1957, p. 295), which agrees with those of Winchell (1956, p. 493).

11) Tremolite

The identification of this mineral is hampered by the lack of sufficient material.

In thin section it is generally difficult to distinguish between tremolite and manganoan cummingtonite (Klein, 1964, p. 970). Tremolite has the smaller extinction angle and lower refractive index but owing to the lack of sufficient material these properties could not be determined with any reliability in the material from Hotazel. Jaffe et al., (1961, p. 645) state that they could not distinguish cummingtonite with a lower Mn content than the Nsuta mineral from tremolite by optical properties alone.

For the identification of the material from Hotazel reliance had to be placed on X-ray diffraction (Table 9) only as no reliable chemical or optical data could be obtained. Cummingtonites may be distinguished from all other monoclinic amphiboles by the (310), ($\bar{6}42$) and ($\bar{6}61$) spacings.

TABLE 9. (after Klein, 1964)

The values of d_{310} and $d_{\bar{6}42} - \bar{6}61$ of two monoclinic amphiboles compared with the mineral from Hotazel (in Å).

	x Fluor-tremolite	x Manganoan-cummingtonite Nsuta	Hotazel (114 mm X-ray camera)
d_{310}	3.11 Å	3.06 Å	3.11 Å
$d_{\bar{6}42}$)		1.405 Å	
$\bar{6}61$)	1.43 Å		1.43 Å

x Jaffe et al., 1961, p. 648.

Physical characteristics: It is found as very fine, slender needles (photo 52 - thin sec. TH 2).

Optical properties: The mineral is colourless with n - 1.61, the extinction is oblique and the absence of pleochroism distinguishes it from actinolite.

Occurrence: Tremolite is present only in the 'carbonate-rock' from Hotazel, particularly alongside cracks filled with andradite (photo 53 - thin sec. TH 2).

Diagnosis: The identification in this assemblage is based mainly on X-ray measurements as the crystals are too small for reliable optical observations.

12) Minnesotaite - $Fe_3(OH)_2Si_4O_{10}$

Occurrence: Minnesotaite was positively identified in material from bore-cores from Mamatwan (photo 9) where the mineral is associated with dolomite and rhodochrosite. Some of the X-ray diffraction patterns of material from the other mines also contain the (001) reflection of minnesotaite. X-ray powder data of manganese ore from the Kalahari Manganese-field often show a reflection in close vicinity of 9.5 Å which could be minnesotaite as this reflection cannot always be accounted for by todorokite. Todorokite has its strongest reflection around 9.6 Å.

Diagnosis: The identification is based mainly on X-ray powder data. The minnesotaite occurs dissemminated and in small quantities only. No chemical or optical determinations are possible.

13) Talc - $Mg_3(OH)_2Si_4O_{10}$

Optical properties: Talc is present as minute, slender needles and laths. The extinction is oblique.

Occurrence: The mineral occurs as follows:-

a) In the 'carbonate-rock' from Mamatwan, as rims consisting of aggregates of slender laths that surround lenticular bodies of carbonate minerals (photo 54 - thin sec. TM 16).

b) As groups of laths near bodies of carbonate minerals at Mamatwan (thin sec TM 16).

c) As laths now replaced by opal. It is common in the 'carbonate-rock' from Hotazel, Smartt and Mamatwan.

Diagnosis: The identification is based on X-ray powder data only.

14) Ankerite - $Ca(Mg, Fe^{2-},Mn)(CO_3)2$

Physical characteristics: On a polished surface ankerite has a red colour (photo 9(b) - pol. sec. M 10).

Occurrence: The mineral was found in the 'carbonate-rock' in bore-cores from Mamatwan, along the foot-wall. The ankerite has probably formed as a result of a reaction between dolomite or rhodochrosite and iron-rich material (pol. sec. M10).

Diagnosis: It was identified by means of X-ray powder pattern which agrees with that of ferroan dolomite, ankerite (ASTM 12-88). The presence of Fe as a major constituent was established by means of a qualitative spectrochemical test.

15) The Psilomelane Group

In the past the term 'psilomelane' was commonly used for hard, botryoidal manganese ore. Fleischer and Richmond (1943, pp. 269 - 286) listed a number of minerals in the psilomelane group and recommended that the term 'psilomelane type' be used to include unidentified material. Ramdohr (1956, pp. 64 - 67) states that the 'psilomelane-like' minerals may be separated into four minerals which are very similar in properties:- Psilomelane 'proper', cryptomelane, hollandite and cornadite. He considers that cryptomelane, hollandite and cornadite are closely related structurally and chemically although they do not appear to form extensive series of solid solutions, possibly owing to the very low temperature at which they are generally formed. But what happens with products that are formed at higher temperatures, such as part of the hollandite, is not known.

It is difficult to distinguish by means of optical methods only between the minerals of the psilomelane group, and more so when they are fine-grained. Furthermore, X-ray diffraction patterns are often diffuse and this hampers the identification. However, identification is possible with relatively clear X-ray diffraction patterns.

J.E. de Villiers (1946, p. 20) who made an extensive study of manganese ore in South Africa but examined from the Kalahari Manganese-field only ore from the Black Rock Mine, writes:-
"In the present study which was carried out mainly by ore-microscopic and chemical methods, I have for the most part found it impossible to differentiate between the constituents of psilomelane and the name is therefore used here in the general sense to denote a fine-grained, usually composite substance".

According to Frankel (1953, pp. 577 - 597) cryptomelane is a major constituent of ore from Hotazel, Langdon and Smartt. He identified psilomelane microscopically only in ore from Langdon (p. 592) and gives an X-ray diffraction pattern for cryptomelane. Cameron and Sorem (1960, pp. 278 - 310) found cryptomelane to be one of the major constituents in ore from the Nsuta Mine, Ghana. They do not report the presence of psilomelane. According to Fleischer and Richmond (1943, pp. 269 - 286) cryptomelane is generally more common than psilomelane. Psilomelane does therefore not seem to be so widely distributed as is generally assumed.

The mineral cryptomelane is present throughout the entire Kalahari Manganese-field. Hollandite was identified once only. No other mineral from the psilomelane group was identified either by means of X-ray or optical methods. One of the D.T.A. curves (H3) suggests the presence of psilomelane in some of the ores. This could not be verified by means of X-ray diffraction. For further information the reader is referred to the results of the thermal studies (chapter VI).

a) Cryptomelane - $K_2Mn_8O_{16}$ ------ (simplified to MnO_2)

Physical characteristics: According to Ramdohr (1956, p. 65) the crystal structure of cryptomelane tends to have a very fine acicular development parallel to the c-axis. In the Kalahari Manganese-field certain botryoidal aggregates of cryptomelane consist of very fine needles (photo 55 - pol. sec. H4) which are frequently perpendicular to the botryoidal surface. Cryptomelane is nearly always secondary and of supergene origin. The metallic lustre is steel gray and the fracture conchoidal. It is non-magnetic and takes a good polish. Hardness 5 - 6.

Chemical properties: According to Frankel (1958, p. 535) the K_2O content of ore from the Kalahari Manganese-field, being composed essentially of cryptomelane, is as low as 0.3 to 1.7 per cent. Mathieson and Wadsley (1950, pp. 99 - 101) suggest that the potassium in cryptomelane is distributed at random and is not a~~f~~ fixed quantity. This may possibly explain the low K_2O content (0.38 per cent) of sample H6 (Table 18) which consists of 55 - 65 per cent cryptomelane. In addition it can be pointed out that this high percentage of cryptomelane is present in the few chips selected for ore-microscopical examination from the bulk-sample submitted for chemical analysis. These chips were, however, considered representative of the sample. The powder of the bulk-sample was examined goniometrically by X-rays and the material proved to be essentially cryptomelane.

Optical properties: It is found in most ores from the Kalahari Field in the following associations:-

i) Replacement-ore (photos 57, 58, 59, 60 - pol. secs. BRVI, D6, A4)
ii) Veins of various ages (photos 61, 62, 63 - pol. secs. H10, vuggy-ore)
iii) Colloform and cavity fillings (photo 65 - pol. secs. H4, BR 1)
iv) In rarer samples as massive, cryptocrystalline ore (pol. sec. H6).

Diagnosis: Cryptocrystalline cryptomelane may be mistaken for pyrolusite or nsutite. The reflectance of coarse-grained material is slightly but distinctly darker gray. Hematite is readily distinguished from cryptomelane by means of its higher relief. Spectrochemical determinations were carried out for potassium.

b) *Hollandite* - Approximately $Ba(Mn^{2+},Fe^{2+})Mn_7^{4+}\ O_{16}$

Physical characteristics: It takes a good polish.

Optical properties: The colour in reflected light is gray-black. The bireflectance and the anisotropism are distinct. It shows polysynthetic twinning (photo 66 - pol. sec. H 10a).

Occurrence: The mineral has been identified in one sample from Hotazel only.

Diagnosis: The identification was carried out by means of optical methods only as the sample was too small for X-ray methods, **or spectrochemical determinations for barium.**

16) Manganite - MnO(OH)

Physical characteristics: Small crystals in vugs are found associated with quartz. The crystals are striated parallel to the elongation and are rarely twinned. Manganite polishes with difficulty.

Optical properties: The reflective power is low, the colour in reflected light is gray and the bireflectance is distinct. The anisotropism is strong and the polarization-colours vary between different shades of gray.

Occurrence: The mineral has been identified in ore from Hotazel and Adams only, and then as veins (photo 67 - pol. sec. H7) and as irregular grains in pyrolusite associated with braunite. Transformation to pyrolusite is in various stages from the edge inwards.

Diagnosis: It may be confused with hausmannite. However, manganite rarely shows twinning and internal reflections common to hausmannite.

17) Pyrolusite - polianite - MnO_2

Pyrolusite and polianite are names for the same mineral although they have different modes of occurrence.

Ramdohr (1956, p. 60) suggested the use of polianite-pyrolusite as a coupled designation; pyrolusite proper for the pseudomorphous and replacement material (photos 68, 69 - pol. secs. H2, 7) and polianite proper for the crystals of primary origin (photo 70 - pol. sec. H5). This designation will be followed except that the term 'proper' will be omitted.

a) Pyrolusite

Physical characteristics: Pyrolusite is always pseudomorphous and with the transformation from other minerals shrinkage-cracks form, owing to contraction. According to Ramdohr (1956, p. 61) these cracks lead to apparent changes in hardness and cause the mineral to polish with difficulty. Pyrolusite often discolours the fingers and is non-magnetic.

Optical properties: The colour in reflected light is white to creamy. The bireflectance is distinct and the anisotropism is strong. Under crossed nicols, if the gypsum place is inserted in the optical system, the change of colour is slight as the stage is rotated.

Occurrence: Replacement-structures are numerous. The mineral is found in many samples from Black Rock, Hotazel, Devon and Langdon, as coarse-grained crystals showing shrinkage-cracks which may be filled with cryptomelane or bixbyite (photo 71 - pol. sec. BR 1D), as slender needles and as veins of various ages (photos 61, 62, 64 - pol. sec. H 10), particularly associated with veins of cryptomelane and nsutite. In ore from Black Rock large areas consisting of pyrolusite are common and in these the mineral forms leaf-like flakes which discolour the fingers.

Diagnosis: The identification of the coarse-grained material is not difficult as the reflective power is very high, the anisotropism is strong and the shrinkage-cracks are diagnostic.

b) Polianite

Physical characteristics: The colour resembles that of pyrite. Hardness < 6.

Optical properties: Same as for pyrolusite.

Occurrence: Found in ore from Hotazel as a vein in which individual crystals show no shrinkage-cracks (photo 70).

Diagnosis: Same as for pyrolusite.

13) Todorokite - Mn-O (generalised formula)

The mineral todorokite was first identified by Yoshimura (1935, p. 673). He considered it to be a hydrothermal alteration product of inesite. The second occurrence of todorokite was described as recently as 1960 by Levinson (1960, pp. 302 - 307). Lawrence (1962, p. 59) considers the Philipsburg todorokite to be of supergene origin. In South Africa the asbestiform mineral was known for a long time but was identified as todorokite by Prof. W.J. van Biljon in ore from the Smartt Manganese Mine (personal communication) and by Mr. R.J. Ortlepp in ore from the Orient Manganese Mine (personal communication). Frankel (1953, p. 533) considers the fibrous mineral to be cryptomelane which is in places replaced by pyrolusite. The additional X-ray reflections could be due to anhydrous montmorillonite, according to Frankel.

Todorokite was identified in all the mines of the Kalahari Manganese-field, except at Black Rock. This fact is considered of interest as the Black Rock Mine is the only mine of the group of mines in the Kalahari Manganese-field where banded ironstone and manganese ore are found outcropping.

The close resemblance of some todorokite to asbestos (photo 72) has been the cause of much speculation and has been used by geologists (John de Villiers, 1960, p. 157) as an argument that the banded ironstone in which the ore is found must be from the Lower Griquatown Stage which is known for its economic deposits of asbestos fibre. However, the todorokite does not seem to represent replaced asbestos fibre. The criss-cross nature of the todorokite shown in photos 73, 74 and 75, and the flaky nature of the todorokite (photos 76, 78 - samples T1, T2, T3) as well as the absence of magnetite which is often associated with asbestos, tends to contradict the replacement theory.

It was considered appropriate to carry out a more detailed investigation of this mineral. This investigation involved X-ray powder data (Table 10), chemical analyses (Table 11), D.T.A. (Table 12) and electron diffraction data. The latter was carried out by the C.S.I.R. and the ISCOR Research Laboratories. Two samples of todorokite (photo 73) from the Hotazel Mine were selected for this investigation. Both samples are relatively free from contaminating material.

Sample A (dog-tooth spar, photos 73, 74 and 75). This sample gives the impression of being harder than sample B.

Sample B consists of fine, fluffy needles, blue ~~of~~ in colour, and resembles asbestos fibre. It was not possible to prepare a polished section of this sample as the material does not lend itself to polishing.

The electron micrographs show both samples A and B to be tabular and flattened on (001) (photos 79, 80) and it appears as if the crystals have two perfect cleavages (001) and (100). Both samples gave similar electron-spot patterns and correspond well with the one published by Straczek (1960, pp. 1180 - 1181). The array of spots along straight lines (photo 80) may be due to stacking faults or twinning.

Straczek (1960, p. 1179) gave the following data for todorokite:-

Monoclinic or orthorombic

$a = 9.75$ Å ; $b = 2.84$ Å ; and $c \sin\beta = 9.59$ Å

The X-ray powder pattern was indexed by Straczek assuming an orthorombic cell ($\beta = 90^{\circ}$)

The method of indexing the electron spot pattern of sample A (photo 80) is illustrated in photo 81. The following calculations were made from the electron diffraction pattern of sample A:-

In the reciprocal latice

$$r_a = 1/a \quad ; \quad r_b = 1/b$$

therefore $$\frac{r_a}{r_b} = {}^{1}/_{a} \Big/ {}^{1}/_{b} = {}^{b}/_{a}$$

In pattern A the repeat distances r_a and r_b measured 0.51 and 1.75 cm respectively.

Assuming the parameters given by Straczek (1960, p. 1179) to be correct and assuming an orthorombic cell the following applies:-

$$\frac{r_a}{1.75} = \frac{2.84}{9.75}$$

$$r_a = \frac{2.84 \times 1.75}{9.75} = 0.509 \text{ cm} .$$

The value agrees well with the measured distance $r_a = 0.51$ cm .

Some of the analyses of Straczek (1960, p. 1177) show 0.14 to 1.05 per cent BaO and 0.2 to 1.45 per cent

Na_2O. There is good agreement between the analyses of sample A and sample B and the ore from Japan as given by Yoshimura (1935) - Table 11.

Physical characteristics: Todorokite discolours the fingers and the colour and lustre is like that of graphite. Electron micrographs of samples A and B show the crystals to be plates flattened on (001) (photo 80). This deduction is made as a great number of the crystals were oriented in such a way as to give electron spot patterns similar to the one of photo 80. Todorokite takes a poor polish and the hardness is $\leqslant$ 2

Optical properties: The reflective colour is white-gray and the bireflectance is medium-weak. By means of a reflectivity meter assembled at the University of Pretoria, the maximum reflectivity was measured at 20.8 per cent and the minimum at 18.5 per cent. The anisotropism is distinct and the polarization colours vary from white to gray (photo 74 - pol. sec. T 1). Under crossed nicols, if the gypsum plate is inserted in the optical system, the change of colour is slight as the stage is rotated.

Occurrence: Todorokite is present in all the mines of the Kalahari Manganese-field except at Black Rock. It is considered to be of supergene origin and occurs as follows:-

a) as veins (photo 82 - pol sec. S5)
b) as a replacement of hausmannite and is common in the mines Smartt, Adams, Mamatwan and Devon (photo 32 - pol. sec D3)
c) in nodules (photo 83 - pol. sec. D1)

It is generally closely associated with gypsum and calcite. Todorokite is replaced by cryptomelane.

TABLE 10.

X-ray powder data for todorokite and woodruffite.

TODOROKITE						WOODRUFFITE	
⊗		Hotazel +		Straczek @		Frondel x	
d.calc.	hkl	d.meas.	I.obs.	d.meas.	I.obs.	d(Å)	I/I_o
9.75	100						
9.589	001	9.578	10	9.6	s	9.51	5
		7.087	2			6.99	4
6.837	101						
		6.549	2				
4.87							
4.794	002	4.784	7	4.77	s	4.77	10
4.34	201						
4.302	102	4.406	2			4.40	3
		4.193	2.5				
						4.08	1
3.42						3.48	2
3.25							
3.19	003	3.166	0.5	3.19	w	3.13	2
3.078	301	3.073	1	3.11- 2.95	band	3.05	1
3.037		3.002	1				
						2.84	0.5
2.73		2.745	broad				
2.69	302			2.7	band		
2.673						2.63	2
						2.56	1
2.449	012			2.448	m	2.466	4
2.397	004	2.397	1.5	2.398	s	2.404	5
2.362	401	2.345	2	2.34	m		
2.328	104	2.312	1.5				
2.188	212	2.23	1	2.21	m	2.225	5
2.172	402			2.16	f-b	2.152	1
2.091	3.11	2.099	0.5	2.11	f-b	2.13	2
1.956	312					1.984	3
1.918	005			1.92	w	1.922	1
1.911	501					1.895	2
1.779	313	1.765	0.5			1.747	2
1.727	412			1.74	wm		

TABLE 10- contd.

Å		Hotazel †		Straczek @		Frondel x	
d.calc.	hkl	d.meas.	I.obs.	d.meas.	I.obs.	d(Å)	I/Io
1.709	404			1.69	f-b	1.68	1
1.652	305	1.641	1.5			1.66	2
						1.636	0.5
						1.592	1
1.525	512			1.53	w		
1.424	020	1.425	0.5	1.423	m	1.423	5
1.409	021	1.408	0.8				
1.393	700	1.385					

Å Calculated at the C.S.I.R. on program 704, using Straczek's parameters $a_o = 9.75$ Å; $b_o = 2.849$ Å; $C_o = 9.59$ Å; $\alpha = 90^\circ$; $\beta = 90^\circ$; $\gamma = 90^\circ$.

@ Straczek et al. (1960, p. 1182).

x Frondel (1953, p. 766).

† Fe K_α - rad. 114 mm camera.

TABLE 11.

CHEMICAL COMPOSITION OF TODOROKITE

	A	B	C
SiO_2	0.25	0.34	1.73[a]
Al_2O_3	0.40	0.33	0.28
Fe_2O_3	1.44	0.20	0.20
P_2O_5	0.07	0.02	-
MnO	7.64	8.23	12.37
MnO_2	73.52	71.17	65.59
MgO	2.72	2.46	1.01
CaO	2.01	3.85	3.28
SrO	0.06	0.03	-
BaO	-	0.20	2.05
LiO_2	0.10	0.10	-
Na_2O	0.49	1.49	0.21
K_2O	0.85	0.45	0.54
SO_3	0.50	1.44	-
CO_2	1.01	1.94	-
H_2O	8.96	7.86	11.28
Cr_2O_3	-	0.001	-
CuO	0.002	0.001	-
Others	-	-	0.70[b]

[a] Includes SiO_2 0.45, insol. 1.28%

[b] Includes P_2O_5 0.42; SO_3 0.28; CO_2 trace, TiO_2 trace.

A - Hotazel sample A

B - Hotazel sample B

C - After Yoshimura, Japan (1935)

(Samples A and B were analysed by Dr. C.E.G. Schutte and Mr. J.L. Pretorius of the Soils Research Institute, Pretoria).

TABLE 11 - contd.

CALCULATED IN TERMS OF 12 O - ATOMS

	A		B		C	
Mn^{2+}	0.65)		0.76)		1.17)	
Mn^{4+}	5.12)	6.18	5.40)	6.57	5.06)	6.40
Mg^{c}	0.41		0.41)		0.17)	
Ca^{d}	0.23)		0.46)		0.48)	
Na	0.10)	0.38	0.32)	0.81	0.05	0.61
K	0.05)		0.03)		0.08)	

c - includes Co and Cu

d - includes Sr and Ba

A spectrochemical test for Zn was negative - samples A and B

Diagnosis: In samples consisting of coarse-grained crystals the identification is easy. However, fine-grained todorokite may be mistaken for cryptomelane but the reflective power is higher than that of cryptomelane. The X-ray powder pattern resembles lithiophorite and particularly woodruffite. However, the anisotropism of todorokite as tested with the gypsum plate is different to that of lithiophorite in the respect that the grains do not discolour to the same extent. Woodruffite differs chemically from todorokite.

Differential thermal analyses: The thermal reactions recorded on todorokite are tabulated in Table 12.

TABLE 12.

D.T.A. of Todorokite

	Hotazel	Straczek et al. (1960, p. 1181)
Endothermic:	80 °C	160 °C
	366 "	292 "
	488 "	437 "
	687 "	673 "
	862 "	
Exothermic:		344 °C
	608 °C	589 "
	967 "	

Straczek did not report results beyond 902 °C. No attempt was made by the author to interpret the complex thermal curve of the todorokite from Hotazel.

19) Lithiophorite - $LiMn_3 Al_2O_9.3H_2O$

Physical characteristics: Lithiophorite takes a fair to good polish.

Optical properties: The reflective power is like that of chalcophanite. However, the bireflectance is strong (from gray to dark-gray) but weaker than that of chalcophanite. The anisotropism is strong and the polarization-colours vary from light-gray to dark-brown and bluish gray. Under crossed nicols, if the gypsum plate is inserted in the optical system, the change of colour is distinct as the stage is rotated. The grains discolour from blue to yellow.

<u>Occurrence</u>: Lithiophorite has been identified in ore from Black Rock, Adams and Mamatwan and usually in microscopic quantities, as veins (photo 84 - pol. sec. BRV1) and as parts of aggregates.

<u>Diagnosis</u>: This mineral may be confused with chalcophanite or fine-grained todorokite. However, the anisotropism as tested with the gypsum plate distinguishes it from todorokite and the X-ray diffraction pattern from chalcophanite.

20) <u>Chalcophanite</u> - $(Zn,Mn^{2+},Fe^{2+})Mn_2O_5.2H_2O$

The presence of chalcophanite is suspected in some of the samples owing to a reflection appearing in some of the diffractometer patterns at 6.75 Å. No chalcophanite could however, be observed optically in these samples, except in material from Hotazel where in a rare case a 'chalcophanite-like' mineral is closely associated with cryptomelane and pyrolusite (photos 85, 86 - pol. sec. H4). The identification of this 'chalcophanite-like' mineral is based on optical observations only as the intimate association with cryptomelane and pyrolusite render identification by means of an X-ray powder camera unsatisfactory. A test for Zn did not yield conclusive results.

<u>Optical properties</u>: The colour in reflected light is variable in shades of gray-white. The bireflection

is very strong and the anisotropism is also very strong but without bright colours. Under crossed nicols, if the gypsum plate is inserted in the optical system, the change of colour is distinct as the stage is rotated (determined on material from outside the Kalahari Manganese-field).

Occurrence: According to Ramdohr (1956, p. 67) this mineral is rarely found alone and it is widely spread as an auxiliary component of many 'psilomelanes'. Chalcophanite is very fine-grained and often devoid of zinc (Ramdohr 1956, p. 67). The ring-like texture observed (photo 86) cannot be explained. Possibly this may be part of a large-scale colloform texture. Similar textures are observed in todorokite.

Diagnosis: The strong bireflectance of chalcophanite is diagnostic except that it may be confused with lithiophorite. However, the X-ray powder pattern of chalcophanite distinguishes it from lithiophorite.

21) Nsutite - MnO_2 (gamma - MnO_2)

The term 'gamma - MnO_2' as first used by Glemster (1939, pp. 1879 - 1881) referred to a specific, artificially prepared manganese dioxide. Later this term was applied to a group of artificial manganese oxides which differed amongst themselves slightly in their X-ray diffraction patterns. The synthetically produced manganese dioxides are classified according to their crystal structure and crystallinity as follows: alpha, beta, gamma and delta of which the gamma and the delta types are suitable for use in dry-cell batteries. Nsutite is the naturally occurring equivalent of 'gamma - MnO_2'. As stated by Zwicker and co-workers (1962, pp. 246 - 266) several authors recognised nsutite in manganese ore from Nsuta, Ghana. Cameron and Sorem (1960, pp. 278 - 210) have also described nsutite from Nsuta, Ghana. They suggested that the term 'gamma - MnO_2' be used for the artificial products only and 'Nsuta - MnO_2' for the naturally occurring equivalent which they separated into "1.64, 1.65 and 1.67" types on the basis of X-ray diffraction spacings. Zwicker and co-workers (1962, pp. 246 - 266) also examined ore from Nsuta and suggested that the name 'nsutite' (pronounced en.sootit) for the naturally occurring equivalent of 'gamma - MnO_2'. On the basis of chemical analyses of the 1.64 and 1.67 types, Zwicker suggested the names 'nsutite' and 'manganoan nsutite' of which nsutite is the more common one. In this treatise the classification of Zwicker will be adhered to i.e. nsutite for the mineral with the 1.64 Å reflection.

In South Africa nsutite was first identified by Ortlepp in ore from the Orient Manganese Mine (in press) and in ore from near Lobatsi (personal communication Mr. R.J. Ortlepp). J.E. de Villiers (1946, p. 20) mentions a 'second constituent of psilomelane' which, according to the description, could be nsutite.

The papers by Zwicker (1962) and Cameron and Sorem (1960) have been concerned with well-crystallised nsutite. In the Kalahari Manganese ore the nsutite is poorly crystallised as determined by its X-ray diffraction pattern and is also intimately intergrown with other manganese minerals. Satisfactory identifications were carried out only with great difficulty and in many samples, owing to lack of sufficient material, were based on optical data only.

Physical characteristics: It is non-magnetic.

Optical properties: Nsutite is opaque and the colour in reflected light is creamy white, very much like pyrolusite, but less creamy. The reflective property is not decreased with oil immersion. The bireflectance is difficult to observe on fine-grained varieties but it is pronounced in the coarser variety. Anisotropic effects are distinct and polarization colours vary between light- and dark-gray. Under crossed nicols, if the gypsum plate is inserted in the optical system, the change of colour is slight as the stage is rotated.

Occurrence: The mineral was only recently recognised in ore from South Africa and apparently it is not rare. In the Kalahari Manganese-field it is of supergene origin and was positively identified only in ore from the Hotazel Mine where it forms veins in the ore and also replaces hausmannite, particularly along cracks and twin lamellae (photos 87 to 91 - pol. secs. H10, a, b, c). A mineral with similar reflectivity was observed at Langdon Mine but the identification could not be verified by X-ray methods owing to the fine intergrowth of minerals. The individual particles vary in size from colloidal to 1 micron and in rare samples only is it coarser grained (photos 92, 93 - pol. secs. H9, a, b, c). The coarse-grained nsutite of photo 93 probably represents vug filling.

Diagnosis: The colour, hardness and reflectivity is very much the same as for pyrolusite and it is therefore difficult to distinguish nsutite from fine-grained pyrolusite. However, the colour of nsutite is less creamy and the X-ray diffraction pattern is distinct in that the reflection at 3.97 Å is not observed in pyrolusite.

22) Cymrite - $2BaO.2\frac{1}{2}Al_2O_3.5SiO_2.3.65H_2O$

Cymrite was originally described by Smith and co-authors (1949) from the Benallt Manganese Mine, Rhiw, Carnarvonshire, Great Britain. The name comes from the Welsh for Wales, Cymru, which is pronounced 'kumry'. The cymrite from Benallt occurs as colourless plates up to 7 mm in diameter and about 0.5 mm thick and hexagonal prisms about 1 mm long. It is restricted to veinlets cutting across hydrothermally-derived manganese ore. Brosge (1960) identified cymrite in his work in the south-central portion of the Brooks Range and mentions that it was present in samples from a pyritized zone near the head of Bonanze Creek in the Wiseman Quandrangle. A third occurrence was described by Runnels (1964, p. 158) in a copper deposit, Brooks Range, Alaska, where it occurs in dolomitic and sideritic wall-rock as crude hexagonal, plate-like crystals up to 4 mm in diameter and 0.5 mm thick.

Smith and co-authors (1949) gave chemical, optical and X-ray data and reported a pseudo-unit cell : $a_0 = 5.33$ Å and $c_0 = 7.67$ Å ; the true cell is stated to have $a = 42$ Å.

According to Smith and co-authors (1949, p. 681) cymrite probably has a very simple type of structure. As far as known no structural analysis of it has yet been published. The two chemical analyses given by Smith and co-authors (p. 678) are not in agreement with each other and do not agree well with the one published by Runnels (1964, p. 163). Runnels states that his formula is to be preferred because of the larger amount of material (780 mg) he used for the analysis as against 7 and 20 mg used by Smith and co-authors. The calculated density of cymrite (calculated for O = 23 after Runnels) is 3.44 which is in good agreement with the measured value of 3.4 and Smith's value of 3.413 (± 0.005).

The formulae of Runnels (1964, p. 163) and Smith (1949, p. 673) are not in agreement with each other. According to Runnels (p. 162) the MgO in his sample is present as dolomite but he does not include any CO_2 in his analysis. According to both Runnels and Smith cymrite does not contain any of the following:- Fe_2O_3, MnO, MgO, CaO, Na_2O, K_2O, P_2O_5, F, FeS_2. The analysis of cymrite from Black Rock was not recalculated for the purpose of determining the empirical unit cell contents because of the uncertainty regarding the formula of cymrite and also on account of the high percentage of impurities present. Dispersed in the cymrite are very fine, red iron oxide and minute grains of hematite. Impurities in the matrix between the grains of the material are albite, orthoclase, piedmontite and sphene. Before submitting the powdered sample (-200 mesh) for a chemical analysis some of the iron was removed by means of a magnetic separator. Some of the powder for the chemical analysis was mounted and polished for examination by reflected light. The polished surface was immersed in dilute hydrochloric acid (10 per cent) for five minutes. The effect of the acid was that scratches on the cymrite became more pronounced. Considering the finely dispersed nature of the iron oxides in the cymrite it was concluded that a fairly drastic treatment with acid would be necessary to remove the iron oxide and this might then have had a detrimental effect on the cymrite.

TABLE 13

CHEMICAL COMPOSITION OF CYMRITE

	1.	2.	3.
SiO_2	26.8	37.65	32.06
Al_2O_3	21.77	14.94	27.00
Fe_2O_3	13.08	9.26	-
MnO	0.17	0.86	-
MgO	0.67	-	0.14
CaO	0.65	-	0.85
Na_2O	0.07	-	0.00
K_2O	0.12	-	0.22
H_2O^+	3.70	5.31	7.03
H_2O^-	0.14		0.00
CO_2	0.76	-	-
TiO_2	0.97	-	0.06
P_2O_5	0.06	-	-
BaO	31.01	31.50	31.36
F	-	-	0.3
FeS_2	-	-	1.46
	99.97	99.52	100.18

1. Impure cymrite from Black Rock Mine (analysed by C.E.G. Schutte and J.L. Pretorius of the Soils Research Institute, Pretoria).

2. Cymrite from Benallt Manganese Min e Rhiv. Carnarvonshire (Smith et al. 1949, p. 678).

3. Cymrite from a copper deposit, Brooks Range, Alaska (Runnels, 1964, p. 162).

TABLE 13b.

X-RAY DIFFRACTION DATA FOR CYMRITE.

Smith et al. (1949)			Black Rock. (57.5 mm camera)	
I.obs.	d.Å	Index	I.obs	d.meas.
S	7.7	0001	6	7.724
VVW	4.6	$10\bar{1}0$	2	4.605
VS	3.95	$10\bar{1}1$	10	3.976
VS	2.95	$10\bar{1}2$	10	2.934
S	2.67	$11\bar{2}0$	9	2.660
VW	2.57	0003		
VW	2.53	$11\bar{2}1$	2	2.530
W	2.32	$20\bar{2}0$	4	2.318
M	2.24	$10\bar{1}3$	6	2.221 B
M	2.21	$20\bar{2}1$		
VW	2.11			
W	1.99	$20\bar{2}2$	3	1.973
MW	1.92	0004	3	1.908
M	1.849	$11\bar{2}3$	5	1.839
VW	1.783	$10\bar{1}4$	1	1.765
MW	1.705	$21\bar{3}1$	4	1.704
MW	1.594	$21\bar{3}2$	4.5	1.589
W	1.565	$11\bar{2}4$	3	1.552
W	1.544	$30\bar{3}0$	3	1.538
W	1.468	$10\bar{1}5$	3	1.456
VW	1.452	$21\bar{3}3$	3	1.443
VW	1.341	$22\bar{4}0$	2	1.334
VW	1.324	$30\bar{3}3$	2	1.321
W	1.283	$31\bar{4}0$	2.5	1.278
VW	1.269	$31\bar{4}1$	1	1.265

B	broad
S	strong
VS	very strong
W	weak

Phase relations between cymrite and celsian, $BaAl_2Si_2O_8$, have been carried out by Seki and Kennedy (1964, pp. 1407 - 1426). They claim to have established that hexagonal celsian (synthetic, and ~~has never been~~ not yet found in nature) forms a complete solid solution series with cymrite by substitution of Al^{3+} for $[Si(OH)]^{3+}$ with increasing water pressure (and/or decreasing temperature). According to Seki and Kennedy (p. 1408) hexagonal celsian has been found to consist of two forms which are hexagonal and orthorombic respectively. Seki and Kennedy have also examined another kind of barium-aluminium silicate, monoclinic celsian, which has been described particularly in manganiferous ore deposits (Vermaas, 1953, p. 845; and J.E. de Villiers, 1951, p. 89). According to Seki and Kennedy the stability relation between hexagonal and monoclinic celsian has ~~never~~ not yet been clarified. However, it is well known that monoclinic celsian and monoclinic feldspar form a complete or partial solid solution through the mineral hyalophane, which is intermediate both in chemical composition and in physical properties (Vermaas, 1953, p. 849).

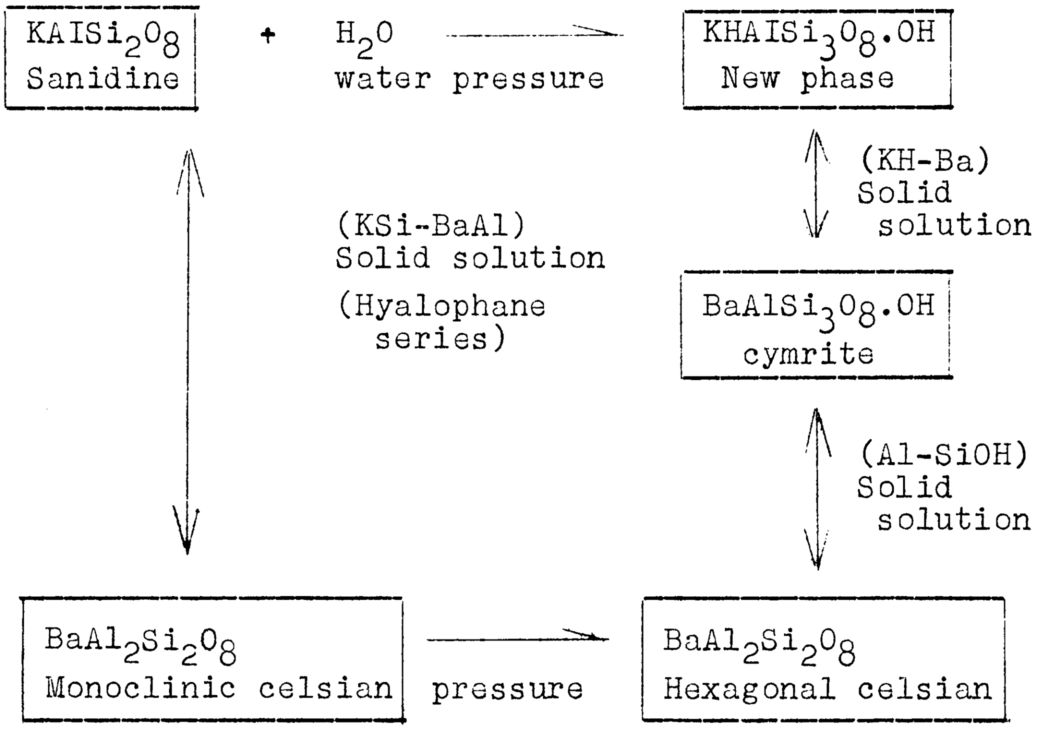
The points of interest in the phase studies of Seki and Kennedy are:-

a) High water pressure or high chemical potential of water is necessary for the formation of cymrite. This may possibly be a reason why the mineral cymrite is so rare in nature.

b) The close relationship between cymrite and the barium feldspars (Table 14).

TABLE 14.

General relationships between potassium and barium feldspars (after Seki and Kennedy, 1964, p. 1407).



Runnels (1964, p. 164) reports that where subjected to supergene processes, cymrite alters to an extremely fine-grained mixture of kaolinite and barite.~~which tends to strengthen the association with feldspar as kaolinite is a common alteratio~~n ~~produc~~t ~~of feldspar.~~

In the Black Rock Mine barite was found close to one of the bostonite bodies and is therefore possibly an alteration product of the cymrite.

Physical characteristics: Cymrite is hexagonal and colourless when pure. It has a perfect basal (0001) cleavage and the lustre is like satin.

Optical properties: The mineral is uniaxial negative, the extinction is straight and the indices of refraction are: $\epsilon = 1.615$ and $W = 1.619$ (± 0.005). Crystals of different habits are shown in photo 94. The mineral contains iron as impurity along the cracks.

Occurrence: It is present in the bostonite at the Black Rock and Hotazel Mines. Some samples contain an odd lath of feldspar (approx. 5%) which is now altered to kaolinite.

Diagnosis: Crystals of cymrite that show cleavage may be mistaken for pyroxene. The colourless crystals with lower relief (photo 94 - thin sec. TH 3) may erroneously be identified as either nepheline or apatite. The X-ray diffraction pattern of cymrite is excellent.

23) Piedmontite - $Ca_2(Al,Fe,Mn)_3(OH)Si_3O_{12}$

Physical characteristics: Piedmontite occurs as small laths.

Optical properties: The mineral is biaxial, 2V(+) is large, the pleochroism varies between lemon, orange and amethyst-pink and the anisotropism is strong. The index of refraction is $n = 1.72$ (±); the small grains do not allow a more accurate determination.

Occurrence: It is present only in the bostonite from Hotazel and then as minute laths (thin sec. TH 4).

Diagnosis: The identification of the mineral from Hotazel is rather difficult owing to the small grain-size (5 μ). The X-ray diffraction pattern is poor owing to lack of sufficient material but a fair agreement with that of the ASTM cards could be recognised.

24) Acmite - $NaFe^{3+}Si_2O_6$

Physical characteristics: Dark-brown crystalline aggregates of acmite are observed in hand-specimens.

Optical properties: The colour is mainly red-brown, also light-brown to yellow, occasionally dark-green. The grain-size ranges from 10 to 100 micron.
$2V(-) = 68^\circ$, weakly pleochroic in shades of brown, and
$X \wedge C = 2 - 15^\circ$ (not accurate); $n\alpha = 1.75$,
$n\beta = 1.77$ (sodium light).

Occurrence: Acmite is present at Black Rock only and then as aggregates in the banded ironstone. Blobs of andradite and acmite are mutually associated (photo 51 - thin sec. TB 2).

Diagnosis: The mineral was identified by means of X-ray, chemical (Table 15) and optical data.

According to Deer, Howie and Zussman (1963, Vol. 2, p. 80) the following applies as far as the nomenclature of acmite and aegirine is concerned:-

> "Although the term acmite has generally been adopted to describe the $NaFe^{3+}Si_2O_6$ 'molecule', both aegirine and acmite have been used for pyroxene of approximately this composition. Aegirine is generally restricted to the green to black bluntly-terminated crystals that are strongly pleochroic in thin section whereas acmite is restricted to the brown variety showing pointed terminations and is only weakly pleochroic."

Considering the general brown colour and weak pleochroism of the mineral from Black Rock the name acmite is adhered to.

TABLE 15.

Chemical composition of acmite

	1.	2.
SiO_2	53.1	52.48
TiO_2	0.02	0.57
Al_2O_3	0.40	0.96
Fe_2O_3	32.42	31.74
FeO	0.008	0.93
MnO	0.54	0.10
MgO	0.11	0.15
CaO	0.63	0.28
Na_2O	11.6	12.05
K_2O	0.07	0.35
H_2O -	.87	
	99.76	99.61

Calculated in terms of 6 O-atoms

	1.		2.	
Si	2.055		2.004	
Al	0.018	0.986	0.043	1.02 @
Ti	0.001		0.016	
Fe^{+3}	0.940		0.912	
Mg	0.006		0.008	
Fe^{+2}	0.003		0.030	
Mn	0.018		0.003	
Na	0.830	0.86	0.892	0.93 x
Ca	0.026		0.011	
K	0.004		0.017	

1.) Acmite from Black Rock (analysed at the Research Laboratories of ISCOR).

2.) Acmite, Quincy, Massachusetts (Deer, Howie and Zussman, 1963, Vol. 2, p. 82). Includes ZrO - 0.41; $(Ce, Y)_2O_3$ - 0.48.

@ Includes Zr - 0.007

x Includes Ce - 0.006

25) Nontronite - montmorillonite

Nontronite is present as an alteration-product of the bostonite at Hotazel, Devon and Black Rock. The mineral is soft, soapy and gives X-ray diffraction and D.T.A. patterns that correspond with montmorillonite and is named nontronite owing to its typical light-green colour. For more detail regarding the mode of occurrence the reader is referred to the heading 'Bostonite' under chapter IV.

26) Hydromica

This mineral is associated with nontronite as an alteration-product of the bostonite from Hotazel and Black Rock. In the material representing the altered bostonite at Devon no hydromica was observed. The mineral was identified by means of X-ray diffraction, D.T.A. and optical methods.

27) Barytes - $BaSO_4$

This mineral is present in ore from Black Rock only. John de Villiers (1960, p. 148) reported barytes to be as common as opal, particularly in material from shaft No. 4. The present investigation disclosed only a few isolated samples containing barytes. However, the chemical analyses tabulated in Table 18 show appreciably more BaO in the ore from Black Rock Mine than in the ore from any of the other mines.

28) Manganous Manganite - $MnO_2.Mn(OH)_2$

During an examination of the oxidation of manganese hydroxide, Feitknecht and Marti (Ljunggren, 1955, p. 145) found the final product of oxidation to be approximately $4MnO_2.Mn(OH)_2$ and named it manganous manganite. The X-ray pattern of their material has only five distinct reflections of which the most diagnostic is the one with a d-spacing of 7.13 Å. Manganous manganite has been reported in manganiferous bog-ore from Glitrevand, Norway (Ljunggren, p. 146) where it seems to be closely related to delta-MnO_2 which has only two X-ray reflections. Little is known about these minerals and even Ramdohr (1956) does not mention manganous manganite or delta-MnO_2.

The d-spacing 7.13 Å as well as the d-spacing 6.95 Å of cryptomelane was found in the ore consisting mainly of cryptomelane and wad which is from Hotazel Mine. The other X-ray reflections corresponding with those of manganous manganite could not be recognised as they coincide with those of cryptomelane and other minerals. Delta-MnO_2 may be present in this ore, but owing to overlapping of reflections a positive identification of this oxide is not possible.

IV. DISTRIBUTION OF THE MINERALS IN THE ORE AND IN THE WALL-ROCK

A. THE MINERALOGY OF THE ORE

The various ores are named according to the chief ore-minerals present (Table 16) and the minerals of the ore are discussed in order of abundance. The description of the ore-body commences with the foot-wall side, and proceeds upwards towards the hanging wall.

THE EASTERN BELT

HOTAZEL MINE

The description of the distribution of the minerals in the ore-body at Hotazel is based on the examination of ten samples representative of the lower and the upper ore-bodies only. The mine was sampled towards the end of 1961 in an area relatively free from ferruginisation. Mining operations only reached the more ferruginised portions towards the middle of 1963.

The lower ore-body

1) Bottom cut

CONTACT-ORE: This ore is situated near the underlying banded ironstone (pol. sec. H1).

a) Amorphous material - is common and probably represents cryptomelane. For further information the reader is referred to the thermal studies (chapter VI).

b) Hausmannite - is present in limited amounts although it is fairly common throughout as remnants. It is

TABLE 16.

Distribution of the manganese ore
in the Kalahari Manganese-field

Mine	Upper ore-body	Middle ore-body	Lower ore-body
HOTAZEL	Ore rich in hausmannite and jacobsite	present but not examined	Bottom cut: Contact-ore Braunite rich ore Cryptomelane-rich ore Top cut: Cryptomelane-rich ore Hausmannite-rich ore Ore rich in cryptomelane and wad Ore rich in cryptomelane and jacobsite
DEVON	not present	not present	Cryptomelane-rich ore Ore rich in braunite and cryptomelane
LANGDON	not present	not present	Cryptomelane-rich ore Ore rich in cryptomelane and jacobsite Hausmannite-rich ore
MAMATWAN ADAMS			Ore rich in cryptomelane and braunite
SMARTT			Ore rich in braunite and todorokite
BLACK ROCK	Ore rich in braunite, hematite and cryptomelane	Ore rich in braunite, hematite and cryptomelane	Ore rich in braunite, bixbyite and cryptomelane

generally altered to cryptomelane and todorokite.

c) Cryptomelane - replaces hausmannite.

d) Goethite - is dissemminated throughout in large patches.

e) Braunite - is present as small crystals in limited amounts and in a few patches.

f) Pyrolusite - constitutes minute inclusions in limited amounts.

g) Todorokite - generally replaces hausmannite.

h) Opal - is fairly common as narrow veins and vug-fillings.

Textural relationships of the contact-ore

The ore is spotted owing to selective weathering (photo 95) and is texturally fine-grained with mottled patches consisting of aggregates of altered hausmannite crystals of which the outlines are irregular.

BRAUNITE-RICH ORE: This ore forms the largest portion of the bottom cut (pol. secs. H2, 3, 4).

a) Braunite - is the chief ore-mineral (5 to 50 micron) and is predominant in some areas where it is closely packed.

b) Pyrolusite - is very fine-grained (1 to 10 micron) and it replaces braunite. It is also associated with cryptomelane in nodules, giving the ore a spotted appearance. Veins of pyrolusite intersect most of the minerals.

c) Cryptomelane - is associated with braunite, mainly as needles and as veins. The mineral is mainly of secondary origin.

d) Goethite - is fine-grained and is present mainly in the ground-mass in between braunite and pyrolusite (photo 22(a) and (b) - pol. sec. H2) and covers large areas. It is also finely dissemminated in patches and as bands.

e) Hausmannite - is present in some of the samples, in clusters and zones and also as scattered remnants (50 to 100 micron).

f) Manganite - is present in some samples as equant grains (10 to 40 micron), in veins and in vein-like bodies. It is also dissemminated in the groundmass.

g) Hematite - is fairly common where associated with braunite although in limited amounts and dissemminated.

h) Chalcophanite - is intergrown with cryptomelane, in aggregates and colloform banding (photo 85 - pol. sec. H4) and as 'cell-like' structures (photo 86 - pol. sec. H4).

i) Bixbyite - is present in hausmannite as a few isolated, small crystals and also in a vein that intersects most minerals.

j) Lithiophorite - constitutes very small crystals in altered hausmannite and was observed in one sample only.

k) Amorphous material - occurs in limited amounts, although it is fairly common and it replaces hausmannite in particular.

Textural relationships of the braunite-rich ore

The ore is massive and has a layered appearance (photo 96 - pol. sec. H3) accentuated by the concentration of goethite, pyrolusite, cryptomelane and manganite along layers and by nodules of pyrolusite, braunite and cryptomelane and also by colloform banding (photo 85 - pol. sec. H4).

2) Top cut

CRYPTOMELANE-RICH ORE: This ore is situated near the bottom cut (pol. sec. H6).

a) Cryptomelane - In certain portions the cryptomelane is free from inclusions and in others it contains equant grains of minute braunite and pyrolusite. Coarser grained cryptomelane in veins intersects most minerals.

b) Braunite - Equant grains of braunite are concentrated along bands. These grains are minute in size.

c) Pyrolusite - is present as veins and also in limited amounts in patches of which the outlines are irregular.

d) Goethite - is dissemminated throughout the groundmass but is also concentrated in patches and in veins.

e) Hematite - occurs mainly as minute inclusions concentrated in banded patches.

f) A 'nsutite-like' mineral - The mineral is found as veins and in patches. (The material is, however, insufficient for X-ray identification).

Textural relationships of the cryptomelane-rich ore

The ore has a massive, dense appearance and slight layering is observed where braunite and goethite are concentrated in zones.

HAUSMANNITE-RICH ORE: This ore is present near the centre of the top cut (pol. sec. H7).

a) Hausmannite - is fairly unaltered and coarse-grained, and is present in closely packed patches.

b) Jacobsite - occurs

   i) as bands resembling veins in hausmannite that have formed as the result of exsolution and give the false impression of being transgressive (photo 39)

   ii) disseminated throughout hausmannite as a product of exsolution (photo 30).

Jacobsite probably crystallised from a residual solution after the hausmannite had formed. For further details regarding the origin, the reader is referred to chapter VI under 'Thermal studies'.

c) Bixbyite - is present in limited amounts:-

   i) in veins, associated with a younger manganite. The bixbyite occurs along the edge and the manganite towards the centre of veins and vugs

   ii) disseminated throughout hausmannite.

d) Manganite - is sometimes associated with bixbyite in veins and vugs.

e) A 'nsutite-like' mineral - is associated with manganite (photo 97) as a replacement intergrowth and is also intergrown with pyrolusite.

f) Cryptomelane - Cryptocrystalline cryptomelane is found in patches and in veins that intersect a 'nsutite-like' mineral.

g) Pyrolusite - is a product of replacement of hausmannite (photo 68) and it is also intergrown with a 'nsutite-like' mineral.

h) Goethite - is disseminated and concentrated in patches.

i) Hematite - is present as minute inclusions in bixbyite and jacobsite.

j) Lithiophorite - is found as isolated, minute crystals.

Textural relationships of the hausmannite-rich ore

The ore has:-

i) a dull but red-brown sheen brought about by the coarseness of the hausmannite

ii) a layered appearance (photo 97) brought about by parallel bands of manganite, a 'nsutite-like' mineral and bixbyite.

ORE RICH IN CRYPTOMELANE AND WAD: This ore is present near the top of the top cut and in certain parts of the bottom cut.

a) Cryptomelane - forms lenticles in parallel bands (photo 18) replacing wad (photo 19). The cryptomelane contains goethite and minute inclusions of hematite.

b) Wad - This earthy material is replaced by cryptomelane. The wad contains cryptocrystalline specks of hematite.

c) Manganous manganite - has been identified in this ore by means of X-ray diffraction only.

Textural relationships of the ore rich in cryptomelane and wad

The ore has a layered appearance brought about by the oriented habit of the cryptomelane which replaces the wad.

ORE RICH IN CRYPTOMELANE AND JACOBSITE: This ore is present near the top of the lower ore-body (pol. sec. H9).

a) Cryptomelane - constitutes patches and also veins. These veins intersect most minerals.

b) Jacobsite - is dissemminated and also in bands resembling veins that have formed as a result of exsolution and give the false impression of being transgressive.

c) Nsutite - is cryptocrystalline and is present in patches.

d) Pyrolusite - is cryptocrystalline and patches of pyrolusite have irregular outlines.

e) Goethite - is dissemminated in the ground-mass and also replaces jacobsite.

f) Hausmannite - was probably early in the paragenetic sequence and only remnants are present.

g) Lithiophorite - constitutes minute crystals.

h) Hematite - is present as minute inclusions.

Textural relationships of the ore rich in cryptomelane and jacobsite

This metallic-bright ore is well jointed and has a spotted appearance brought about by cryptomelane, nsutite and pyrolusite found in spherical patches (photo 98).

The upper ore-body

ORE RICH IN HAUSMANNITE AND JACOBSITE: (pol. sec. H 10).

a) Hausmannite - is present as fine-grained crystals (2 - 20 micron), and is intergrown with jacobsite (photo 29). Hausmannite is also coarse-grained (photos 28 and 30) particularly in 'vugs' (photo 99).

b) Jacobsite - Fine-grained jacobsite is dissemminated and also in bands resembling veins that have formed as a result of exsolution (photos 38 and 39). In certain patches jacobsite predominates over hausmannite and forms closely packed jacobsite. Jacobsite is often riddled with minute inclusions of hematite (photo 37).

c) Cryptomelane - is also a chief ore-mineral and extends over large patches. Veins of relatively younger cryptomelane intersect all the other minerals.

d) Nsutite - is present in vugs (photo 99) and replaces hausmannite.

e) Pyrolusite - is intergrown with nsutite and cryptomelane. Veins of pyrolusite intersect most minerals but is itself intersected by veins of cryptomelane (photos 61 and 62).

f) Goethite - is dissemminated and also in bands (photo 99) where it may be associated with andradite.

g) Andradite - is fine-grained and localised to patches and may be associated with goethite.

Textural relationships of the ore rich in hausmannite and jacobsite

This metallic-bright ore has a layered appearance (photo 99) which is brought out by:-

i) 'vug-fillings' which are parallel to one another.

ii) alternation of bands rich in ore-minerals and in silicates and iron oxides. The bands rich in ore-minerals consist of hausmannite, jacobsite, etc., and the bands rich in silicates consist of andradite, goethite and 'manganese oxide'.

FERRUGINOUS AND SILICEOUS ORE OF HOTAZEL

Hitherto the mineralogy of the ore of the areas free from highly ferruginous and siliceous material has been described. However, during the latter half of 1963 the Hotazel Mine was again visited and at this stage the ore-body revealed many ferruginous (photo 3) and siliceous portions, particularly in the lower ore-body.

Macroscopically the ferruginous portions are often without bedding-planes (photo 3b) are red in colour and have an earthy appearance very much like that of weathered hematite. This ferruginous material is hereafter referred to as the ferruginous ore and is not to be confused with the manganese ore that has been ferruginised and silicified, with a jaspery appearance. Microscopically the ferruginous ore consists mainly of shiny, fine-grained specks of hematite and bright-red iron oxide, probably also hematite, in between. Extending through all this are portions rich in hematite which are without sharply demarcated boundaries. Numerous veins and vein-like bodies of which the boundaries are sharp, intersect the ground-mass. These veins and 'vein-like' bodies are filled with andradite and jacobsite (photo 47). Along the edges of the veins are numerous idiomorphic laths of hematite projecting inwards towards the centre of the vein. As far as the veins are concerned it was not possible to determine the paragenetic sequence of the jacobsite and the andradite. The idiomorphic hematite had obviously formed later than the jacobsite and the andradite.

Samples along the contact between the manganese ore and the ferruginous ore gave little indication of the paragenetic sequence of these two ores. The only indication as to the age of the two ores is the fact that the ferruginous ore is often not lamminated and that the lamminations of the manganese ore terminate against the ferruginous ore (photo 3b). This indicates that the ferruginous ore had formed subsequent to the manganese ore. However, the presence of jacobsite and andradite in veins intersecting the red, ferruginous ore is an indication that the red, ferruginous ore had probably formed during the early stages of formation of the ore (manganese and iron) as andradite is considered to be one of the late metamorphic minerals. Assuming that slumping and leaching had taken place during the early stages of formation of the ore, it seems logical to conclude that the ferruginous ore could have formed in these areas, not excluding the possibility of the ferruginisation of the adjacent areas simultaneously. Ferruginisation of the manganese ore had taken place at some later stage.

The reader is referred to chapter VII on the origin of the ore for more information regarding the slump-structures.

Siliceous portions are present in small, localised areas in the ore-body at Hotazel Mine:-

i) Along the contact between the manganese ore and the ferruginous ore, representing alteration-rims surrounding 'inclusion-like' bodies of the ferruginous ore.

ii) Along the foot-wall of the lower ore-body, particularly along the banded ironstone side.

iii) In the upper- and lower bodies, clearly representing silicification and to a lesser extent ferruginisation of the manganese ore.

DEVON MINE

There is only one ore-body at the Devon Mine and it is considered to be the equivalent of the lower ore-body of the Hotazel Mine although in comparison, as far as the mineralisation is concerned, it is more monotonous. The ore-body of the Devon Mine is less layered than the Hotazel ore-body and consists mainly of ore rich in cryptomelane and braunite.

Ferruginisation of the ore-body is practically absent except for a narrow zone along a vertical fissure and also near the foot-wall along the eastern rim of the workings where it is found in large irregular areas.

ORE RICH IN CRYPTOMELANE AND BRAUNITE:

a) Cryptomelane - occupies large patches. It also replaces braunite and hausmannite.

b) Braunite - is mainly present as equant grains.

c) Goethite - is fine-grained and dissemminated in the ore but is also concentrated in patches of irregular outline. Goethite is more common near the hanging wall.

d) Hematite - occurs as minute inclusions in the groundmass . Hematite is also concentrated in patches of irregular outline and in layers. The outlines of some of the crystals of hematite are irregular owing to corrosion.

Textural relationships of the ore rich in cryptomelane and braunite

The ore has a layered appearance caused by alternating layers of cryptomelane, hematite and goethite (photo 100 - pol. sec. D1). The hematite and the goethite also build nodules which accentuate the layering of the ore.

CRYPTOMELANE-RICH ORE

a) Cryptomelane - patches of irregular outline are associated with iron oxides. Nodules and lenticular nodules (photo 101) are closely associated with goethite and relic hausmannite.

b) Iron oxides (goethite) - The iron oxides consist mainly of goethite and under conditions much the same as in the ore rich in cryptomelane and braunite.

c) Hematite - is present under conditions very much the same as in the ore rich in cryptomelane and braunite.

d) Hausmannite - builds clusters and is generally replaced by todorokite and cryptomelane (pol. sec. D1). It is also found in the ore rich in cryptomelane and braunite.

e) Todorokite - is mainly a replacement product. In nodules it replaces hausmannite (photo 32).

Textural relationships of the cryptomelane-rich ore

This ore is generally less layered than the ore rich in cryptomelane and braunite (photo 100), although anomolous cases were observed.

LANGDON MINE

This mine is just across the fence to the east of Devon and is on the same manganese ore-body. The minerals of the ore-body are the same as at Devon except for the faulted area along the eastern rim of the workings where the ore is brecciated in parts and has been subjected to supergene mineralisation. In this fault-zone hausmannite-rich ore is found.

HAUSMANNITE-RICH ORE: (polished sections N1 and N2)

a) Hausmannite - constitutes large crystals and is closely associated with jacobsite (as in photo 29). It is present also as small idiomorphic crystals in the larger crystals of hausmannite and also as angular fragments in the brecciated portion of the ore.

b) Todorokite - is mainly secondary and replaces hausmannite and 'nsutite'. Todorokite is present along shrinkage-cracks in the pyrolusite and as cementing material in the brecciated portions.

c) 'Nsutite-like' mineral - This mineral replaces hausmannite (like photo 91). X-ray diffraction patterns of this mineral gave strong reflections of cryptomelane and very diffuse ones of nsutite. Optically it resembles nsutite.

d) Jacobsite - constitutes small irregular bodies in and near hausmannite. It often contains minute inclusions of hematite (as in photo 37) and occassionally fills shrinkage-cracks in pyrolusite (rare) and is present as angular fragments in the brecciated portion of the ore.

e) Pyrolusite - is fine-grained and patches of pyrolusite have irregular outlines.

f) Hematite - is disseminated as minute inclusions.

Textural relationships of the hausmannite-rich ore

This metallic-bright ore is massive with little layering. It is present only along the faulted area over a width of approximately 20 feet. The ore is high-grade, and the brecciated portion consists mainly of aggregates of angular hausmannite and jacobsite. The large crystals of hausmannite and jacobsite and also the 'nsutite' are considered to post-date the brecciation. Todorokite constitutes the cementing material.

From the paragenetic sequence mentioned above it is evident that some of the hausmannite and jacobsite must have formed after the tectonic movements had taken place and only along the zone of faulting where solutions could penetrate more freely.

THE CENTRAL BELT

The mines Mamatwan, Adams and Smartt are situated in the Central Belt. Noteworthy of the ore from the Central Belt are the high values of CaO and CO_2 in the chemical analyses (Table 18). These are the highest for the Kalahari Manganese-field. For further information the reader is referred to chapter V dealing with the geochemistry of the ore.

MAMATWAN - ADAMS

The mines Mamatwan and Adams are just across the fence from each other and as they are on the same ore-body the mineralogy of the two mines will be dealt with together.

ORE RICH IN BRAUNITE AND CRYPTOMELANE

a) Braunite - constitutes small, equant grains.

b) Cryptomelane - is present as follows:-

  i) in nodules, where it replaces hausmannite, giving the ore a mottled appearance (photo 60)

  ii) as cementing material between grains of braunite (photo 59 - pol. sec. M7a)

  iii) along grain boundaries of calcite (photo 102b - pol. sec. M7a)

  iv) in veins which are intersected by a later calcite

  v) sometimes along cleavage-planes of calcite.

c) Todorokite - replaces hausmannite and minerals of the ground-mass and is associated with pyrolusite in nodules. A structure somewhat like the cells of a plant is observed in places.

d) Hematite - occurs mainly as minute inclusions in braunite and also as laths that replace carbonate minerals in nodules (photos 102 and 103 - pol. sec. M7a) and along edges of carbonate veins and also as idiomorphic crystals probably of secondary origin.

e) Iron oxides (goethite) - These oxides are mainly goethite and are fine-grained and dissemminated.

f) Hausmannite - Clusters of hausmannite, particularly in nodules, are generally replaced by cryptomelane and todorokite.

g) Manganite - is present in limited amounts and then in nodules only.

h) Bixbyite - in nodules replacing hausmannite. It is also associated with manganite and in rare instances the odd grain is dissemminated in the ground-mass.

i) Lithiophorite - constitutes lenticles.

j) *Pyrolusite* - occurs mainly in nodules.

k) *Magnetite* - was observed in one vein and also in a few odd grains in the ground-mass.

Gangue-minerals

i) *Calcite* - is common in the ore as a primary constituent and is dissemminated amongst the other minerals. It is also present in vein-like bodies in the ore and in the 'carbonate-rock' (photo 9). Calcite also formed at a later stage in veins.

ii) *Rhodochrosite* - occurs as vein-like bodies in the 'carbonate-rock' (photo 9) and also in nodules.

Textural relationships of the ore rich in braunite and cryptomelane

The ore is massive and has a lenticular appearance when observed in reflected light. The lenticles are elongated parallel to the bedding of the ore (photos 104 and 105).

SMARTT MINE

This is the only mine of the Central Belt where banded ironstone is exposed on the hanging wall side. In the suboutcrop the ore-body is greatly enriched in manganese.

ORE RICH IN BRAUNITE AND TODOROKITE (pol. secs. S 1, 2, 3, 4).

a) *Braunite* - occurs as equigranular grains, occassionally with minute inclusions of hematite. The braunite is loosely and densely packed, with many remnants of carbonate in between, and in places it is replaced by todorokite, cryptomelane and bixbyite.

b) *Todorokite* - is mostly fine-grained, particularly where it is associated with cryptomelane. In nodules it is more coarse-grained. The mineral replaces braunite and bixbyite as well as minerals of the ground-mass, e.g. carbonate minerals. The veins of todorokite intersect most minerals.

c) Cryptomelane - is fine-grained but massive where associated with todorokite and is difficult to identify. It also builds nodules and veins.

d) Goethite - is mainly dissemminated in the ore, replaces cryptomelane and in vugs, bixbyite and braunite (photo 107). Goethite, pseudomorphous probably after bixbyite, is present in a vein of todorokite (photo 82).

e) Bixbyite - replaces braunite.

f) Hematite - occurs as minute inclusions in braunite and also in some veins.

g) Pyrolusite - The odd small grain of pyrolusite is present in veins of cryptomelane.

Gangue-minerals

The gangue-minerals are mainly carbonate minerals, e.g. calcite and rhodochrosite and are present under the same conditions at Smartt as at the Mamatwan and Adams Mines. The chemical composition of one of the vein-like bodies indicates that it is free from magnesia (chapter V).

Textural relationships of the ore rich in braunite and todorokite

The ore has a layered appearance which is accentuated by the many nodules (photo 108 - pol. sec. S2). In places lenticular veins of limestone (low in magnesia) are common (photo 8).

THE WESTERN BELT

BLACK ROCK MINE

There are two main groups of ore-bodies at Black Rock:-

a) The ore-bodies of the 'hogback'. Samples of this ore were examined during the course of this investigation.

b) The ore-bodies encountered in bore-holes and shafts situated to the east of the 'hogback'. This material was not available to the author.

THE 'HOGBACK'

There are three consistent ore-bodies and the samples examined were taken in the open-cast workings along the line AB (Folder 2). Also examined were the samples taken along the strike of the ore-bodies and taken underground from the lower ore-body down dip to 900 feet. No variation was observed in the minerals of the ore from 900 feet or those from the lower ore-body near the surface.

1) The lower ore-body

This ore-body consists mainly of braunite and/or bixbyite. Cryptomelane replaces both these minerals in varying degrees.

ORE RICH IN BRAUNITE, BIXBYITE AND CRYPTOMELANE

(pol. secs. BR 1a, b, c, d).

a) Braunite - is common in all the ores and may in places form the major constituent.

i) Braunite (ordinary)
Coarse-grained crystals of this mineral are in places free from braunite-II. Braunite (ordinary) is irregularly replaced by cryptomelane (photo 56). It may be intergrown with bixbyite and braunite-II.

ii) Braunite-II
Coarse-grained crystals of braunite-II are 50 - 100 micron in size. In places braunite-II is intergrown with braunite (ordinary).

b) Bixbyite - In places bixbyite forms a major constituent of the ore, but generally it is less common than braunite. In some specimens bixbyite and braunite are intergrown and then they have mutual boundary relationships (photo 27).

c) Cryptomelane - is common in all the ores and may even predominate. It is generally later than braunite and bixbyite. Cryptomelane replaces braunite along certain (200) crystallographic directions (photo 57) and also irregularly (photo 56) as well as along grain boundaries. It is also present as 'rims' around braunite (photo 25) as well as in cracks in the pyrolusite (photo 71).

d) Hematite - is present mainly as minute laths but also as large crystals in braunite.

e) Goethite - is mainly secondary and replaces cryptomelane in particular.

f) Pyrolusite - occurs in between bixbyite (photo 71) but is also dissemminated.

g) Lithiophorite - is associated with cryptomelane in vugs. The formation of lithiophorite post-dates that of cryptomelane.

h) Hausmannite - is present as remnants and then only as the odd grain.

Textural relationships of the ore rich in braunite, bixbyite and cryptomelane

The ore has a layered appearance (photo 109) and near the hanging wall the layering becomes more pronounced (photo 110) where it has many patches that presumably represent remnants of the banded ironstone.

2) The middle ore-body

ORE RICH IN BRAUNITE AND CRYPTOMELANE

(pol. secs.BR 2a, b, c)

a) Braunite - only ordinary braunite was found in the middle ore-body. It is both coarse- and fine-grained and is replaced by cryptomelane in varying degrees. It contains numerous minute inclusions of hematite, the number of which increases as the hanging wall is approached and in certain areas it is associated with andradite (photo 49).

b) Cryptomelane - replaces braunite in varying degrees.

c) Andradite - is present in certain patches only and it is apparently later than the braunite (photos 48 and 49).

d) Hematite - occurs as minute inclusions in the braunite and the andradite (photo 46).

e) Lithiophorite - Traces of lithiophorite are present.

Textural relationships of the ore rich in braunite and cryptomelane

The ore is massive (photo 111) and in places it is layered (photo 112).

3) The upper ore-body (pol. secs.3a, b, c, d).

This ore-body contains numerous remnants of banded ironstone.

ORE RICH IN BRAUNITE, HEMATITE AND CRYPTOMELANE

a) Braunite - is in places idiomorphic and appears to show an affinity for the siliceous portions of banded ironstone (photo 114). The braunite, both fine- and coarse-grained, is replaced by cryptomelane. Sometimes it is associated with andradite.

b) Hematite - occurs as minute inclusions particularly in braunite and andradite (as in photo 46). Where hematite is present in veins it is coarse-grained and secondary in origin.

c) Cryptomelane - is generally secondary in origin. It is disseminated in the ore but is more concentrated in patches of which the outline is irregular. In places it may be almost densely packed. The mineral is also present as slender crystals along the edges of vugs.

d) Andradite - is localised in certain patches and also in cracks where it is sometimes associated with bright-red iron oxide, evidently hematite (photo 115).

e) Opal and chalcedony - is generally later than most minerals and fills vugs (photo 114) and cracks.

Textural relationships of the ore rich in braunite, hematite and cryptomelane

The ore is layered and in certain samples the original structure of the replaced banded ironstone is still to be seen (photos 113, 114, 115).

AREA OF INTENSE FOLDING AT BLACK ROCK

As already explained in chapter II (the geology of the Western Belt) recumbent and asymmetrical folding of the ore-body was observed in open-cast working No. 2 and No. 4 (Folder 2). Specimens of the ore from this area were examined (samples a to e, photo 13) to determine whether the folding pre- or post-dates the formation of the ore. The ore consists mainly of braunite and cryptomelane and subordinate quantities of hematite, iron oxide, andradite and hausmannite. It is considered representative of the middle ore-body of the Black Rock Mine except for the many signs of brecciation.

Sample a - represents a relatively unaltered ore, rich in braunite with few signs of fracturing.

Sample b - This ore is rich in braunite and is much brecciated. The brecciated areas and fractures are recemented by a later cryptomelane and iron oxide (photo 116). It appears as if this cementation by cryptomelane and iron oxide may be relatively recent in the paragenetic sequence (photos 47 and 118).

Sample c - shows much brecciation and the andradite is found along cracks (photo 48).

Sample d - The braunite of this sample is relatively unaltered. However, diffuse signs of fracturing are to be seen.

Sample e - is much brecciated and more altered than any of the other four samples. The braunite is almost completely altered to cryptomelane and the andradite presumably to iron oxide. The iron oxide in the cracks and the brecciated areas has a bright red colour. This alteration may be attributed to some extent to the presence of fault f2 (Folder 2) which is near by. Veins of cryptomelane intersect the breccia (photo 119).

Textural relationships of the minerals in the area of intense folding

The degree of brecciation of the samples corresponds with their respective structural positions. There seems to have been two periods of brecciation subsequent to which the fragments were recemented. Andradite appears to be younger than one of the periods of brecciation as it fills many of the cracks. It is also presumably older than the younger period of brecciation although there is little evidence to verify this.

B. THE MINERALOGY OF THE WALL-ROCKS

1) 'Carbonate-rock'

A brick-red, brown and purplish, layered rock (photo 9) sometimes forms the foot-wall of the ore-bodies of Hotazel, Devon, Langdon, Mamatwan and Smartt. At Hotazel it is also present in the hanging wall of the lower ore-body. In these mines this rock is present in the open-cast workings except at Mamatwan where it was encountered only in bore-holes. No drilling results for Adams are available and this rock was not found in the open-cast working.

The thickness of this layer ranges from 3 to 5 feet. The sample from Mamatwan is relatively soft and consists mainly of hematite and a little minnesotaite with lenticular bodies and streaks of dolomite, rhodochrosite, ankerite and talc (photos 9, 54 - thin sec. TM 16). No quartz or any clastic material was ever found in any of the samples examined.

The 'carbonate-rock' from <u>Mamatwan</u> is of a brick-red colour and is less altered than the 'carbonate-rock' from <u>Hotazel, Devon and Langdon Mines</u> which is ferruginised and of a more purplish colour. The ferruginised rock consists mainly of microscopic flakes of hematite ~~and iron oxide~~ and some opal. The opal is probably pseudomorphous after talc. At Devon, Langdon and Hotazel only minor quantities of the mineral minnesotaite were found. The 'carbonate-rock' of these ~~latter~~ three mines has numerous lenticular streaks of a red jasper. The rock is often replaced by cryptomelane (photo 7).

At <u>Smartt Mine</u> the 'carbonate-rock' is even more altered to iron and manganese oxides than at Hotazel and it is also much harder. Macroscopically it consists of pencil-slim streaks showing a metallic reflectance in a dull, fine-grained material. The metallic streaks are mainly hematite, cryptomelane and pyrolusite.

2) Bostonite (albitised)

An intrusive rock forms a sheet-like body at Hotazel and dykes at Black Rock. At Devon similar material is found in the rubble ~~of~~ along a fault (photo 6).

This intrusive rock is brown in colour and when in an altered state (often) it is red to red-brown or bluish of colour. Microscopically it is porphyritic with a spherulitic matrix. The matrix consists of slender laths of alkali feldspar, partially sericitised (photo 120 - thin section TBH1), in which are

up of aggregates of albite, small crystals of iron oxide and an odd crystal of sphene. The feldspar of the matrix consists mainly of albite and very little orthoclase-microcline. This identification of the feldspar (possible on one sample only) is based on X-ray diffraction analyses as well as staining tests (Bailey and Stevens, 1960, pp. 1020 - 1025) as the fine texture of the matrix does not lend itself to reliable optical observations. The predominance of alkali feldspar as well as the sub-parallel arrangement of the laths in the matrix suggest that the rock is a bostonite.

<u>Footnote</u>: After completion of the text it occurred to the author that the term 'proto-carbonate' would be more correct.

According to Moorhouse (1950, p. 300) bostonite is characterized by a trachytic or flow-texture, in which lath-shaped feldspar are arranged in a rough, but not perfect, parallelism or in radiating patterns.

Flame-photometric determinations (carried out at the Research Laboratories of ISCOR) indicate that the rock contains 5.04 per cent Na_2O and 5.42 per cent K_2O. From these values the quantity of albite and potassium-feldspar in the rock was calculated as 42 per cent and 32 per cent respectively (by weight) assuming that all the K_2O is present as orthoclase and not as sericite. However, X-ray diffraction analyses indicate that not more than 5 per cent orthoclase is present and therefore much of the K_2O must be present as sericite. The sericite most probably represents sericitised potassium feldspar. The rock may therefore be termed a bostonite that has been albitised and sericitised.

Altered bostonite

At Hotazel certain portions along the centre of the bostonite body are in a fairly advanced stage of alteration. It is altered to characteristic soapy material, purplish to red-brown or greenish-yellow in colour, and identified as nontronite.
Cymrite is present in the bostonite body at Hotazel and at Black Rock as plate-like crystals (photo 94 - thin sec. TH3) where it is associated with a dense matrix in which small crystals of piedmontite (thin section TH4) and a 'sphene-like' mineral (not fully identified, being too small) are present. No cymrite or piedmontite was observed in the spherulitic matrix.

The alteration of the bostonite has apparently taken place in stages, and probably as follows:-

jasper alternating with glistening bands of iron oxide. This rock is similar to the banded ironstone except that the siliceous portions are bright red and tend to predominate over the iron oxide. This scarlet jaspery rock is found only locally and little of it has been observed on the surface. The most striking example as far as the red colour is concerned was observed on the dump alongside shaft No. 3 (Folder 2 - pol. sec. BR B1).

Altogether 25 samples of banded ironstone representative of the various mines of the Kalahari Manganese-field (excluding Adams and Mamatwan Mines) were examined by means of thin sections, X-ray diffraction, spectroscopy and wet chemical methods. In five of the seven samples from Black Rock acmite, and occasionally also andradite, (photo 51 - thin secs. TB2, 3, 4) were found as aggregates in place of the siliceous bands. Apparently acmite replaces the chert. Unaltered banded ironstone crops out near by. These samples from Black Rock are considered representative of the banded ironstone as they were taken along and across the strike of the formation. The indications on the surface are that acmite is present in a certain portion of the body of banded ironstone (approximately one half). No acmite was observed in the ore-body.

In order to determine the possible source of the sodium for the acmite in the banded ironstone, determinations were carried out for Na_2O on twelve of the 25 samples of banded ironstone from the Kalahari Manganese-field (Table 17). The average percentage Na_2O of the chert of the banded ironstone as calculated from the percentages of Na shown in tables 15 and 17, is 0.47 for the Eastern Belt and the Central Belt (not Mamatwan and Adams), and 4.45 for the Western Belt. It is evident that not all the sodium of the banded ironstone at Black Rock can be of a sedimentary origin. The manganese ore of the Kalahari Manganese-field contains on an average 0.3 per cent Na_2O (Table 18) and the 'carbonate-rock' 0.07 per cent Na_2O (Table 20). Much of the sodium found in the acmite at Black Rock was probably introduced hydrothermally, and if so, then probably during the late stage of the intrusion of the bostonite, although there is no evidence in favour of this. However, this seems to be a logical conclusion considering the albitised nature of the bostonite present at Hotazel. Grout (1946, p. 130) also considered that the acmite from Cuyuna Range, Minnesota, resulted from the action of hot sodic waters on hematitic chert.

4) Inclusion of muscovite-garnet rock

At Black Rock Mine a soft, creamy-white rock is present in the southern section of level 2. It forms an irregular body, approximately 10 to 15 feet thick and cuts obliquely across the ore-body. The rock is sheared.

Microscopically it consists mainly of muscovite flakes which are distorted in places, numerous fine crystals of garnet and fine-grained chlorite (photo 50).

TABLE 17.

Minor element content of banded ironstone and 'carbonate-rock'.

	EASTERN BELT							WESTERN BELT			CENTRAL BELT
	HOTAZEL					DEVON		BLACK ROCK			SMARTT
	% per cent										
	HB3	HB4	HB6	HB8	HB10	DB1	DB2	BB1	BB2	BB3	SB1
Na	.31	.15	.68	.20	.14	.86	.41	.11	.12	6.8	1.0
Mn	1	.01	.1	.05	.01	.05	.01	.005	.05	.05	.01
Ca	.01	.01	1	.01	.005	.005	.005	.005	.01	.05	.01
Sr	.01	-	.005	.005	-	-	-	-	.005	.005	-
Al	.01	.01	.05	.01	.01	.05	.01	.005	.01	.01	.05
Cu	.005	.005	-	.005	-	-	-	-	-	-	.005
Pb	.005	-	.005	.005	-	.005	-	-	-	-	-
Cr	.005	.005	.01	.005	.005	.005	.005	.005	.01	.01	.01
Ni	.005	.005	.005	.005	.005	.005	.005	.005	.005	.005	.005
Co	.005	-	-	-	-	-	-	-	-	-	-
Sn	.005	-	-	.005	-	-	-	-	-	-	-
Ti	.005	.005	.01	.005	.005	.005	.005	.005	-	-	.01
V	.01	-	.005	.005	.005	.005	-	.005	-	-	.005
Ag	.005	-	-	.005	-	-	-	-	-	-	-
Li	.08	.10	.11	.13	.10		.035	.10			

All the samples are of banded ironstone except HB3 (jaspilite) and HB6 ('carbonate-rock').

Na was determined by flame-photometry and the other elements were determined spectrochemically (semi-quantitatively).

W, K, Mo, In, Bi, Sb, Te, As, Ce, Ga, Eu, Ba, Hf, La were looked for but could not be detected.

(-) looked for but not detected.

Accomplished at the Research Laboratories, ISCOR.

V. THE GEOCHEMISTRY OF THE MANGANESE ORE

The following constituents were determined in representative samples from the mines Hotazel, Devon, Langdon, Smartt, Adams, Mamatwan and Black Rock, by means of:-

1) Wet chemical techniques -
SiO_2, Fe_2O_3, MnO, MnO_2, MgO, CaO, Na_2O, K_2O, H_2O, CO_2, P_2O_5, SO_3, BaO, SrO and Li_2O.

and 2) Semiquantitative spectrochemical methods:-
Cu, Pb, Cr, Ni, Co, Mo, Sn, Ti, V and B.

The results are tabulated in Tables 18 and 19. The data given in Table 18 are presented graphically on Folder 3 in order to facilitate the interpretation of the chemical composition and to demonstrate the characteristics of the ore of the various mines. The graphs, from left to right for each individual mine, represent the ore sampled from the foot-wall upwards to the hanging wall contact.

A. THE VARIOUS COMPONENTS

1) Iron, manganese and silicon

The quality of manganese ore depends to a large extent on the iron content which can be kept low by selective mining. High-grade ore is found at Devon, Langdon, Hotazel and Black Rock. Silica also tends to lower the grade of the ore and on Folder 3 it is shown that only the ore from Hotazel and Devon is high in silica. Much opal is seen at Hotazel, particularly near the base of the bottom cut.

Folder 3 also shows that at Hotazel the iron and the manganese increase sympathetically from the bottom of the ore-body to the top with a somewhat inverse relationship between iron and manganese on the one hand and silica on the other. At Devon the iron and the silica increase sympathetically but there is an inverse relationship between manganese and iron. At Black Rock the ore is low in silica, but high in iron and there is an inverse relationship between iron and manganese in the No. 3 ore-body.

These variations in the chemical composition of the ore may be explained in terms of the component minerals (set out in chapter IV - distribution of the minerals in the ore and in the wall-rock). Inverse relationships between elements such as manganese, iron and silica, are dependent on the presence of hematite and opal, for instance.

2) Alkaline Earth Metals (Ca, "Mg", Sr, Ba)

Magnesium is not an alkaline earth metal but is grouped with these metals for the sake of convenience. Calcium and magnesium are major constituents of most rocks in the earth's crust whereas strontium and barium are common, although only as minor constituents.

A close geochemical relationship between calcium and magnesium is evident from Folder 3. In the Kalahari Manganese-field the highest values for calcium were detected at the mines Adams and Smartt. In these mines calcium predominates considerably over magnesium. Mookherjee, (1961, p. 725) also reported a preponderance of calcium over magnesium in gonditic ore from India. At Adams there is a sudden increase of calcium and magnesium as the cover of Kalahari limestone is approached. At Smartt, where there is no cover of Kalahari limestone, only magnesium increases near the top. The higher calcium and magnesium contents may be explained by:

a) contamination from the cover of limestone, and

b) the presence of 'oolitic' remnants of carbonate in the ore-body (applicable to the mines of the Central Belt).

Barium is generally more common than strontium in igneous rocks. However, the low solubility of barium sulphate may account for the small quantity of this element in natural waters.

According to Rankama and Sahama (1949, p. 471) strontium accompanies calcium consistently in minerals and rocks of both igneous and sedimentary origin. There are no strontium-bearing minerals present in the ores although strontium was detected, and the strontium determined chemically must have been concealed within the rock-forming minerals. At Adams Mine the ore is markedly higher in calcium, but lower in strontium than at any of the mines in the Kalahari Manganese-field.

At Black Rock Mine the highest barium values for the area were encountered and it is in this mine only that barytes is present, but not the barium-bearing mineral, psilomelane. Some of the barium must, however, be concealed in the rock-forming minerals as the SO_3 content is too low (Table 18) to satisfy all the BaO as barytes. The average percentage BaO is 0.34 which requires 0.15 per cent SO_3 but only 0.05 per cent is available. According to Ljunggren (1955 B, p. 35) many sedimentary manganese ores have a remarkably high content of barium. He reported 0.01 to 0.1 per cent barium in bog-ores from Sweden.

3) The Alkali Metals (Na, K, Rb, Li)

Sodium and potassium are amongst the main constituents of the lithosphere. Rubidium is one of the more abundant trace-elements, about the same as strontium, whereas <u>lithium</u> is relatively rare (Rankama and Sahama, 1949, p. 422).

In the ore of the Kalahari Manganese-field potassium predominates over sodium. Higher values for potassium were encountered at the mines Devon, Black Rock and Hotazel where cryptomelane is the host for potassium. At the mines Adams and Smartt where braunite predominates, the potassium values are relatively low. Mookherjee, (1961, p. 725) reported a preponderance of K over Na in gonditic manganese ore from India.

Why more sodium is present in ore from the mines Devon, Adams and Black Rock is not fully understood. At Black Rock Mine the sodium-bearing mineral, acmite, occurs in the banded ironstone but not in the ore.

Rubidium was detected in trace-quantities in most of the samples from the various mines. It is, however, probably concealed in the rock-forming minerals as no rubidium-bearing minerals were detected in the ores. Only the most sensitive lines of rubidium around 7800 Å were detected by means of spectrochemical tests. The less sensitive lines of rubidium, which occurs in the ultraviolet region of the optical spectrum were not detected and this would indicate that only trace-quantities of rubidium are present in the samples. Ljunggren (1955 B, p. 41) reported trace-quantities of rubidium in bog-ores from Sweden.

Lithium is present in all the samples in percentages varying from 0.01 to 0.14. The lithium-bearing mineral lithiophorite is fairly common in the ores.

4) <u>Trace-elements</u> (Cu, Pb, Cr, Ti, V, Ni, Co, B and P)

No minerals were found in which these ions are present in any noteworthy quantities and they must therefore be concealed within the rock-forming minerals.

The relatively high values for copper (0.008%) in the ore from Black Rock Mine are noteworthy and in conjunction with the fact that andradite at Black Rock Mine suggest a higher grade of metamorphism than at most of the other mines of the Kalahari Manganese-field.

The highest values for boron were found in the ore rich in braunite, which is from the mines Adams and Smartt. This corresponds with the findings of Wasserstein (1943, pp. 389 - 398) who examined a number of manganese samples from Postmasburg as well as some foreign ores. He concluded that braunite is the sole carrier of boron. The presence of boron in the ores (braunite) of the Kalahari Manganese-field somewhat suggests that it is a primary constituent.

Titanium was detected in all the samples (Table 19) whereas vanadium was detected in 31 of the 36 samples. The ions cobalt and nickel are consistently present and a preponderance of Co over Ni is indicated in Table 19. Mookherjee (1961, p. 725) reports similar relationships for titanium, vanadium, cobalt and nickel in gonditic ore.

Phosphorus is universally present in samples of ore from the Kalahari Manganese-field.

B. GEOCHEMICAL AFFINITIES OF THE COMPONENTS

The pattern of the distribution of the minor elements may be summarized as follows:-

1) K_2O Na_2O, and K^+ concentrated mainly in cryptomelane and its allied manganese minerals.
2) CaO MgO and both predominate in the ore of the Central Belt.

3) Pb is present in all the samples except those rich in wad (Table 19).

4) The ion Pb^{++} shows a dependance on the amount of Fe present in the ore. According to Mookherjee (1961, p. 726), who examined manganese ore from India, the adsorption of the ion Pb^{++} on colloidal $Fe(OH)_2$ represents a case of chemisorption and not a Van der Waals' type of bonding.

According to Ljunggren (1955 B, p. 36) the adsorbing power of manganese dioxide has been examined from a chemical point of view by various workers and it has been shown that, **inter alia**, barium, radium, ionium, nickel and cobalt have been strongly adsorbed. He also states that it is difficult to predict which elements ought to be enriched and why certain elements have a higher enrichment with respect to others irrespective of whether they have almost the same chemical behaviour, such as the enrichment of Co over Ni in manganese bog-ore from Sweden. Ljunggren (p. 38) claims that the adsorbing power of hydrous ferric oxide is not as pronounced as that of manganese dioxide and that the adsorbing power of MnO_2 has been of great importance in the formation of several manganese ores (p. 40).

In the Kalahari Manganese-field the Mn and Fe probably were in a colloidal state during the formation of the ore and the manganese probably was deposited as carbonates and oxides.

It is significant that the ore from certain mines have a higher content of certain trace-elements. The enrichment in the source-material probably accounts for the higher content of some elements in the ore in respect of others.

TABLE IX

THE CHEMICAL COMPOSITIO THE KALAHARI MANGANESE FIELD

SAMPLE NO.		SiO_2	Al_2O_3	Fe_2O_3	MnO	MnO_2	MgO	CaO	Na_2O	K_2O	Li_2O	H_2O	CO_2	P_2O_5	SO_3	BaO	SrO	TOTAL
								HOTAZEL										
H1	Bottom Cut	21.64	0.42	9.82	7.98	46.93	2.30	2.47	0.11	0.84	-	7.26	0.14	0.16	0.16	0.08	0.29	100.60
H2		4.07	0.61	7.62	17.68	59.09	2.00	1.88	0.12	1.20	-	4.91	0.33	0.05	-	0.16	0.16	99.88
H3		17.19	0.51	6.52	11.92	52.17	2.30	2.00	0.16	1.73	-	4.80	0.18	0.05	-	0.08	0.28	99.89
H4		8.19	0.81	7.23	21.73	50.98	1.80	2.04	0.08	0.37	-	6.31	0.16	0.20	-	0.08	0.28	100.26
H5	Top Cut	0.85	0.79	11.05	9.25	71.05	1.23	1.54	0.03	0.21	-	2.98	0.17	0.64	-	0.12	0.18	100.09
H6		16.04	1.06	10.47	6.26	58.12	0.80	1.84	0.03	0.33	-	3.95	0.44	0.23	0.12	0.08	0.08	99.85
H7		1.07	1.06	10.01	51.72	32.45	0.50	1.10	0.00	0.00	-	1.24	0.39	0.01	-	0.12	0.06	99.73
H8		4.73	0.82	15.10	4.67	59.80	2.10	2.01	0.07	2.70	-	5.90	1.86	0.16	-	0.12	0.39	100.43
H9		2.32	0.32	13.92	10.60	67.61	0.78	1.53	0.03	0.17	-	2.50	0.24	0.004	-	0.08	0.19	100.29
H10	Upper Body	1.42	0.77	13.37	23.69	54.76	0.87	1.93	0.08	0.19	-	2.14	0.13	0.10	0.07	0.32	0.11	99.95
								DEVON										
D1		5.83	0.44	10.83	6.62	63.90	2.17	2.17	0.44	1.64	0.05	5.40	0.00	0.07	0.26	0.09	0.38	98.12
D2		11.09	0.32	9.01	2.78	63.24	2.22	2.74	0.24	1.20	0.05	5.51	1.03	0.09	0.37	0.13	0.41	100.43
D3		3.49	0.40	10.54	12.55	58.24	2.43	2.01	0.39	2.00	0.05	7.05	0.22	0.09	0.38	0.38	0.25	100.47
D4		12.08	0.40	17.28	9.56	50.08	1.67	2.48	0.48	1.10	0.05	4.20	0.37	0.08	0.32	0.06	0.22	100.43
D5		10.69	0.44	20.85	3.54	51.60	2.19	2.54	0.19	1.92	0.03	5.39	0.15	0.14	0.36	0.19	0.19	100.41
D6		15.37	0.64	7.95	2.97	59.55	2.20	3.44	0.50	2.18	0.03	4.20	0.29	0.06	0.28	0.07	0.25	99.98
D7		3.24	0.44	21.59	7.01	53.47	2.19	2.30	0.18	2.48	0.03	5.81	0.66	0.11	0.27	0.03	0.31	100.12
D8		26.78	0.44	16.93	1.76	43.64	1.43	2.17	0.15	2.30	0.03	3.44	0.40	0.13	0.38	0.03	0.28	100.29
								ADAMS										
A1		6.00	0.59	6.46	28.78	35.64	3.01	7.33	0.26	0.24	0.09	1.87	9.48	0.12	0.10	0.11	0.04	100.12
A2		4.71	0.47	5.85	25.96	33.28	3.17	10.93	0.24	0.17	0.08	2.24	11.70	0.07	1.03	0.08	0.04	100.03
A3		7.10	0.37	5.93	17.16	50.81	2.53	5.22	0.72	0.26	0.09	5.68	3.54	0.07	0.54	0.00	0.02	100.04
A4		3.59	0.48	6.18	19.45	41.98	2.42	10.55	0.48	0.22	0.08	3.24	10.67	0.12	0.40	0.19	0.04	100.09
A5		2.61	0.42	5.15	14.12	26.32	4.09	21.75	0.21	0.39	0.06	2.24	21.97	0.07	0.74	0.00	0.10	100.24
A6		2.35	0.43	5.06	15.03	28.27	4.24	19.83	0.27	0.46	0.06	2.34	20.76	0.05	0.90	0.00	0.08	99.52
								SMARTT										
S1		6.09	0.28	9.33	22.41	32.25	3.00	13.13	0.18	0.23	0.04	2.88	10.05	0.08	0.26	0.05	0.22	100.48
S2		6.31	0.56	7.38	23.03	31.07	2.68	15.71	0.18	0.23	0.04	2.12	10.52	0.05	0.24	0.07	0.22	100.41
S3		5.00	0.20	11.02	20.60	39.64	2.10	9.93	0.27	0.21	0.05	3.90	6.97	0.06	0.28	0.05	0.10	100.38
S4		5.44	0.24	14.18	15.45	28.99	2.51	14.68	0.14	0.26	0.05	7.06	10.49	0.08	0.21	0.10	0.25	100.13
S5		5.61	0.16	7.19	23.34	33.78	3.43	12.75	0.21	0.19	0.05	2.67	10.05	0.09	0.46	0.04	0.22	100.24
								BLACK ROCK										
B1-a	Lower Body	4.85	0.12	29.40	12.80	44.04	1.17	3.60	0.07	1.08	0.04	2.10	0.01	0.07	0.10	0.35	0.06	99.86
B1-b		3.69	0.20	28.62	11.92	46.78	1.16	3.74	0.16	1.54	0.03	1.94	0.22	0.08	0.02	0.18	0.06	100.34
B1-c		7.92	0.32	28.44	18.39	36.66	0.89	4.16	0.19	0.84	0.04	1.56	0.36	0.14	0.01	0.20	0.06	100.18
B2-a	Middle Body	4.94	0.08	27.62	14.97	44.12	0.93	3.95	0.15	1.08	0.03	1.94	0.02	0.14	0.08	0.31	0.05	100.41
B2-b		4.15	0.04	26.59	14.69	45.77	0.99	3.49	0.16	1.22	0.04	2.24	0.26	0.16	0.06	0.24	0.08	100.18
B2-c		5.28	0.12	28.30	13.45	44.33	0.57	4.20	0.18	1.30	0.04	1.76	0.03	0.16	0.03	0.15	0.08	99.98
B3-a	Upper Body	4.88	0.04	28.26	11.06	45.64	1.16	3.10	0.08	0.84	0.04	1.90	2.54	0.07	0.10	0.44	0.06	100.21
B3-b		5.53	0.08	51.84	7.96	27.58	0.71	2.88	0.16	0.70	0.04	2.06	0.02	0.04	0.02	0.74	0.06	100.42
B3-c		9.29	0.12	57.13	8.09	17.47	0.68	4.00	0.58	0.34	0.01	1.88	0.40	0.14	0.02	0.18	0.06	100.39
B3-d		5.15	0.04	50.42	8.04	28.62	0.84	3.40	0.16	0.69	0.01	2.14	0.02	0.04	0.06	0.59	0.06	100.29
L1	Langdon	1.24	0.36	8.05	11.90	65.46	2.32	2.30	0.24	1.12	0.05	5.90	0.22	0.09	0.16	0.48	0.22	100.11
L2		0.91	0.54	7.21	26.63	55.94	0.97	1.59	0.28	0.82	0.14	4.24	0.48	0.07	0.13	0.03	0.03	100.01

Analysts: Dr. C.E.G. Schutte, Messrs. J.L. Pretorius and E.C. Haumann, Soils Research Institute, Pretoria.

TABLE 19

SEMI-QUANTITATIVE SPECTROCHEMICAL ANALYSES

OF THE ORE FROM THE K.M.F.

SAMPLE NO.	Cu %	Pb %	Cr %	Ni %	Co %	Mo %	Sn %	Ti %	V %	B %	
H 1	<.005	<.005	<<.005	.005	.01	<.005	.005	.005	.01	.1)	Bottom Cut
H 2	<.005	<.005	<<.005	.005	.01	.005	.005	.005	.005	.3)	
H 3	<.005	<<.005	<<.005	.005	.005	<<.005	<.005	.005	.005	.1)	
H 4	<.005	<.005	<<.005	.005	.01	<<.005	.005	.005	.05	.3)	
H 5	<.005	.005	<<.005	.005	.005	.005	.005	.005	.01	.1	Top Cut
H 7	<.005	.01	<.005	.005	<.005	.005	.005	.005	<.005	.1	
H 8	<.005	x	<.005	<.005	.005	.005	.005	.01	.1	.01	
H 9	<.005	.1	<.005	.005	.005	.005	.005	.005	.05	.1	
H10	<.005	.1	x	.005	.005	.005	.005	.005	.01	.1	Upper body
D 1	<.005	.005	<.005	.005	.01	<.005	.005	.005	.01	.08	
D 2	<.005	.005	<<.005	.005	.01	<.005	.005	.005	.01	.08	
D 3	<.005	.005	x	.005	.005	.005	.005	.005	.05	.1	
D 4	<.005	.005	<<.005	.005	.005	<.005	.01	.005	.01	.08	
D 5	.005	<<.005	<<.005	.005	.005	<.005	.005	.005	.05	.01	
D 6	.005	<<.005	x	.005	.005	<.005	.005	.005	.01	.01	
D 7	.005	<<.005	<.005	.005	.005	<.005	.01	.005	.005	.01	
A 1	<.005	<.005	<.005	.005	.01	<.005	.005	.005	<.005	.1	
A 2	<.005	<<.005	<.005	<.005	.01	<.005	.005	.005	.005	.1	
A 3	<.005	<.005	<.005	<.005	.01	<.005	.005	.01	x	.5	
A 4	<.005	<.005	<.005	.005	.01	<.005	.005	.005	x	.4	
A 5	<.005	<<.005	<.005	.005	.005	<.005	.005	.01	.005	.1	
S 1	<.005	.01	<<.005	.005	.01	<.005	.005	.01	.01	.5	
S 2	<.005	<.005	<.005	<.005	.01	.005	.005	.01	<.005	.5	
S 3	<.005	.01	<.005	.005	.01	<.005	.005	.01	.005	.5	
S 4	.005	<.005	<.005	.01	.01	.005	.005	.01	.005	.5	
S 5	<.005	<<.005	x	.005	.005	<<.005	<.005	<.005	<.005	.05	
B1-a	.005	.01	.005	.005	.01	<.005	.01	.01	x	.1	Lower Body
B1-b	.01	.01	<.005	.005	.01	<.005	.01	.01	x	.15	
B1-c	.005	.005	<.005	.005	.01	<.005	.01	.005	x	.1	
B2-a	.01	.01	<.005	<.005	.005	<.005	.005	.005	<.005	.1	Middle Body
B2-b	.01	.01	<.005	.005	.01	<.005	.005	.01	.01	.05	
B2-c	.01	.01	<.005	.005	.01	<.005	.005	.01	.01	.05	
B3-a	.01	.01	<.005	.005	.01	<.005	.01	.01	.005	.2	Upper Body
B3-b	.01	.005	<.005	<.005	.005	<<.005	.005	.005	<.005	.08	
B3-c	.01	.01	<.005	.005	.005	.005	.005	.01	.005	.05	
B3-d	<.005	.01	<.005	.005	<.005	.005	.005	.01	<.005	.04	

H - Hotazel D - Devon A - Adams S - Smartt BR - Black Rock

x - below detection limit. < - Less than.

Cd, Zn, As, W, Sb, Zr were looked for but could not be detected

Accomplished at the Research Laboratories, ISCOR.

C. DISCUSSION OF THE NORMATIVE MINERALS

The ore of the Kalahari Manganese-field in all probability has resulted from metamorphism of sedimentary material which consisted of carbonates and oxides. The 'carbonate-rock' (Table 20 - analyses 1 and 2) evidently represents the more ferruginous and siliceous portions of this sedimentary material of which the lime and the magnesium content may vary. No clastic material was found in the 'carbonate-rock' and the normative quartz is to a great extent present as opal. Talc, and in places the iron-rich form, minnesotaite, is characteristic of the 'carbonate-rock' which with the hematite had most probably formed as a result of later metamorphism of the original sedimentary material. The high manganese content of the 'carbonate-rock' of Hotazel (Table 20 - analysis 1) is the result of later manganisation (photo 7), and that of the limestone in the manganese ore of Smartt Mine (analysis 3) is most likely the result of artificial contamination from the manganese ore in which bands of limestone are present. The material of analysis 1 probably has more talc and less magnesite than is shown in the norm (Table 20b). The normative rhodochrosite (Table 20b) could also represent some of the original sedimentary material. No albite or kaolinite was detected in the 'carbonate-rock'.

The low values for sodium and potassium shown in the analyses (Table 20) are noteworthy as they seem to support the idea of Ljunggren (1955 B, p. 38) that hydrous ferric oxide has a low adsorbing power for certain ions.

An analysis of the limestone of the Upper Griquatown Stage (Table 20 - No. 6) is included for comparative purposes. ~~as far as its manganese content is con-~~

Boardman (1964, p.438) postulates that the reason for the attenuation of bodies of manganese ore in the banded ironstone or the Upper Griquatown Stage of the Olifantshoek area is the low manganese content of the limestone in this area.

TABLE 20.

Chemical composition of 'carbonate-rock' and associated carbonates.

	1	2	3	4	5	6
SiO_2	14.12	41.25	2.95	19.2	3.29	8.36
Al_2O_3	1.12	0.31	-	-	-	-
Fe_2O_3	30.02	40.40	1.86	0.57	0.52	0.07
FeO	0.00	1.98	-	0.83	0.11	1.91
P_2O_5	0.10	-	-	-	-	-
MnO	19.87	0.07	6.82	0.18	46.4	0.38
MnO_2	0.00	-	7.19	-	1.81	-
MgO	12.84	10.95	1.16	20.1	6.81	19.42
CaO	2.46	0.81	43.7	17.3	9.4	27.1
Na_2O	0.07	0.12	-	-	-	-
K_2O	0.00	0.03	-	-	-	-
SO_3	0.00	-	-	-	-	-
CO_2	14.52	2.16	36.1^x	29.62^x	32.3^x	42.8^x
H_2O^+	4.96	1.79	0.05	0.13	0.14	0.01
TiO_2	-	-	-	-	-	-
	100.08	99.87	99.87		100.78	100.05

1) Manganised 'carbonate-rock' (brick-brown) (as photo 7), Hotazel Mine.

2) 'Carbonate-rock' (brownish-red), Mamatwan Mine.

3) Limestone ('oolites' - photo 8) in manganese ore, Smartt Mine.

4) Dolomitic limestone (thin band) in 'carbonate-rock' (as photo 9 b), Mamatwan Mine.

5) Rhodochrosite-rock (thin band) in 'carbonate-rock' (as photo 9 b), Mamatwan Mine.

6) Limestone, Upper Griquatown Stage, Olifantshoek.

x - % determined by loss upon ignition.

Analysts: Analyses 2, 3, 4, 5, 6: the Research Laboratories, S.A. Iron and Steel Industrial Corporation.

Analysis 1: the Soils Research Institute, Pretoria.

TABLE 20(b)

C.I.P.W. Norms.

	1	2	3	5	6
Quartz	-	19.23	2.95	3.29	7.65
Albite	0.52	1.05	-	-	-
Olivine (probably as serpentine)	-	-	-	-	1.58
Talc	19.60	29.86	-	-	-
Minnesotaite	-	2.97	-	-	-
Kaolinite	2.58	0.26	-	-	-
Hematite	30.02	40.40	1.86	0.52	0.07
Rutile	-	-	-	-	-
Apatite	0.34	-	-	-	-
Calcite	4.30	1.40	77.9	16.80	48.34
Magnesite	13.61	2.96	2.35	14.20	38.72
Rhodochrosite	14.38	-	1.61	45.54	0.55
Siderite	-	-	-	0.11	3.02
Mn_2O_3	-	-	12.96	3.32	-
MnO	11.01	0.07	-	16.63	-
P_2O_5	-	-	-	-	-
K_2O	-	0.03	-	-	-
H_2O	3.67	1.26	-	0.14	0.01
	100.03	99.49	99.63	100.55	99.94

VI. THERMAL STUDIES

Detailed descriptions of the thermal properties of the individual manganese oxides MnO_2, Mn_2O_3 and Mn_3O_4 are found in the literature, but little is said about the interaction of these oxides in mixtures. This question is however of value in the elucidation of the mineral paragenesis which resulted from metamorphism of sedimentary manganese deposits. Thermal investigations were therefore carried out on the manganese ore from the Kalahari Manganese-field to assist in the identification of the various minerals as well as to study the mineral paragenesis of the manganese oxides. The instruments used were a differential thermal apparatus, a Reichert high-temperature microscope and a Leitz heating microscope.

A. DIFFERENTIAL THERMAL ANALYSIS (D.T.A.)

Since manganese minerals often give diffuse X-ray diffraction patterns owing to poor crystallinity, with the result that identification of fine-grained aggregates is not always reliable, other methods of attack had to be resorted to. Differential thermal analysis is ideally suited for the study of fine-grained substances.

The empirical nature of the method gives rise to difficulties for example the peak temperature which is used for reporting the differential thermal results is rather variable and depends on many factors, i.e. the amount of thermally active material, the heating rate, packing, etc. For this reason the accuracy of the 'characteristic' temperature was investigated. This method of reporting was first suggested by Murray and Fischer (Mackenzie, 1957, p. 17), that is the temperature at which a line at 45° to the base-line of the thermal curve becomes tangential to the commencement of the peak, is more accurately determinable and should be less variable and therefore preferable to the peak temperature. The 'characteristic' temperature may be suitable for pure materials, particularly the carbonates, but for mixtures of manganese minerals it was found to be less reliable than the peak temperature.

The results of the present investigation indicate that in the case of mixtures the D.T.A. is suitable for the identification of certain of the manganese minerals only. This is to a great extent due to difficulties in the classification, particularly the poorly crystallised manganese oxides, variation in the composition of the individual manganese minerals and the fact that some minerals, which generally give characteristic thermal curves in the pure form, often do not show up in the mixtures (also applicable to non-manganese minerals). It is therefore not surprising at all that differential thermal curves reported in the literature for different specimens of reputedly the same manganese mineral do not always agree, e.g. cryptomelane. (The thermal data contained in Table 21 are given for comparative purposes). Kulp and Perfetti (1950) made a thermal study of some manganese minerals using the D.T.A. apparatus. Their results on the trio, pyrolusite, bixbyite and hausmannite, agree well with the thermal study carried out by Grasselly and Kliveni on the synthetic substances of ~~the~~ similar oxides. On comparing D.T.A. curves for pyrolusite and synthetic MnO_2 a difference can be observed in the initial endothermic peaks of the natural and the synthetic substances, i.e. the thermal temperatures for the synthetic substances are lower. This may possibly be explained by the fact that the size of the granules of the artificial compound is more minute than that of the natural mineral (Foldvari, Vogl and Koblencz, 1956, p. 7).

The following sequence will elucidate most of the thermal reactions of the manganese minerals appearing in the oxide form:-

$$6\ MnO_2 \longrightarrow 3Mn_2O_3 + 3O \longrightarrow 2\ Mn_3O_4 + O \longrightarrow \text{spinel}\ (2XO.Mn_2O_3)$$

(cryptomelane, pyrolusite) or nsutite)	(bixbyite)	(hausmannite)	(jacobsite)

(Jacobsite contains some iron in its structure).

The transformation from hausmannite to spinel (jacobsite) is not only a function of the temperature, but is also dependent on the chemical composition as has been confirmed by tests in the laboratory.

The peak temperatures of the thermal curves (Folder 4) for the ore from the Kalahari Manganese-field are tabulated in Table 22.

Discussion of the results of the diffential thermal analyses

1) Most of the cryptomelane from the ore of the Kalahari Manganese-field shows endothermic peaks at 670 to 695°C and at 745 to 825°C except in the case of sample H6 which shows thermal peaks at 580, 615 and 1050°C. The lower peak temperatures cannot be explained. It is however, noteworthy that all the prominent reflections of the X-ray diffraction pattern of cryptomelane for sample H6 are present whereas certain reflections of cryptomelane for samples H1, 2, 3 and 4 are absent (not basal). This is probably due to the

TABLE 21

THERMAL DATA (IN DEGREES CENTIGRADE)

MINERAL	1ST ENDOTHERMIC PEAK	2ND ENDOTHERMIC PEAK	REFERENCE
Pyrolusite	660 to 680	1030 and 1040	Fig. H5 and 6
(MnO_2)	660 to 705	970 to 1040	Kulp and Perfetti
Cryptomelane	580 and 615	1050	Fig. H6
(Gen. - MnO_2)	540 and 615	910	Mackenzie (p. 323)
	670 to 695	745 to 825	Fig. H2 and 3, B3b, B3c
	?	750 to 850	Rode (Grasselly and Klivenyi, 1957, p. 36)
Nsutite (MnO_2)	596 to 624	1000 to 1018	Zwicker et al. (p.258)
Psilomelane	750 to 850	1000	Rode (Grasselly et al.)
(Gen.-MnO_2)	710	950 (exothermic)	Mackenzie (p. 323)
Bixbyite (Mn_2O_3)	-	1020 ? (weak)	Mackenzie "
Hausmannite	-	960	Mackenzie "
(Mn_3O_4)	-	- (inert)	Kulp and Perfetti
Braunite	-	- (inert)	Kulp and Perfetti
($Mn_2O_3 \cdot MnSiO_3$)	-	960 (exothermic)	Mackenzie
Jacobsite ($FeO \cdot Mn_2O_3$)	610 (exothermic)	820 (exothermic)	Heystek and Schmidt
Manganite	380	960	Mackenzie
$MnO.(OH)$	380 and 560	960 (exothermic)	Mackenzie
Goethite	380	-	Mackenzie (p. 301)
Calcite	-	870	Fig. S2
	-	890 to 1010	Mackenzie
Ankerite	-	725,820 and 880	Fig. A3
	-	700,840 and 915	Mackenzie (p. 342)

FOOTNOTE:

The thermal data for some of the minerals are included for comparative purposes when considering the data given in Table 22.

TABLE 22

COMPARISON OF THERMAL, X-RAY AND OPTICAL AND CHEMICAL DATA ON ORE FROM THE KALAHARI MANGANESE-FIELD

SAMPLE	MINERALS ACCORDING TO D.T.A. (FOLDER 4)		MINERALOGICAL COMPOSITION ACCORDING TO X-RAY AND OPTICAL DATA	CHEMICAL DATA (FOLDER 3)	REMARKS
	MINERALS Major	Minor			
H1	-	Cryptomelane	Amorphous manganese and opal	More potassium than any of the other samples from Hotazel. Cryptomelane is a potassium - bearing mineral	The broad endothermic peak at 240°C is due to dehydration i.e. loss of adsorbed water and hydroxyl. This also applies to the endothermic peak at 310°C for H2, 3 and 4 and 240°C for H.10 (Folder 5).
H2	-	Cryptomelane	Cryptomelane		The endothermic peaks at 919 and 1000°C cannot be explained. The one at 910°C is too high for the first peak of dolomite. X-ray diffraction failed to detect the presence of carbonate minerals.
H3	Cryptomelane	?	Cryptomelane		The large peak at 820°C is most likely due to cryptomelane
H4	-	Cryptomelane	Cryptomelane and braunite	More potassium than H1, 2 and 3	The lesser endothermic reaction at 910°C possibly indicates less cryptomelane which agrees with the lower potassium value. Braunite is thermally inert.
H5	Pyrolusite	Goethite or manganite	Cryptomelane, braunite and pyrolusite (goethite)	Rich in Mn_2O_3 and P_2O_5	The peak temperatures agree also with nsutite but the asymmetry of the first endothermic peak indicates the presence of pyrolusite.
H6	Cryptomelane	?	Cryptomelane		A mixture, in which cryptomelane is dominant (55-65% -estimated). The impurities are braunite, goethite and nsutite which may explain why the peak at 580 is much more prominant than the 615 peak. Mackenzie (p. 323) reports the more prominent peak for cryptomelane at 615°C. The peak temperatures are lower than those for H2 and 3.
H7	Hausmannite	Manganite or goethite	Hausmannite (bixbyite, jacobsite, nsutite, manganite)		The doublet at 1000°C is probably due to oxidised "Mn_3O_4" reverting to Mn_3O_4. Hausmannite oxidises to Mn_2O_3 upon heating in air in presence of bixbyite.
H8	-	Cryptomelane psilomelane?	Wad, cryptomelane and hematite	Much CO_2 and lesser Ca and Mg	The peak at 190 - dehydration. The endothermic peak at 920°C cannot be explained.
H9	Pyrolusite	?	Cryptomelane, jacobsite, nsutite and pyrolusite.		Apparently the concentration of cryptomelane and jacobsite is too low to show in the DTA.
H.10	Hausmannite	?	Hausmannite, jacobsite, and nsutite	Much BaO	The thermal curve shows traces of MnO_2 which may possibly represent the nsutite.
D1	-	Cryptomelane	Cryptomelane, hausmannite and braunite	?	The endothermic peak at 200 is the result of dehydration. The peak at 950°C cannot be explained.
D2	Cryptomelane	?	Cryptomelane	More K than D1	A higher concentration of cryptomelane is apparently the reason for the prominence of the peak at 795°C. This agrees with the chemical data. Dehydration took place up to 250°C.
D3	Cryptomelane	?	Cryptomelane and braunite	More K than D1	The shift of the peaks to higher temperatures is similar to that of H3 and cannot be explained.
A1	Calcite + Ankerite	?	Braunite, cryptomelane, dolomite and calcite	Much more Ca and Mg in the ore than at Hotazel, Devon and Black Rock.	Schwod and Kulp, Kent and Kerr (Mackenzie p. 341) postulated that the two initial peaks of ankerite are due to disintegration of the primary rhombohedral structure forming calcite and calcium or magnesium complexes, with subsequent decomposition of the remaining calcite.

TABLE 22 (Continued)

	MINERALS ACCORDING TO D.T.A. (FOLDER 4)		MINERALOGICAL COMPOSITION ACCORDING TO X-RAY AND OPTICAL DATA	CHEMICAL DATA (FOLDER 3)	REMARKS
SAMPLE	MINERALS Major	Minor			
A2	-	Calcite + (cryptomelane)	Braunite, cryptomelane and calcite	Much Na	The low peak temperature (810°C) for the calcite may be due to the high sodium content.
A3	Calcite + Ankerite	?	Braunite, cryptomelane todorokite, dolomite and calcite	Much Ca and Mg	Part of the peak at 700 may be due to todorokite. The peak at 170 is due to loss of adsorbed water.
A4	Ankerite	?	Cryptomelane, hausmannite, bixbyite, dolomite and calcite	Much Ca and Mg	A typical curve for ankerite. X-ray diffraction shows a more prominent reflection for dolomitic carbonate than for calcite. The calcite, hausmannite and bixbyite do not show in the DTA owing to their low concentrations.
S1	Calcite	Ankerite	Braunite, goethite, calcite and dolomite	Much Ca and Mg	X-ray diffraction shows a more predominent peak for calcite than for dolomitic carbonate.
S2	Calcite	?	Braunite and calcite	Much Ca and Mg	X-ray diffraction does not show a reflection for dolomitic carbonate
B1	Pyrolusite + bixbyite	?	Bixbyite and pyrolusite	?	The peak at 1010°C is due to pyrolusite as well as bixbyite.
B2	-	Cryptomelane	Bixbyite and braunite	?	The peak at 980°C cannot be explained.
B3	Pyrolusite	Cryptomelane	Braunite, iron oxide, pyrolusite (cryptomelane)	Much CO_2	One of the peaks at 1000°C is due to pyrolusite - the other cannot be explained. X-ray diffraction does not indicate carbonate or hausmannite
B3b	Cryptomelane	?	Iron oxide, braunite and cryptomelane	Much Fe	The peak at 1020°C cannot be explained. Hematite is thermally inert.
B3c	-	Cryptomelane	Iron oxide, braunite (cryptomelane)	Much Na	The relatively low second endothermic peak for cryptomelane at 745°C may be due to the high Na_2O content (Folder 4).

The thermal curves for samples from Devon, Adams, Smartt and Black Rock show a small exothermic peak at 320°C which is most likely instrumental. The thermal curves for Hotazel do not show this peak. They were taken on a different apparatus.

structure being incomplete. The structure was restored to normal after 'heat-treating' the samples H2, 3 and 4 for half an hour at 600°C.

2) Shifting of peaks - The peak temperature for pure calcite is 890 to 1010°C (Table 21) whereas in sample A2 it shifted to as low as 810°C (Folder 4). This may possibly be due to the high Na_2O content (Table 18). Similar observations have been reported by Berg (Mackenzie, 1957, p. 339). He found that as little as 0.01 per cent NaCl lowers the temperature of the onset of the first peak of dolomite.

3) The masking of the thermal reactions, e.g. sample H 10 contains more than minor quantities of jacobsite and nsutite but shows little or no thermal reactions for these minerals. The masking may possibly be due to the minerals being dispersed, particularly the jacobsite.

B. Observations on the REICHERT HIGH-TEMPERATURE MICROSCOPE

In order to observe the thermal changes that manganese minerals undergo whilst being subjected to heat-treatment, investigations were extended to an examination of these minerals under the Reichert high-temperature microscope. As far as is known no data have been published on high-temperature microscopy of manganese ore-minerals in reflected light.

The Reichert Vacutherm micro-vacuum furnace is used on the Reichert Metallurgical Microscope of the inverted type (photo 121). The equipment consists of a furnace (photo 122) in which the specimen is placed on a quartz ring (photo 123) and which in turn rests on the specimen carrier. The heating is done by two molybdenum elements surrounding the specimen. The temperature is measured by a thermocouple inserted into a small hole at the side of the specimen close to its polished surface. The experiment may be carried out either in a vacuum or in an inert atmosphere.

As the equipment is designed to accommodate metal specimens (5 mm in diameter - photo 123) and owing to the low thermal conductivity of rocks various modifications had to be made for this investigation. A problem that had to be overcome was the preparation of the sample, in particular the small shoulder near the polished surface and also the hole for the thermocouple (photo 123). Metal specimens are machined on a lathe to the required diameter but with rock specimens this is not possible. After experimenting with supersonic and diamond drills as well as grinding tools, a rotary drill with abrasive powder was found most effective for the preparation of the sample which in the case of rock specimens should not exceed 2.5 mm in diameter.

One of the initial tests was carried out on a sample of bixbyite containing some massive cryptomelane, dissemminated hematite and cryptomelane, the latter along grain boundaries (photo 124). The specks and streaks along grain boundaries were too small to be identified by means of X-ray methods. Upon heating (in argon at approximately 5°C per minute), some of the massive cryptomelane changed to a cryptocrystalline bixbyite (subsequently identified by X-ray diffraction) between 480 and 780°C (photos 125, 126 and 127). During this heating experiment it was observed that the cryptomelane became dull and darker in colour. The reflectivity diminished as the polished surface became dull owing to the loss of such constituents as oxygen and potassium. Grasselly and Klivenyi (1956, p. 16, 17) reported that MnO_2 loses an appreciable quantity of oxygen at 460°C. Some of the potassium was probably also lost at this temperature. The dissemminated white specks remained unchanged at high temperatures and are therefore evidently hematite. The white streaks along the grain boundaries of the bixbyite changed at 460°C to a darker colour and is therefore regarded as cryptomelane. At 1150°C the polished surface of the specimen became covered with a liquid of molten material appearing from the rear, nearer the elements (photos 128, 129). During cooling, which took approximately fifteen minutes, hausmannite crystallised from the molten material on to the polished surface of the specimen (photo 130). The flow of argon was continued until the sample had reached room temperature which took approximately 15 minutes. Subsequently the sample was again polished and this time at right angles to the previous polished surface, after which it was examined at room temperature in order to have a complete picture of the thermal changes that had taken place, as well as the relative positions of the minerals with respect to the heating elements and the polished surface that was under observation initially. It was observed that the transition from cryptomelane to bixbyite is incomplete (photo 131) and that the transition to hausmannite had taken place only in the hot zone where the sample had melted (photo 132).

Although a phase change was noticed (cryptomelane becoming transformed to bixbyite), this experiment was actually disappointing. The phase change from Mn_2O_3 to Mn_3O_4 was not observed although the thermocouple registered 1150°C. The reason for this is the thermal gradient in the specimen which results from the low thermal conductivity of the ore. Thus the rear portion of the specimen which was in the hot zone of the elements melted (1567°C is the melting point of the pure material), whilst the thermocouple which is placed more or less at the edge of the heating zone, registered only 1150°C and the thermal gradient between the hot zone and the polished surface would be even greater as it is still farther away from the elements. The following alterations were then made to reduce thermal gradients in the specimen:-

i) The outer diameter of the sample was reduced to 3 mm and that of the polished surface to 2.5 mm.

ii) The thermocouple was placed nearer the polished surface. To prevent the thermocouple from making contact with the sample holder a slot was cut as shown in photo 123-5.

iii) The sample was built into a small furnace of its own and the polished surface was raised to be nearer the heating elements (photo 123-~~5~~3).

Various materials were tested for this small furnace:

<u>A quartz tube</u> - For this experiment the sample was cemented inside a quartz tube using alundum cement. Greater stability of the sample was attained as the sample was placed in direct contact with the elements. However, this method was not satisfactory as the quartz reacted with the manganese oxides at high temperatures.

<u>An alundum tube</u> - The most satisfactory material for a furnace proved to be alundum. The same assembly was used as with the quartz. No reaction was observed between the sample and the alundum. Temperatures of 1150°C were registered without melting the rear portion of the sample and upon repolishing one of the samples it was observed that the phase change:

$$3Mn_2O_3 \text{ (approx. } 877^{\circ}C) \longrightarrow 2Mn_3O_4 + O$$

had been affected at the polished surface (photo 133), although this was not observed in the high-temperature microscope during the heating experiment. The polished surface had gradually become dull from 900°C onwards whereafter it was unsuitable for observations in reflected light.

Experiments on manganese minerals carried out in a vacuum gave slightly better results although not yet satisfactory. It is a recognised fact that crystal size is dependent on temperature and not on time (Keyser, 1961, p. 196). Unless the surface under observation can be kept clear during the heating experiment it appears as if phase changes at only relatively low-temperature may be observed in manganese minerals. The high-temperature microscope may however, prove to be a valuable tool for the identification of minute inclusions. Experiments in an inert atmosphere (argon) and in a vacuum were also carried out on iron ores. The surfaces under observation remained relatively unaffected ~~by~~ at temperatures between 1100 and 1200°C.

Discussion of results

In view of the fact that apparently only relatively low-temperature transformations may be observed on manganese minerals by means of the high-temperature microscope and as the observations discussed here were made at room temperature after the samples had been repolished after the heating test, no absolute temperatures can be given. The rate of heating was approximately 5°C per minute and the cooling of the sample took approximately 15 minutes, relatively fast down to 200°C and thereafter fairly slowly.

No systematic thermal investigation was carried out on the manganese minerals; only a few observations were made which will now be discussed.

1) The transformation

Bixbyite (Mn_2O_3) $\xrightarrow{877^{o}}$ Hausmannite (Tetragonal Mn_3O_4)

The initial stage of this transformation is illustrated in photo 134. Although a few small crystals of hausmannite are found along grain boundaries, the main mass consists of bixbyite and a partly altered bixbyite. Except hat according to the X-ray data a reflection is present at 3.67°A and that differences were observed in the intensities of some of the reflections compared with standard bixbyite, it is evident that the partly altered bixbyite is nearer to bixbyite than to hausmannite (Table 23).

In areas of higher temperatures the transformation is more complete. Well-twinned, granular hausmannite formed where a melting temperature had been attained. It is noteworthy that the hausmannite which has crystallised from a melt is sometimes riddled with pores (photo 132). The pores could have formed during the reduction of bixbyite to hausmannite, possibly owing to the speed of the reduction. Brill-Edwards and co-authors (1965, p. 368) found that magnetite formed by fast reduction of hematite at 1000°C contained pores. According to Edwards these pores are believed to develop from vacancies generated in the structure as a result of differences in ionic diffusion or during the atomic rearrangement.

TABLE 23.

X-ray powder data of various manganese oxides.

BIXBYITE.		PARTLY ALTERED BIXBYITE.		HAUSMANNITE (SYNTHETIC)	
I	d	I	d	I	d
	ASTM 8-10				ASTM 1-1127
10	4.68			20	4.92
10	4.21	10	4.15		
60	3.83	10	3.87		
		20	3.67		
10	3.35	20	3.35		
30	2.99			31	3.08
				8	2.87
100	2.72	100	2.71	63	2.75
20	2.51	10	2.52	100	2.48
40	2.35	40	2.35	13	2.36
20	2.21	10	2.22		
10	2.11	10	2.08		
40	2.01	10	2.00	15	2.03
10	1.924	10	1.91		
40	1.873	10	1.85		
25	1.719	10	1.81	18	1.79
90	1.657	50	1.67	5	1.70
20	1.617			5	1.64
20	1.567			50	1.57
30	1.530			50	1.54
20	1.483			3	1.47
30	1.454	10	1.45	18	1.44
80	1.421	40	1.42		
40	1.388	10	1.39	4	1.38
30	1.359	10	1.36		
10	1.330			8	1.34
20	1.307			3	1.30
30	1.282			13	1.28
20	1.258			4B	1.24
20	1.196			5B	1.19
40	1.177	10	1.18		
40	1.157				
30	1.141				
30	1.125			4	1.12
70	1.079	20	1.081		

2) The transformation:

Hausmannite (tetragonal Mn_3O_4) $\xrightarrow{\pm 1160^{\circ}C}$ Jacobsite (cubic Mn_3O_4)

Certain samples examined under the heating microscope were subsequently examined at room temperature and the hausmannite and the jacobsite were observed to be closely associated with hematite. Jacobsite occurs mainly in between hausmannite and hematite (photo 135). According to the phase diagram (iron oxide - manganese oxide in air) of Muan and Somiya (1962, Fig. 2, p. 232) this assemblage of minerals (photo 135) indicates that the temperature must have been above 1000°C as only components stable above this temperature are present. The other equilibrium phases at 1000°C shown on the diagram of Muan and Somiya such as spinel ___ Mn_2O_3 could not be observed as the rate of reaction was possibly too slow.

Vredenburgite which is composed of jacobsite (principal constituent) with minute lamellae of hausmannite, was observed in one sample only.

Hausmannite

Upon heating, the regular twin lamellae of hausmannite (photo 136a) are replaced by intermittent twinned units that make angles of 60 and 120° with each other (photo 136 b); anomalous cases have, however, been observed. Noteworthy is the complete absence of clearly demarcated boundaries between individual units. Certain of the units show strong internal reflections along some of the twin-lamellae (photo 137). This cannot be explained.

C. Observations on the LEITZ HEATING MICROSCOPE (model IIa)

The microscope consists of an electric furnace with a variable heating-rate and a ground glass-screen on to which the magnified image of the sample is projected for observation during the heating experiment. The sample is prepared by passing it through a 200-mesh sieve after which it is packed into a square 3 x 3 mm in size. By evaluating the volume changes of the specimen a melting curve in relation to temperature is easily plotted. The temperature at which softening commences, the 'hemisphere point' which is the officially accepted melting point, and the flow temperature were determined in air for 5 manganese minerals (photo 138). The results are tabulated in Table 24.

TABLE 24.

Softening temperature, melting point and flow temperature of 5 manganese minerals (determined in air).

Mineral	Softening Temperature	Melting point	Flow Temperature	Recognised Melting point for pure Minerals.
Cryptomelane	1560°C	1562°C	1564°C	1567°C
Pyrolusite	1574°C	1576°C	1580°C	
Todorokite	1560°C	1564°C	1566°C	
Hausmannite	1574°C	1576°C	1580°C	
Braunite	1476°C	1500°C	1501°C	

The samples of cryptomelane and todorokite were fairly pure and the melting temperatures as tabulated above correspond well with the generally accepted melting point of manganese oxides (1567°C). The low melting point of braunite may be due to impurities that are present. The impurities may be hematite or Si_2O. According to Muan (1959, p. 309) the liquidus temperature of manganese oxide decreases sharply as SiO_2 is added and with the SiO_2 content increasing above 34 weight per cent the liquidus temperatures start to rise.

Why the pyrolusite and the hausmannite melted at higher temperatures than 1567°C is not fully understood. However, the hausmannite-rich sample contains more MnO than the other samples from Hotazel (H7 - Table 13).

VII. THE ORIGIN OF THE ORE

A. Previous theories on ore-genesis

According to John de Villiers (1960, p. 157) the gradation from manganese ore into banded ironstone along strike, frequently at an angle to the bedding, is proof that the ore is not syngenetic in origin, but was formed by metasomatic replacement of the banded ironstone.

Boardman (1961, p. 214) contends that the ore from Black Rock could have received much manganiferous material from the dissolution of manganese-bearing dolomite over wide areas to the south and the east. This, according to Boardman, would have required local interformational erosion if an early period of weathering of the dolomite coincided with the sedimentation of the Upper Griquatown Stage in the Black Rock area i.e. if the manganese ore is considered syngenetic. He reckons that it is more likely that most of the additional manganese for secondary enrichment could have seeped into the exposed banded ironstone of the Upper Griquatown Stage during the erosion which followed the post-Matsap orogenic period. He also points out that the precise length of strike of highly manganiferous formations is not yet known owing mainly to imcomplete exploration to the north of the Kuruman River and that at the southern end the ore belt appears to be terminated suddenly immediately to the south of the Adams Mine by powerful faulting.

According to Boardman it would appear that in this particular area the banded ironstone was interbedded with highly manganiferous, well-laminated, calcareous beds which became enriched to varying grades of manganese ore in the present zone of weathering. The major part of the enrichment was due to solution and removal of calcium from the original rock. Local migration and precipitation of manganese, no doubt, assisted the enrichment, and adsorption of extraneous manganese also probably contributed to an unknown extent. The absence of any notable concentration of manganese ore in the extensive outcrop of the Upper Griquatown Stage along the eastern flank of the Langberg in the vicinity of Olifantshoek is explained by Boardman on the basis that the Upper Griquatown Stage in this area lacked the peculiar highly manganiferous limestone facies which seems to have been necessary for the concentration of manganese ore in the Black Rock area.

B. Conclusions drawn from the present investigation.

1) Evidence in favour of a metasomatic origin

In this instance the ore-bodies would be subsequent or hypogene deposits formed by the percolation of solutions containing manganese. The ore-bodies would probably be characterised by irregularities in occurrence and in shape.

At Black Rock the upper ore-body in places transgresses across the laminations of the banded ironstone; the transgression is gradual. However, this localised transgression is not representative of the ore-bodies of the Kalahari Manganese-field and it is noteworthy that there is a complete absence of veinlets of manganese ore protruding into the banded ironstone. Furthermore, no evidence was found to indicate that the manganese deposits were formed by replacement resulting from injections of magmatic emanations from deep-seated igneous intrusions.

2) Evidence in favour of a sedimentary origin

In this case the ore-bodies would represent sediments and would have been formed under conditions similar to those under which the sedimentary rocks accompanying them formed, with the exception that they might have been subjected to later metasomatism. They would therefore be true syngenetic deposits.

That the manganese ore formed simultaneously with the enclosing banded ironstone, which is generally accepted to have formed by chemical precipitation, is supported by the following evidence:-

a) The interbedded nature of the ore-bodies with the banded ironstone.

b) The persistence of the ore-bodies along strike for a distance of more than 20 miles and down dip for at least 1,000 feet, for example the lower ore-body at Black Rock.

c) The distinctly layered nature of the ore conforms in dip and strike with the enclosing rocks.

d) The folding of the ore-body is in conformity with that of the banded ironstone.

That the manganese ore formed by sedimentary processes is supported by the following evidence:-

a) The lower manganese ore-body, which is by far the thickest and the most persistent, thickens eastwards from Black Rock to Hotazel and in particular in the direction of Adams and Mamatwan. This suggests that the source of the material forming the ore-body was introduced from the east and the southeast.

b) The increase of calcium in the ore from Black Rock to Smartt, Adams and Mamatwan (Folder 3) is in conformity with the postulated direction from which the source-material could have come, that is the dolomite situated to the east and the southeast.

On the whole, the evidence is in favour of a sedimentary origin for the ore of the Kalahari Manganese-field.

C. Possible sources of material for the sediments of the Upper Griquatown Stage

As far as tonnages of manganese ore are concerned, Boardman (1964, p. 426) estimated 50 million tons for the Postmasburg area, taking ore down to 30 per cent Mn. In the Kalahari Manganese-field Boardman's estimate is much larger, i.e. 1,000 million tons (p. 439).

The following formations could have contributed material to the basin of deposition:

1) The dolomite of the Transvaal System

In the Postmasburg area Nel (1929, p. 39) regarded the underlying dolomitic formation as a possible source of the manganese and quotes analyses of Campbell Rand limestone in which the content of manganese varies from 0.39 to 2.12 per cent. The dolomite is therefore a likely source of manganese. However, in the Kalahari Manganese-field the dolomite lies 5,000 feet stratigraphically below the manganese-bearing banded ironstone, a relationship which is in strong contrast with the close association of the ore and the dolomite in the Postmasburg area. Nevertheless, erosion of dolomite to the east could have yielded solutions charged with calcium, magnesium and manganese. On the basis of analyses of the dolomite and the composition and the specific gravity of both the dolomite and the manganese ore Nel (1929, p. 89) calculated that 1 cubic foot of ore (50 per cent metallic manganese) would require 58.6 cubic feet of dolomite. Therefore, an enormous volume of dolomite must have been decomposed and eroded away to provide the known manganese ore of the Kalahari Manganese-field.

2) The rocks of the Lower Griquatown Stage

a) The banded ironstone and jasper

The banded ironstone and jasper contain much iron but only a little manganese, and these rocks could therefore have been a major source only of iron for the sediments of the Upper Griquatown Stage.

b) The tillite

Glacial debris containing fresh minerals and oxygen-rich meteoric water is another possible source of manganese and iron in considerable quantity. Hewett (quoted by Krauskopf, 1957, p. 76) pointed out that it is perhaps not accidental that bog-ore of manganese is concentrated in areas underlain by the latest Pleistocene till.

It has been found by Borchert (1960, p. 262), Krauskopf (1957) and Schweigart (1965, p. 291) that iron in the trivalent state is practically insoluble in the presence of oxygen and that solutions in continental regions would therefore not transport significant quantities of dissolved iron. Hence it is highly unlikely that the rocks of the Lower Griquatown Stage contributed much ferruginous material in solution to the sedimentation of the Upper Griquatown Stage.

3) The Ongeluk lava

The Ongeluk lava is a likely source of manganese and iron for the Kalahari Manganese-field because shortly after its formation, the Ongeluk lava contained an abundance of fresh ferromagnesian minerals readily accessible to circulating water. The lava has a considerable total thickness. Nel (1929, p. 27) considers it to be 3,600 feet thick and Wessels (in press) estimates its thickness at 7,000 feet. The lava was erupted subaqueously and repeated lava flows could have contributed progressively towards the enrichment of the water in manganese, iron, calcium, magnesium and silica, mainly by solutions and gases and by extraction processes.

Manganese in surface water seldom has a concentration greater than 5 p.p.m. of water (Krauskopf, 1957, p. 65). The manganese content of the Ongeluk lava (Table 24) is many times in excess of this figure.

TABLE 24.

Manganese and iron content of bore-cores of Ongeluk lava from the farm Bonetsfontein near Postmasburg

Mn %	Fe %
0.17	9.0
0.09	10.0
0.09	10.2
0.03	4.3
0.15	9.6

(Depth 1,300 to 1,450 feet)
Analyses at the Research Laboratories, ISCOR.

The balance of the evidence seems to favour a sedimentary origin for the rocks of the Kalahari Manganese-field. Thus far evidence has been presented suggesting that the Campbell Rand Dolomite and the Ongeluk lava could at some stage have contributed material for the deposition of the sediments constituting the rocks of the Upper Griquatown Stage. It would appear that the manganese could have come from both the dolomite and the lava and the iron mainly from the lava.

Trace-quantities of elements such as Cu, Pb, Cr, Ti, V, Ni, Co and B which were detected in the banded ironstone are considered by Schweigart and others (Schweigart, 1965, p. 295) as diagnostic of sediments derived from volcanic exhalations.

It is of interest to note that no clastic material was found in either the ore-bodies or the banded ironstone which may indicate that the material in solution extracted from the dolomite was transported over an area of low relief in which case the clastic material in the rivers would have separated from the material in solution.

D. The transportation of iron and manganese

The chemical similarity between manganese and iron is shown by their close association in rocks. In igneous rocks the ratio Mn/Fe varies between 1/100 and 1/10 (Krauskopf, 1957, p. 61). The chemistry of iron and manganese during sedimentation is well explained by many authors, but why the two elements become separated under conditions of sedimentation is still somewhat of an enigma. Manganese in solution may be deposited as carbonate or silicate under reducing conditions, or as an oxide under oxidising conditions, but why iron is not always deposited at the same time is not clear. Many suggestions have in the past been put forth, for example:-

a) The absence of either iron or manganese in the source-material. This argument may be rejected on the grounds that manganese and iron are often found together in rocks.

b) Selective removal of say, only iron (iron is far more common in rocks than manganese). This is contradicted by the fact that compounds of manganese are uniformly more soluble than the corresponding compounds of iron (Lindgren, Rankama and Sahama and Goldschmidt - as quoted by Krauskopf, 1957, p. 69).

c) Bacteria furnish a reasonable explanation for the curious fact observed by Ljunggren (Krauskopf, 1957, p. 71), that in some lakes in Sweden iron-rich deposits in one part and manganese-rich deposits in another are apparently produced simultaneously from the same inflowing water. However, the assumption that the particular kind of bacteria that precipitate manganese as present in all the environments where manganese deposits are found and that they were present in excess of bacteria that precipitate iron and sometimes even to the exclusion of iron-bacteria, is not to be rejected but is more likely applicable to smaller localised deposits such as bog-ore deposits and not to large deposits (Krauskopf, 1957).

d) Meteoric waters containing carbonic acid may redissolve the iron and the manganese from consolidated material, particularly during supergene enrichment. This may lead to enrichment either in manganese or in iron as is the case at Smartt Mine where the ore-body is progressively enriched in manganese as the sub-outcrop is approached, whereas prolonged leaching in certain areas resulted in detrimental ferruginisation of the manganese ore in other areas (Boardman, 1964, p. 434).

e) Catalytic action of MnO_2 already precipitated could accelerate the oxidation of manganese.

f) Physico-chemical conditions during precipitation. Ferric oxide and hydroxide have a greater insolubility than the manganese equivalents and the most important reason for vertical and lateral variation in distribution of the iron ore, the manganese ore and the banded ironstone, are changes in sea currents, each with its own characteristic physico-chemical conditions.

It is contended that the rocks of the Upper Griquatown Stage represent chemical precipitates and that various processes could have contributed towards the separation of the iron and the manganese, e.g. physico-chemical conditions of precipitation and to a lesser extent bacteria and also the catalytic action of MnO_2. The hypothesis of separation of manganese from iron oxide by precipitation (prior) is particularly suited to explain manganese deposits associated with submarine lava flows. This separation would be most effective where manganese is supplied by the weathering of volcanic material and by exhalative processes to meteoric water in amounts slightly greater than normal. Excessive amounts of manganese are probably not essential if the necessary physico-chemical condition is maintained for a prolonged period.

E. The environment and the mode of deposition of the Upper Griquatown Stage

The sediments of the Upper Griquatown Stage of the Kalahari Manganese-field were probably deposited in a marine basin partly or wholly separated from the open sea and it is possible that some blending of the facies took place in the basin. Depending on the prevailing pH manganese carbonate or calcium carbonate can be deposited in colloidal form (Deer, Howie and Zussman, 1963, vol. 5, p. 268).

In the Hotazel area slump-structures, due to contemporaneous slumping, for instance the presence of contorted bands of magnetite (photo 41) and patches of ferruginous material in the ore-body (photo 3), suggest the prevalence of unstable conditions in the areas of carbonate deposition. These slump-structures were not observed anywhere outside the Hotazel Mine.

1) The banded ironstone

Cullen (1963, p. 387) considers that the banded ironstone formations of Precambrian age may be of a sedimentary origin. Woolnough, Sakamoto, Alexandrov and Hough (quoted by Cullen, 1963) all agree that the ironstones represent the products of advanced chemical weathering under warm, humid conditions and that they were deposited in large enclosed basins.

According to Cilliers (1961, p. 79) the material from which the banded ironstone of the Lower Griquatown Stage was formed, must have been transported over an area of low relief so that the load of clastic material in the rivers could be separated from the material in solution. He came to the conclusion that the banded ironstone was formed from material precipitated chemically in a restricted and shallow basin of deposition and that the banding resulted from slight variations in chemical conditions. Cullen attributes the banding to differential influx of material controlled by recurrent isostatic readjustments and not to seasonal climatic fluctuations in the manner described by Alexandrov and Hough (quoted by Cullen, p. 386).

2) The manganese ore

Drilling at Smartt Mine revealed that the grade of the ore deteriorates as the ore-body is followed down-dip under cover of the banded ironstone (Boardman, 1961, p. 215). It then becomes a laminated rock with a high lime content and is composed mainly of compacted laminae of manganese oxides cemented with streaks of calcite and elongated oolites along the bedding planes.

The following evidence was found in the Kalahari Manganese-field to support Boardman's theory that the original material of the ore-body was calcareous:-

a) The presence of calcareous material in the oolites and the lenticular inclusions in the ore (photos 8, 9, 54, 99, 102, 107).

b) The high carbonate content of the ore from the mines Smartt and Adams (Folder 3).

Considering this evidence it seems possible that the manganese ore-body originated from manganiferous limestone intercalated in the banded ironstone. It is not clear what the original composition of the limestone was but it probably consisted of a high proportion of rhodochrosite, calcite, dolomite and in places siderite. Boardman (1964, p. 437) considers that the manganese content of this limestone could have been in the region of 20 per cent or more. It is not certain whether the wad present in some of the mines (Devon, Langdon and Hotazel) represent some of the original material that was deposited as oxides. Should this be the case then it may be concluded that precipitation took place along the zone bordering the carbonate-oxide field of physico-chemical conditions e.g. South Klingan and Central Kazakhstan; U.S.S.R. (Roy, 1965, p. 1255).

F. The mode of formation of the ore-minerals and their distribution

1) The possible temperature of formation of some of the minerals

a) The minerals of the ore

Much has been published on the origin of certain manganese oxides and on whether the manganese ore is supergene or hypogene in origin. Hewett and Fleischer (1960, p. 1 - 55) carried out an extensive investigation on the manganese minerals and arrived at the following conclusions:-

i) Some manganese oxide minerals appear only in deposits of supergene origin, e.g. lithiophorite, chalcophanite and wad.

ii) Others are present only in deposits of hypogene origin, e.g. hausmannite (?), bixbyite and jacobsite.

iii) Lastly, some are present both in deposits of supergene origin and in deposits of hypogene origin, e.g. pyrolusite, manganite, cryptomelane, psilomelane, hollandite and braunite.

Hewett and Fleischer (p. 51) consider other manganese minerals also but they are not included in the above list as they were not found to be present in the Kalahari Manganese-field.

J.E. de Villiers (1946, p. 40 - 41) considers bixbyite, hausmannite and jacobsite as minerals that form at high temperatures.

The formation and the transformation of the different manganese oxides are explained in chapter VI on the thermal studies. Extensive data are contained in the literature on phase-equilibrium studies of systems involving manganese, iron and silica which indicate the transformation of manganese dioxide minerals at high~~er~~ temperatures to lower oxides, for example pyrolusite, cryptomelane or nsutite are transformed to bixbyite at 600°C (photo 71) and bixbyite is transformed to hausmannite at 877°C (Hahn and Muan, 1960). Pyrolusite and cryptomelane together with silica may be transformed to braunite at elevated temperature. The formation of braunite and bixbyite from each other has been reported in the literature but could not with certainty be verified in the ore from the Kalahari Manganese-field. Roy and Mukherjee (Mitra, 1965, p. 212) reported abundant braunite as the only lower oxide in the chlorite zone of progressive regional metamorphism. Braunite may also be stable at higher grades of metamorphism as its stability range is very wide. It is present together with andradite at Black Rock (photo 45, 46, 48, 49). The absence of jacobsite at Black Rock may be due to the lack of suitable material, i.e. braunite was present initially and jacobsite does not readily form from braunite. Under reducing conditions braunite is formed in a sedimentary environment at low temperatures (Betekhtine - Mitra, 1965, p. 312). Bixbyite was not found together with andradite in ore from the Kalahari Manganese-field.

The temperatures at which the pyrolusite, cryptomelane and nsutite transform to bixbyite (600°C) and bixbyite to hausmannite (877°C) are beyond the limit of natural metamorphic processes. Nevertheless, the trend of the different transformations is variable according to the partial pressure of oxygen during the metamorphic processes.

Not a single example could be found in the literature where doubt has been cast on the origin, at high temperature, of the manganese oxide minerals bixbyite, hausmannite and jacobsite. Also, the mineral andradite which is present in the Kalahari ore-bodies is generally regarded as a high-temperature metamorphic mineral.

It is concluded that the formation and transformation of some of the different manganese oxides and minerals of the ore of the Kalahari Manganese-field had taken place under metamorphic conditions of changing temperature and it is considered that the temperature probably did not exceed 500°C at any time.

b) <u>The minerals of the banded ironstone</u>

In a noteworthy paper on the genesis of marine sedimentary iron ores Borchert (1960, pp. 261 - 277) quotes work of Krumbein and Garrels, and of Huber, and emphasizes the existence of a CO_2 - zone at moderate depths in the ocean. In this zone abundant iron is dissolved and in response to the normal ocean currents moves towards the oxygen-rich shallow sea. Here the iron is deposited as limonite ooliths. However, Borchert maintains that a considerable proportion of the dissolved iron is precipitated in the CO_2 - zone itself to form sideritic clay.

According to John de Villiers (1960, p. 132) the ferruginous bands of the banded ironstone of the Upper Griquatown Stage are composed almost entirely of fine-grained, compact, crystalline hematite with a subordinate quantity of tiny crystals of magnetite. According to Visser (1958, p. 14) the ferruginous bands of the banded ironstone of the Lower Griquatown Stage are composed mainly of hematite, limonite and small crystals of magnetite. Frequently the rock is strongly magnetic. Cilliers (1961, p. 19) reported siderite in fresh samples of banded ironstone from the Lower Griquatown Stage. The present author found much siderite in samples of the upper portion of the Lower Griquatown Stage, ~~from~~ at a depth of approximately 400 feet.

The ferruginous bands of the banded ironstone of the Upper Griquatown Stage are composed of closely packed, fine grains of idiomorphic hematite. There appears to be no reason to assume that the hematite is pseudomorphous after magnetite. In fact, no magnetite was found in the banded ironstone, not even in samples from a depth of 450 feet. Furthermore, the banded ironstone is virtually non-magnetic.

It is contended that the hematite of the Upper Griquatown Stage is a product of a sedimentary process in which predominantly iron hydroxide was precipitated along the zone bordering the oxide-carbonate field of marine deposition i.e. in an oxidising environment. The banded ironstone of the Lower Griquatown Stage on the other hand formed most likely along the zone bordering the carbonate-oxide field i.e. more reducing in character.

2) The paragenetic sequence

A close study of the mutual relationship of the manganese minerals of the Kalahari Manganese-field reveals that some occur in two generations, e.g. braunite, also braunite-II, occurs as encrustations on andradite which in turn encrusts ordinary braunite (sample B 1).

Time-relations among the minerals are clearly indicated in most of the samples by veins of one mineral intersecting others and by pseudomorphs, although in the case of the pseudomorphs the sequence is not so easily established. From the mineralogical investigation a broad sequence is recognised:-

a) Original sedimentary material

It would appear that the ore from the Kalahari Manganese-field represents original sedimentary rocks which consist of oolitic carbonate in a matrix of gelatinous manganese and iron hydroxide, manganese and iron carbonate and in places hydrous silicates of magnesium and iron.

b) Minerals formed by lithification

During diagenesis the gels were evidently dehydrated and owing to ultimate lithification, wad (photos 13, 19), rhodochrosite (photo 9) and calcite (photo 8) were formed. Of these minerals only rhodochrosite and calcite and possibly wad are still present in the ore and the wall-rock.

c) Metamorphic minerals

i) An early stage - The minerals braunite, magnetite (photo 41), cryptomelane, pyrolusite, goethite, talc and minnesotaite were formed as a result of low-grade metamorphism, most likely from the wad (photo 18, 19) and from leached material.

ii) <u>A Main Stage</u> - During the **main** metamorphic period hausmannite, jacobsite, hematite, andradite, tremolite, talc, bixbyite, braunite and manganite were formed. These minerals are to some extent metasomatic in origin. They are listed in a sequence suggested by the mineralogical evidence

d) <u>Supergene minerals</u>

Cryptomelane, nsutite, todorokite, pyrolusite, hematite, lithiophorite and goethite possibly originated under supergene conditions as replacement-minerals and as cavity fillings.

e) <u>Hydrothermal minerals</u>

Acmite seems to have made its appearance in the banded ironstone owing to hydrothermal actions, most likely at some time after the main period of ore formation.

The above paragenetic sequence applies more or less to the ore of the Kalahari Manganese-field as a whole. Local departures are numerous and the full sequence cannot be established for any one mine, for example, andradite was found at Black Rock and at Hotazel and manganite at Hotazel and at Adams only. Moreover, no todorokite is known at Black Rock.

3) <u>The distribution of the minerals</u>

<u>The Eastern Belt</u> - The ore from Hotazel is complex (photo 99) and the full sequence of minerals, excluding the primary carbonates, can be traced. Braunite-rich ore (photo 22) is present although generally much altered. It is noteworthy that only at Hotazel are presumed slump-structures

present in the ore (photo 41).

The Central Belt - The ore from this area is mainly a braunite-rich ore and it is only in this area where the primary carbonates were observed (photos 102, 106, 107). Hausmannite is represented mainly by relics (early oxide - photo 31).

The Western Belt - The ore from this belt is mainly a braunite-rich ore. There is very little wad in the ore from Black Rock. Isolated crystals of hausmannite are present but no jacobsite or todorokite. No marked difference could be observed between ore taken near the surface and underground along the incline at 450 and 900 feet (450 feet vertical depth). This fact as well as the absence of todorokite even in the late oxides tend to indicate that the ore from Black Rock was not greatly altered by late supergene solutions.

G. The metamorphism of the Upper Griquatown Stage

The evidence presented thus far is in accordance with a sedimentary origin of the rocks of the Upper Griquatown Stage. In the Kalahari Manganese -field there is no obvious crustal deformation and no structural features were found that could be associated with regional metamorphism. The evidence indicates that the manganiferous sediments together with the enclosing rocks most probably have subsequently been subjected to varying degrees of thermal metamorphism in different parts of the Kalahari Manganese-field, as indicated by the presence of various metamorphic minerals, e.g. andradite at Hotazel (photo 99) and at Black Rock (photos 45,46, 48, 49), tremolite at Hotazel (photos 52, 53) and talc at Mamatwan (photo 54) and at Adams. The high-temperature manganese oxide minerals like hausmannite (photo 99) and jacobsite (photo 47) are associated with the metamorphic silicate minerals. No high-temperature manganese silicate minerals like rhodonite or tephroite are known to have been formed either in the ore or in the enclosing rocks.

1) <u>The non-manganiferous minerals</u>

The minerals andradite and tremolite which are associated with the manganese ore of the Kalahari Manganese-field are generally accepted to indicate the prevalence of high temperature at the time of their formation. It is generally assumed that tremolite is a lower grade metamorphic mineral than andradite.

<u>Andradite</u> - It is generally assumed that andradite is not a product of regional metamorphism but of high-grade contact- or thermal metamorphism. Typical occurrences of this mineral are in metamorphosed, impure calcareous sediments and can be ascribed to a reaction between calcite, iron oxide and silica.

$$\underset{\text{calcite}}{3CaCO_3} + Fe_2O_3 + 3SiO_2 \longrightarrow \underset{\text{andradite}}{Ca_3Fe,Si_3O_{12}} + 3CO_2$$

<u>Tremolite</u> - Occurrences of this mineral similar to those in the Kalahari Manganese-field are found in metamorphosed carbonate-rocks and its presence can be ascribed to a reaction between dolomite, silica and water.

$$\underset{\text{dolomite}}{5CaMg(CO_3)_2} + 8SiO_2 \longrightarrow \underset{\text{tremolite}}{(OH)_2CaMg_5Si_8O_{22}} + \underset{\text{calcite}}{3CaCO_3} + 7CO_2$$

Talc - minnesotaite - These are low-grade metamorphic minerals and may, as far as the Kalahari Manganese-field is concerned, be ascribed to a reaction between dolomite, silica and water.

$$\underset{\text{dolomite}}{3CaMg(CO_3)_2} + 4SiO_2 \longrightarrow \underset{\text{talc}}{(OH)_2Mg_3Si_4O_{10}} + \underset{\text{calcite}}{3CaCO_3} + 3CO_2$$

With sufficient iron present minnesotaite may be formed:

$$(OH)_2Fe_3Si_4O_{10}$$

2) The manganese minerals

Braunite is the most widely distributed of these minerals in the ore of the Kalahari Manganese-field, particularly in the Central Belt and the Western Belt. With the onset of metamorphism and the consequent increase in temperature the higher oxides of the manganese minerals with Mn^{4+} in the structure combined with the available silica to form braunite which is stable at high grades of metamorphism. Braunite is present in the ore together with andradite (photos 45, 46, 48, 49) and it is intergrown with bixbyite at Black Rock (photo 27). The indications are that in places at Black Rock the two minerals, braunite and bixbyite, originated simultaneously. Dunn (quoted by Mitra, 1960, p. 305) describes intergrowths of sitaparite (bixbyite) and braunite in ore from India and considers the two minerals there to have formed simultaneously. On the other hand, Mitra (1960, p. 305) ascribes similar textures to replacement.

At the peak of metamorphism andradite was formed as well as hausmannite-jacobsite (photo 99) and Korannaberg ranges. The maximum intensity of the anomaly was found to be in the Olifantshoek area. This location of the anomaly apparently does not agree with the metamorphic aureole of the area.

H. The geological history of the Upper Griquatown Stage

It would appear that the manganiferous chemical sediments were laid down under oxidising conditions and that braunite was one of the early metamorphic minerals to be formed from the original sedimentary material. Subsequent to the formation of the sediments they were subjected to post-Transvaal folding. In chapter II on the geology of the Kalahari Manganese-field it is explained that the rocks of the Upper Griquatown Stage were folded and eroded before the deposition of the sediments of the Gamagara Formation. Subsequent to the folding of the Upper Griquatown Stage much material such as manganese, iron and 'mud' with a composition close to andradite was introduced into open cavities and fissures (photo 48) and in certain areas iron oxide (hematite) was precipitated in what appears to have been cavities formed presumably by leaching and slumping (photos 3, 41). Subsequently, but probably before the deposition of the sediments of the Gamagara Formation, certain areas were subjected to high-grade metamorphism (thermal) during which the minerals andradite, hausmannite and jacobsite were formed.

At a later stage the area was subjected to epeirogenesis, possibly uplift, and the rocks of the Upper Griquatown Stage were eroded. This is proved by the basal conglomeratic breccia of the Gamagara Formation located on the farm Eersbegint in which are present rounded pebbles of manganese ore and banded ironstone. This manganese ore already contains the minerals hausmannite and jacobsite (photos 35, 36). Most likely towards the waning stage of this period of erosion of the rocks of the Upper Griquatown Stage, the manganiferous ore-bodies were subjected to supergene enrichment and the minerals such as cryptomelane, pyrolusite, todorokite and nsutite could have been formed. (The various stages in the history of the Kalahari Manganese-field are schematically represented in Table 25).

It is therefore evident that there is some relationship between the geological structure (folding) and the grade of metamorphism. High-grade ore is encountered in areas that were subjected to folding (Eastern and Western Belts) and it is in these areas that the mineral andradite is present. No andradite is known in the ore from the Central Belt. In fact this ore which is of a low grade corresponds somewhat with the original composition of the sediments from which it originated.

H1. A comparison with the Postmasburg Manganese-field

According to J.E. de Villiers (1946, p. 41) the Postmasburg ores have been deposited from circulating, hot solutions. He quotes the opinion of others: L.T. Nel - replacement by meteoric water; H. Schneiderhöhn - metamorphosed sediments; A.L. du Toit - replacement deposits that have undergone metamorphism.

~~The present author had the opportunity of visiting the Postmasburg Manganese-field on several occasions and also to examine some of the ore. He is of the opinion that the ore is a product of replacement and has subsequently undergone thermal metamorphism.~~

It is of interest to note that the Eastern Belt of the Postmasburg-field compares favourably with the Central Belt of the Kalahari Manganese-field in this respect that in both areas the mineral braunite is predominant. Furthermore, the Western Belt of the Postmasburg-field compares favourably with the Eastern - and Western Belts of the Kalahari Manganese-field in so far that the minerals bixbyite, hausmannite and jacobsite are present in both areas. Garnet was not found in the ore from the Postmasburg-field.

According to J.E. de Villiers (1946, p. 40) certain features of the ore from the Postmasburg area militate against a metamorphic origin. They are:-

1) "Small druses in the ore are not uncommon". In the Kalahari Manganese-field andradite is found in some of the vugs and in the Postmasburg-field ephesite, bixbyite and diaspore. In this connection it should be pointed out that under conditions of thermal metamorphism the pressure need not be exceptionally high as under conditions of regional metamorphism. However, according to Barth (1962, p. 234) shearing stress in rocks greatly facilitates the process of recrystallization and the 'pore fluid' will escape from places of high pressure, even in gneiss and schist. Moreover, it is quite conceivable that in a carbonate environment a gaseous phase under metamorphic conditions would create and maintain drusy cavities.

2) "In a few specimens coarse- and fine-grained sitaparite ores of similar mineralogical constitution occur in juxtaposition". Although under the same conditions of metamorphism a uniform grain-size would result, local variations in physical conditions caused by fracturing or bedding could however, account for a variation in grain-size.

TABLE 25

THE VARIOUS STAGES IN THE HISTORY OF THE KALAHARI MANGANESE-FIELD

GEOLOGICAL FORMATION OR STRUCTURE	PROCESS	CONDITIONS AND ENVIRONMENT	MINERALS FORMED IN THE MANGANESE ORE OF THE UPPER GRIQUATOWN STAGE
Gamagara Formation	Sedimentation	Conditions favourable for deposition of clastic material (contains pebbles of manganese ore and banded ironstone)	Supergene minerals.
Unconformity	Epeirogenesis	Uplift and erosion	
Bostonite	Intrusion of dykes and sills	Hydrothermal alteration of bostonite	In bostonite - cymrite, nontronite piedmontite and hydromica.
Hidden igneous rocks	Plutonic intrusion	Scanty evidence suggests thermal metamorphism to have taken place before the deposition of the Gamagara Formation	Main metamorphic minerals : hausmannite, jacobsite, hematite, andradite, tremolite, talc, bixbyite, braunite, and manganite.
Folds and breccia	Vein and cavity filling conditions	Addition as well as leaching of material	
	Pressure from the west - long and continued	Compression	
Upper Griquatown Stage	Lithification	Low grade metamorphism (load?)	Early metamorphic minerals : braunite, magnetite, cryptomelane, pyrolusite, goethite, talc and minnesotaite.
		Dehydration, compaction and recrystallation	Minerals owing to lithification : wad, manganese oxide, rhodochrosite and calcite.
	Chemical precipitation	Marine basin of deposition - oxidising environment.	Original sedimentary material : oolitic carbonate, gelatinous manganese and iron hydroxide, manganese and iron carbonate and hydrous silicates of magnesium and iron.
Ongeluk lava	Successive flows, subaqueously	Exhalative conditions and weathering processes (Enrichment of water in Fe, Mn and SiO_2).	
Campbell Rand Dolomite	Erosion and weathering	Highland towards east. (Enrichment of water in Mn, Ca and Mg).	

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PHOTO 2

HOTAZEL MINE, SOUTHERN FACE. SEPTEMBER, 1963

s = Sand
l = Limestone (Kalahari)
u = Upper Manganese Body
b = Bostonite
i = Banded Ironstone
c_2 = Top cut
c_1 = Bottom cut.

Photo 3(a). Manganese ore (blue-black) and iron ore (red). Bottom cut, approximately 25 feet high. Hotazel.

Photograph missing

Photo 3(b). Close-up of contact area between manganese (bluish) and iron ore (red). The laminations of the manganese ore terminate against iron ore. The patch of iron ore is approximately 3 feet across. Hotazel.

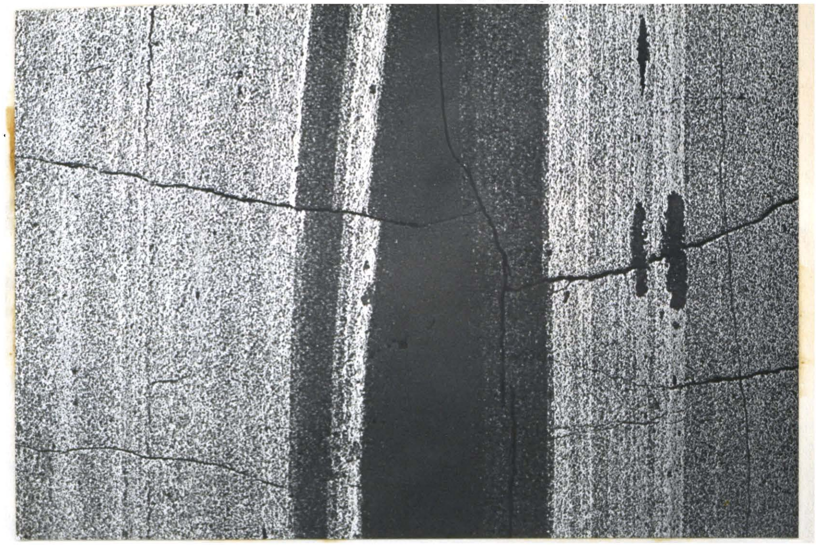


Photo 4. Martitised banded ironstone. The two dark bands are partially replaced jasper (black). Refl. light. Hotazel - HB 1 15 x

Photo 5. Kalahari limestone (white-gray) replacing banded ironstone from above (black squares). The dark-gray strip on the top is Kalahari sand.
Hotazel.

Photo 6. Transverse fracture, striking east - west, filled with surface rubble. Devon.

Photo 7. 'Carbonate-rock' (black) partially replaced by cryptomelane (gray-white). The thin bands (black) are red-brown jasper.
Devon. 2/3 x

Photo 3. Manganese ore showing remnants of limestone (white) and 'oolites'. Smartt ½ x

Photo 9(a). 'Carbonate-rock' (left) from footwall of ore-body, with strips of dolomite (white) and rhodochrosite (dark-gray). At right ~~is~~ manganese ore overlying the 'carbonate-rock'.
Mamatwan.

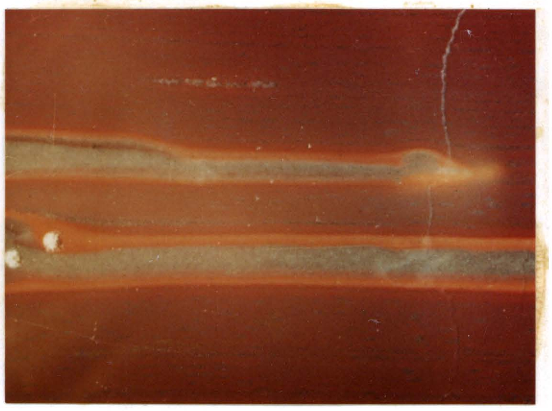


Photo 9(b). Rhodochrosite (gray) with reaction rim of ankerite (yellow-red), all in groundmass of hematite and minnesotaite. The two holes were drilled for X-ray identification. Oblique illumination. Mamatwan - M 10. 10 x

Photo 10. Manganese ore-body (m) with intercalation of banded ironstone (jointed) dipping to the west. The banded ironstone is approximately 5 feet across. Black Rock.

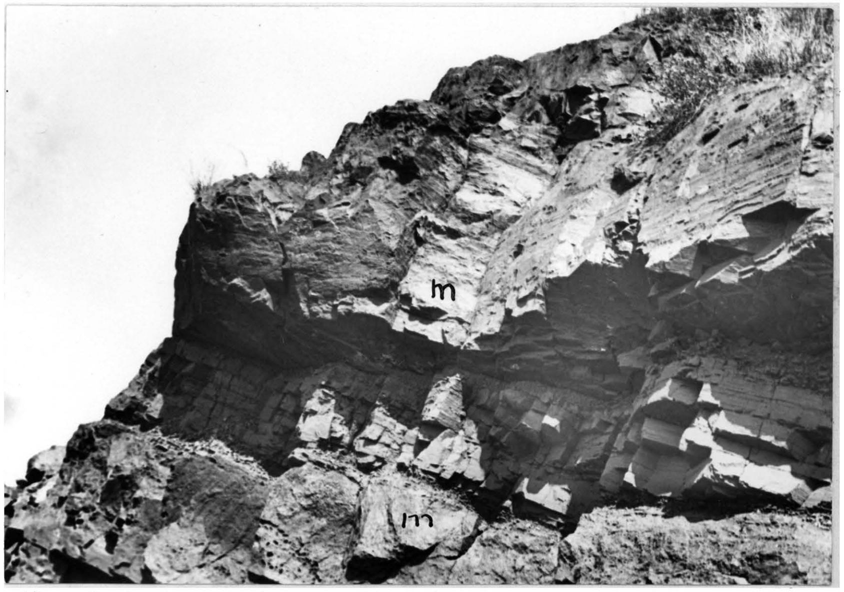


Photo 11. Banded ironstone dipping westwards at 35° beneath manganese ore-body. The entrance to underground workings in ore-body is seen. Black Rock.

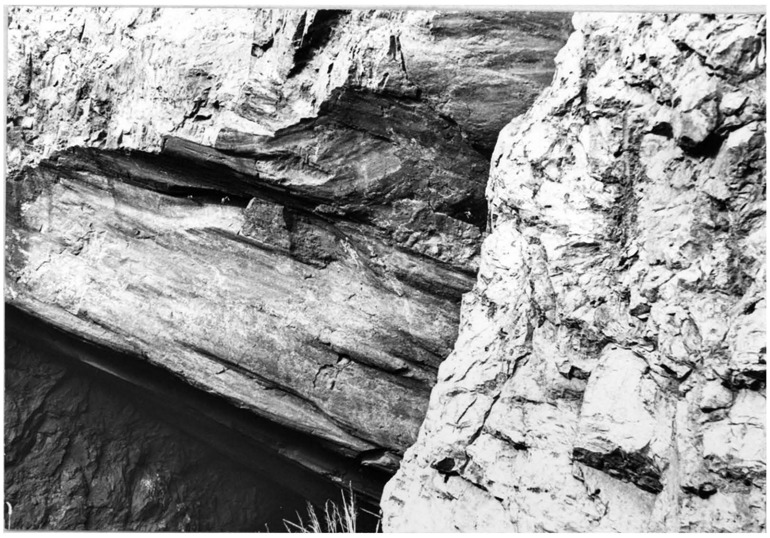


Photo 12. Coarse slickensides in manganese ore-body. Black Rock.

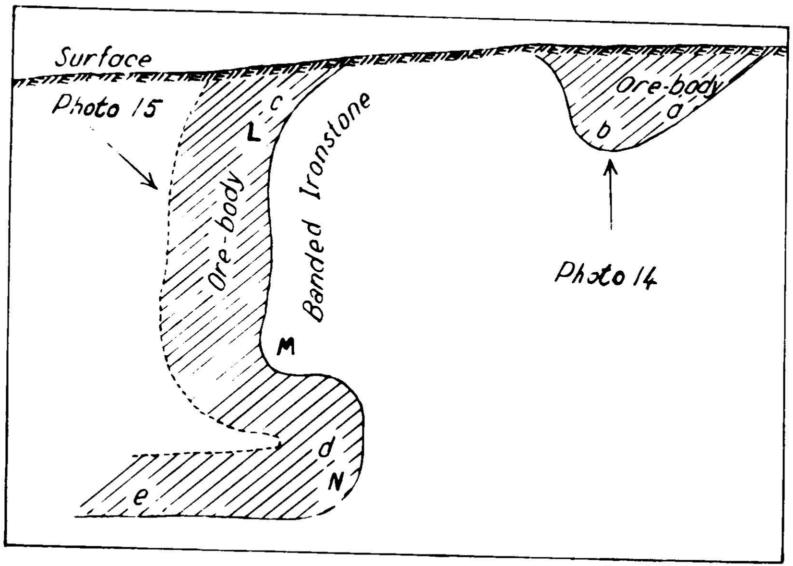


Photo 13. Cross section across folded ore-body depicting relationship of photos 14 and 15. This area is situated along the open-cast workings 4 and 2 (Folder 2) east of the beacon N'chwane (samples were taken at a to e). Black Rock.

Photo 14. Excavation along asymmetrical fold of small amplitude (position indicated on photo 13). To the left the foot-wall contact of the manganese ore is almost vertical. Banded ironstone at bottom of excavation. Size of fencing poles indicate scale. Black Rock.

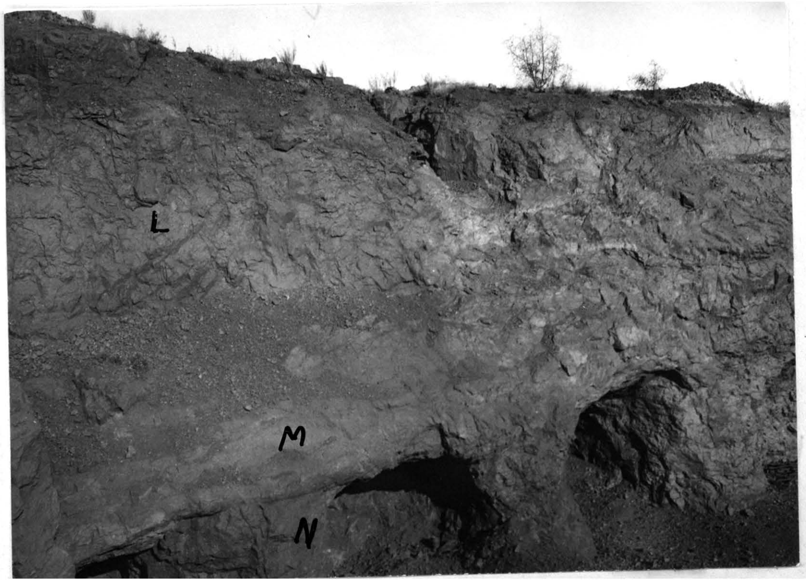


Photo 15. Recumbent fold of banded ironstone (M) and manganese ore (L and N). Black Rock.

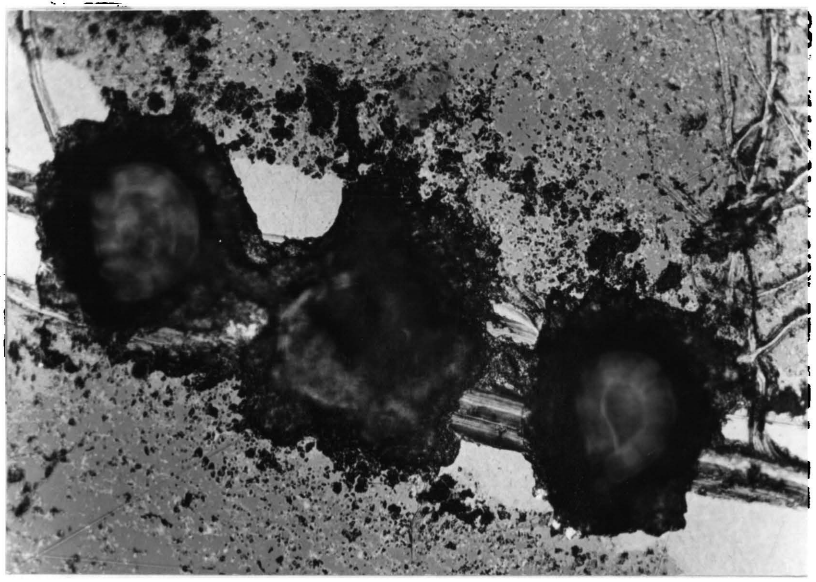


Photo 16. Holes 0.3 mm in diameter formed by diamond-tipped objective. Refl. light. 300 x

Photo 17. Scratches 0.1 mm in width by 'micro-manipulator' and sapphire stylus.
Refl. light. 300 x

Photo 18. Ore rich in cryptomelane and wad. Cryptomelane (white) forming in wad (black). Top cut, Hotazel - H8. Refl. light.   15 x

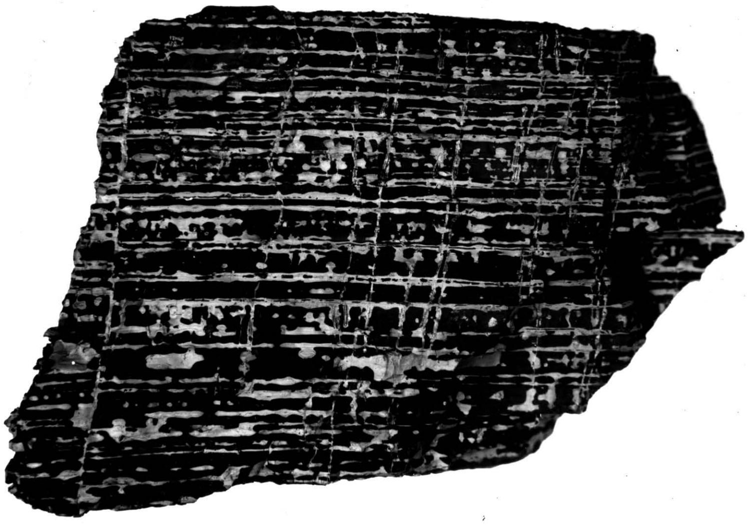


Photo 19. Cryptomelane (light-gray) forming in wad (black). Oblique illumination.
Langdon.   Actual size.

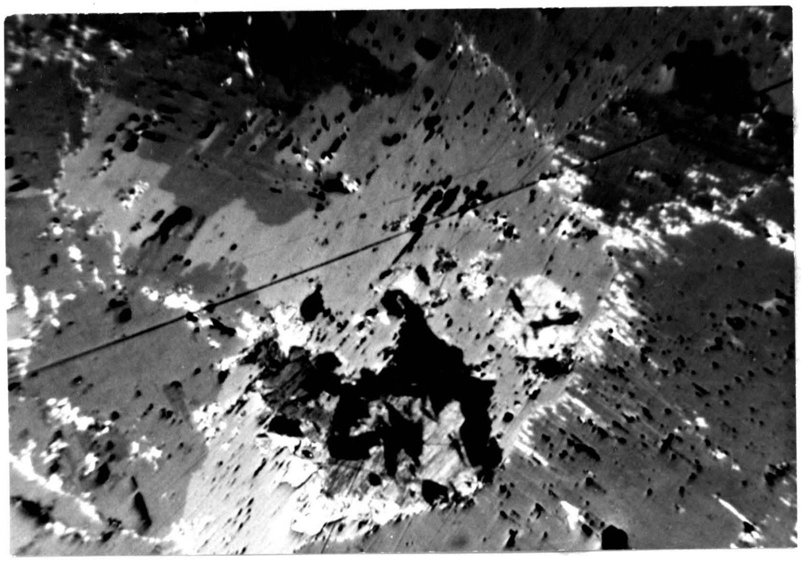


Photo 20. Anisotropism in braunite (ordinary). The white is pyrolusite. Black Rock - BR 2. Crossed nicols, refl. light, oil imm. 300 x

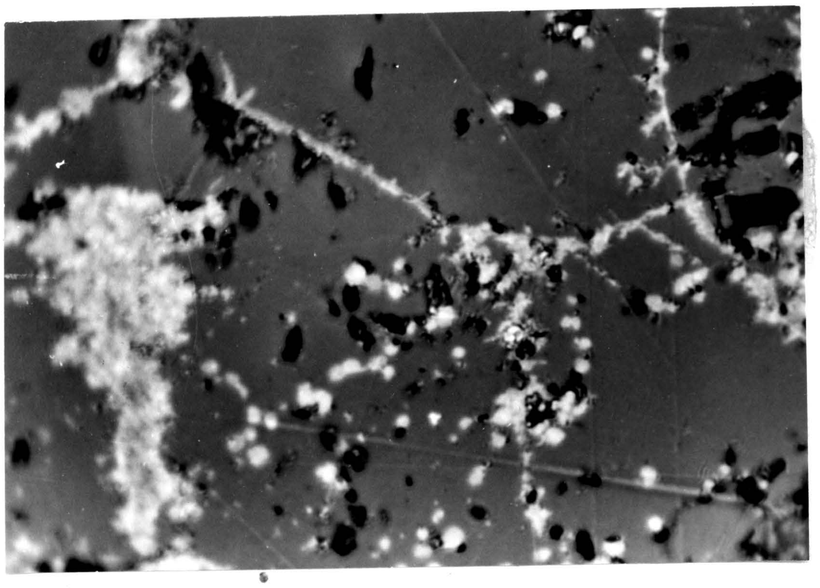


Photo 21. Cryptomelane (white) replacing braunite particularly along grain boundaries (supergene). Hotazel - H3. Refl. light, oil imm. 300 x

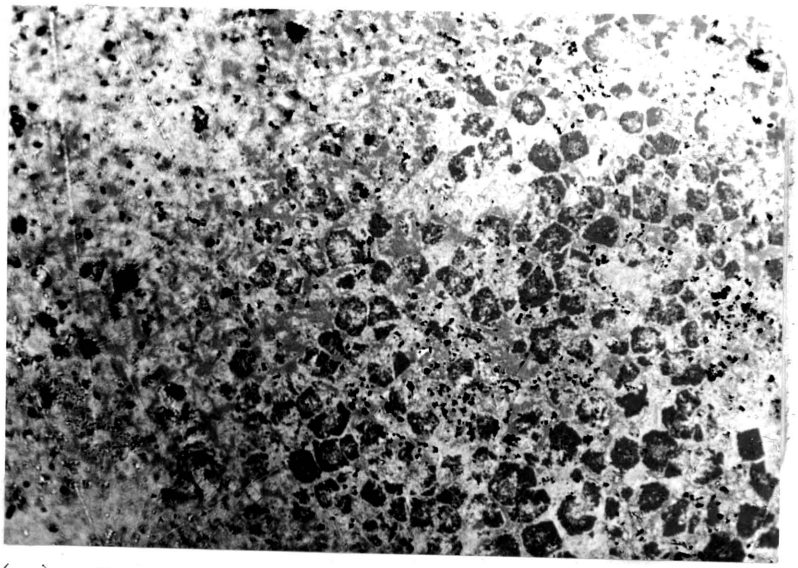


Photo 22(a). Equant grains of braunite replaced by pyrolusite (white). The gray material in the groundmass is goethite. Hotazel - H2.
Refl. light, oil imm. 300 x

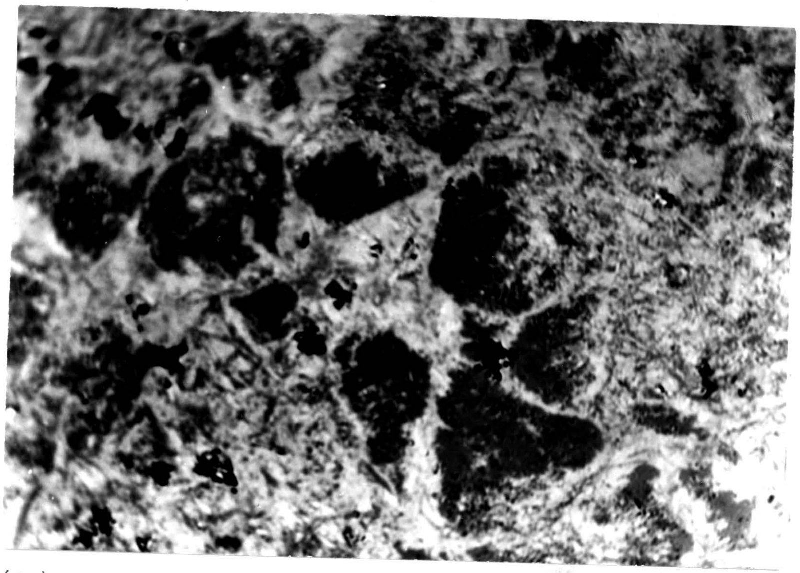


Photo 22(b). Same as photo 67 but higher magnification, showing partial replacement of braunite (gray) by pyrolusite (light-gray). Hotazel - H2.
Refl. light, oil imm. 1800 x

Photo 23. Crystals of braunite-II.
Black Rock - BB 1. 100x

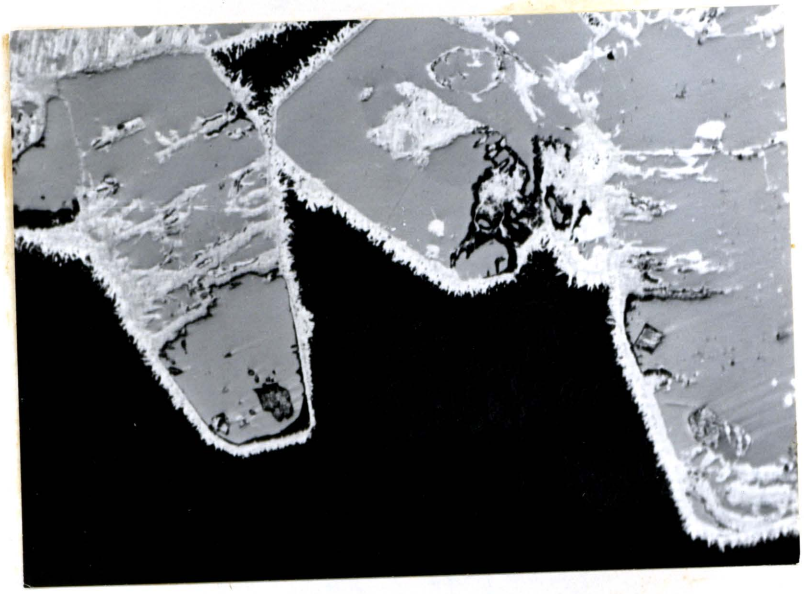


Photo 24. Interpenetrating twin of braunite-II.
Black Rock - BB 1. 100 x

Photo 25. Vug filled with crystals of braunite-II (gray) which are replaced and surrounded by a rim of cryptomelane (white). Massive black is chalcedony. Black Rock - BR 1. Refl. light, oil imm.
300 x

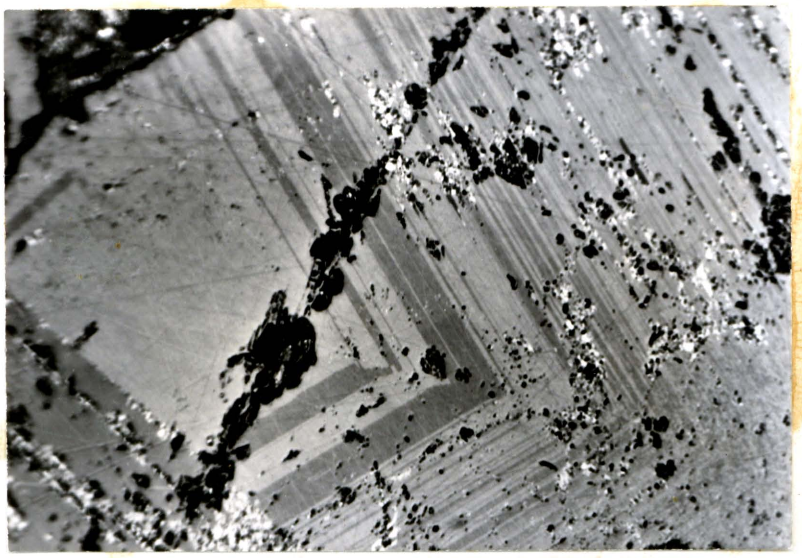


Photo 26. Bixbyite twinned. Black Rock - BR 1.
Half-crossed nicols, refl. light, oil imm. 300 x

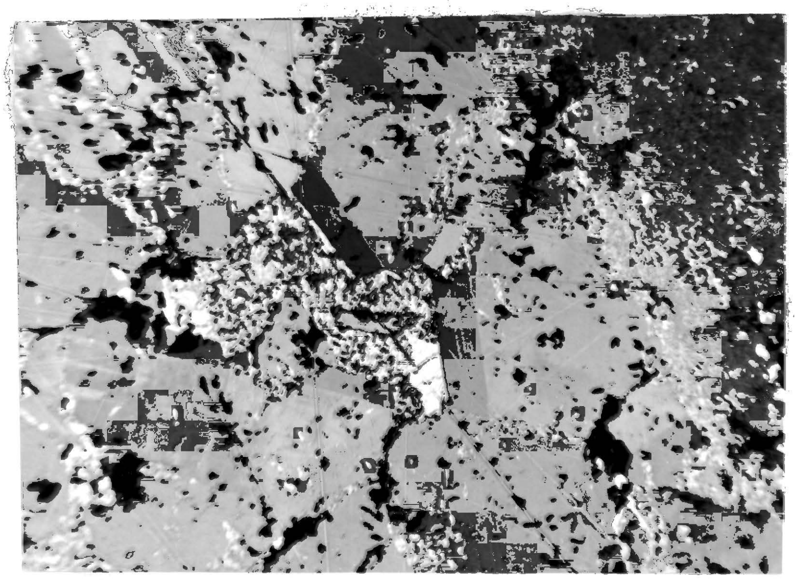


Photo 27. Bixbyite (gray) and braunite (dark-gray) having mutual boundary relationship. The white is pyrolusite and the light-gray (mottled) is cryptomelane. Black Rock - BR 1. Refl. light, oil imm. 300 x

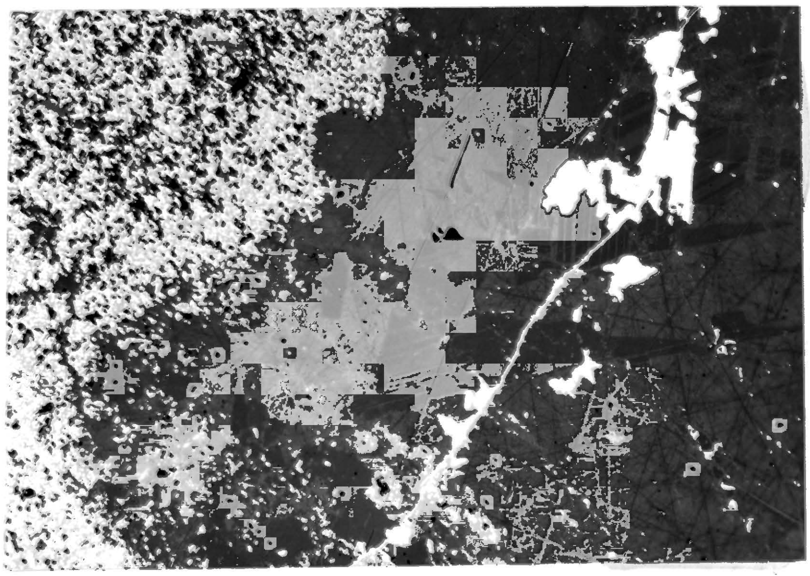


Photo 28. Hausmannite (with characteristic scratches and twinning) and jacobsite which contains hematite (white) and goethite (dark). Lower left is nsutite (white). Hotazel - H 10. Refl. light, oil imm. 300 x

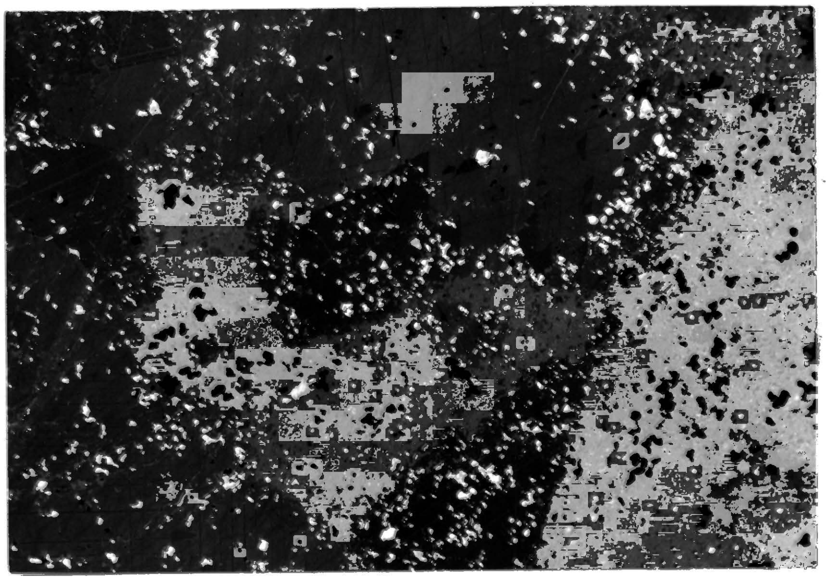


Photo 29. Coarse-grained hausmannite (dark-gray) partially surrounding jacobsite (light-gray) and fine-grained hausmannite (dark-gray specks in jacobsite). The black is goethite and the white spots are pyrolusite and hematite. Hotazel - H 10. Refl. light, oil imm. 300 x

Photo 30. Coarse-grained hausmannite (twinned) partially surrounding jacobsite (gray) which contains hematite (white). Hotazel - H 10. Refl. light, oil imm. 300 x

Photo 31. A relic of hausmannite (idioblastic) now replaced by cryptomelane in braunite ore. Adams - A4. Refl. light, oil imm. 150 x

Photo 32. A relic of hausmannite (twinned) now replaced by todorokite and cryptomelane in cryptomelane ore. Devon - D3. Refl. light, oil imm. 450 x

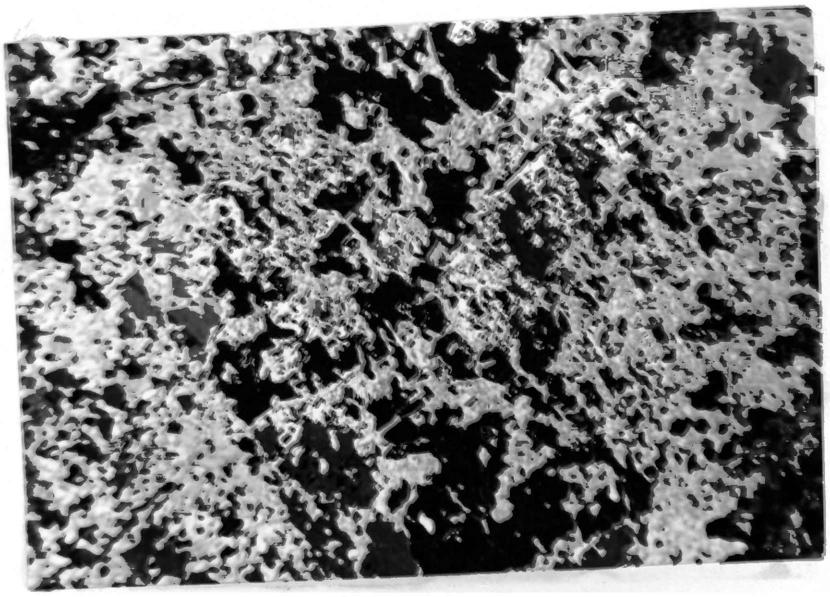


Photo 33. Relic of hausmannite (dark and gray) now replaced by cryptomelane (light-gray and white). Devon - D6. Refl. light, oil imm. 300 x

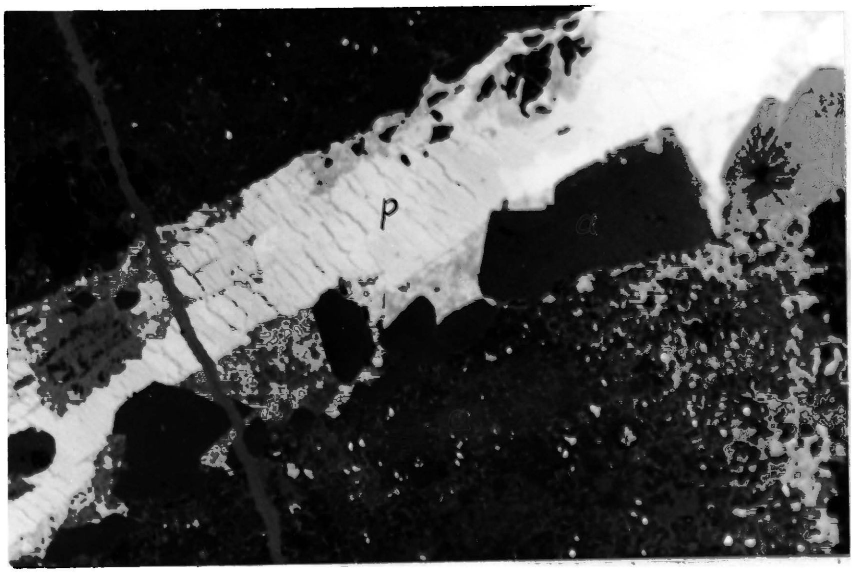


Photo 34. A vein of pyrolusite (white with shrinkage cracks) cutting a ground-mass of fine-grained hausmannite and jacobsite. The idiomorphic crystals (dark-gray) are bixbyite. Hotazel - H 10. Refl. light, oil imm. 300 x

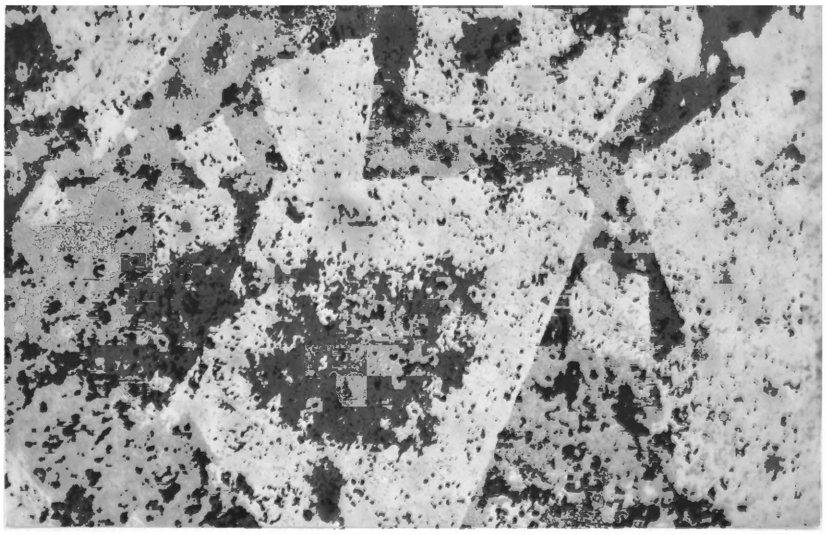


Photo 35. Jacobsite (gray) replaced by hematite (white). The white crystals are not idiomorphic single crystals but are aggregates of crystals of hematite. Eersbegint. Refl. light, oil imm. 150 x

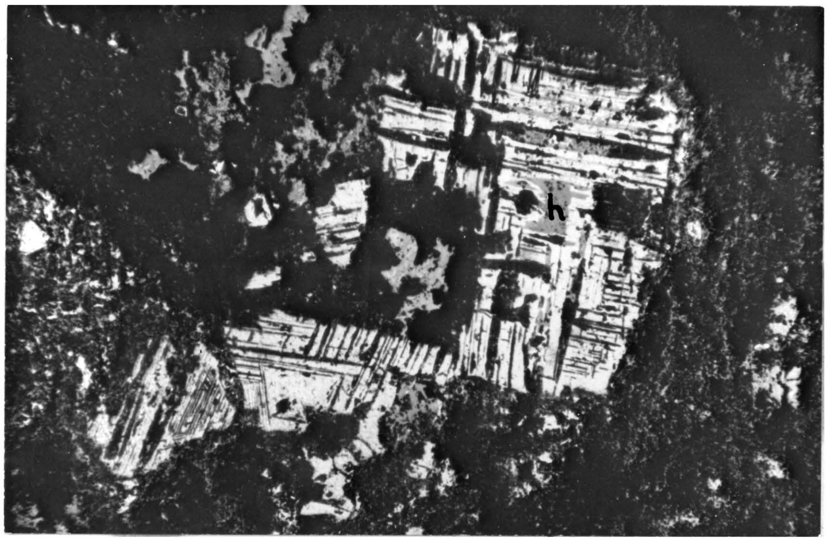


Photo 36. Vredenburgite consisting of jacobsite, hausmannite (h) and hematite (white).
Eersbegint. Refl. light, oil imm. 150 x

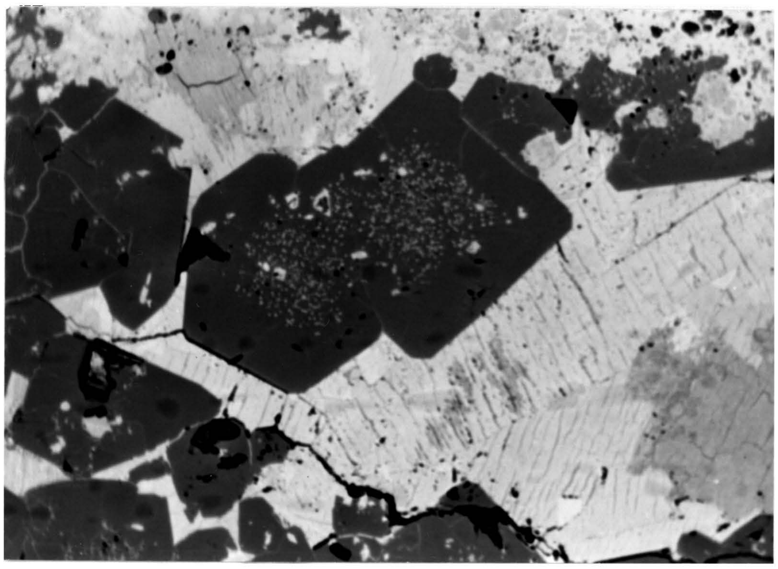


Photo 37. Idioblastic jacobsite (gray) with spots of hematite and pyrolusite (white).
Hotazel - jacobsite. Refl. light, oil imm. 150 x

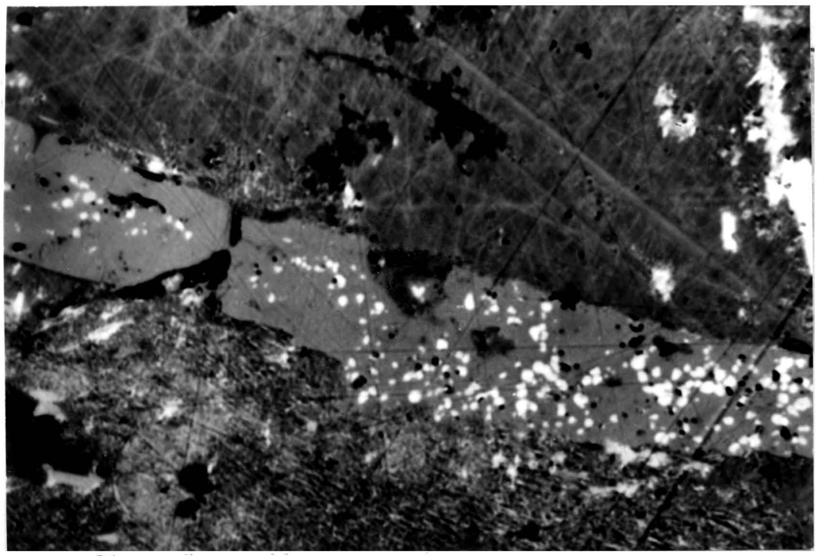


Photo 33. A vein of jacobsite (gray) with spots of hematite (white) in hausmannite (dark-gray). The white patch in the top righthand corner is pyrolusite. Hotazel - H7. Refl. light, oil imm. 300 x

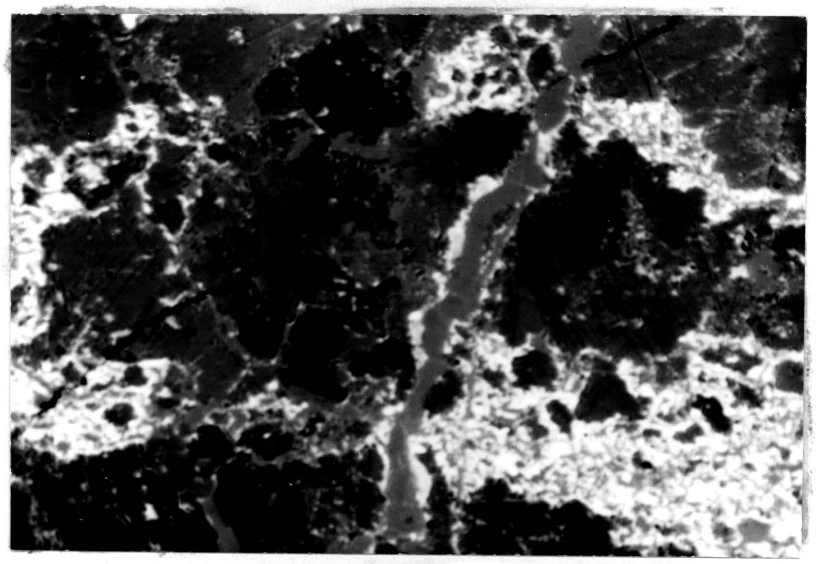


Photo 39. A vein of jacobsite (gray) cuts across hausmannite (dark and gray) which in turn is replaced by nsutite (white). The dark and gray of the hausmannite is due to its bireflectance. In the hausmannite is the odd grain of jacobsite. Hotazel - H 10. Refl. light, oil imm. 1800 x

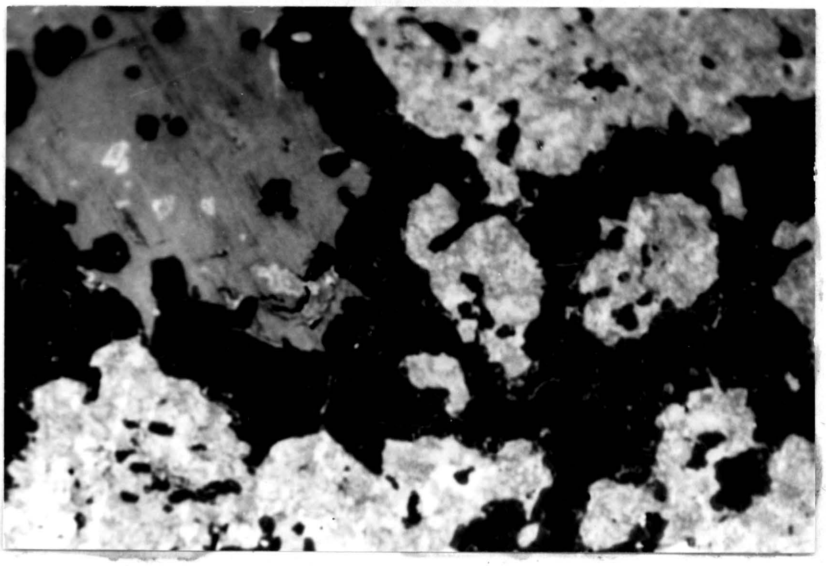


Photo 40. Magnetite (dark) cracked, replaced by possibly nsutite (white) and cryptomelane (gray). Hotazel - H9. Refl. light, oil imm. 1800 x

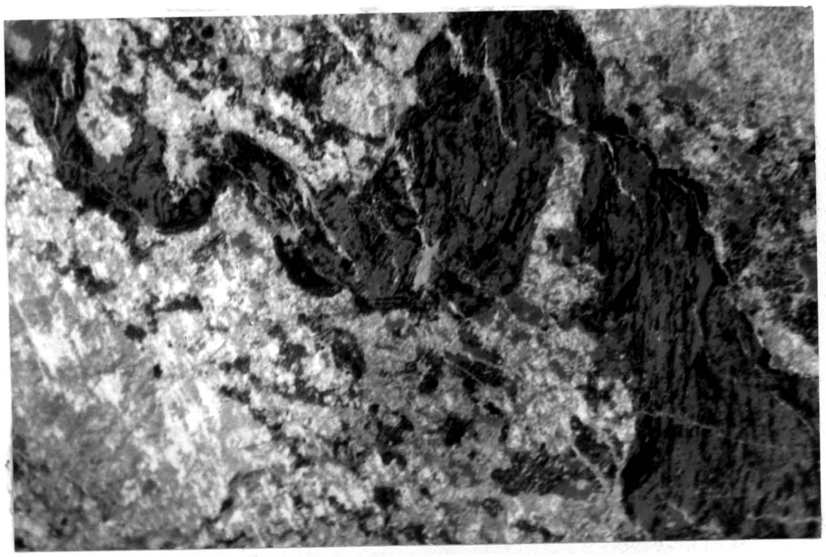


Photo 41. Magnetite (dark-gray) in cryptomelane (light-gray). The wavy texture is considered to be due to slumping. Hotazel - H9. Refl. light, oil imm. 1800 x

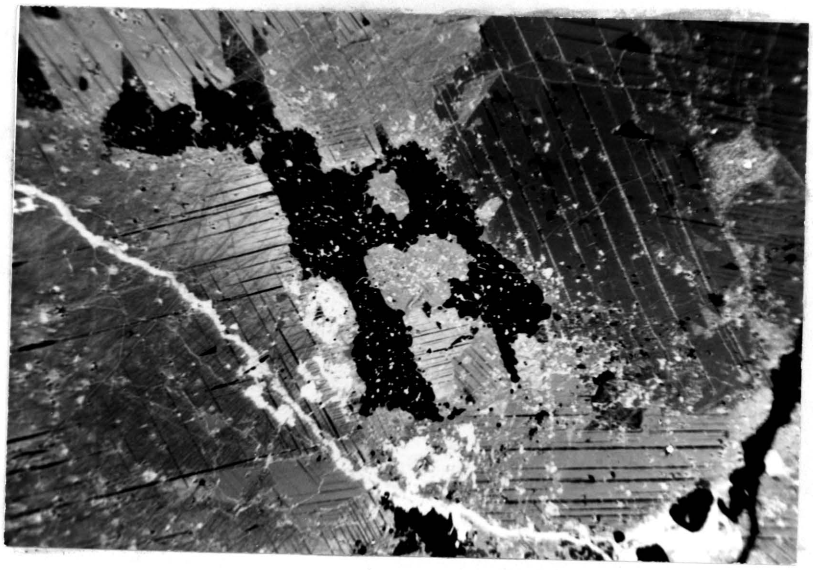


Photo 42. Hausmannite (twinned) and goethite (dark). The white spots are hematite and the vein is nsutite (white). Hotazel - H 10. Refl. light, oil imm. 300 x

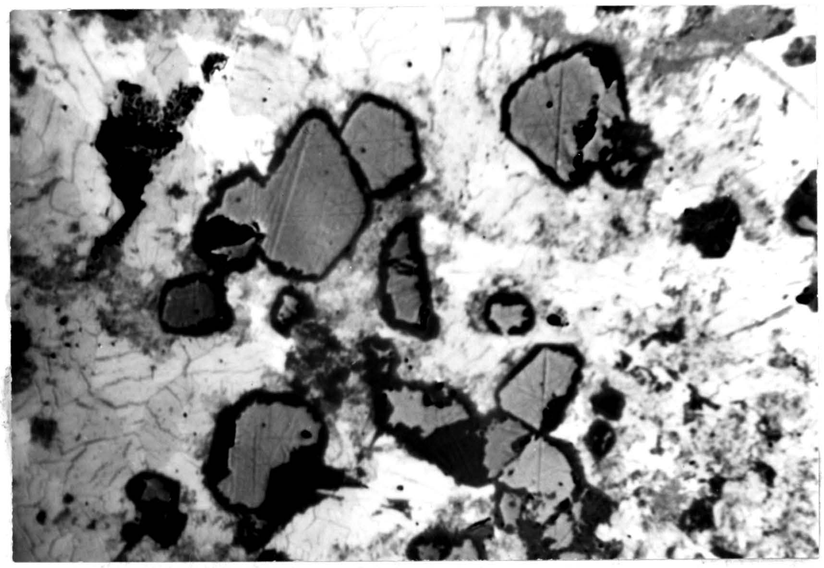


Photo 43. Pyrolusite (white) with shrinkage cracks filled out with cryptomelane. Also idioblasts of hematite (gray) with rims of 'jacobsite' (dark). Hotazel - H5. Refl.light, oil imm. 1300 x

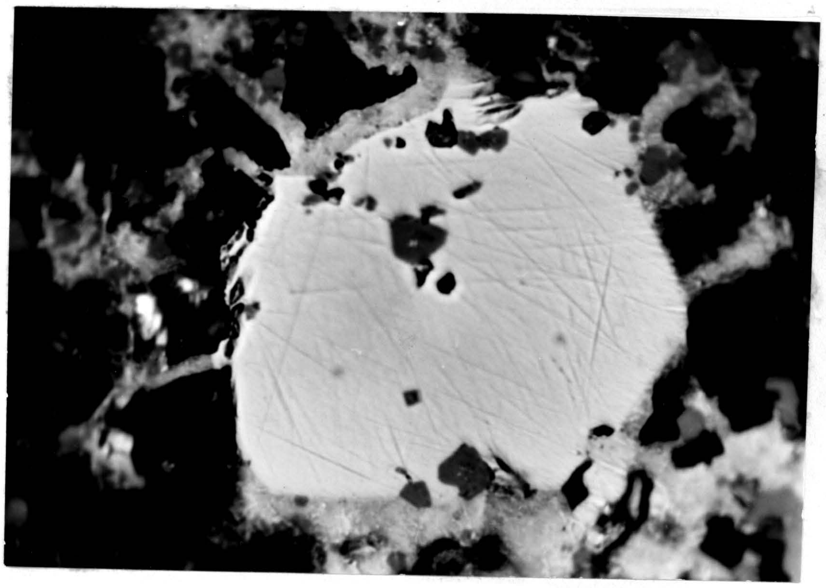


Photo 44. Grain of hematite (white) containing idiomorphic crystals of either bixbyite or jacobsite. Devon - D2. Refl. light, oil imm. 1300 x

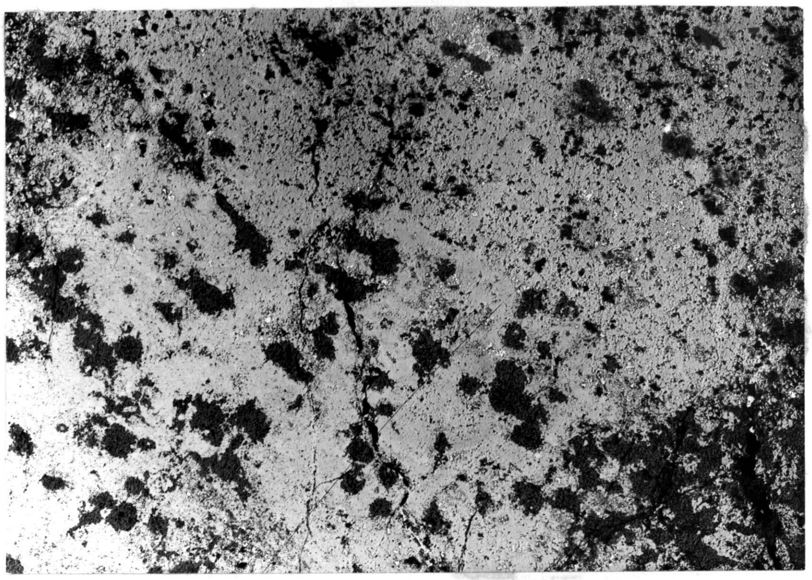


Photo 45. Braunite (gray) and andradite (dark).
Black Rock - BR 3E. Refl. light. 8 x

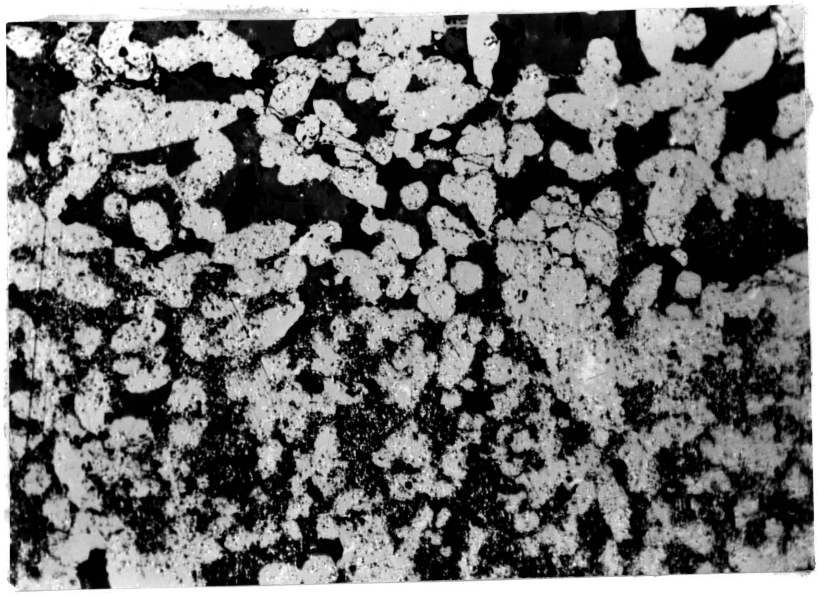


Photo 46. Same as photo 45 but higher magnification showing braunite (gray-white) and andradite (dark-gray). The hematite is white.
Black Rock - BR 3E. Refl. light, oil imm. 150 x

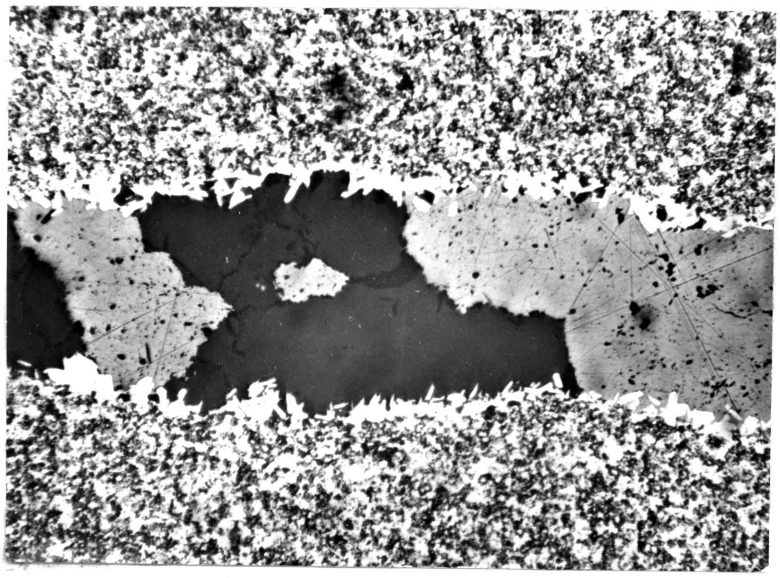


Photo 47. Andradite (dark) and jacobsite (even gray) veining hematite. The idiomorphic crystals along the edge of the vein are hematite. The hematite obviously formed after the garnet. Hotazel. Refl. light.
150 x

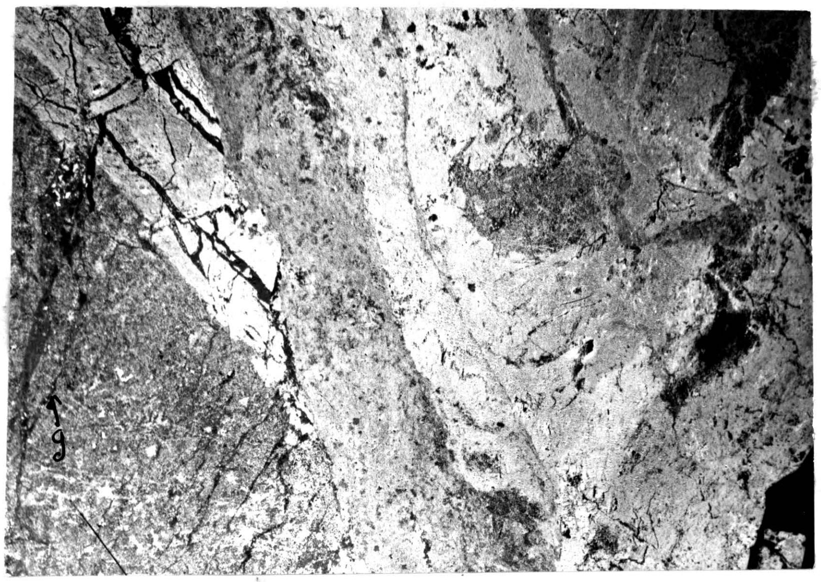


Photo 48. Brecciated braunite. Also andradite (dark, along cracks on left), and some cryptomelane (disseminated) and goethite (G). Sample (c), folded area. Black Rock. Refl. light. 8 x

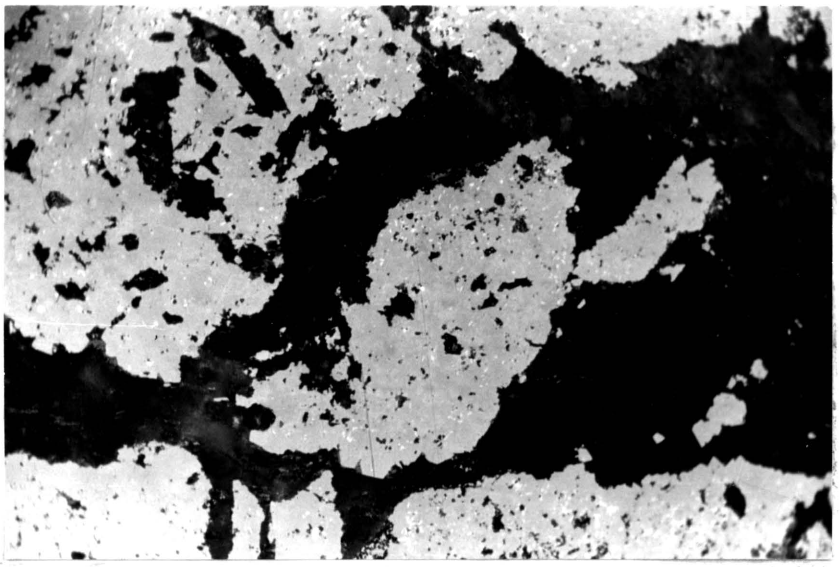


Photo 49. Cracks shown on photo 48 enlarged. Andradite (dark) and braunite (gray). Black Rock. Refl. light, oil imm. 300 x

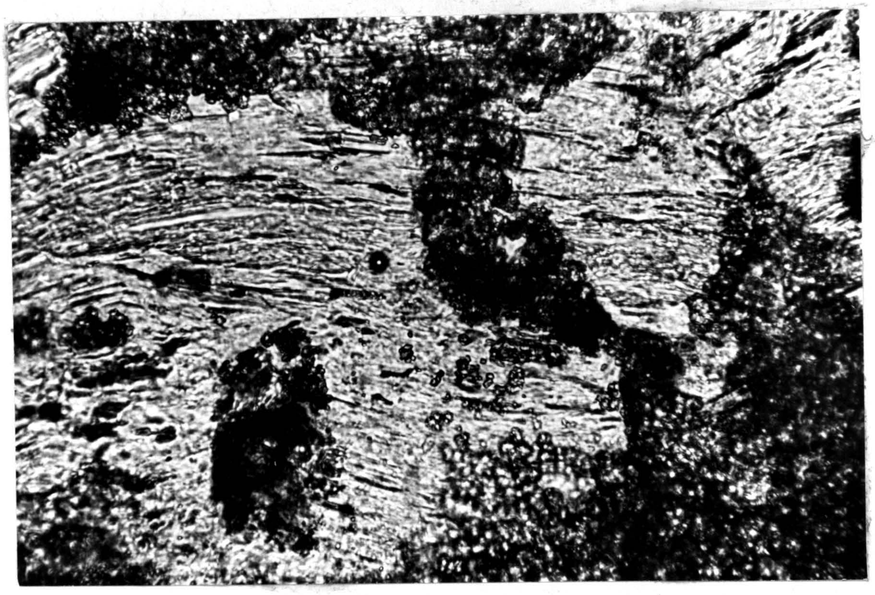


Photo 50. Inclusion in ore-body consisting of garnet (finely granular) replacing muscovite (light-gray striped).
Black Rock - BRIB.s 1 (thin sec.). Trans light.
150 x

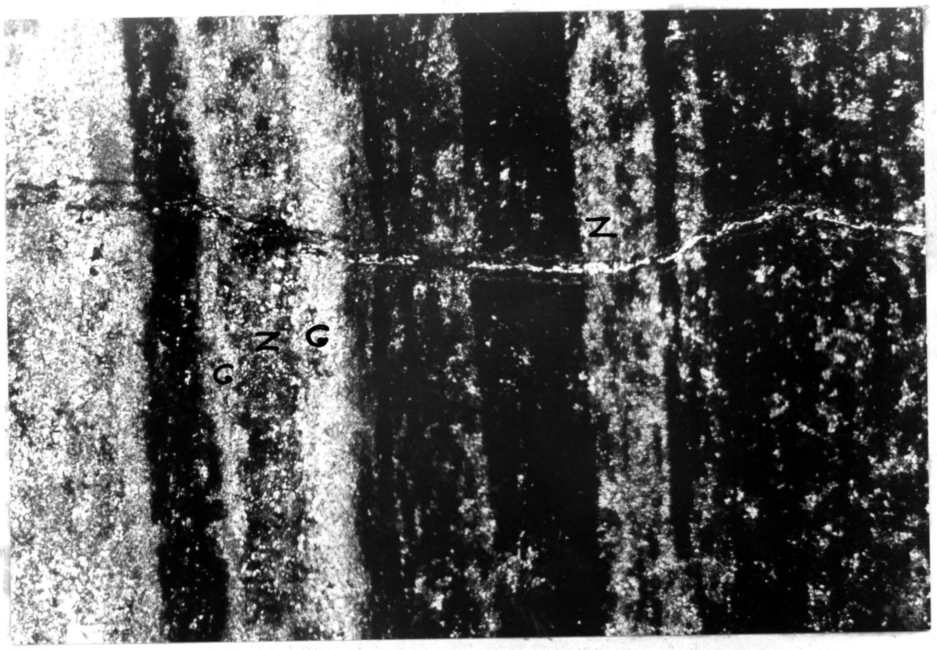


Photo 51. Andradite (g) and acmite (z) formed along the siliceous portion of the banded ironstone. Hematite (dark). Black Rock - TB2 (thin sec.). Trans light.
20 x

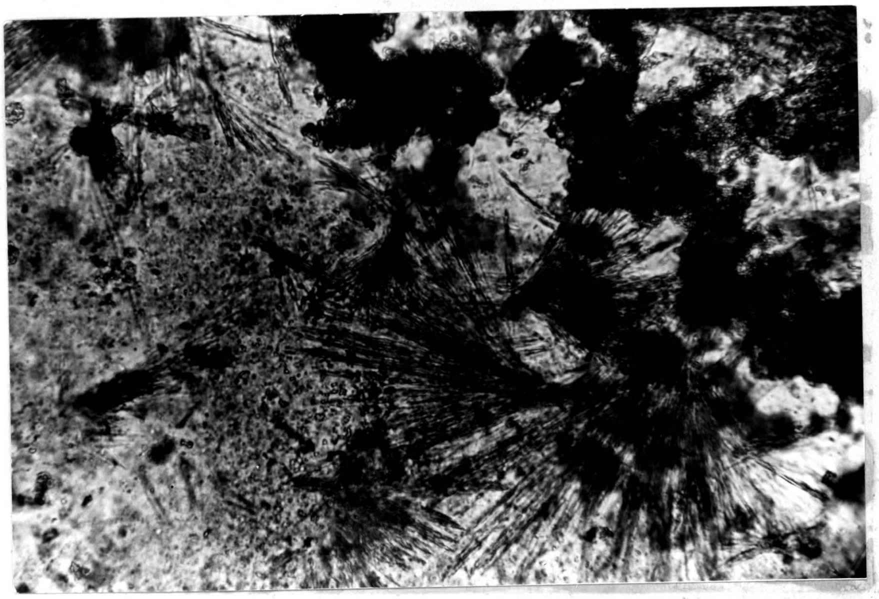


Photo 52. Needles of tremolite, and garnet (dark)
in altered 'carbonate-rock'.
Hotazel - TH 2 (thin sec.). Trans light. 150 x

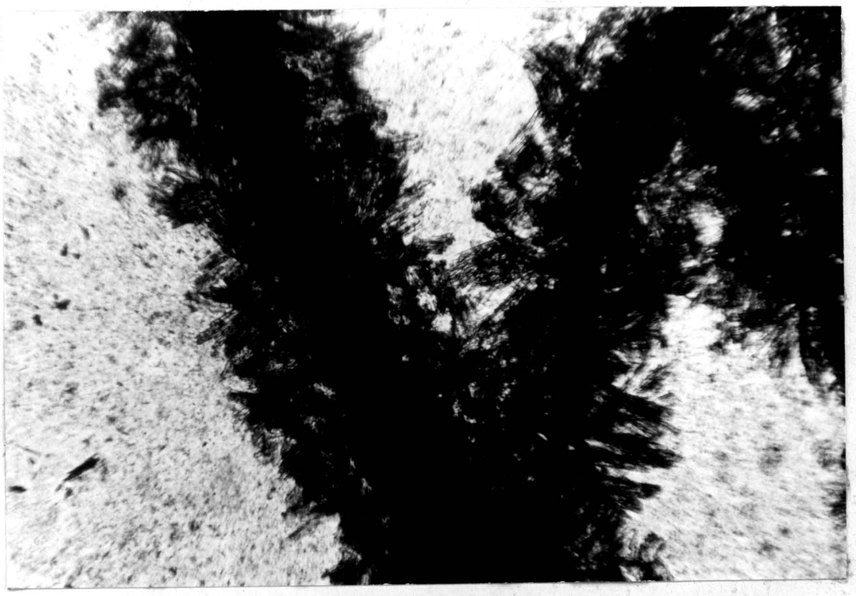


Photo 53. Needles of tremolite along cracks in
altered 'carbonate-rock'. Hotazel - TH 2.
Trans. light. 150 x

Photo 54. Carbonate (light-gray stippled) surrounded
by reaction rim of talc (white) all in mass of minnesotaite (dark). Mamatwan - TM 16 (thin sec.).
Crossed nicols, trans. light. 50 x

Photo 55. Fibrous cryptomelane part of the colloform banding of photo 85. Hotazel - H4.
Crossed nicols, refl. light, oil imm. 1800 x

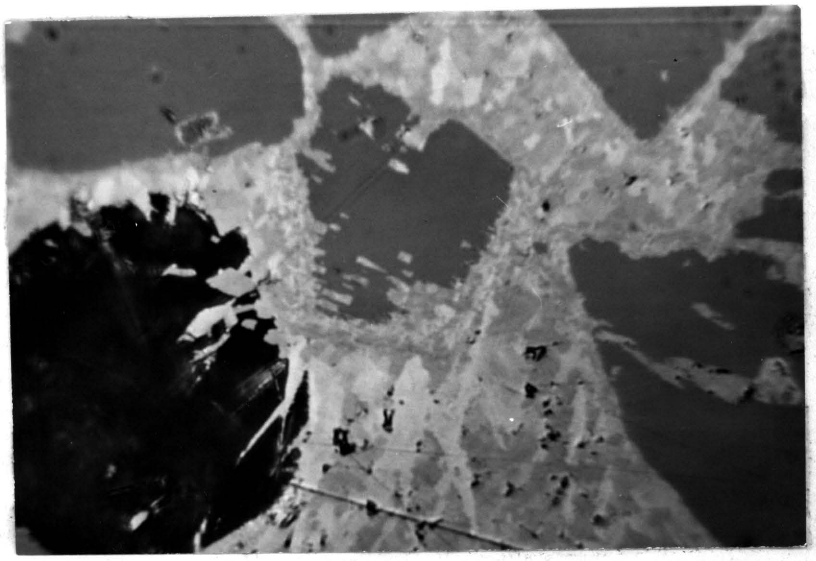


Photo 56. Cryptomelane (white) replacing braunite (dark-gray). The black is goethite.
Black Rock - BR 1D. Refl. light, oil imm. 300 x

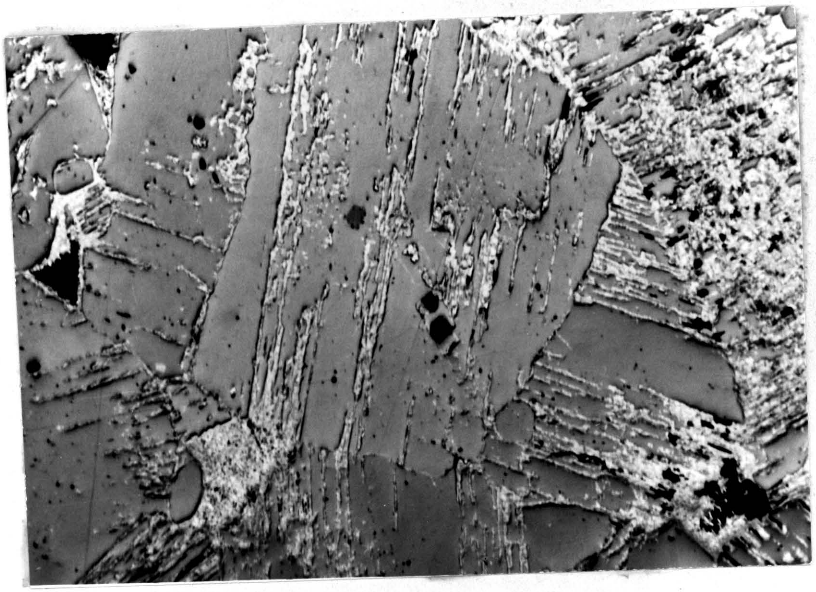


Photo 57. Cryptomelane (white) replacing braunite-II (gray). Black Rock - BR 1E. Refl. light, oil imm.
1800 x

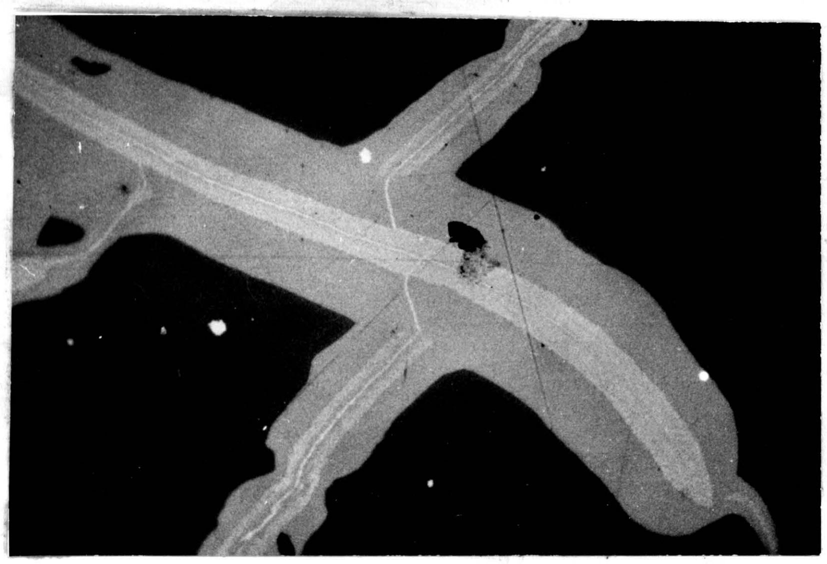


Photo 58. Braunite (dark) replaced by cryptomelane (gray) which in turn contains secondary pyrolusite (light-gray). Black Rock - BR V1.
Refl. light, oil imm. 300 x

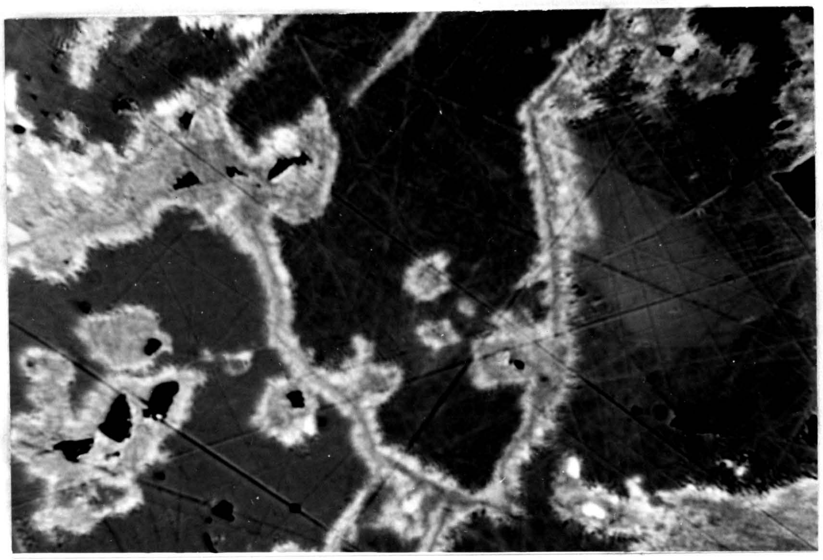


Photo 59. Cryptomelane (light-gray) and pyrolusite (white) replacing braunite.
Devon - D6. Refl. light, oil imm. 300 x

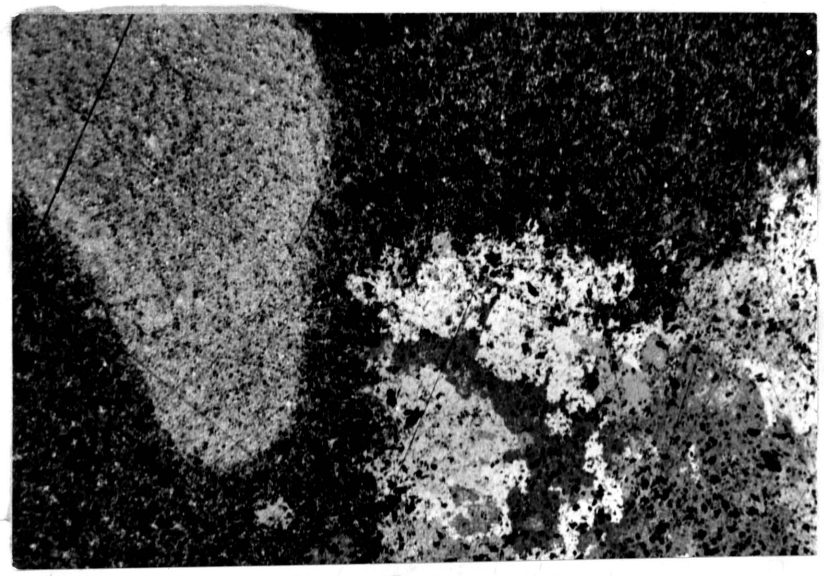


Photo 60. Nodule of fine-grained cryptomelane (gray) and 'mottled cryptomelane' (light-gray) in fine-grained ground-mass of braunite-rich ore. The 'mottled cryptomelane' represents an aggragate of replaced hausmannite. Adams - A4.
Refl. light, oil imm. 140 x

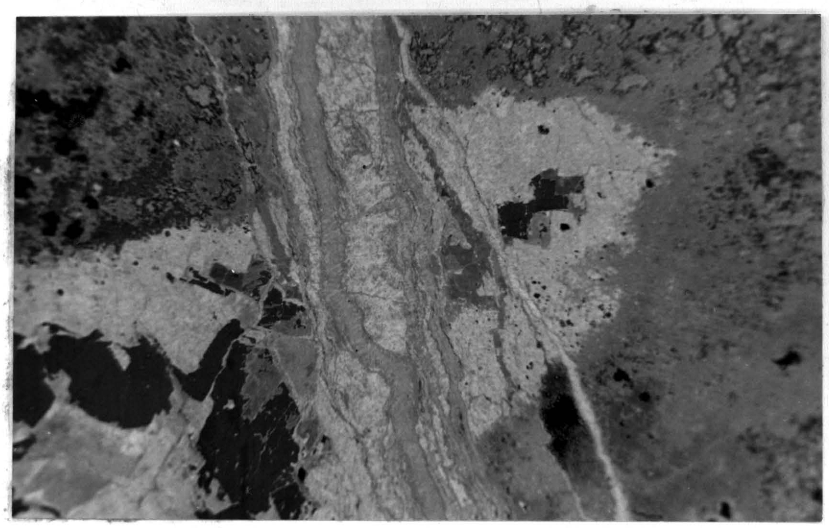


Photo 61. Cryptomelane (gray) and pyrolusite (white) veining a large mass of nsutite (white) which again replaces hausmannite (dark). The surrounding mass is jacobsite, hausmannite and cryptomelane.
Hotazel - H 10. Refl. light, oil imm.   300 x

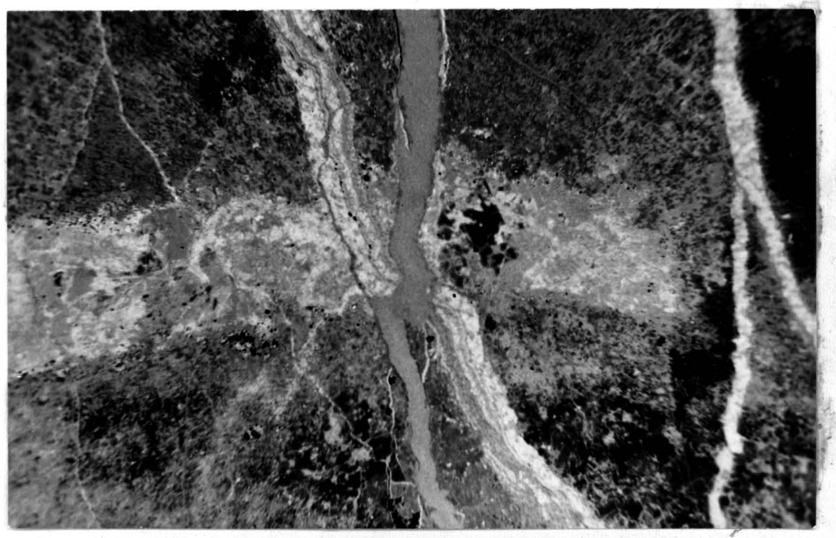


Photo 62. Vein of cryptomelane (gray) intersecting vein of pyrolusite (white), both veining nsutite (light-gray). All in jacobsite and hausmannite.
Hotazel - H 10. Refl. light, oil imm.   300 x

Photo 63. Todorokite-like mineral (white), also braunite and veins of braunite and cryptomelane.
Hotazel - vuggy ore. Refl. light, oil imm.   300 x

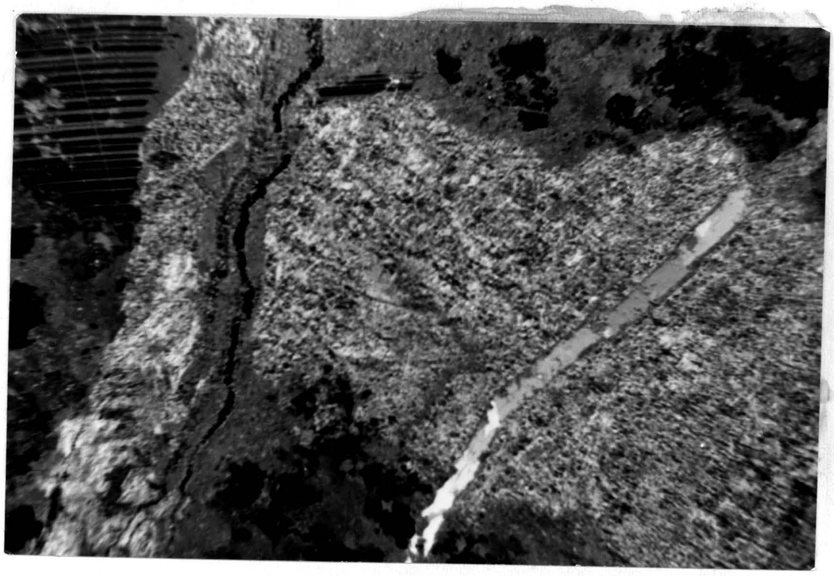


Photo 64. Pyrolusite (white) veins nsutite (mottled light-gray), bixbyite (gray) and goethite (black). The gray spots in the vein are crystals of bixbyite or jacobsite. The twinned mineral is hausmannite. Hotazel - H 10. Refl. light, oil imm. 300 x

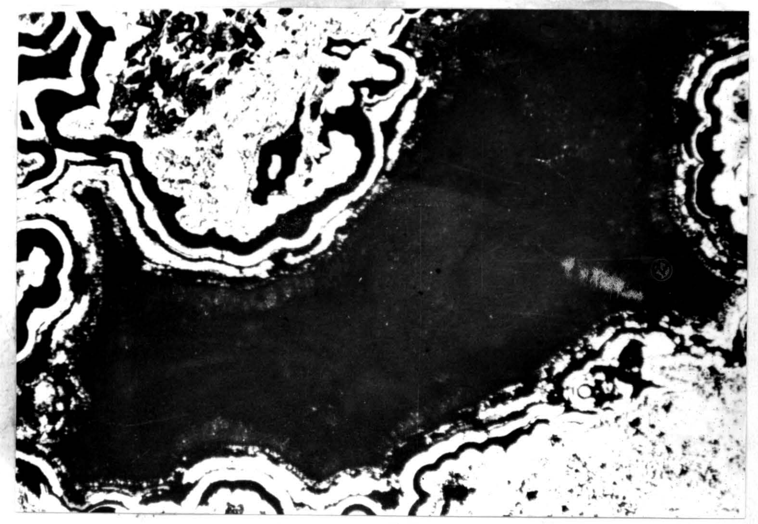


Photo 65. Vug filled with chalcedony (dark) and cryptomelane (white). Black Rock - BR 1. Refl. light. 300 x

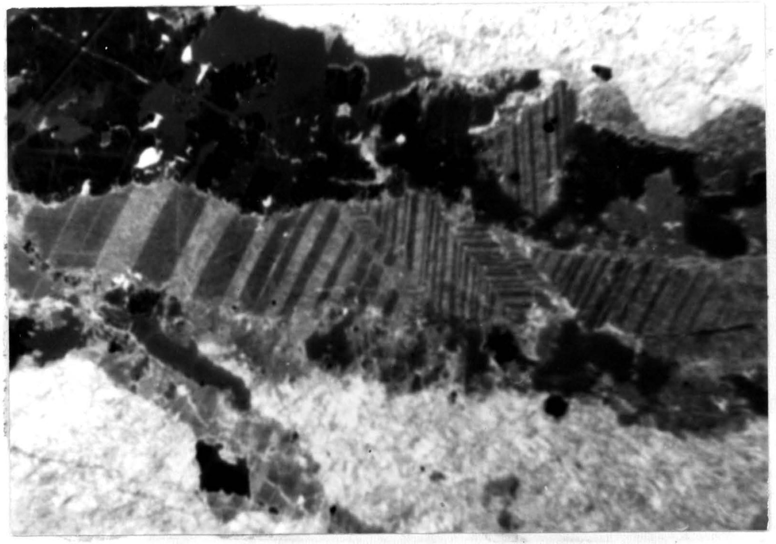


Photo 66. Hollandite polysynthetically twinned (herringbone), in hausmannite (dark). The minerals alongside are bixbyite (dark-gray) and nsutite (white). Hotazel - H 10. Half crossed nicols, refl. light, oil imm. 1300 x

Photo 67. Manganite veining hausmannite (dark-gray) and bixbyite (gray). The manganite is replaced by pyrolusite (white). Hotazel - H7.
Half crossed nicols, refl. light, oil imm. 300 x

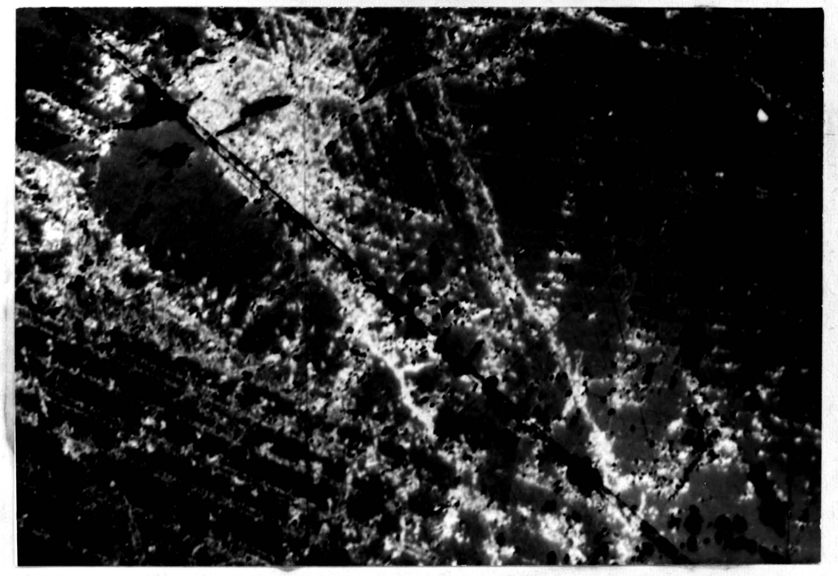


Photo 68. Hausmannite replaced by pyrolusite (white). Hotazel - H7. Refl. light, oil imm. 300 x

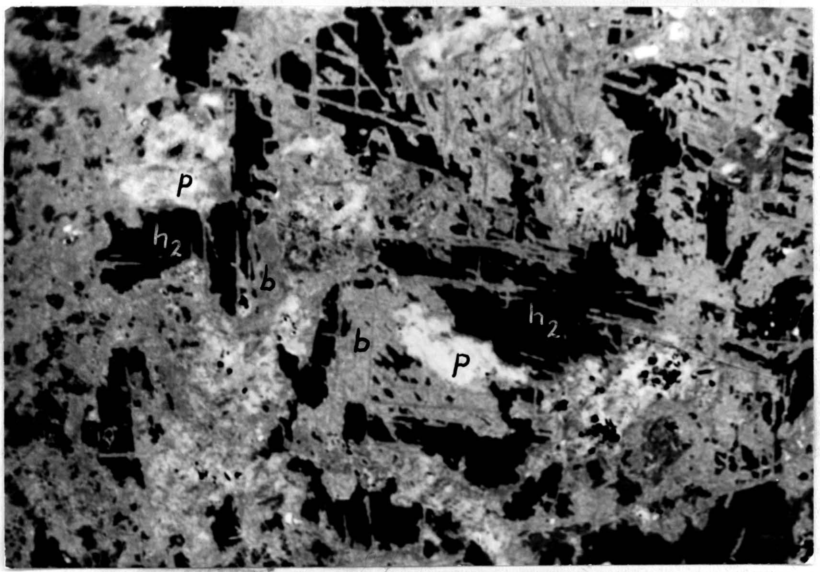


Photo 69. Hausmannite (dark-gray) replaced by braunite (b) which is in turn replaced by pyrolusite (p). Hotazel - H2.
Refl. light, oil imm. 500 x

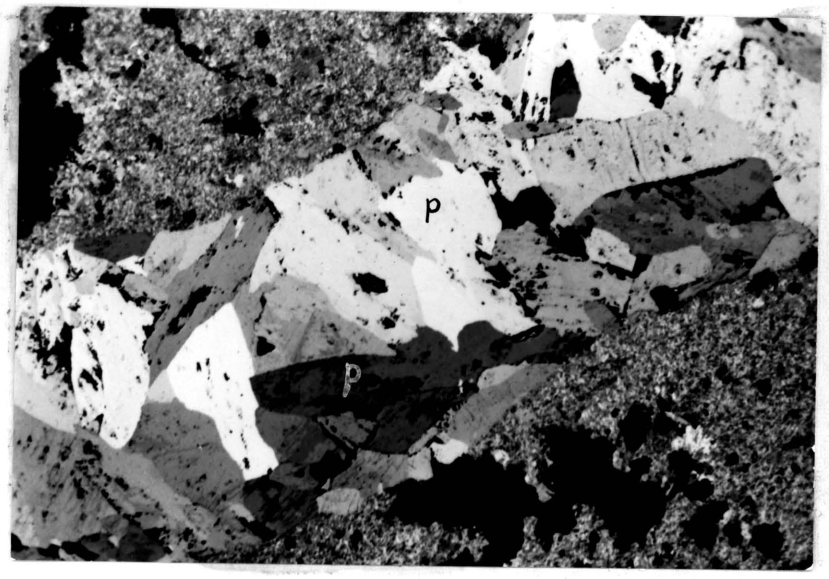


Photo 70. Vein of coarse-grained polianite (p) in braunite and nsutite. The black represents pits. Hotazel - H5. Crossed nicols, refl. light, oil imm. 300 x

Photo 71. Idioblastic bixbyite surrounded by pyrolusite (white) and cryptomelane in the shrinkage cracks. Black Rock - BR 1D. Refl. light, oil imm. 300 x

Photo 72. 'Asbestiform' todorokite. Hotazel - HT 1. 2/3 x

Photo 73. Dog-tooth spar todorokite.
Hotazel - HT 2. 2/3 x

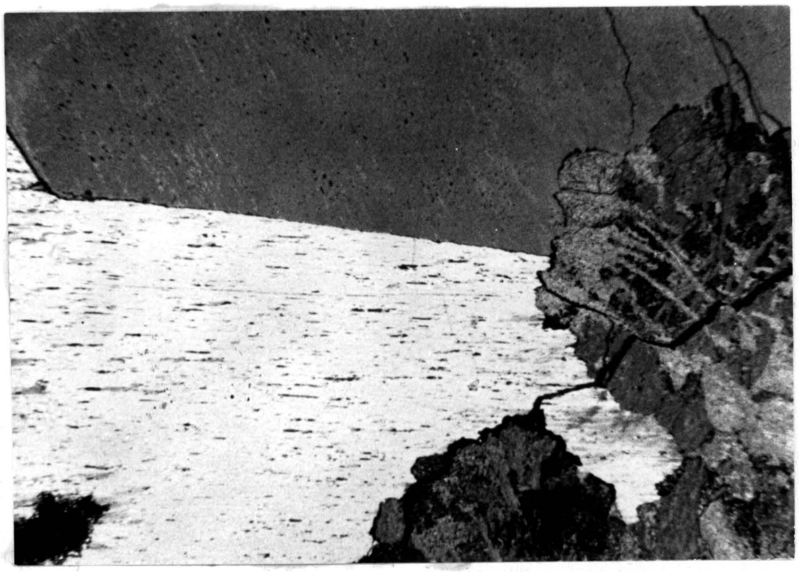


Photo 74. Polished surface of dog-tooth spar todorokite showing fine- (left) and coarse-grained crystals (right). Pits - black. Hotazel - Pol. sec. Todo. Half crossed nicols, refl. light, oil imm. 150 x

Photo 75. Polished surface of dog-tooth spar todorokite - fine-grained. Hotazel - pol sec. Todo. Half crossed nicols, refl. light, oil imm. 300 x

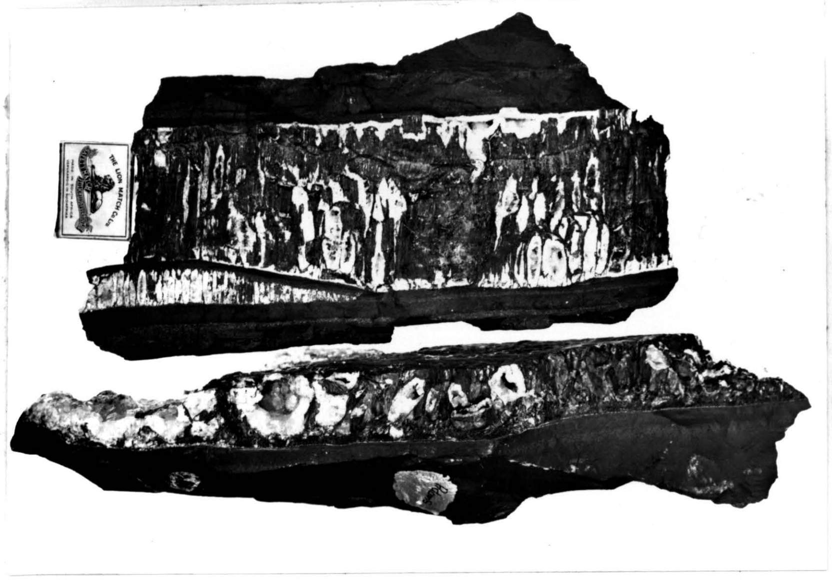


Photo 76. 'Asbestiform' (alongside matchbox) and 'flaky' todorokite (L) from the same vein. The todorokite is replaced by calcite (white). Adams - AT 1 and 2.

Photo 77. Fibrous 'asbestiform' todorokite shown in photo 76, enlarged. Adams - AT 1. 8 x

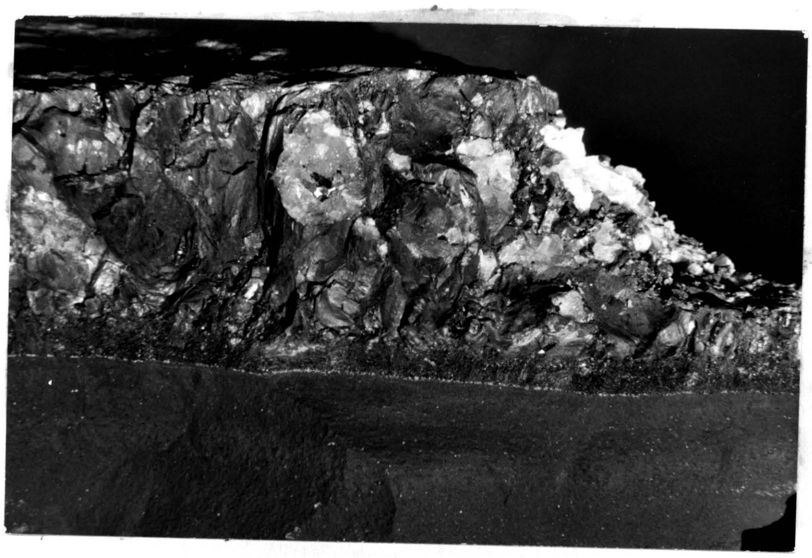


Photo 78. 'Flaky' todorokite shown in photo 76, enlarged. Adams - AT 2. 4 x

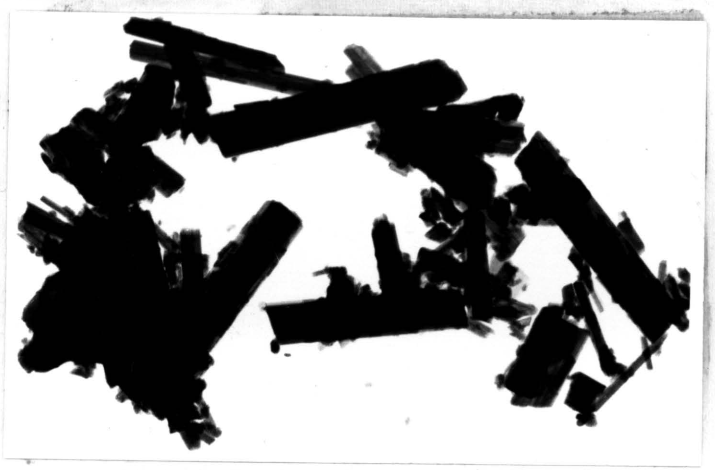


Photo 79. Electron micrograph of todorokite. ~~Examination of~~ The structure indicates that there are bundles of fibres rather than single crystals. Hotazel.

Photo 80. Electron diffraction pattern of an orientated 'single crystal' of todorokite which consists of a bundle of fibres. The incident electron beam is perpendicular to the (001) plane and the array of spots indicate stacking faults in the bundle.

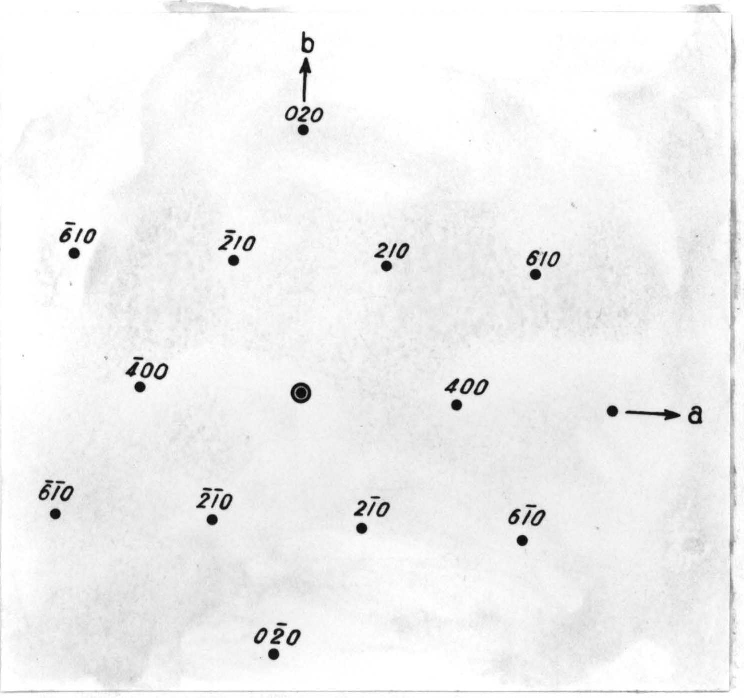


Photo 81. Indices of the electron spot pattern shown in photo 80.

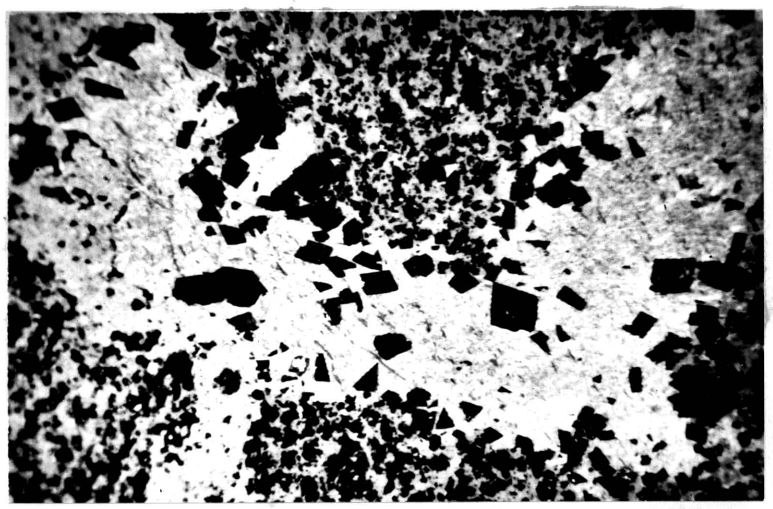


Photo 82. Crystals of goethite possibly pseudomorphous after bixbyite, in vein of todorokite in braunite ore.
Smartt - S5. Refl. light, oil imm. 300 x

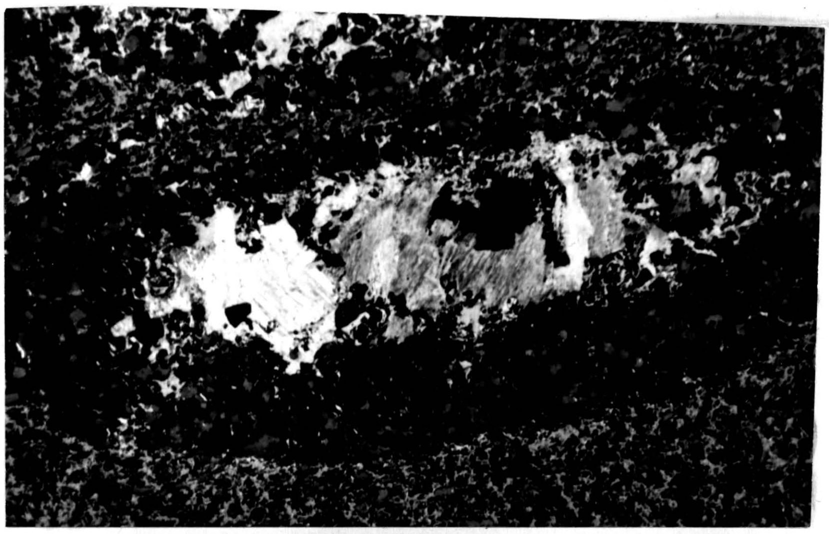


Photo 83. Nodule in braunite ore, now filled with todorokite. Devon - D1. Refl. light, oil imm. 150 x

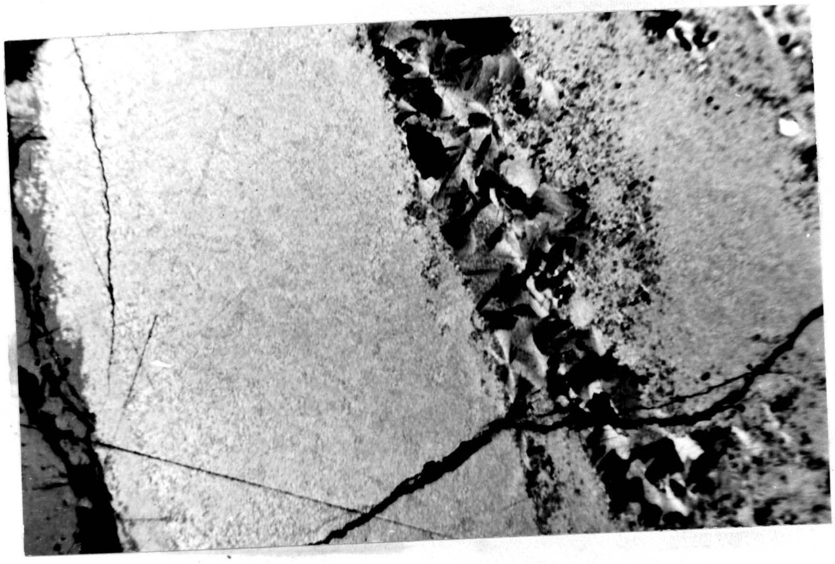


Photo 84. Fine-grained pyrolusite (light-gray) and lithiophorite (wavy).
Black Rock - BR V1. Refl. light, oil imm. 300 x

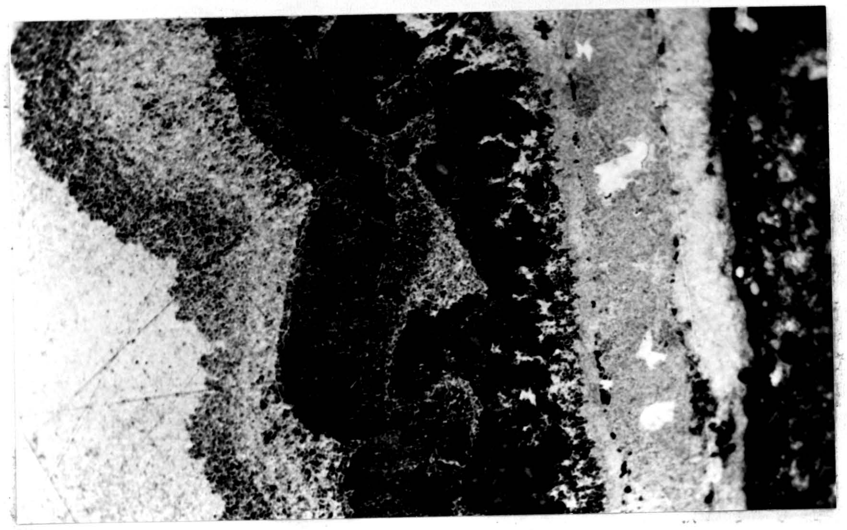


Photo 85. Colloform banding. The Black is mainly goethite, the gray-white is cryptomelane, the white is pyrolusite and the gray is 'chalcophanite' (C). Hotazel - H4. Refl. light, oil imm. 150 x

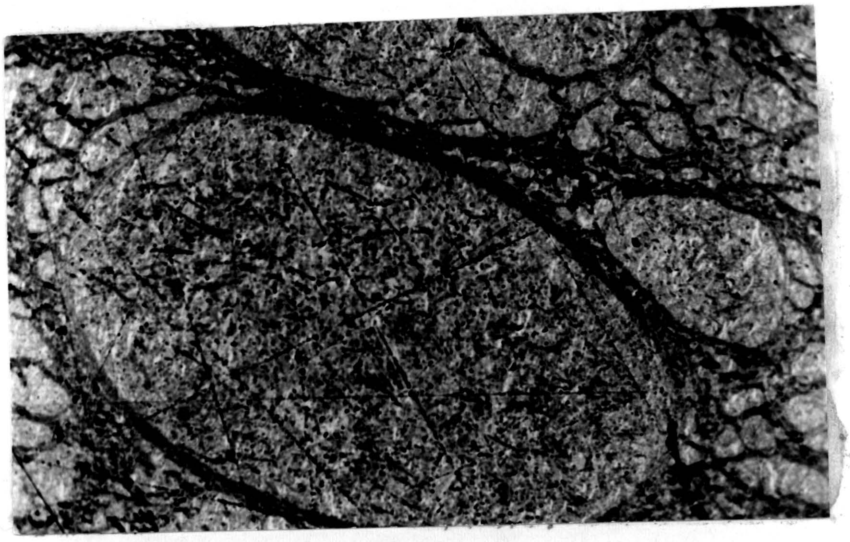


Photo 86. Spherial units consisting of 'chalcophanite' (oval, dark strip), needles of pyrolusite and cryptomelane as well as goethite.
Hotazel - H4. Refl. light, oil imm. 300 x

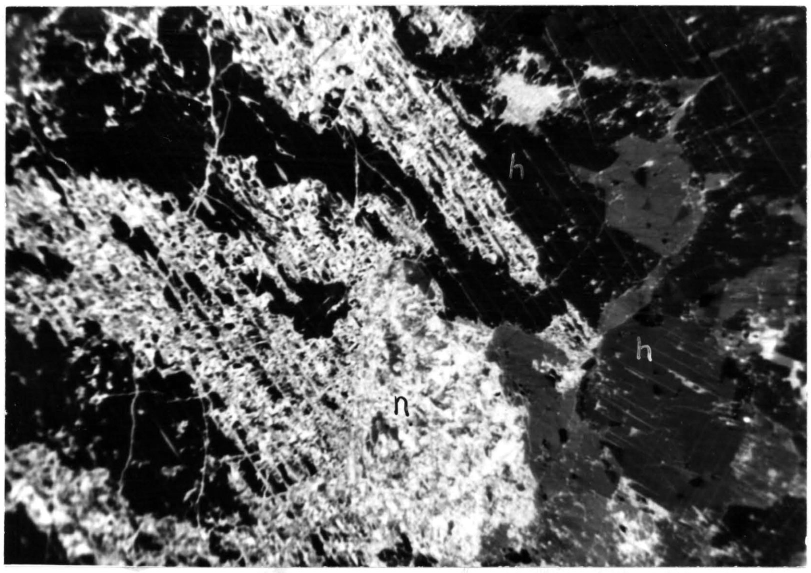


Photo 37. Coarse-grained hausmannite (h) replaced by nsutite (n). The light-gray is jacobsite.
Hotazel - H 10. Crossed nicols, refl. light, oil imm.
300 x

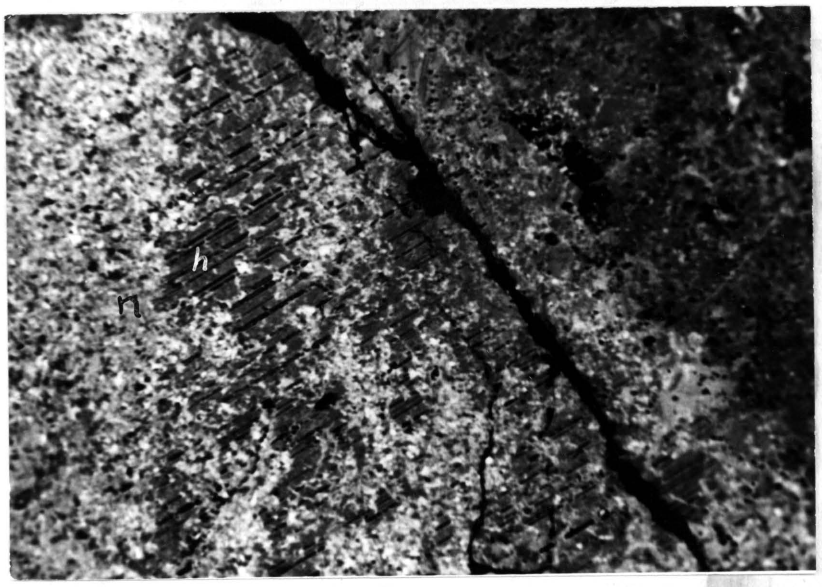


Photo 38. Nsutite (n) replacing hausmannite (h).
Hotazel - H 10. Refl. light, oil imm. 300 x

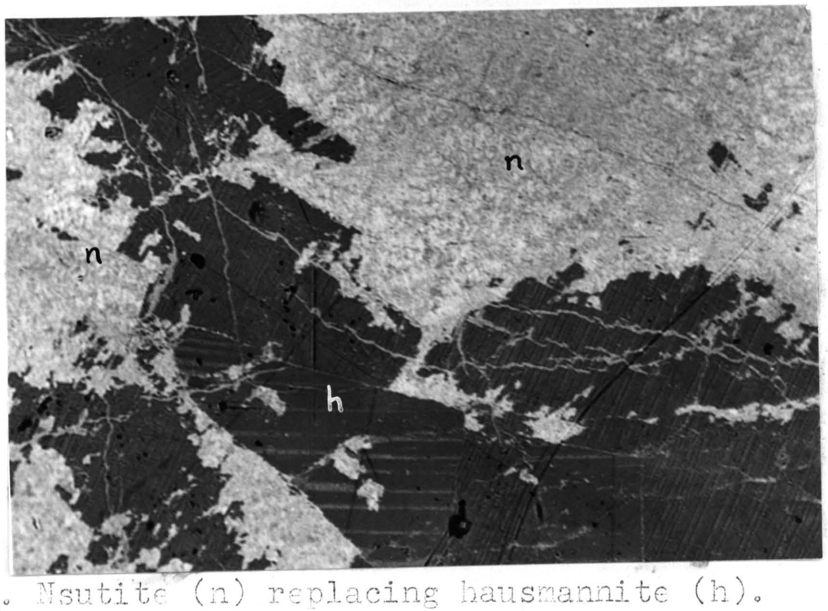


Photo 39. Nsutite (n) replacing hausmannite (h).
Hotazel - H 10. Refl. light, oil imm. 300 x

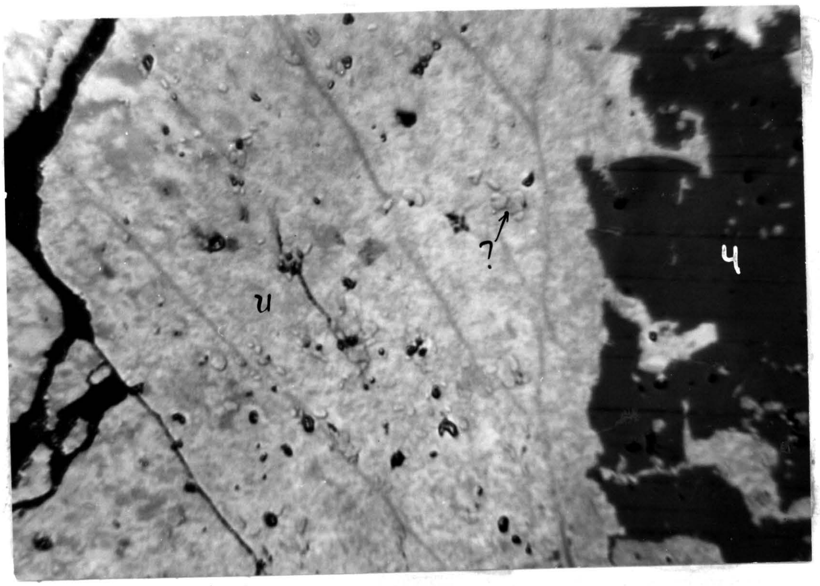


Photo 90. Nsutite (n) replacing hausmannite (h). The small inclusions (i) in the nsutite are probably relics of hematite.
Hotazel - H 10. Refl. light, oil imm. 1800 x

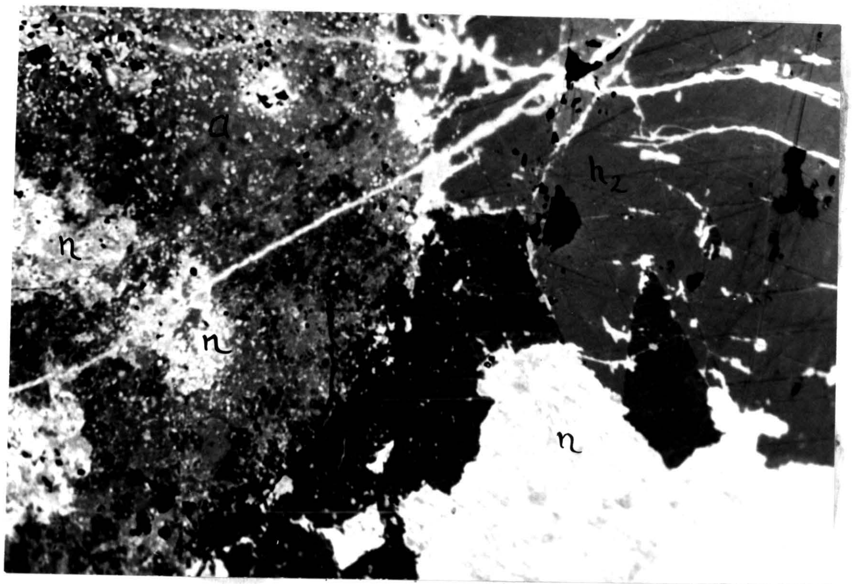


Photo 91. Coarse-grained hausmannite-h_2(dark-gray) and jacobsite (gray with spots of hematite), all partially replaced by nsutite-n(white).
Hotazel - H 10. Refl. light, oil imm. 300 x

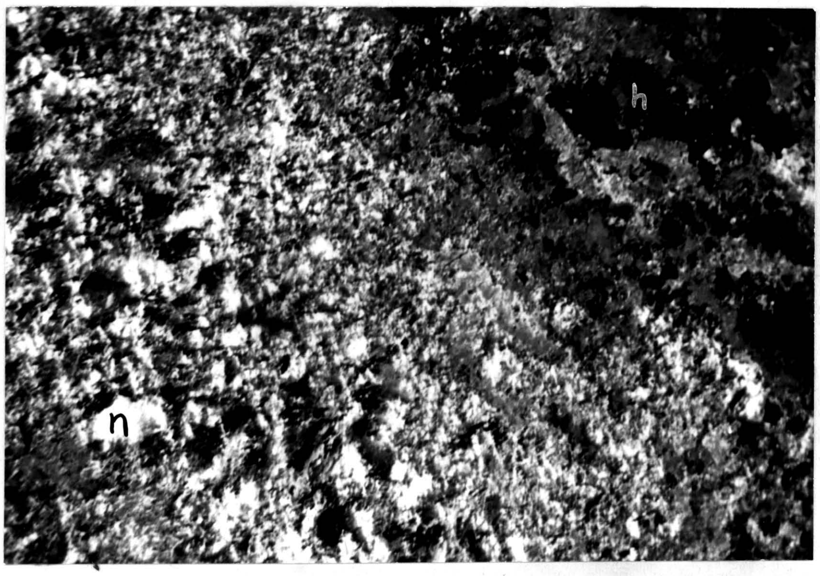


Photo 92. 'Velvety' nsutite (n) in contact with hausmannite (h). Hotazel - H9.
Crossed nicols, refl. light, oil imm. 300 x

Photo 93. Fine-grained nsutite (n1) in contact with coarse-grained nsutite (n2). Hotazel - H9.
Crossed nicols, refl. light, oil imm. 300 x

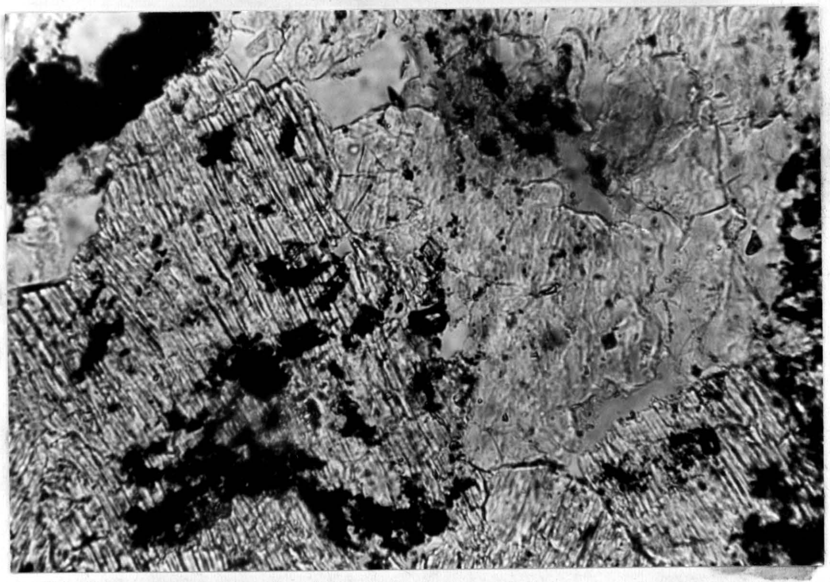


Photo 94. Different habits of cymrite - closely spaced prismatic cleavage in foreground and in upper half, on approximately basal section. ~~The black~~ ~~is~~ Iron oxide (black). Hotazel - TH 3 (thin sec.).
Trans. light. 150 x

Photo 95. Ore situated near the underlying banded ironstone. Mainly amorphous material in respect to X-ray diffraction, some hausmannite and goethite. Hausmannite replaced by cryptomelane (light-gray). Cracks (black). Bottom cut, Hotazel - H1. Refl. light. 15 x

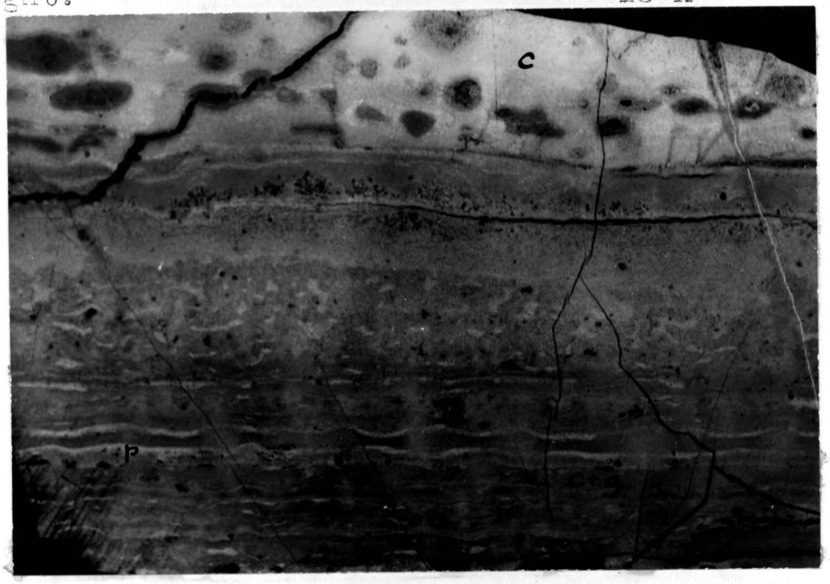


Photo 96. Braunite-rich ore. Cryptomelane (c), goethite (g) and pyrolusite (p) and braunite (disseminated). Bottom cut, Hotazel - H3. Refl. light. 15 x

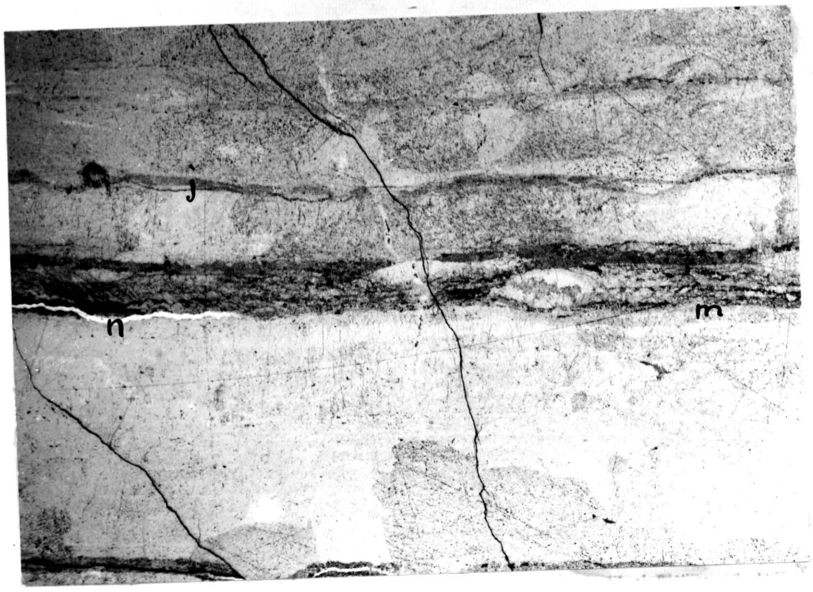


Photo 97. Hausmannite-rich ore. Predominantly coarse-grained hausmannite, also veins of jacobsite (j), manganite (m) and nsutite (n). The shadowy areas are where the hausmannite contains more goethite. Top cut, Hotazel - H7. Refl. light. 15 x

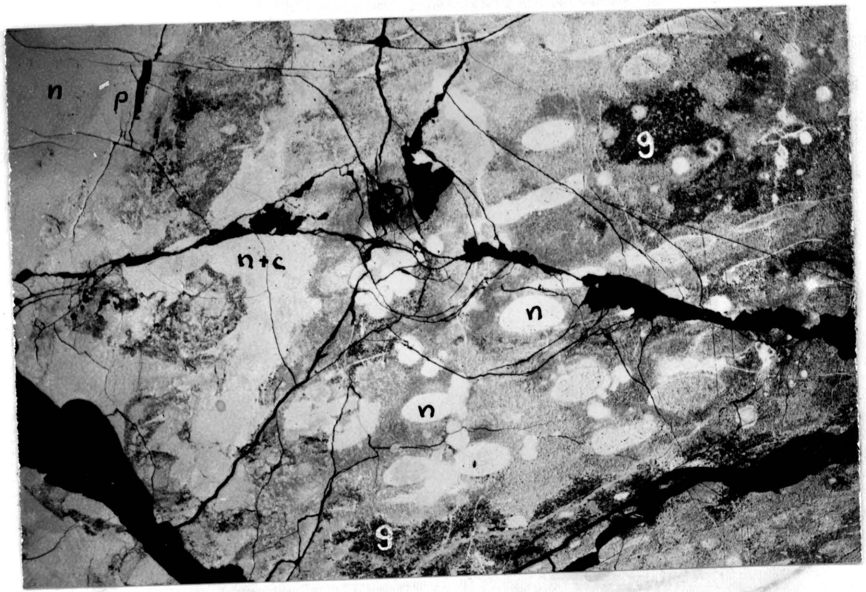


Photo 93. Ore rich in cryptomelane and jacobsite. The spherical units mainly nsutite (n), cryptomelane (c) and pyrolusite (p) in a ground-mass of cryptomelane, jacobsite and iron hydroxides (g). Cracks (black). Top cut, Hotazel - H9. Refl. light. 15 x

Photo 99. Ore rich in hausmannite and jacobsite. Mainly fine-grained hausmannite (h1), cryptomelane (c), jacobsite (j), nsutite (n), andradite (1) and coarse-grained hausmannite (h2). The nsutite and hausmannite (h2) are mainly 'vug fillings'. Upper body, Hotazel - H 10. Refl. light. 15 x

Photo 100. Ore rich in cryptomelane and braunite, showing remnant structures. Near foot-wall, Devon - D1. Refl. light. 15 x

Photo 101. Cryptomelane-rich ore. Some of the nodules (possibly remnant structures) are filled with hausmannite.
Near hanging wall, Devon - D4. Refl. light. 15 x

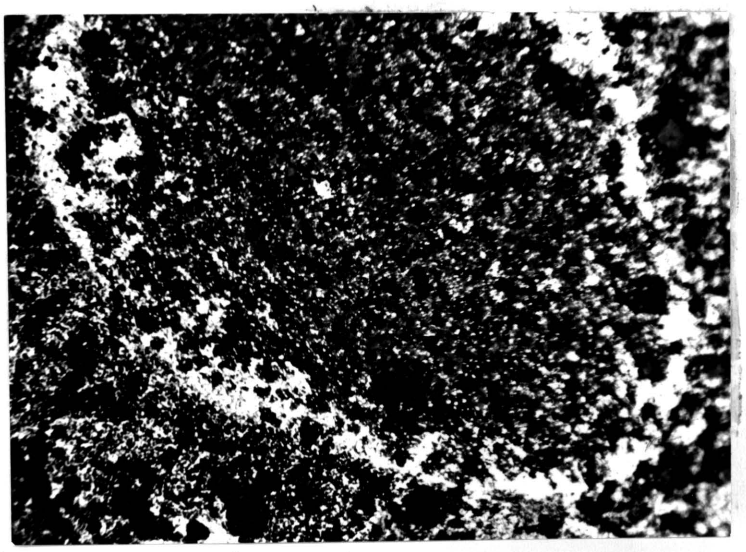


Photo 102(a). Hematite (white) in partially replaced nodule of carbonate from 'carbonate-rock'. Mamatwan - M 7a (pol. sec.). Refl. light, oil imm. 150 x

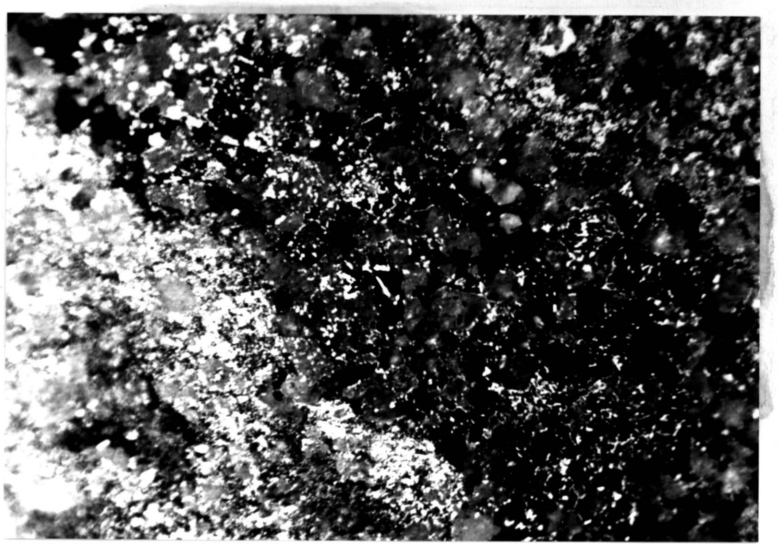


Photo 102(b). Enlargement of photo 102(a). Hematite (white) and cryptomelane (streaks) along grain boundaries of carbonate (dark and gray). Mamatwan - M 7a (pol. sec.) Refl. light, oil imm. 150 x

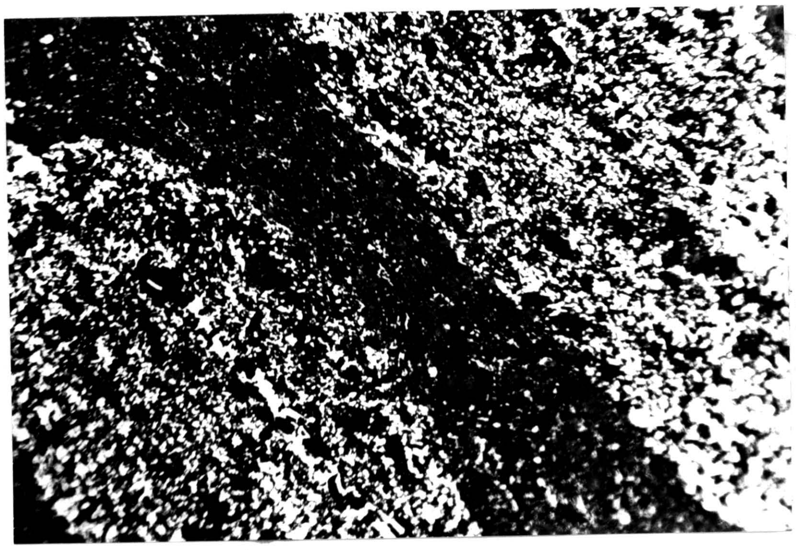


Photo 103. Nodules filled with hematite, cryptomelane and carbonate (black). All in 'carbonate-rock'. Carbonate is also in ground-mass. Mamatwan - M 7a (pol. sec.). Refl. light, oil imm. 150 x

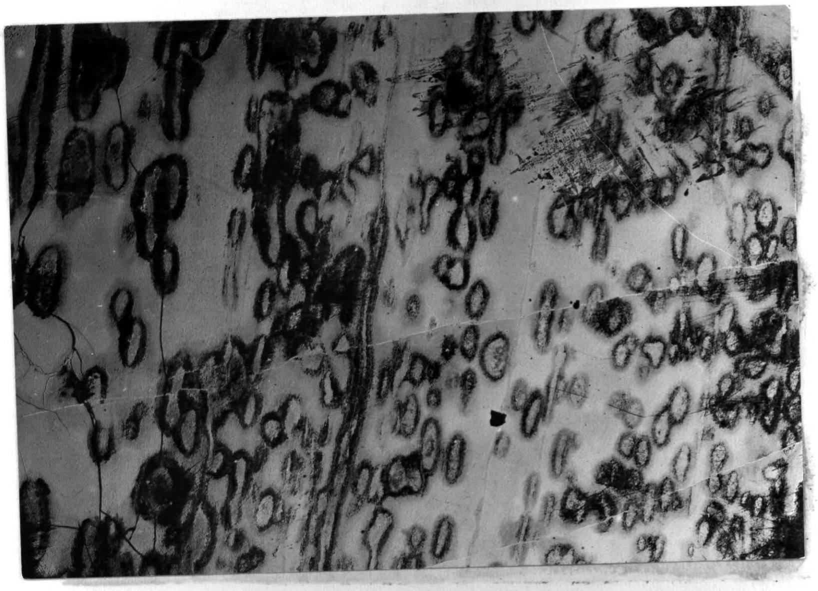


Photo 104. Ore rich in braunite and cryptomelane. The nodules are filled with todorokite, cryptomelane, hausmannite and hematite. Near foot-wall. dark: wad. Adams - A1. Refl. light. 15 x

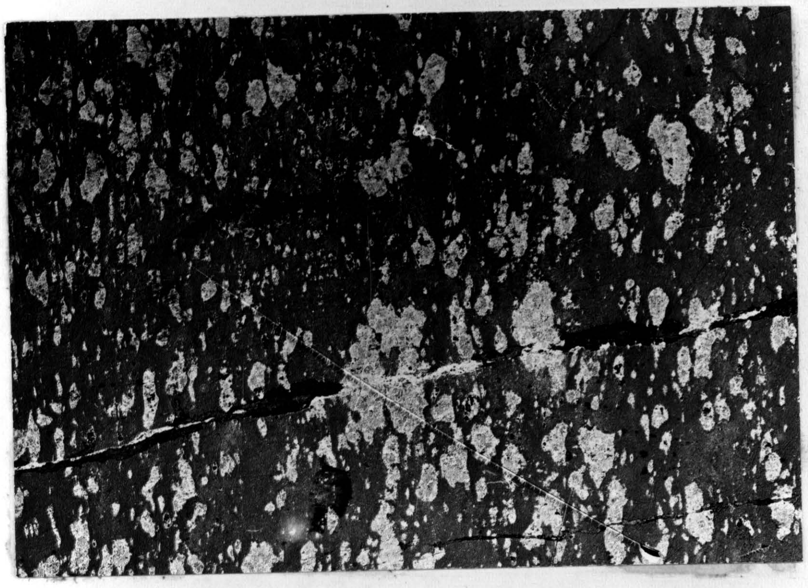


Photo 105. Ore rich in braunite and cryptomelane. The shiny, bright nodules are filled with todorokite, cryptomelane, hausmannite and hematite. Near hanging wall. Adams - A6. Refl. light. 15 x

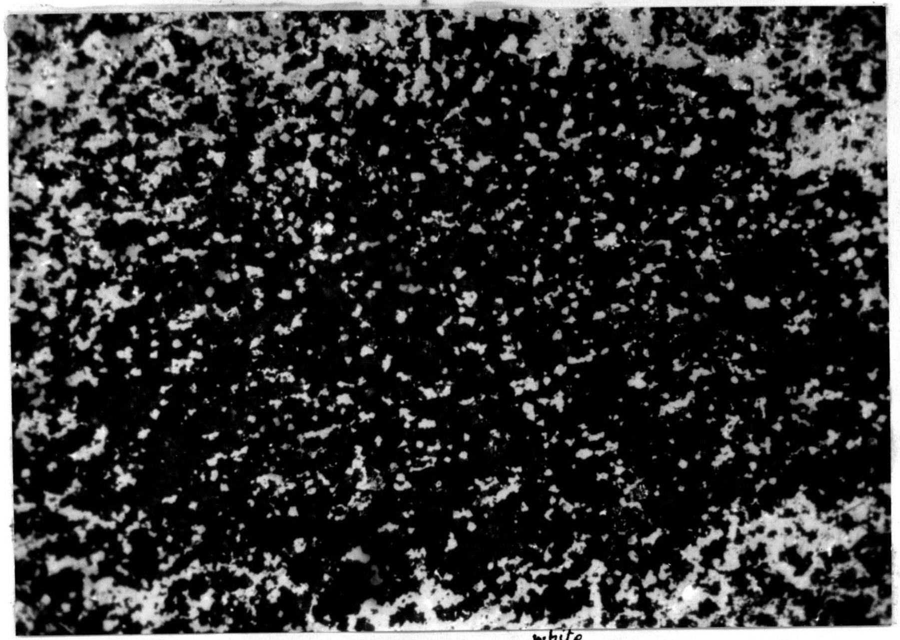


Photo 106. Idiomorphic braunite (~~gray~~ white) less densely packed in nodular carbonate (dark). Smartt - S2. Refl. light, oil imm. 300 x

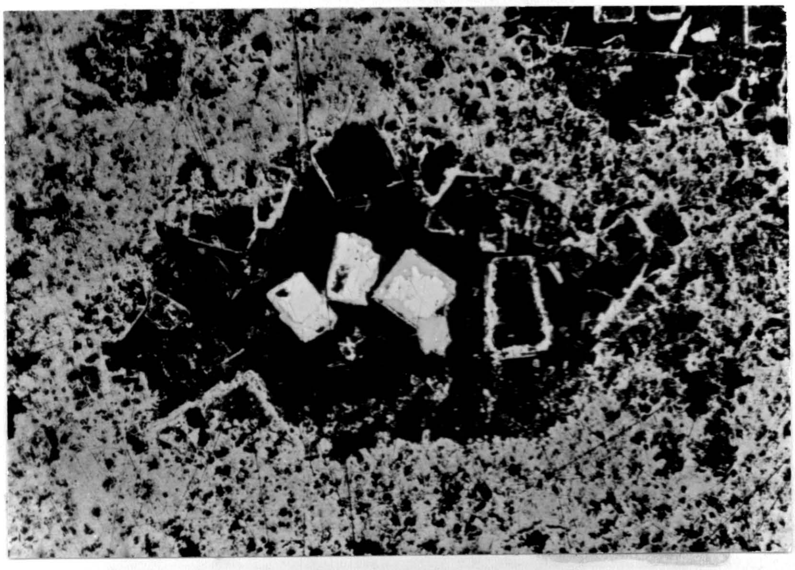


Photo 107. Vug filled with carbonate (dark) and crystals of 'bixbyite'. The latter replaced by cryptomelane and goethite (dark). All in braunite ore. Smartt - S3. Refl. light, oil imm. 140 x

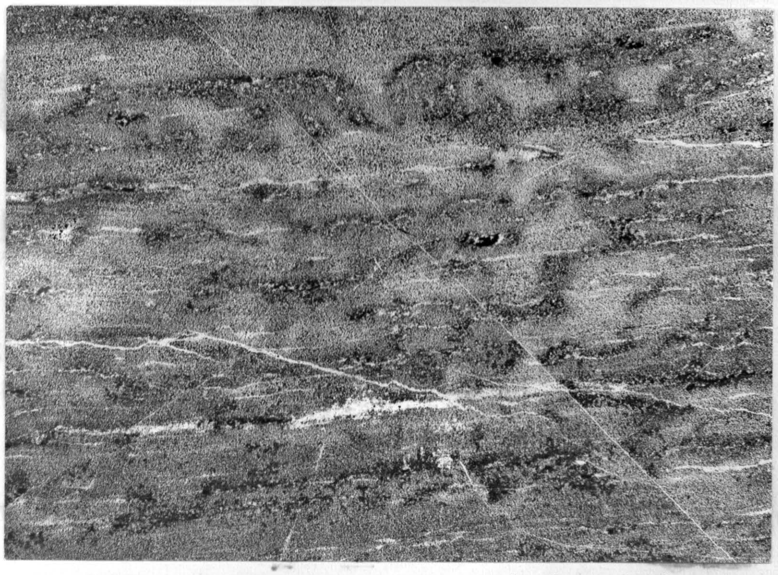


Photo 108. Ore rich in braunite and todorokite. The dark nodules are filled with carbonate minerals. Braunite and cryptomelane are concentrated along the white streaks. Smartt - S2. Refl. light. 15 x

Photo 109. Ore rich in bixbyite, braunite and cryptomelane. The white streaks mainly pyrolusite and cryptomelane. Black areas are vugs filled with silica and iron oxide. Lower ore body near foot-wall. Black Rock - BR 1B. Refl. light. 15 x

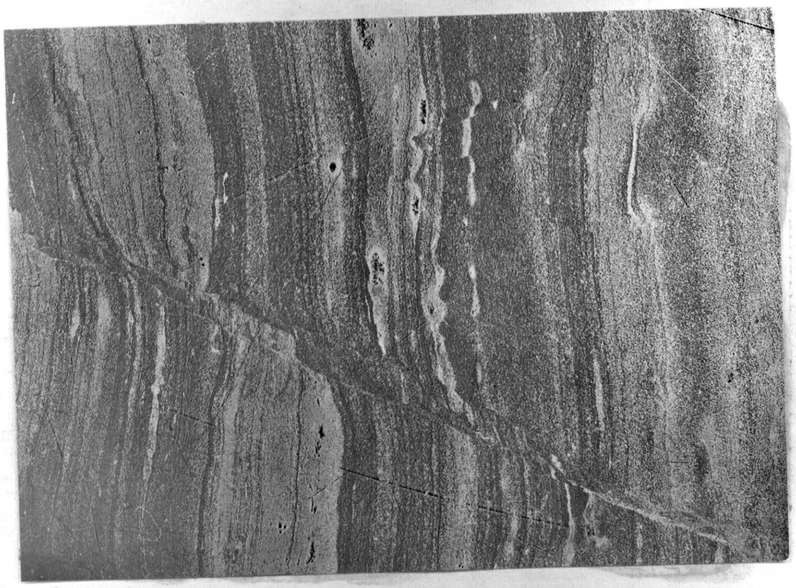


Photo 110. Layered manganese ore consisting of fine-grained hematite and braunite. Remnant structure of banded ironstone. Near hanging wall of lower ore body, Black Rock - BR 1D. Refl. light. 15 x

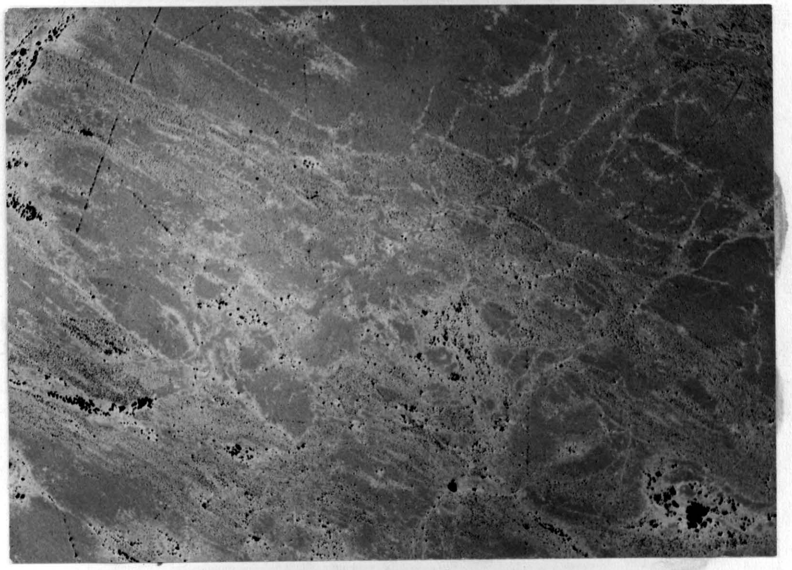


Photo 111. Ore rich in braunite and cryptomelane. Braunite ore (gray) incipiently replaced by cryptomelane (white). Near foot-wall of middle ore body. Black Rock - BR 2b. Refl. light. 15 x

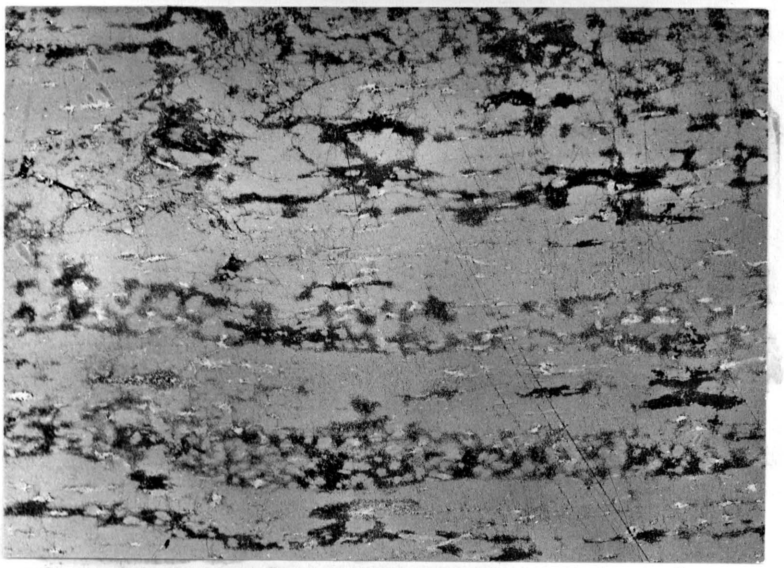


Photo 112. Ore rich in braunite and cryptomelane. Braunite (gray), cryptomelane (white) and andradite (dark). Near hanging wall of middle ore body. Black Rock - BR 2c. Refl. light. 15 x

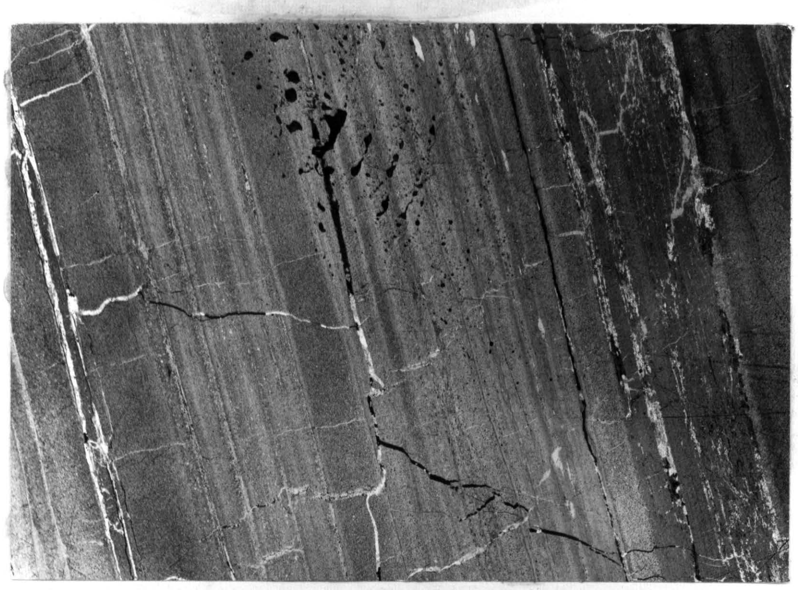


Photo 113. Ore rich in braunite, hematite and cryptomelane, remnant structure of banded ironstone. Near foot-wall of upper ore-body. Bands (dark-gray) filled with red earthy hematite, fine-grained cryptomelane and braunite alternate with bands (gray) ~~more~~ rich ore in braunite. Cracks are filled with pyrolusite (white), opal (black) and braunite (white-gray). Black Rock - BR 3a. Refl. light. 15 x

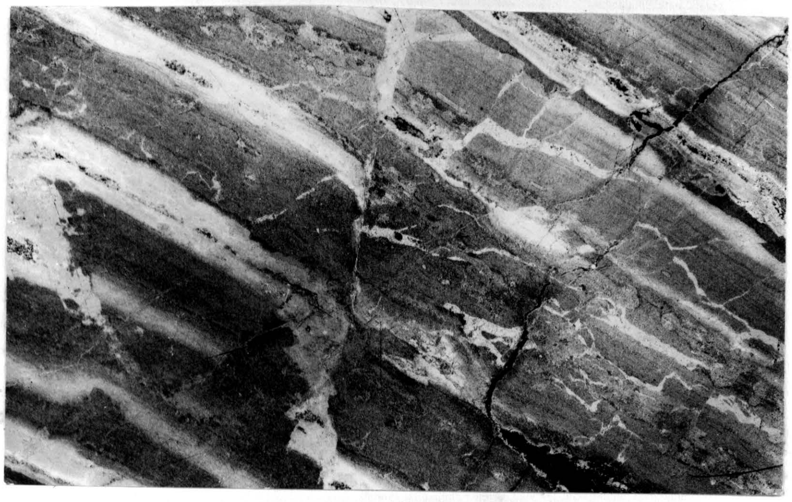


Photo 114. Ore rich in braunite, hematite and cryptomelane. The white strips are braunite and cryptomelane whereas the gray material consists of specks of hematite, goethite, dissemminated braunite and cryptomelane. Bottom richt is chalcedony in a vug. Upper ore-body, Black Rock - BR 3B. Refl. light. 15 x

Photo 115. Ore rich in braunite and cryptomelane. The cracks extending across the layering are filled with andradite and a little iron oxide. Near hanging wall of upper ore-body, Black Rock - BR 3c. Refl. light. 15 x

Photo 116. Cryptomelane (light-gray), cementing brecciated braunite/pyrolusite/cryptomelane fragments. All in braunite ore. Sample (b) folded area. Black Rock - Fol.b. Refl. light, oil imm.
150 x

Photo 117. Cryptomelane (white), formed along fractures in braunite ore. Sample (b) folded area. Refl. light, oil imm.
150 x

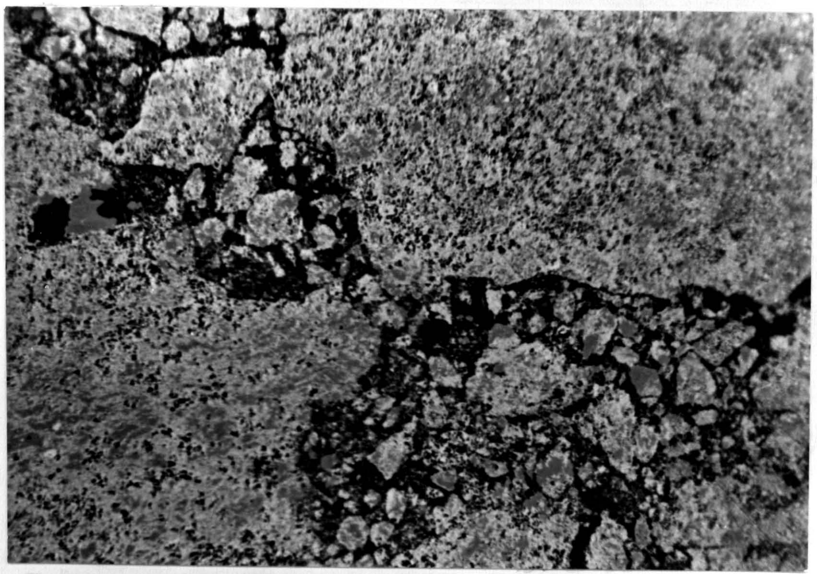


Photo 118. Iron oxide (black - in brecciated areas). Andradite (black - top left) in contact with braunite (gray). All in partially altered braunite-rich ore Sample (b) folded area. Black Rock - Fol.b. Refl. light, oil imm.
150 x

Photo 119. Fractures filled with iron oxide, intersected by cryptomelane (white). All in altered braunite ore. Sample (e) folded area. Black Rock - Fol.e. Refl. light, oil imm. 150 x

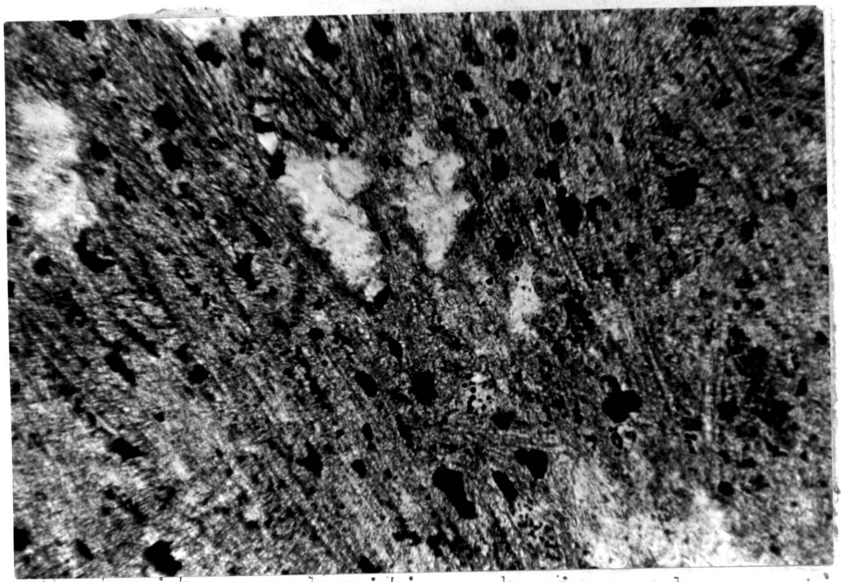


Photo 120. Bostonite porphyritic, showing subparallel arrangement of laths of partially albitised and serisitised alkali feldspar. Also aggregates of albite (white) and iron oxides (black). Hotazel - TBH 1 (thin sec.).
Trans. light. 300 x

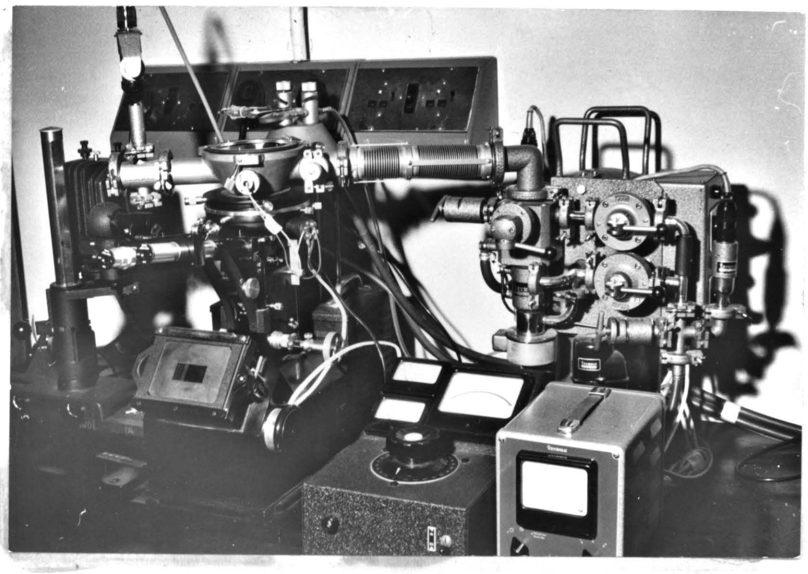


Photo 121. The Reichert Metallurgical Microscope and the Vacutherm Micro-Vacuum Furnace with evacuating unit.

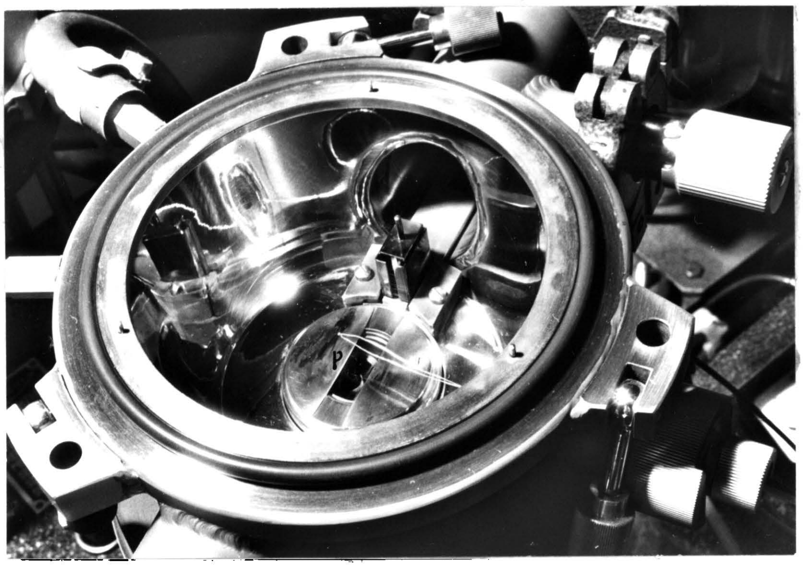


Photo 122. The lower half of the Vacutherm Micro-Vacuum Furnace with observation port (P) and thermocouple.

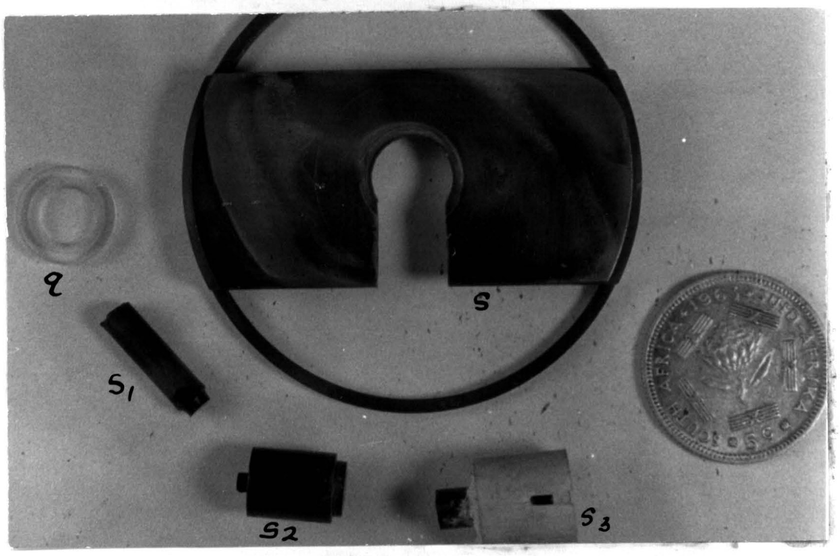


Photo 123. Various forms of samples and holders used in vacutherm and micro-vacuum furnace: the sample carrier (s), the quartz ring (q), the 2.5 mm ore sample (S 1), the 5 mm metal sample (S2) and the 2.5 mm ore sample cemented into the alundum tube (S3).

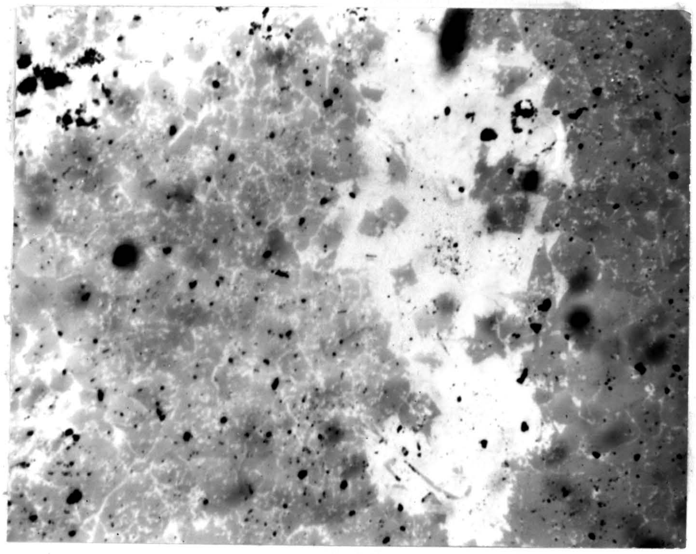


Photo 124. Bixbyite (gray) with cryptomelane (white) and streaks of cryptomelane along grain boundaries. The disseminated white specks are hematite. Refl. light, Reichert high-temp. microscope. 160 x

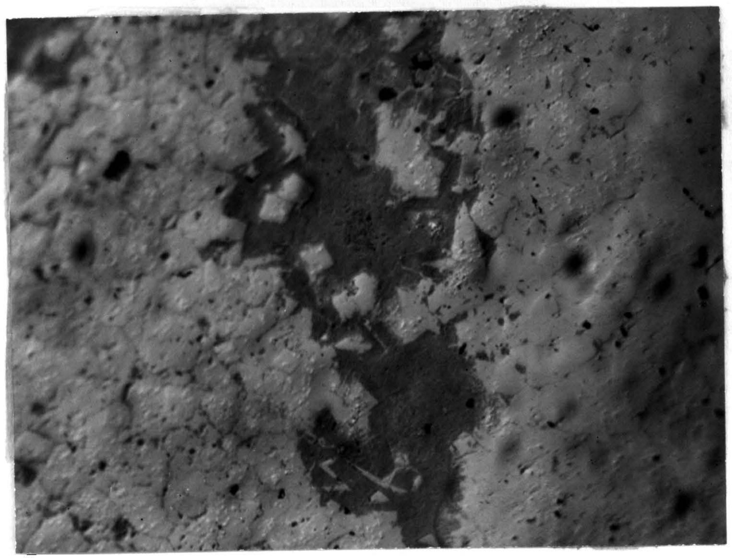


Photo 125. Cryptomelane partly altered to cryptocrystalline bixbyite (dark - centre of plate) and along grain boundaries (dark-gray). At this temperature the cryptomelane has lost some of its oxygen. Refl. light, Reichert high-temp. microscope. 480°C 160 x

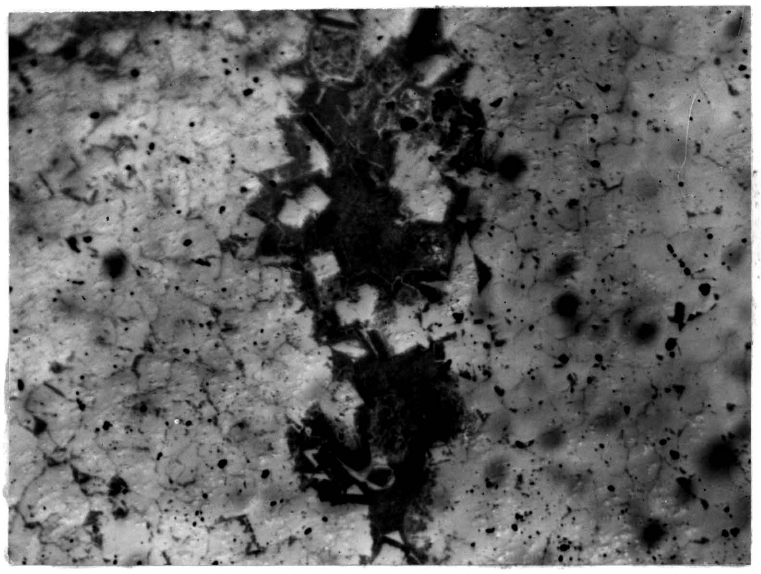


Photo 126. Altered cryptomelane (dark) showing negative relief, and hematite (white) positive relief, and bixbyite (gray). Refl. light, Reichert high-temp. microscope. 560°C 160 x

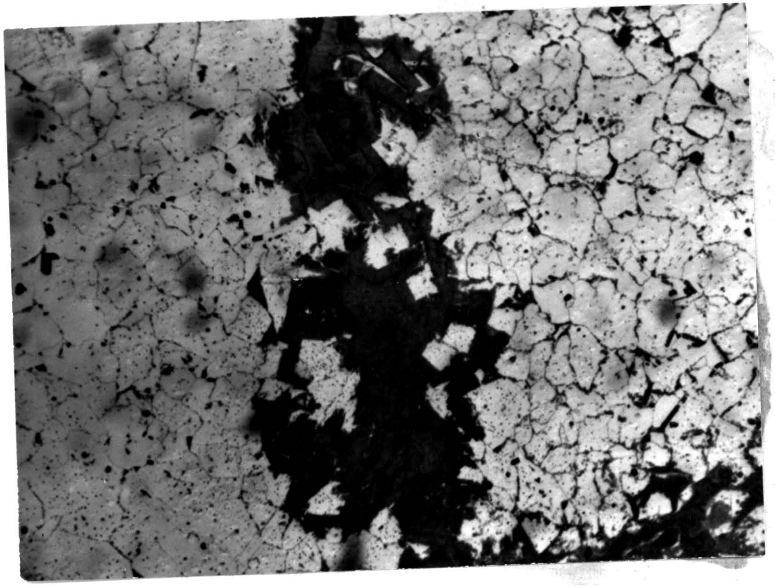


Photo 127. Cryptocrystalline bixbyite (dark) formed from cryptomelane clearly visible at 780°C also along crystal boundaries of original bixbyite. Refl. light, Reichert high-temp. microscope. 160 x

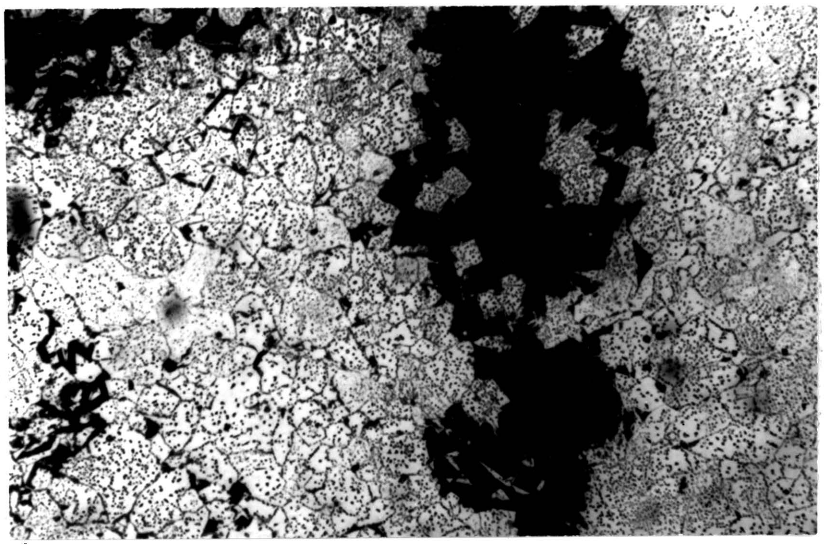


Photo 128. At 900°C the polished surface of the specimen became spotted. Refl. light, Reichert high-temp. microscope. 160 x

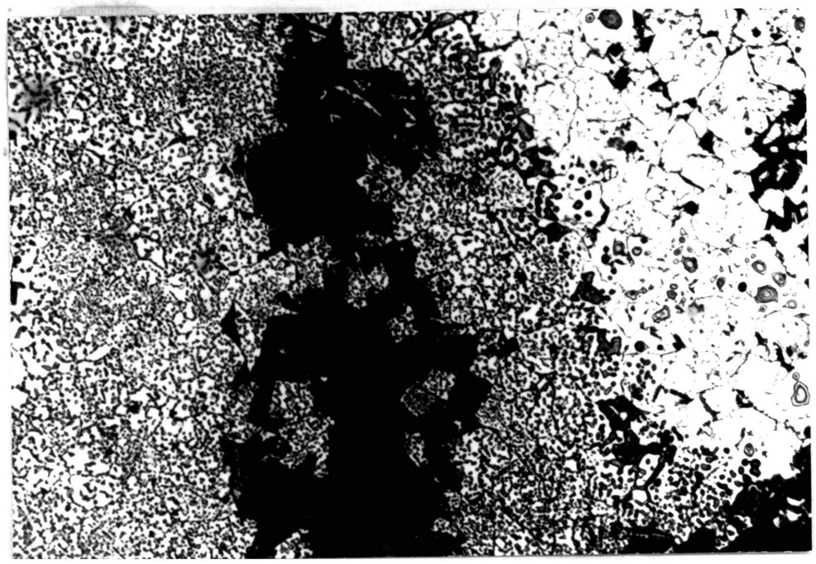


Photo 129. At 1030°C the spots on the polished surface are identified as a liquid. This observation was made shortly before the surface became covered by molten ore coming from the rear, nearer the elements.
Refl. light, Reichert high-temp. microscope 160 x

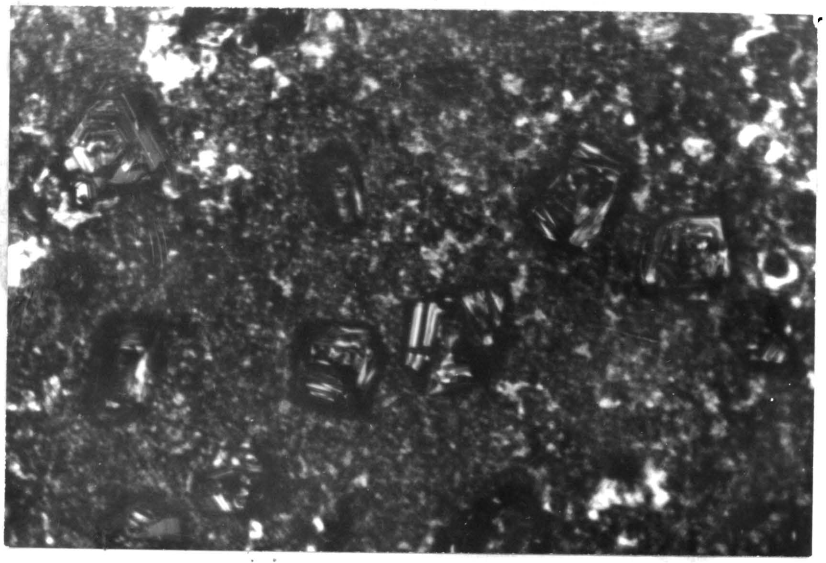


Photo 130. After cooling from a melt (ore), hausmannite ~~has~~ crystallised from the molten material on the surface under observation.
Refl. light, Reichert high-temp. microscope.
Room temp. 160 x

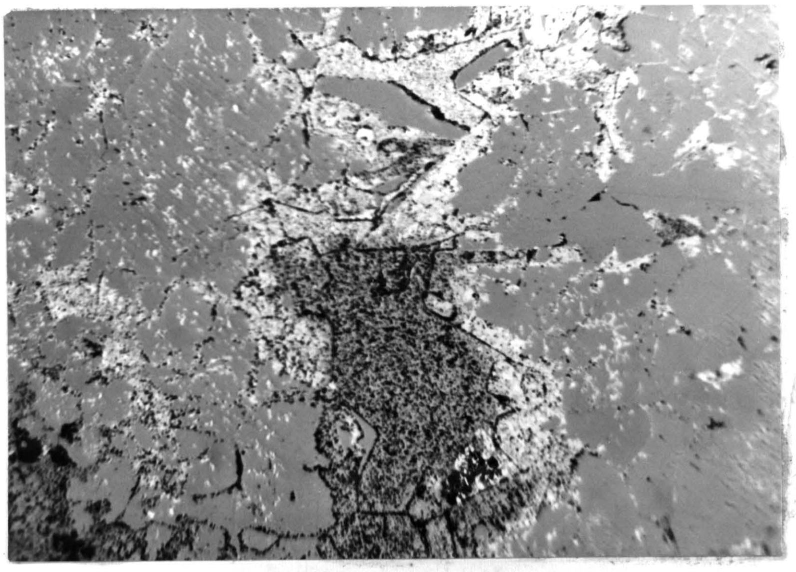


Photo 131. Partial alteration of cryptomelane. During heating the cryptomelane (white) ~~had~~ altered to cryptocrystalline bixbyite (mottled, dark). All in primary bixbyite (gray). Refl. light, oil imm. Repolished after heating.
Room temp. 300 x

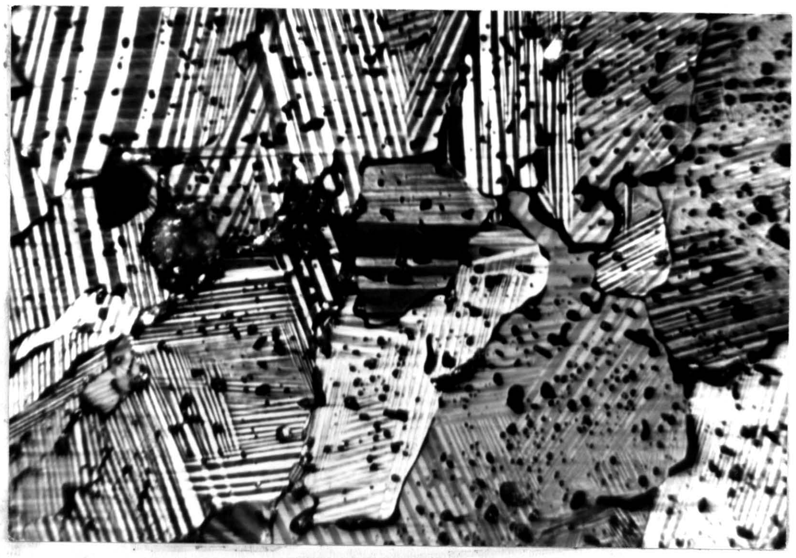


Photo 132. In areas of sufficiently high temp. hausmannite (twinned) has formed. The black spots are pores. Refl. light, oil imm. Repolished after heating. Room temp. 300 x

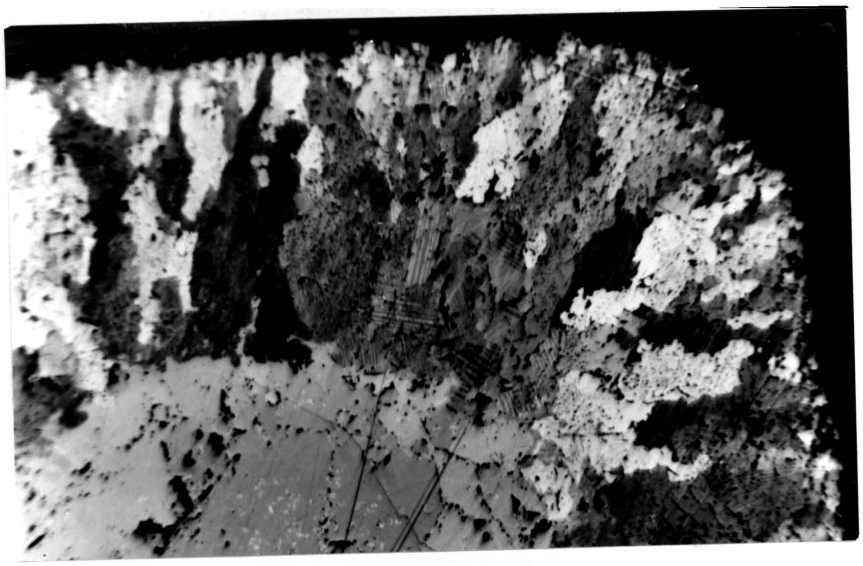


Photo 133. Hausmannite (white and dark) and bixbyite (gray). The hausmannite ~~h~~a~~s~~ formed along the peripheral portion of the specimen owing to alteration of the bixbyite.
Refl. light, oil imm. Repolished after heating.
Room temp. 300 x

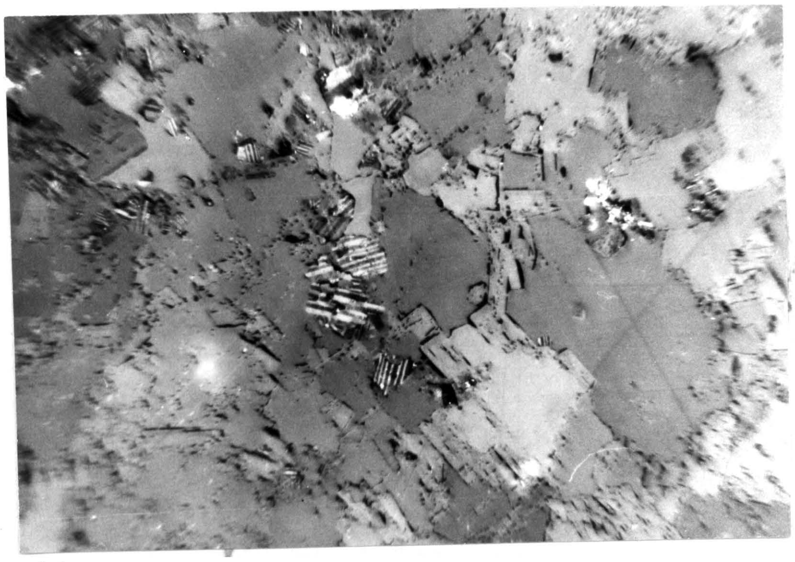


Photo 134. Alteration of bixbyite (gray) to partially altered bixbyite (dark-gray) and hausmannite (twinned). Refl. light, oil imm. Repolished after heating. Room temp. 300 x

Photo 135. Hematite (white) with jacobsite (gray -j), surrounded by jacobsite (j) and hausmannite (h). All in ground-mass of hausmannite (h). Refl. light, oil imm. Repolished after heating. Room temp. 300 x

Photo 136 (a). Hausmannite before heating. Photos 136 (a) and (b) do not represent the same sample. Refl. light, oil imm. 300 x

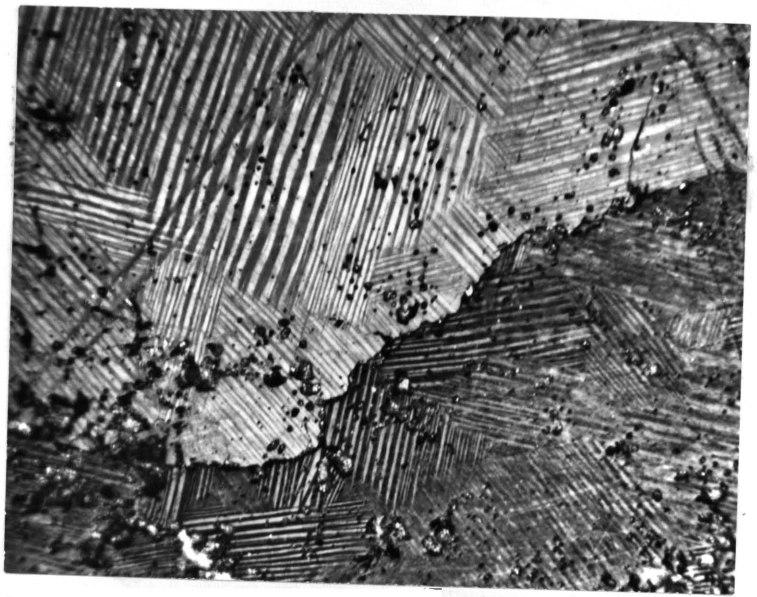


Photo 136 (b). Hausmannite after heating contains units with individual twinning. The twinning lamellae of the individuals in a unit make angles of 60 and 120° with each other. Clearly demarcated boundaries between the separate units are absent but one such unit has been linked. Refl. light, oil imm. Repolished after heating. Room temp. 300 x

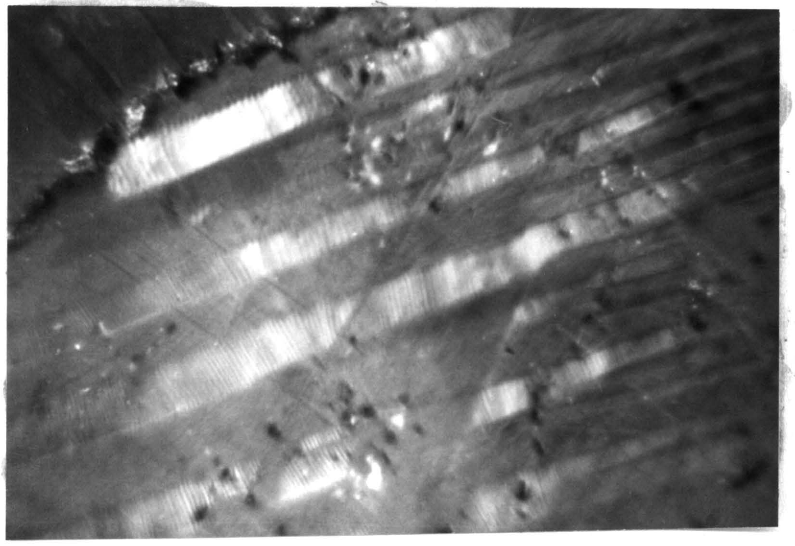
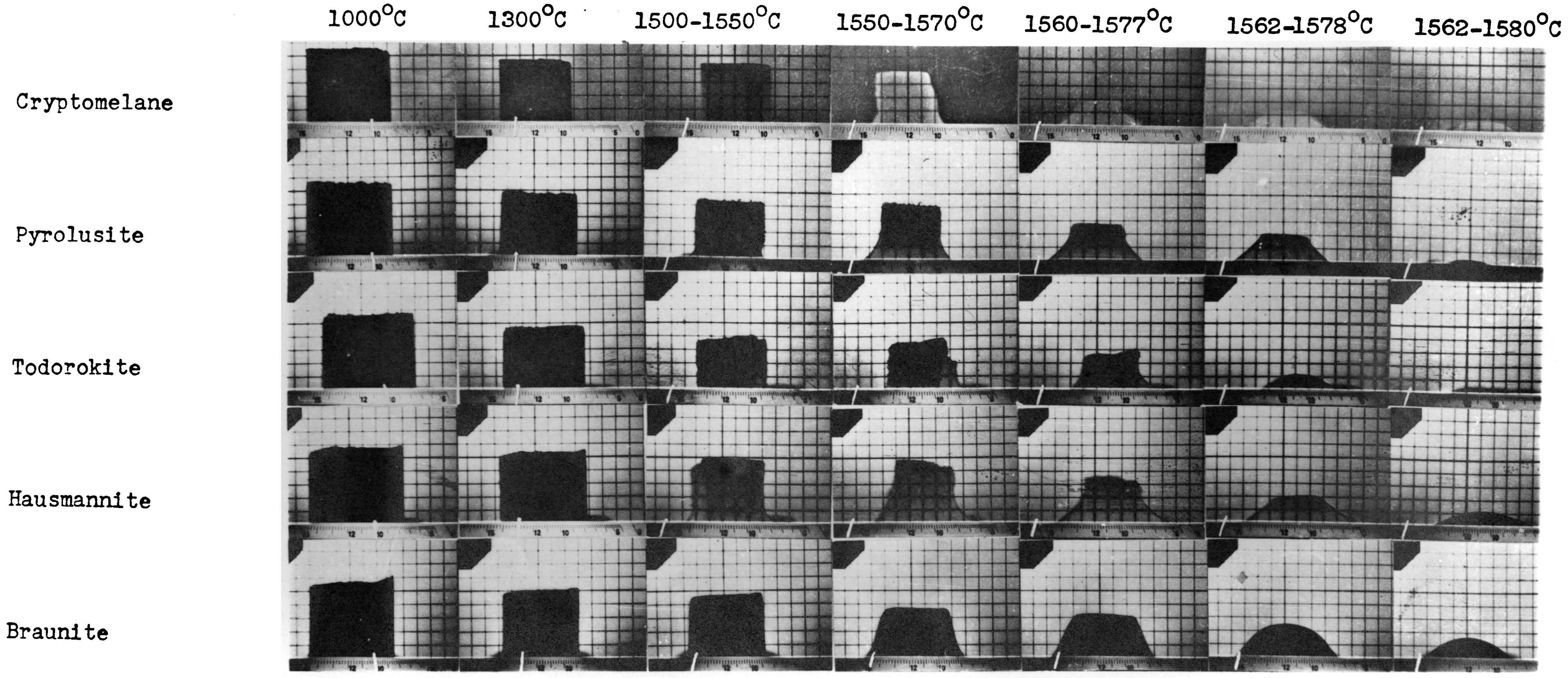


Photo 137. Twinning in hausmannite displaying pronounced internal reflections (see photo 136b). Refl. light, oil imm. Repolished after heating.
Room temp. 1,000 x

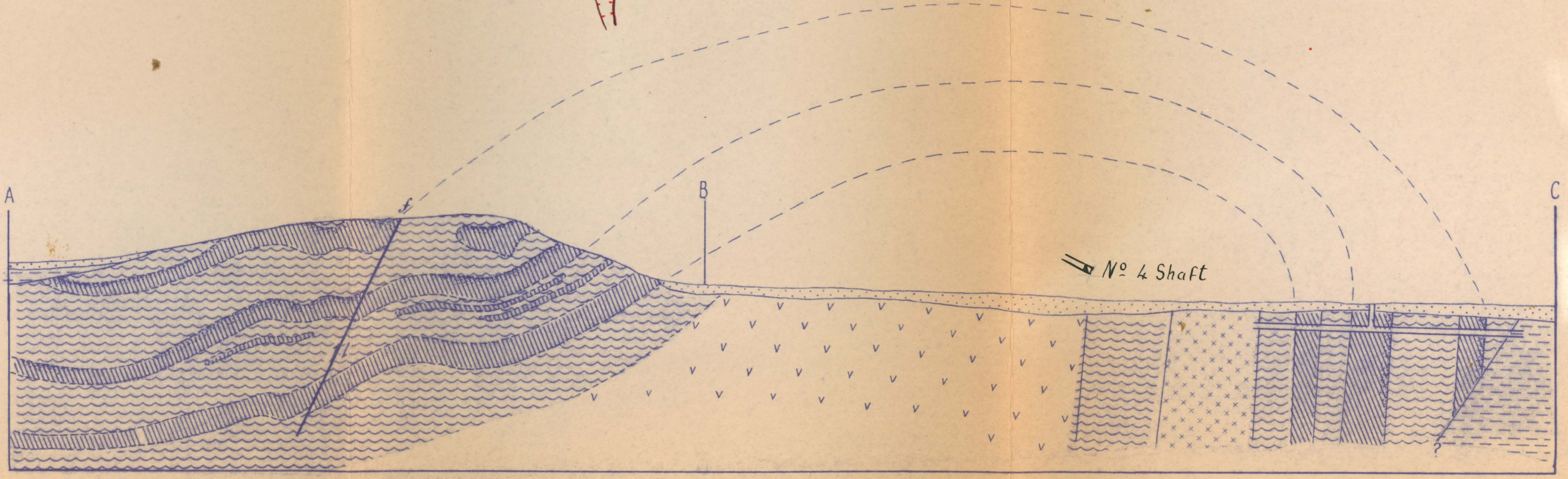
Photo 138.

Determination of softening temperature, hemisphere point and flow temperature.



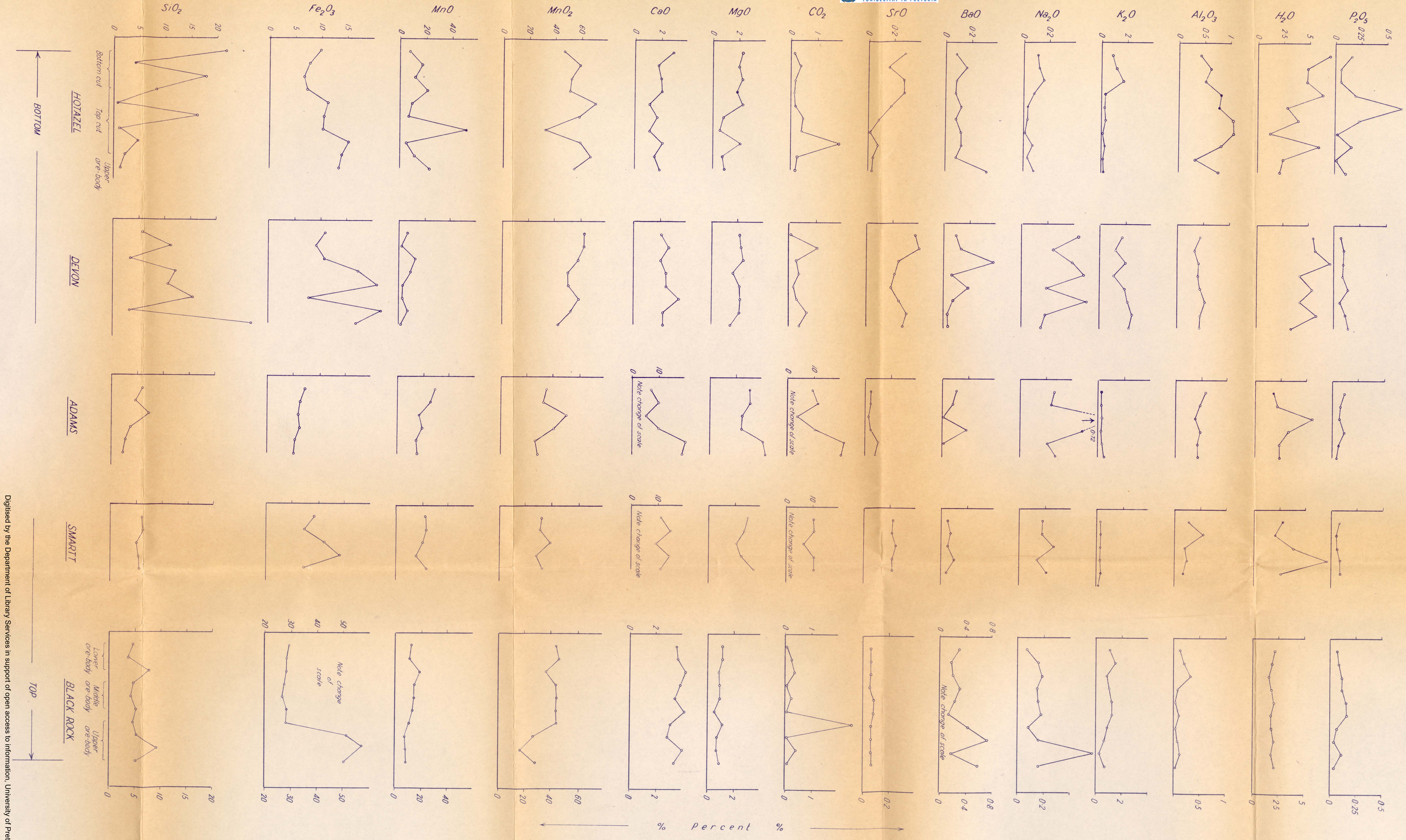
SURFACE GEOLOGY
of the
BLACK ROCK MINE

Scale 1:2,000



— Section A-B-C —

VARIATION IN THE CHEMICAL COMPOSITION OF ORE
FROM THE
KALAHARI MANGANESE-FIELD



MAJOR CONSTITUENTS

Amorphous manganese oxide and opal
Cryptomelane
Cryptomelane
Cryptomelane and braunite
Cryptomelane, braunite and pyrolusite
Cryptomelane
Hausmannite
Wad, cryptomelane and hematite
Cryptomelane, jacobsite, pyrolusite and nsutite
Hausmannite, jacobsite and nsutite

Cryptomelane, hausmanite and braunite
Cryptomelane
Cryptomelane and braunite
Cryptomelane, braunite and hausmannite
Cryptomelane and iron oxide
Cryptomelane and iron oxide
Cryptomelane and goethite
Cryptomelane and goethite

Braunite, cryptomelane, dolomite and calcite
Braunite, cryptomelane and calcite
Braunite, cryptomelane, todorokite, dolomite & calcite
Cryptomelane, hausmannite, bixbyite, dolomite & calcite
Braunite, cryptomelane and todorokite
Cryptomelane, hausmannite and bixbyite

Braunite, goethite, calcite and dolomite
Braunite and calcite
Braunite and goethite
Todorokite, cryptomelane and goethite
Braunite

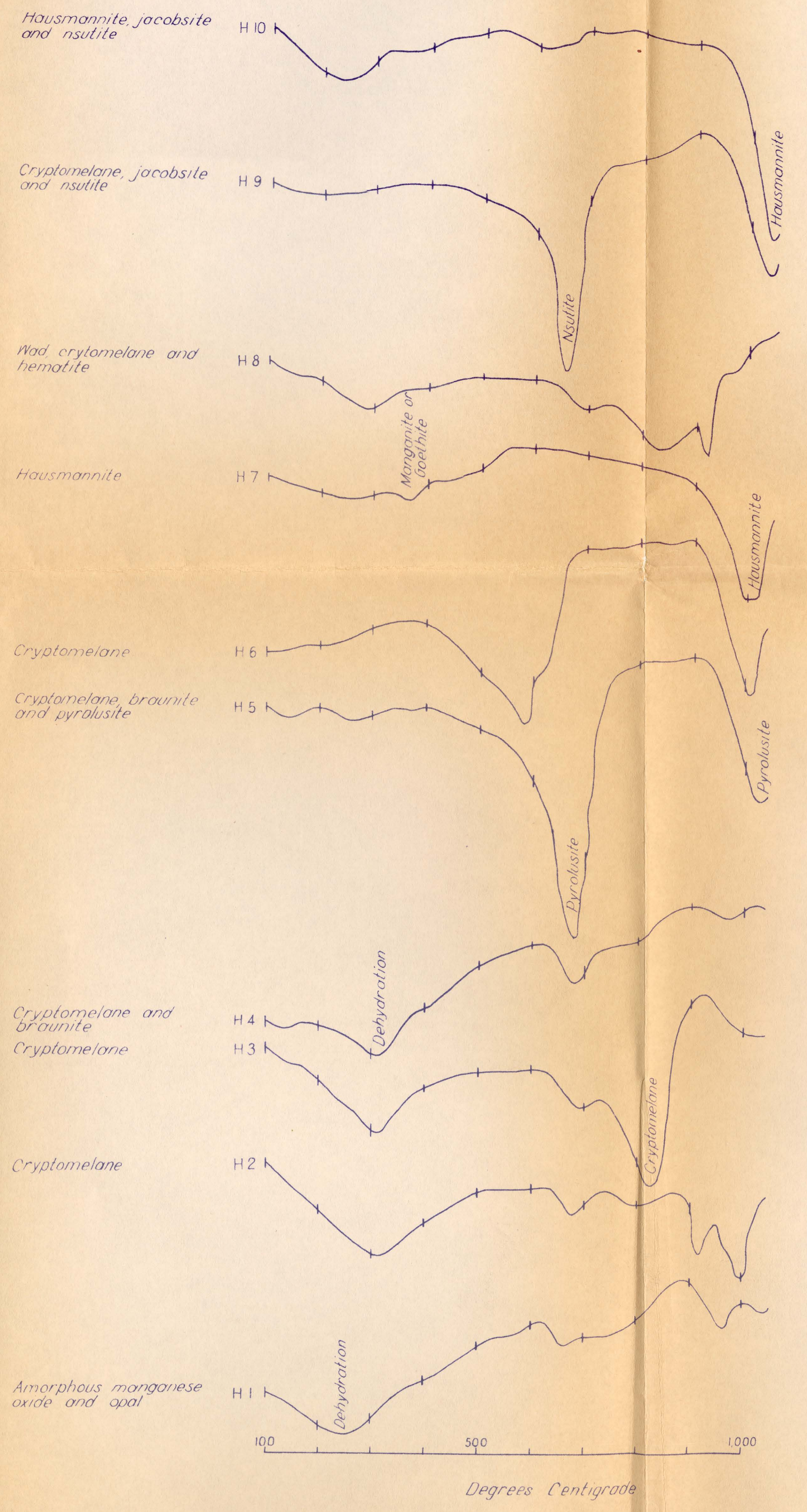
Bixbyite and pyrolusite
Bixbyite and braunite
Braunite, iron oxide, pyrolusite (cryptomelane)
Braunite and cryptomelane
Braunite
Braunite and iron oxide
Braunite and iron oxide
Iron oxide and braunite
Iron oxide and braunite
Iron oxide and braunite

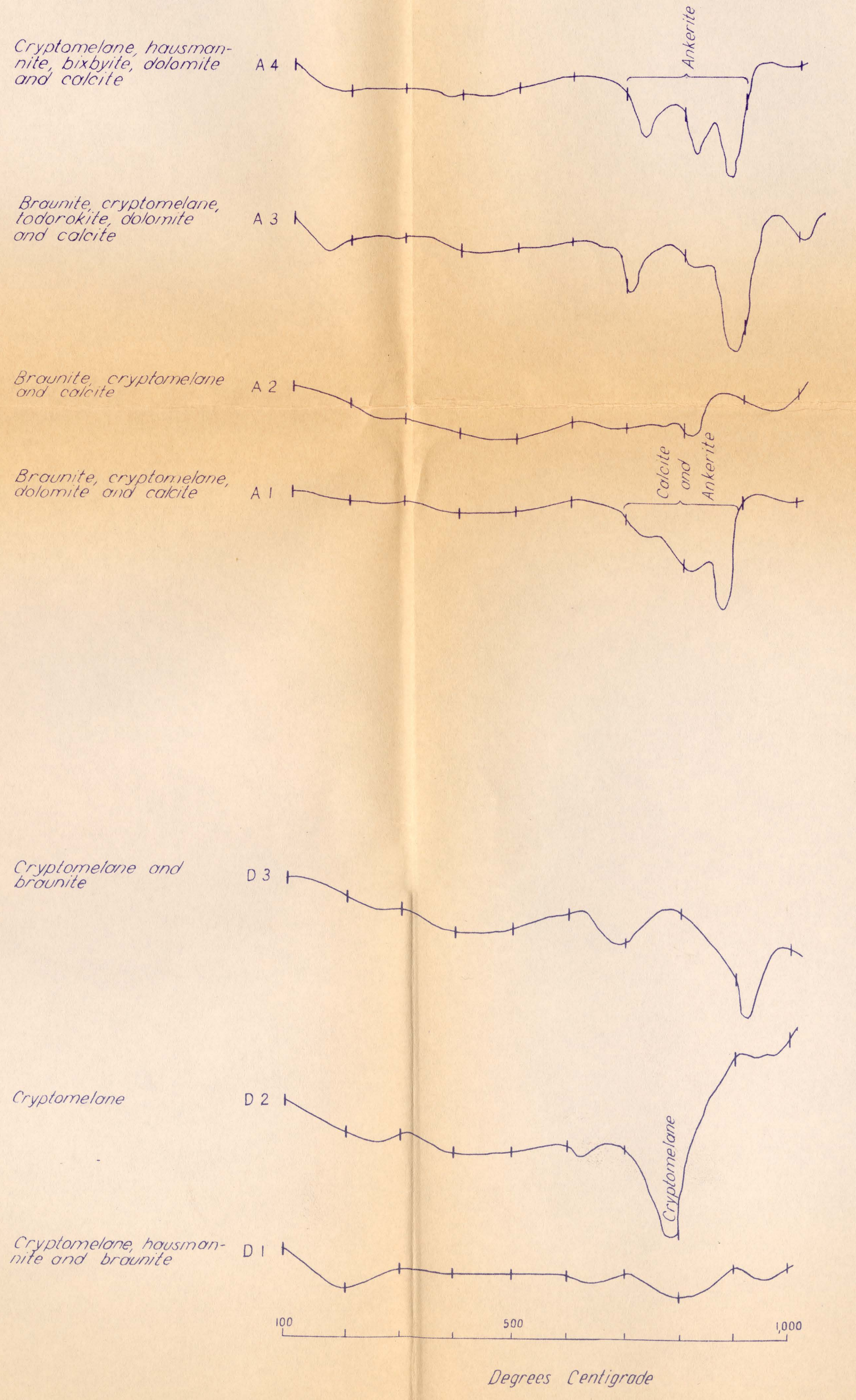
FOLDER 4

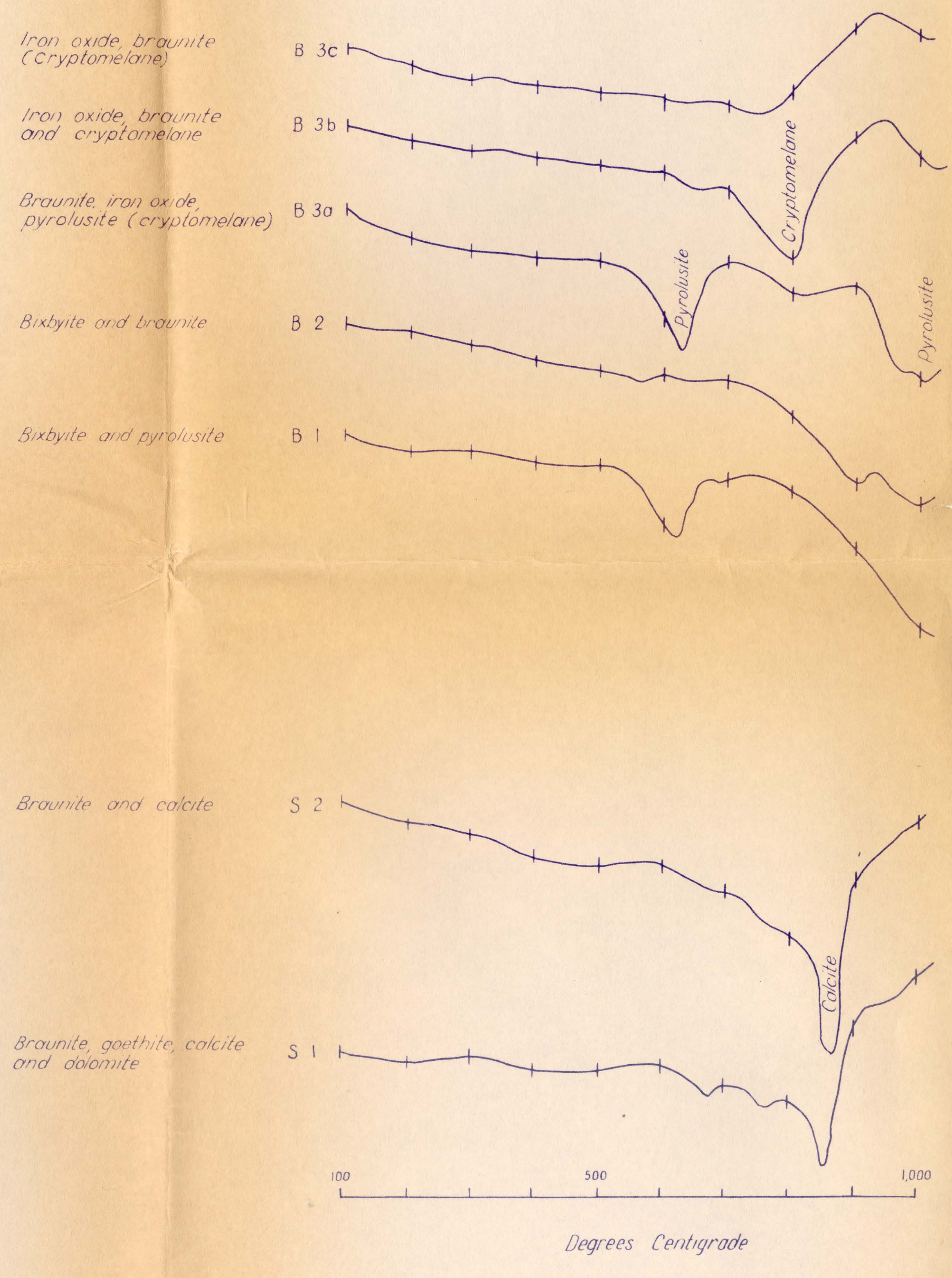
DIFFERENTIAL THERMAL CURVES OF ORE

from the

KALAHARI MANGANESE - FIELD







H : Hotazel
- H10 Upper body
- H5-9 Top cut
- H1-4 Bottom cut

D : Devon

A : Adams

S : Smartt

B : Black Rock
- B3a-3c Upper body
- B2 Middle body
- B1 Lower body

Analyst :-
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The major mineral constituents (written horizontal) are according to X-ray diffraction

The mineral names (written vertical) alongside the peaks are according to the thermal curves