CANADA

DEPARTMENT OF MINES AND TECHNICAL SURVEYS

OTTAWA

MINES BRANCH INVESTIGATION REPORT IR 60-39

A MINERALOGICAL ANALYSIS OF TWO SAMPLES OF OOLITIC IRON ORE FROM THE CLEAR HILLS AREA OF ALBERTA

by

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MINERAL SCIENCES DIVISION

COPY NO. 23   MARCH 17, 1960

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SUMMARY OF RESULTS

The mineralogical compositions of two samples of oolitic iron ore from the Clear Hills area of northwestern Alberta have been determined by utilizing the results obtained from several techniques, including microscopy, X-ray diffraction, chemical analysis, differential thermal and thermogravimetric analysis. It has been found that the ore consists of a fine-grained matrix consisting chiefly of a glauconitic silicate and goethite, in which are embedded oolites and other coarse mineral grains. The oolites, which exhibit a wide range in composition, are estimated to comprise from 60 to 70% of the ore.

The mineralogical composition of sample labelled NE, which is considered to be the more representative of the deposit, is estimated to be as follows: goethite 53%; glauconite 19%; gibbsite 8%; calcite 6%; quartz 5%; siderite 2%; apatite 2%; excess water 4%; and other minerals 1%. The sample labelled OP was found to have an essentially similar composition to that of sample NE.

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CONTENTS

INTRODUCTION

A number of deposits of iron-rich sandstone occur in the Clear Hills area of the Peace River district in northwestern Alberta. According to Kidd (1), two large deposits have been outlined, each of which contains 500 million to 1000 million long tons with a grade of about 33% iron.

In September, 1959, Mr. G.R. Heffernan of Premier Steel Mills Limited, Edmonton, Alberta, submitted to the Mines Branch for beneficiation tests, two samples of iron ore from one of these deposits. The samples were labelled NE and OP. In a letter to Dr. John Convey dated October 1, 1959, Mr. Heffernan stated that one of the samples had been taken from an open pit by a farmer, and that the other was taken by a Mr. Norman Edgar, consultant, by a bulldozer cut through the deposit from top to bottom. Although Mr. Heffernan made no reference to the labelling of the samples , OP probably refers to "open pit", and NE probably refers to the sample taken by Mr. Norman Edgar. The latter sample was considered by Mr. Heffernan to be more representative of the deposit.

The investigation covered by this report was conducted jointly by officers of the Mineralogy, Physical Chemistry, and Analytical Chemistry Sections of the Mineral Sciences Division, Mines Branch. The microscopic study, X-ray diffraction analyses

and mineralogical calculations were done by Dr. E.H. Nickel.

The thermal studies and some of the X-ray diffraction analyses

were performed under the direction of Dr. N.F.H. Bright in the

Physical Chemistry Section; this work is described in the Appendix

(see pages 24 to 41). Miss E.E. Lepine, assisted by some other

members of the Analytical Chemistry Section staff, made the

chemical analyses.

PROCEDURE

Considerable difficulty was encountered in preparing

suitable polished sections from the ore because of its tendency to

crumble under even slight pressure. A procedure that proved to

be satisfactory consisted of impregnating small lumps of the ore

with bakelite varnish, under vacuum. After heat-curing the bakelite-

impregnated fragments, a flat surface was slowly ground on each

of them, with further impregnations whenever the surface showed

signs of deterioration. This alternating grinding and impregnation

resulted in surfaces suitable for polishing. The completed polished

sections were studied under an ore microscope to identify the

minerals and to determine their associations.

X-ray powder diffraction analysis was used to

identify minerals in the samples and in the polished sections

prepared from the samples.

Additional information on the composition of the samples was provided by the thermogravimetric and differential thermal analyses. A detailed discussion of the results and interpretations of these analyses are given in the Appendix (pages 24 to 41).

Both samples were subjected to complete chemical analysis (see Table 1, page 6). These analyses were used as a basis for calculating the mineralogical compositions of the samples which are shown in Tables 2 and 3 (pages 7 and 8). The method of calculation, and the reasons for the steps taken are as follows:

1) All the sulphur was calculated as pyrite (FeS_2) since this was the only sulphide mineral recognized in the polished sections.

2) All the P_2O_5 was calculated as hydroxyl apatite ($10CaO.3P_2O_5.H_2O$), since apatite was the only phosphate mineral recognized in the ore.

3) The ferrous oxide not accounted for as pyrite was calculated as siderite ($FeO.CO_2$), since the presence of this mineral had been established by X-ray diffraction and microscopy. There is a possibility that some of the ferrous iron may also be present in the glauconitic silicate, discussed below, in which case the siderite content would be somewhat lower than that given. This is probably not very significant, however, since the calculated percentage of siderite in both samples is less than two per cent.

4) The CO_2 remaining after the siderite calculation was calculated as calcite $(CaO.CO_2)$, the amount of calcite so obtained was in close agreement with that obtained from the TGA results.

5) All the Fe_2O_3 was calculated as goethite $(Fe_2O_3.H_2O)$, since this was the only ferric oxide recognized in polished sections and by X-ray diffraction. However, the goethite probably contains more water than that given by the stoichiometric formula, since this is commonly the case in hydrated ferric oxides of sedimentary origin. Furthermore, the X-ray diffraction patterns of the mineral are weak and diffuse, which is characteristic of a high degree of hydration. It is probable, therefore, that most of the water remaining after calculation of the other mineral species, is associated with the goethite as adsorbed or capillary water.

6) The percentage of silica as quartz was determined by the Trostel and Wynne method of differential solubility.

7) The remaining silica was presumed to be present as a silicate or silicates. Since the silicates present yield only very diffuse X-ray patterns with few diffraction lines, and are indurated with goethitic stain, it has not been possible to identify them positively. However, the X-ray powder patterns suggest the presence of a micaceous mineral. A mica which has a sufficiently flexible composition to accommodate the oxides remaining from the preceding calculations, and which is commonly found in sedimentary

deposits, is glauconite. According to Struntz (2), a typical

formula of glauconite can be given as $(K, Ca, Na)_{<1}$ $(Al, Fe^{+2}, Fe^{+3},$

$Mg)_2(OH)_2Al_{0.35}Si_{3.65}O_{10}$. Assuming that the silicate mineral

present has such a formula, the CaO and SiO_2 remaining from the

preceding calculations, all the K_2O, Na_2O and MgO reported by

the analyses, and sufficient Al_2O_3 and H_2O to satisfy the formula

were combined to give the percentage of a material which will

be referred to as glauconite in the samples. This calculation

involves some uncertainties, one of which is the amount of chemically

combined iron in the mineral. This will be discussed more fully

under "Mineralogical Composition", (see page 6).

8) The alumina remaining after the glauconite

calculation is assumed to be present as $Al_2O_3 . 3H_2O$, or gibbsite.

This interpretation is consistent with the DTA and TGA results,

and with the geological environment of the deposit, although the

presence of gibbsite in these ores has not been positively established.

Following these calculations, there remained only

the excess water, MnO and TiO_2 to be accounted for. The majority

of the water is probably contained by the goethite as adsorbed or

capillary water, as noted above. The manganese could possibly

occur in the goethite, likely in partial substitution for the iron

or alternatively in one or other of the carbonate minerals. The

mode of occurrence of the TiO_2 is not known .

DETAILS OF INVESTIGATION

Mineralogical Composition

Chemical analyses of samples NE and OP are given in Table 1.

TABLE 1

Chemical Analyses of Samples NE and OP

	NE		OP	
	Analyzed %	Calculated to 100%	Analyzed %	Calculated to 100%
FeO	1.30	1.29	0.65	0.65
Fe_2O_3	48.03	47.74	46.03	46.26
✶SiO_2	16.64	16.54	22.0	22.11
Al_2O_3	8.26	8.21	8.44	8.48
CaO	4.34	4.31	4.67	4.69
MgO	2.69	2.67	1.85	1.86
MnO	0.10	0.10	0.14	0.14
K_2O	0.64	0.64	0.69	0.70
Na_2O	0.08	0.08	0.11	0.11
TiO_2	0.32	0.32	0.36	0.36
P_2O_5	0.80	0.79	0.78	0.78
S	0.11	0.11	0.11	0.11
H_2O	13.7	13.62	10.4	10.46
CO_2	3.28	3.26	2.88	2.89
C	0.32	0.32	0.40	0.40
Total	100.61	100.00	99.51	100.00
✶ SiO_2 as quartz 4.73%			9.15%	

TABLE 2

The Calculated Mineral Composition of Sample NE

	Fe_2O_3	FeO	SiO_2	Al_2O_3	CaO	MgO	MnO	K_2O	Na_2O	TiO_2	P_2O_5	S	H_2O	CO_2	C	Totals
Apatite					1.04						0.79		0.03			1.86
Pyrite		0.13										0.11				0.24
Siderite		1.16												0.71		1.87
Calcite					3.25									2.55		5.80
Goethite	47.74												5.38			53.12
Quartz			4.73													4.73
Glauconitic silicate			11.81	3.07	0.02	2.67		0.64	0.08				0.97			19.26
Gibbsite				5.14									2.72			7.86
Water													4.52			4.52
Carbonaceous material															0.32	0.32
Other							0.10			0.32						0.42
Totals	47.74	1.29	16.54	8.21	4.31	2.67	0.10	0.64	0.08	0.32	0.79	0.11	13.62	3.26	0.32	100.00

TABLE 3

The Calculated Mineral Composition of Sample OP

	Fe_2O_3	FeO	SiO_2	Al_2O_3	CaO	MgO	MnO	K_2O	Na_2O	TiO_2	P_2O_5	S	H_2O	CO_2	C	Totals
Apatite					1.03						0.78		0.03			1.84
Pyrite		0.13										0.11				0.24
Siderite		0.52												0.32		0.84
Calcite					3.27									2.57		5.84
Goethite	46.26												5.21			51.47
Quartz		---	9.15													9.15
Glauconitic silicate			12.96	4.70	0.39	1.86		0.70	0.11				1.06			21.78
Gibbsite				3.78									2.00			5.78
Water													2.16			2.16
Carbonaceous material															0.40	0.40
Other							0.14			0.36						0.50
Totals	46.26	0.65	22.11	8.48	4.69	1.86	0.14	0.70	0.11	0.36	0.78	0.11	10.46	2.89	0.40	100.00

The mineralogical compositions of the samples were calculated from the chemical analyses with the aid of other supporting data, as described above. The calculated mineral composition of sample NE is given in Table 2; that of OP, in Table 3. The figures in these tables are given in two decimal places for convenience in tabulating and addition, and are not meant to indicate the degree of confidence.

A degree of uncertainty in these calculations is unavoidable because some of the minerals are fine-grained, partially amorphous, and intergrown with others. The greatest uncertainty probably resides in the assumed composition of the silicate mineral (or minerals). For the reasons detailed above, the silicate has been designated as a glauconitic silicate and has been assumed to be iron-free. It is more likely, however, that this mineral contains at least some chemically combined iron. If the mineral actually is a glauconite, then the maximum amount of iron present is that which, together with magnesium, totals 2 atoms in the glauconite formula, viz $(K, Ca, Na)_{<1} (Al, Fe, Mg)_2 (OH)_2 (Al, Si)_4 O_{10}$. According to this, the maximum amount of iron possible in the glauconite is 4% Fe, although the actual value is probably lower. The amount of iron combined in the glauconite would correspondingly reduce the amount of goethite and/or siderite, and increase the amount of gibbsite shown in Tables 2 and 3.

The amount of goethite in samples NE and OP is probably somewhat higher than that shown in Tables 2 and 3 if the excess water is considered to be part of this mineral. On the other hand, the goethite content could be reduced a little if some of the trivalent iron is combined with the glauconite.

No gibbsite or other aluminum hydroxide could be recognized, either microscopically or by X-ray diffraction, but its presence is consistent with the DTA and TGA results; the chemical analyses show aluminum in considerable excess over that required by the glauconitic silicate. Therefore, the gibbsite, if present, is probably amorphous, and could be closely intergrown with the partially amorphous groundmass which is composed largely of goethite and glauconite.

Association of the Minerals

The two samples described in this report consist of a brown, earthy, friable groundmass in which are embedded oolites and other sand-like mineral particles. Examination of screened fractions of lightly crushed ore reveals that the -28+65 mesh fractions consist largely of unbroken oolites, while the finer sizes consist largely of the fine-grained groundmass minerals, and the coarser sizes, of combined oolites and groundmass. This screen separation of oolites and matrix permits the proportion of oolites to groundmass to be estimated. An evaluation of the

screened products of the ore indicates that samples NE and OP

consist of about 72% and 62% oolites, respectively.

The mineralogical composition of the groundmass

or matrix is in some doubt, since it is too heavily indurated by

goethite to permit an identification of the components by the petro-

graphic microscope, and X-ray powder patterns of the matrix

minerals are generally very weak and diffuse. The latter suggest

that the matrix consists predominantly of amorphous material

which, for the reasons cited above, is probably composed chiefly

of goethite and glauconite.

The goethite in the matrix varies from sub-microscopic

particles and films indurating the glauconite, through fine-grained

disseminations (Figs. 1 and 2), to almost solid goethite (Figs. 3 and 4).

Analyses show that the iron content of the matrix assemblage is

similar to that of the samples as a whole. For example, the NE

and OP head samples contain 34.6% Fe and 32.7% Fe, respectively,

while the -200 mesh fractions of the same samples contain 32.9% Fe

and 30.6% Fe, respectively.

A small proportion of the matrix is composed of

fine-grained apatite. This apatite occurs, at least in part, as

large masses, and one fragment 10 mm in diameter, consisting

largely of fine-grained apatite with a few oolites, was observed.

Embedded in the matrix which, as stated previously, consists largely of goethite and glauconite, are oolites and relatively coarse, angular mineral grains.

The oolites vary from spheroidal to ellipsoidal, and fall within a narrow size range, ie, between 28 and 65 mesh. They vary greatly in composition, and generally consist of several minerals, frequently in concentric arrangement and rimmed by goethite. Many oolites are built around a quartz core (Figs. 2, 5 and 7); some consist largely of calcite (Fig. 1); others of glauconite (Figs. 1 and 7); and still others, of goethite (Figs. 5 and 7). Figure 6 illustrates the fragmental nature of some of the ore.

The range in iron content of the oolites has been determined by screening out the oolites from the matrix, separating them into gravity fractions by heavy liquids, and analyzing them for iron. The results are shown in Table 4.

TABLE 4

Iron Distribution in Oolites from Samples NE and OP

Density Range	Wt % of fraction	Fe % in fraction	% Iron Distribution		
			In Lighter Fractions	In This Fraction	In Heavier Fractions
Sample NE					
< 2.8	37.3	24.40	--	24.0	76.0
2.8-3.0	4.7	36.29	24.0	4.5	71.5
3.0-3.3	21.1	43.29	28.5	24.1	47.4
3.3-3.6	17.7	47.88	52.6	22.4	25.0
>3.6	19.2	49.42	75.0	25.0	--
Sample OP					
<2.8	23.7	16.94	--	10.9	89.1
2.8-3.0	5.6	27.99	10.9	4.3	84.8
3.0-3.3	28.9	38.74	15.2	30.6	54.2
3.3-3.6	32.7	46.52	45.8	41.5	12.7
>3.6	9.1	51.01	87.3	12.7	--

Table 4 shows that the iron content of the oolites ranges from about 17% Fe to 51% Fe, although some oolites both higher and lower in iron content could probably have been isolated if lighter and heavier liquids had been used. Table 4 also indicates that the oolites can be up-graded by gravity methods. For example, the separation of sample NE at a density of 3.0 resulted in the removal of 42% (37.3% + 4.7%) of the sample weight as a float tailing, with an iron recovery, in the sink concentrate, of 71.5% of the iron. In sample OP, a separation at the same density removed 29.3% of the sample weight, with a recovery of 84.8% of the iron. These results, of course, apply only to the oolites, and not to the ore as a whole.

The only apatite recognized in the polished sections was in the 10 mm ore fragment which consisted largely of fine-grained apatite with embedded oolites. Analyses of some of the separated fractions, however, indicate that the apatite occurs both in the oolites and the groundmass, but that the heavy, or iron-rich, oolites contain less P_2O_5 than the samples as a whole. Analyses of heavy oolites (ie, those with a specific gravity greater than 3.3) from both samples indicate P_2O_5 contents of about 0.3%, which is appreciably lower than that of the head samples, which contain 0.8% P_2O_5.

The carbonate minerals calcite and siderite appear to be present largely as coarse angular particles and, to a lesser extent, as oolite components.

The quartz occurs as discrete, angular, mineral grains in the groundmass, and as cores in the oolites.

The pyrite also occurs as discrete mineral grains.

No graphite was observed in the ore, so the non-CO_2 carbon is probably present as amorphous carbonaceous matter in the groundmass.

The manganese is most likely combined with the goethite, in substitution for the iron. The titanium content, on the other hand, is higher than that normally found in goethite, so that it may be present as a distinct titanium mineral, possibly as rutile or anatase.

CONCLUSIONS

Samples NE and OP are similar with respect to their chemical and mineralogical compositions. They consist of extremely friable oolitic iron ore consisting of about 60 to 70% oolites in a fine-grained matrix. The matrix consists largely of a fine-grained silicate mineral, or mineral mixture, and goethite. The oolites, which range in size from 28 to 65 mesh, exhibit considerable variations with respect to their mineralogical composition and iron content. Goethite, which is the only iron ore mineral present in

significant amounts, varies in grain size from sub-microscopic amorphous material to solid oolites and coarse fragments over 1 cm in diameter.

The oolitic fraction of the ore can probably be beneficiated by standard ore dressing methods, but the beneficiation of the fine-grained matrix is likely to present rather serious difficulties.

REFERENCES

1. D.J. Kidd, Iron Occurrence in the Peace River Region, Alberta. Research Council of Alberta, Geological Division, Preliminary Report 59-3 (1959).

2. H. Struntz, Mineralogische Tabellen, 3rd ed., Akad. Verlag., Leipzig (1957).

Fig. 1. - Photomicrograph of polished section of ore,
showing oolites rimmed by goethite (white)
in a matrix of glauconitic silicate (grey)
with disseminated goethite. The oolite
in the centre of the photograph consists
largely of calcite; the others, largely
glauconitic silicate. Pits are black.

- -

Fig. 2. - Photomicrograph of polished section of ore
        showing oolites in a glauconitic matrix (grey)
        with disseminated goethite (white). The two
        oolites near the centre of the photograph have
        quartz cores. Pits are black.

- -
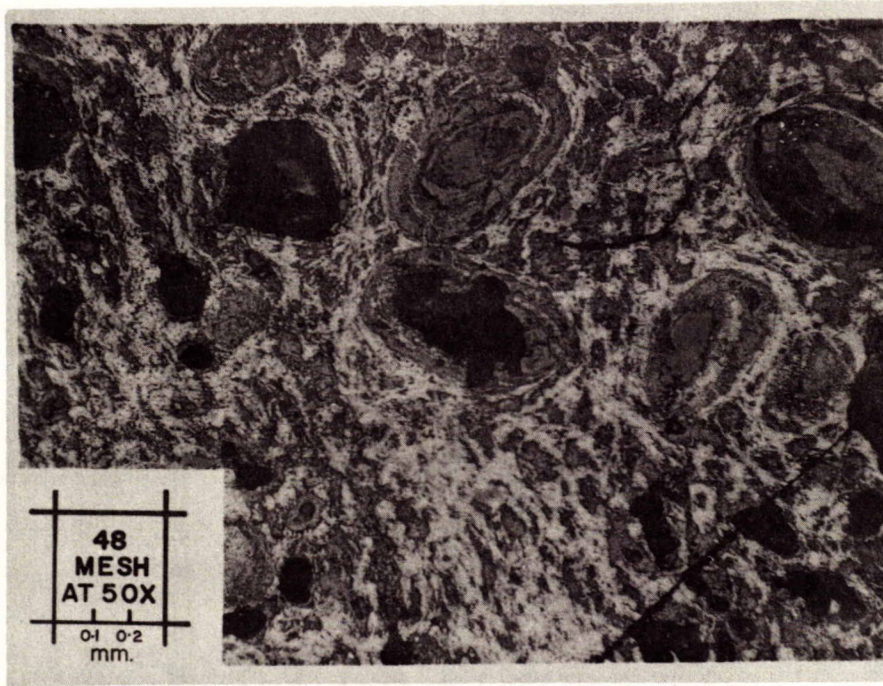
Fig. 3. - Photomicrograph of polished section of ore, showing concentrically-banded oolites in a matrix containing abundant coarse goethite (white). X-ray diffraction patterns indicate the presence of some siderite in the matrix. Pits are black.

- -
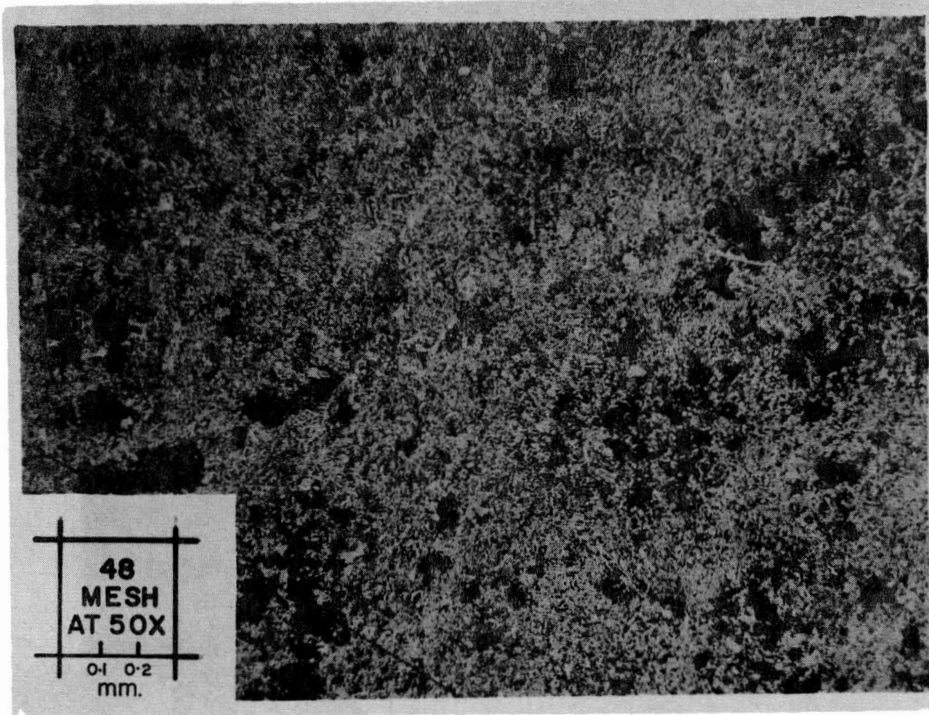
Fig. 4. - Photomicrograph of polished section of ore
consisting largely of fine-grained goethite
(white). Polishing pits are black.

- -

48
MESH
AT 50X

0·1 0·2
mm.

Fig. 5. - Photomicrograph of polished section of ore,
showing variety of oolites in a glauconitic
matrix. Some of the oolites consist largely
of goethite (white), while others have only a
narrow goethite rim. Some of the oolites have
quartz cores (smooth, grey), and an angular
quartz grain rimmed by goethite can be seen
near the centre of the photomicrograph.

- -

Fig. 6. - Photomicrograph of polished section of ore,
showing an aggregate composed of angular
quartz and calcite grains (light grey) in a
fine-grained glauconitic matrix.

- -
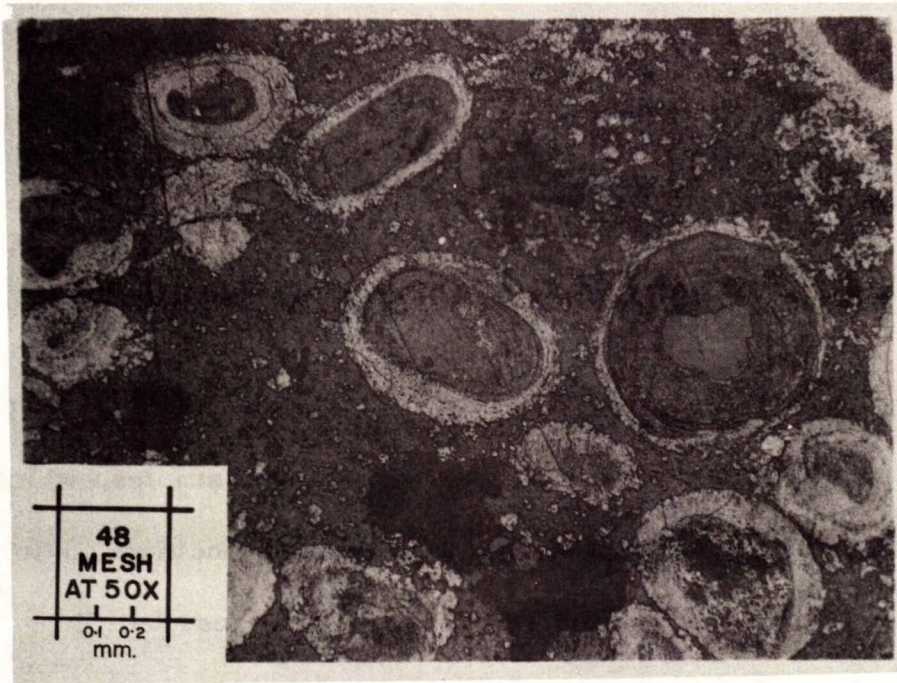
Fig. 7. - Photomicrograph of polished section of ore,
showing a variety of oolites in a matrix of
glauconite and goethite. The oolites vary
from glauconitic silicate rimmed by goethite
to solid goethite (white). The largest oolite
has a quartz core (smooth grey). Pits are
black.

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APPENDIX

THERMOGRAVIMETRIC, DIFFERENTIAL THERMAL AND X-RAY DIFFRACTION ANALYSES OF CLEAR HILLS OOLITIC IRON ORE

by

Norman F.H. Bright

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INTRODUCTION

This Appendix gives details of work done in the Physical Chemistry Section, Mineral Sciences Division, in support of the mineralogical work on two oolitic iron ore samples, which forms the subject of the main report. This work includes mainly thermogravimetric and differential thermal analyses, but, in addition, some chemical and X-ray diffraction work was done.

EXPERIMENTAL PROCEDURES

The thermogravimetric and differential thermal analyses were conducted in air, and also in a flushing carbon dioxide atmosphere. The CO_2 atmosphere served to sharpen up any reactions due to carbonate decomposition, and to suppress any reactions dependent on atmospheric oxidation, such as that of sulphide(s) or of any organic material present. The details of the techniques will not be described here as they have been adequately described in various well-known text-books and in many recent research publications. Suffice it to say here that a Stanton

thermobalance was used for the thermogravimetric work, and that, for the differential thermal analyses, an equipment of Mines Branch construction was used, embodying a palladium sample holder in a horizontal orientation, a heating rate of 12 deg C per minute, and Pt:Pt/13% Rh thermocouples for recording the differential and sample temperatures.

In order to destroy any carbonate and/or sulphide(s) and to dissolve much of the goethite and thereby concentrate the siliceous components of the ore as far as possible, for study by differential thermal analysis, a 5 g sample of the NE ore was leached in approximately 100 ml of concentrated nitric acid for 24 hr. After standing for several hours, the mixture was heated to boiling, allowed to cool and to stand overnight. After diluting with water and filtering, the residue was dried and weighed. It was found to comprise about 28% of the weight of the original sample. This residue was subjected to differential thermal analysis in an air atmosphere, and also to a qualitative emission spectroscopic analysis.

The final technique that was applied to the study of these iron ores was thermogravimetric analysis (TGA). In this technique, the changes in weight of the samples were studied as they were subjected to a pre-determined thermal programme; in this instance, heating at the rate of about 375 deg C per hour to approximately 1100°C was employed. For each material, air and CO_2 atmospheres were employed.

EXPERIMENTAL RESULTS AND INTERPRETATIONS

a. Spectrographic Analysis

The two original samples, NE and OP, when examined by qualitative emission spectroscopic analysis both gave the following results:-

Fe, Ca - major constituents

Si, Mg, Al - significant minor constituents

The leach residue from the NE ore gave the following result:-

Fe, Si - major constituents

Mg, Al - significant minor constituents

This is as would be expected from the destruction of any calcium carbonate by the HNO_3 leach.

b. Differential Thermal Analysis

The results of the differential thermal analyses are as follows:-

Ore Sample OP

Examined in air		Examined in CO$_2$	
Nature of peak	Temperature of peak	Nature of peak	Temperature of peak
Moderate endothermic	151°C	Moderate endothermic	150°C
Smaller endothermic	308°C	Smaller endothermic	309°C
Moderate endothermic	363°C	Moderate endothermic	360°C
Small, broad exothermic	438°C	--	--
Broad, moderate endothermic	560°C	Small to moderate, broad endothermic	575°C
V. small sharp endothermic	585°C	V. small sharp endothermic	579°C
Moderate endothermic	831°C	Sharp endothermic	915°C
Small endothermic	862°C	--	--

Ore Sample NE

Examined in air		Examined in CO_2	
Nature of peak	Temperature of peak	Nature of peak	Temperature of peak
Fairly large endothermic	151°C	Fairly large endothermic	138°C
Moderate endothermic	303°C	Moderate endothermic	306°C
Moderate endothermic	355°C	Moderate endothermic	360°C
Small broad exothermic	455°C	--	--
Small broad endothermic	570°C	Small broad endothermic	540°C +
V. small sharp endothermic	580°C	V. small sharp endothermic	581°C
Moderate endothermic	839°C	Sharp moderate endothermic	929°C

Ore Sample NE - Residue from HNO$_3$ leach - examined in air

Nature of peak	Temperature of peak
Moderate endothermic	135°C
Smaller endothermic	348°C
Small broad endothermic	560°C approx.
V. small sharp endothermic	581°C
Nothing further up to 1080°C	

From a consideration of the nature and position of the peaks detailed in the preceding tables, from their relative sizes and their presence or absence when the sample was examined in a carbon dioxide atmosphere, and also from their presence or absence in the case of the HNO$_3$-leached material, it is possible to draw the following conclusions:

(i) The moderately large, endothermic peaks at about 140-150°C and at about 350-360°C are both associated with the dehydration of the same material; this material is present in both samples and also in the HNO$_3$-leached material.

(ii) The moderate-sized endothermic peak at about 305-310°C is associated with the dehydration of a different material, which is not present in the HNO$_3$-leached product, but is present in both samples as received.

(iii) The broad, exothermic peak at about 440-450°C is probably associated with the oxidation of pyrite or other sulphide mineral, and/or of any organic carbonaceous material that might be present. It is observed with both ores as received, but is not present in the HNO_3-leached material.

(iv) The broad, small, endothermic peak in the 540-570°C temperature range is probably associated with the loss of chemically bound water from a clay mineral; this peak is observed in all samples.

(v) The very sharp, small endothermic peak at about 580°C, superimposed on the immediately preceding peak, is attributed to the $\alpha \rightarrow \beta$ quartz inversion and is observed in all samples.

(vi) The fairly large, endothermic peak observed at 830-840°C in the samples as received, when tested in air, and as a noticeably sharper peak at about 920-930°C when tested in CO_2, is attributed to the decomposition of calcite. As expected, this peak is not observed in the HNO_3-leached material. Calcium carbonate alone decomposes at a temperature of 950-1000°C; the fact that this peak is observed at significantly lower temperatures with these ores, is to be expected from the presence of other materials, particularly the siliceous constituents of the ores.

c. X-ray Diffraction Examinations

X-ray diffraction work was done on the samples as received, and after heating to various temperatures in the differential thermal analyses. The results of these X-ray examinations are listed below.

In assessing the relative abundance of the constituents mentioned in these lists, only the intensity of the X-ray diffraction pattern has been considered. It must be borne in mind that such factors as crystal symmetry, the presence of heavy atoms, the particle size of the material and its degree of crystallinity, the presence of amorphous material, preferred orientation and matrix effects could all play a part in affecting the validity of these assessments of relative abundances. Hence, these statements of abundances should be considered in a qualitative sense only.

Sample OP

1. <u>As received:-</u> Major constituents:- Goethite, $Fe_2O_3.xH_2O$.

Quartz, SiO_2

Small minor constituent:- Calcite, $CaCO_3$

Extra lines that could possibly correspond to small amounts of pyrite, apatite, and a micaceous material, perhaps of the glauconite type.

2. <u>After heating to 750°C in air in DTA equipment</u>

Major constituents:- Hematite, Fe_2O_3

Quartz

Small minor constituent:- Calcite

Extra lines that could possibly correspond to small amounts of apatite and a mica.

3. <u>After heating to 1055°C in air in DTA equipment</u>

Major constituent:- Hematite

Minor constituent:- Quartz

Extra lines that could possibly correspond to small amounts of lime, apatite, and feldspar.

4. <u>After heating to 1080°C in CO_2 in thermobalance (see later)</u>

Major constituent:- Hematite

Minor constituent:- Quartz

Extra lines that could possibly correspond to small amounts of apatite, feldspar and cristobalite.

<u>Sample NE</u>

1. <u>As received:</u>- Major constituent:- Goethite

Minor constituent:- Quartz

Small minor constituent:- Calcite

Extra lines that could possibly correspond to small amounts of pyrite, apatite and the same micaceous mineral.

2. <u>After heating to 720°C in air in DTA equipment</u>

Major constituent:- Hematite

Small minor constituents:- Quartz

Calcite

Extra lines that could possibly correspond to small amounts of apatite and a mica.

3. **After heating to 1060°C in air in DTA equipment**

> Major constituent:- Hematite
>
> Minor constituent:- Quartz
>
> Extra lines that could possibly correspond to small
>
> amounts of apatite, feldspar, and lime.

4. **After heating to 1240°C in air in DTA equipment**

> Major constituent:- Hematite
>
> Trace :- Quartz
>
> Extra lines that could possibly correspond to small
>
> amounts of feldspar and other undetermined materials.

5. **After heating to 1100°C in CO_2 in thermobalance (see later)**

> Major constituent:- Hematite
>
> Minor constituent:- Quartz
>
> Extra lines that could possibly correspond to small
>
> amounts of feldspar, apatite and cristobalite.

Sample NE - Residue from HNO_3 leach

> Major constituent:- Quartz
>
> Other lines that could correspond to the micaceous
>
> type of material, possibly glauconite, and other
>
> unspecified materials.

Sample NE - Residue from HNO_3 leach after heating to 1080°C in air in DTA equipment

> Major constituent:- Quartz
>
> Minor constituent:- Hematite

d. **Thermogravimetric Analyses**

> The results obtained by the use of the Stanton thermo-

balance with these samples are as detailed in the following tables.

1. Sample OP, heated in air

Total loss in weight = 17.55% (based on as-received weight)

Highest temperature used = 1130°C

Temperature Range (deg C)	Observation	% Loss in weight (thermogravimetric)	Remarks
100-360	Large, rapid weight loss.	12.75%	Not resolvable into discrete stages, although indication of a complex phenomenon, particularly above 250°C.
360-710	Slower, continuous weight loss.	2.47%	- -
710-925	More rapid weight loss.	2.29%	Loss mostly completed by 820°C.
925-1130	- -	- -	No further weight change.

By comparing these results with the DTA results already given for this material in air, it will be seen that the first major loss in weight corresponds to the endothermic peaks observed at 151°C, 308°C and 363°C. The slow loss in the range 360°C to 710°C corresponds to the broad flat endothermic peak at 560°C, while the final loss in the 710°C to 925°C corresponds to the endothermic peak(s) at 830-860°C. The major loss is probably due to water from the goethite and any other hydrous mineral present, the second loss to combined water from the clay mineral, and the final loss is due to CO_2 from the carbonate present.

2. <u>Sample OP, heated in CO_2</u>

Total loss in weight = 17.62% (based on as-received weight)

Highest temperature used = 1150°C

Temperature Range (deg C)	Observation	% Loss in weight (thermogravimetric)	Remarks
100-355	Rapid weight loss.	12.40%	Probably complex at upper end of range.
355-720	Slow loss.	2.40%	Possibly also complex.
720-950	More rapid loss.	2.40%	- -
950-1150	- -	- -	No further change in weight.

The general form of the curve and the location of the changes in slope followed very closely the pattern of the results obtained for this material heated in air. The figures for the weight losses are very similar to those obtained in the air test and the same diagnosis as to their significance is considered to apply.

3. Sample NE, heated in air

Total loss in weight = 19.5% (based on as-received weight)

Highest temperature used = 1095°C

Temperature Range (deg C)	Observation	% Loss in weight (thermogravimetric)	Remarks
100-360	Rapid weight loss.	13.52%	Probably complex in the range 240-360°C, but not resolvable into discrete stages.
360-710	Slower loss.	3.13%	Probably also complex.
710-910	More rapid loss.	2.54%	Mostly complete at 820°C.
910-1095	- -	- -	No further weight change.

Again, the pattern followed by the TGA trace showed the same form and characteristics as those already described.

4. Sample NE, heated in CO_2

Total loss in weight = 19.45% (based on as-received weight)

Highest temperature used = 1180°C

Temperature Range (deg C)	Observation	% Loss in weight (thermogravimetric)	Remarks
100-350	Rapid weight loss.	13.11%	Not resolvable into discrete stages.
350-720	Slower loss.	3.43%	Possibly also complex, with one stage virtually complete at 650°C.
720-950	More rapid loss.	2.64%	- -
950-1180	- -	- -	No further loss in weight.

In all cases, the form of the curve followed very much
the same pattern and the same interpretations apply throughout.
It will be observed that, for each specimen, the aggregate of the
gravimetric weight losses was quite close to the direct total weight
loss obtained by independent measurement of the initial and final
weights of the samples. This is good confirmation of the reliability
of the above data.

DISCUSSION

A full quantitative interpretation of the thermo-
gravimetric data is rendered impossible by several factors:
firstly, the lack of resolution of the various decomposition stages;
secondly, the indeterminate composition, particularly as regards
degree of hydration, of some of the minerals known or suspected
to be present. This consideration applies in particular to the
micaceous mineral which is present and to the goethite, both of
which might have a variable proportion of water of hydration.
In addition, the amount of other elements in the micaceous mineral
e.g., the degree of substitution of alkalis for lime, of magnesia
for ferrous iron, and of alumina for ferric iron, are all also
strictly unknown quantities, although a reasonable typical formula for a
glauconite is assumed for this material in calculating the mineral
balance in the body of the report. All these factors would have a

bearing on the weight losses occurring in the various temperature ranges.

From the differential thermal analysis traces, it appears that both the OP and NE samples contain quartz as a significant minor constituent, with the amount in the OP sample being larger than the amount in the NE sample; this is supported by the chemical analysis quoted in the body of the report, viz., 9.15% as against 4.73%.

If the losses of weight in the temperature range 720°C to 1100°C are due solely to CO_2 evolution from calcium carbonate, then calculation shows that the percentages of $CaCO_3$ in the two samples are as follows:-

Sample	Thermogravimetric $CaCO_3$ % content	Direct Chemical $CaCO_3$ % content
OP	5.34%	5.84%
NE	5.89%	5.80%

These figures show very satisfactory agreement.

The amount of water lost from the clay mineral and from the apatite in the range 360-720°C is about 2.44% for the OP sample and 3.28% for the NE sample; these figures must be approximate only owing to the difficulty of deciding where the various loss stages start and finish. This H_2O loss is consistent with the figure of about 20% quoted for the micaceous mineral content of the two samples, assuming this mineral to be of a

glauconitic mica type.

The low-temperature water losses (below 350-360°C) are about 12.58% for the OP sample and about 13.32% for the NE sample. If we assume that the ferric iron contents, calculated as Fe_2O_3, are as quoted in the body of the report, and that the formula of the goethite is strictly stoichiometric, viz., $Fe_2O_3 \cdot H_2O$, then this will account for 5.21% and 5.38% of the H_2O loss, respectively.

As mentioned above, part of the H_2O loss in this temperature range appears to be from one constituent of the ore and part from a different constituent. It is considered that the residual water losses not accounted for by the goethite, viz., 7.37% and 7.94% respectively are due partly to loss from a hydrated alumina, possibly gibbsite, and partly to water which is attached to the goethite in proportions in excess of the stoichiometric $Fe_2O_3 \cdot H_2O$ formula. This is in accord with the rather diffuse, ill-defined X-ray diffraction pattern exhibited by this constituent of the ore.

In conclusion, it may be stated that the X-ray diffraction, thermogravimetric, differential thermal, and emission spectrographic data are all consistent with the mineralogical findings detailed in the body of the report and with the mineral compositions calculated from the chemical analyses quoted therein.

EHN:NFHB:EEL/DV