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MINERALOGICAL CHARACTERISTICS OF AN OOLITIC IRON DEPOSIT IN THE PEACE RIVER DISTRICT, ALBERTA*

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ABSTRACT

A minette-type oolitic iron deposit in the Peace River district, Alberta, occurs as flat-lying ironstone beds up to 10.6 m thick which contain 32-34 wt. % Fe *in situ* or 36–38 wt. % Fe after drying for 3 hours at 105°C. The ironstone beds consist of ooliths, siderite, and clastic material embedded in a clastic matrix and ferruginous cement. The ooliths consist of concentric layers of intimately intergrown goethite, nontronite, and amorphous phosphate around cores which are generally quartz. The goethite contains 46–56 wt. % Fe (mean 49 wt. %) and about 1.6 wt. % P_2O_5, the nontronite contains about 36.7 wt. % Fe and 0.8 wt. % P_2O_5, and the amorphous phosphate contains 4.4–22.9 wt. % Fe and 15.4–35.0 wt. % P_2O_5. The clastic matrix and cement are largely a ferruginous opal that contains 24 wt. % Fe. About 44% of the Fe in the ironstone beds occurs as goethite, 35% as nontronite, 13% as ferruginous opal, and 8% as siderite. The ironstone beds *in situ* are greenish black, difficult to break, and have high water and ferrous iron contents. Upon exposure to atmospheric conditions the ferrous iron is apparently oxidized and causes the material to turn brown. Concurrent with oxidation, the adsorbed water escapes and causes shrinkage cracks in ferruginous opal.

SOMMAIRE

Un gisement de fer oolitique du type minette, situé dans la région de Peace River, en Alberta, se présente sous forme de couches ferrifères horizontales dont l'épaisseur va jusqu'à 10.6 m. La teneur en fer varie de 32 à 34% en poids *in situ*, soit de 36 à 38% après séchage de trois heures à 105°C. Les couches ferrifères se composent d'oolites, de sidérite et d'un matériau clastique dans une pâte clastique et un ciment ferrugineux. Les oolites sont formés d'une fine intercroissance de goethite, nontronite et phosphate amorphe, en couches concentriques autour d'un noyau généralement de quartz. Les teneurs, en poids, sont les suivantes: 46–56% Fe (moyenne, 49%) et ~1.6% P_2O_5; nontronite: ~36.7% Fe et 0.8% P_2O_5; phosphate amorphe: 4.4–22.9% Fe et 15.4–35.0% P_2O_5. La pâte clastique et le ciment ferrugineux consistent principalement en opale ferrugineuse tenant 24% de fer en poids. Le fer se répartit comme suit: 44% dans la goethite, 35% dans la nontronite, 13% dans l'opale et 8% dans la sidérite. Les couches ferrifères, d'un noir verdâtre *in situ*, sont difficiles à briser; elles contiennent une forte proportion d'eau et de fer ferreux. Ce dernier s'oxyde à l'air et le minerai passe au brun. Au cours de cette oxydation, le départ de l'eau adsorbée provoque des fissures de retrait dans l'opale ferrugineuse.

INTRODUCTION

Oolitic iron deposits in the Clear Hills area, Peace River district, Alberta were discovered in 1924 (Bertram & Mellon 1975), but were not seriously investigated as a source of iron until they were encountered in 1953 during exploration for oil and gas. However, the deposits have not been brought into production because of metallurgical problems in recovering the iron.

Renewed interest in establishing a steel industry in western Canada resulted in an agreement between the Provincial Government of Alberta and the Federal Government of Canada to evaluate the potential of the Peace River oolitic iron deposits. The evaluation included an assessment of the deposits by Krupp Industries Limited of Germany, studies of the mineralogy, ore dressing and smelting of the ore by CANMET, and ore dressing research by CANMET and Alberta Research Council. This paper gives the characteristics and mineralogy of the deposits. The mineralogy was determined from material obtained through a sampling program by the Alberta Research Council. The geological setting of the deposits summarizes reported geological data (Kidd 1959; Mellon 1962; Green & Mellon 1962; Bertram & Mellon 1975), and the chemical analyses are from unpublished industrial, Alberta Research Council, and Mines Branch reports.

LOCATION AND GENERAL GEOLOGY

The Peace River iron deposits are in northestern Alberta, about 80 km northwest of Peace River, and about 485 km northwest of Edmon-

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*Mineral Research Program, Processing Contribution No. 27.

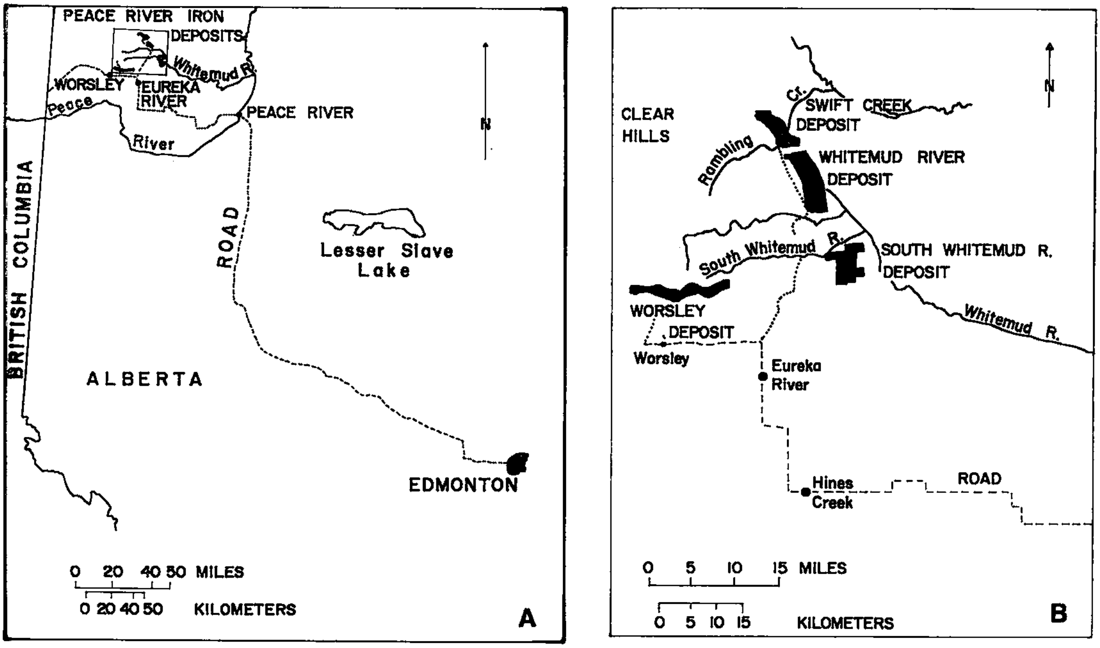


FIG. 1. Location (A) and distribution (B) of the Peace River iron deposits.

ton, Alberta (Fig. 1A). They are in the Clear Hills area, a gently rolling upland 1100 m above sea level, that rises from the surrounding wooded plain (about 750 m above sea level), and is dissected by streams. Oolitic ironstone beds are exposed along streams at 788 m above sea level near the eastern margin of Clear Hills (Swift Creek deposit), and at 795 to 830 m above sea level at the southern margin near Worsley (Mellon 1962).

The area is underlain by gently dipping Late Cretaceous sandstones and shales, and is covered by thin deposits of unconsolidated gravel, sand, and clay largely of glacial origin. The strata are soft and tend to slump; thus, bedrock exposures are scarce and are confined largely to small cuts along recently incised stream valleys (Green & Mellon 1962). The Cretaceous rocks form a sequence of alternating marine and nonmarine sandstones and shales that have been divided into six formational units (Green & Mellon 1962; Table 1). The main oolitic ironstone beds are in the Bad Heart sandstone, and minor ones are intercalated with sandstone of the Kaskapau Formation. The ironstone beds of the Bad Heart sandstone are locally up to 10.5 m thick and form iron deposits. According to Hamilton (1974) there are four known iron deposits: Swift Creek, Whitemud River, South Whitemud River, and Worsley (Fig. 1B).

A drilling program between 1953 and 1962 indicated that the oolitic ironstone horizons in the Swift Creek, Whitemud River, and South Whitemud River deposits are 4.5 to 10.5 m thick, and in the Worsley deposit are up to 9 m

TABLE 1. UPPER CRETACEOUS STRATA IN CLEAR HILLS
(from Green & Mellon 1962)

ROCK UNIT			THICKNESS (M)	LITHOLOGY
Wapiti Formation			0-120	soft, whitish sandstone; grey, blocky, carbonaceous shale; thin coal seams (continental)
Smoky River Group	Puskwaskau Formation		90-180	dark grey, fissile shale (marine)
	Bad Heart Sandstone		0-9	green, ferruginous, oolitic sandstone and mudstone (marine)
	Kaskapau Formation	upper member	45-125	dark grey, fissile shale (marine)
		lower member	12-147	whitish sandstone; grey, sandy shale; oolitic siderite (marine)
Dunvegan Formation			150-235	soft, grey sandstone with calc. concentrations; grey, silty, carbonaceous shale (deltaic)
Shaftesbury Formation		upper member	99-165	grey, silty shale; thin, laminated siltstone (marine)
		lower member	180-320	black, fissile shale; numerous fish scales (marine)

TABLE 2. STRATIGRAPHY OF THE OOLITIC IRON HORIZON*

Depth from Top of Horizon in Metres	Description
0 to 0.15	Earthy, very crumbly, rust-colored material.
0.15 to 0.6	Friable, brittle, reddish brown material that rips easily with a bulldozer; small pieces disintegrate after exposure to air for several hours.
0.6 to 0.9	Reddish to greenish brown material, has a sub-metallic lustre on broken surfaces.
0.9 to 3.4	Dark green to black, friable, brittle, dense; oolitic texture evident on broken surfaces; difficult to rip with a bulldozer; 60 vol.% ooliths.
3.4 to 6.4	Dark green to black, subconcoidal fracture, breaks across oolitic grains rather than around them; cannot be ripped with a bulldozer; 60 vol.% ooliths.
6.4 to 8.2	Dark green to black; 20 vol.% ooliths; high mudstone content.

*Summarized from Hamilton (1974).

TABLE 3. SAMPLES OF OOLITIC IRON ORE

Sample No.	Barrel No.	Depth Interval of Sample (metres)
1	1 to 21	1 to 1.5
2	26 to 46	1.5 to 3.0
3	51 to 71	3.0 to 4.5
4	75 to 93	4.5 to 5.8
5	94 to 96 and 101 to 114	5.8 to 7.0
6	116 to 122 and 126 to 135	7.0 to 8.2

thick, but average 2 m (Kidd 1959). Proven ore reserves are 206 million tonnes, and combined probable and possible ore reserves are 815 million tonnes (Bertram & Mellon 1975).

Hamilton (1974) reported that the ironstone beds of the Swift Creek deposit are massive, with only a vaguely defined stratification near the top and bottom of the horizon. The stratigraphic sequence is summarized in Table 2. The oolitic ironstone beds have a sharp contact with the underlying bluish grey shale.

Bulk samples were taken from the Swift Creek deposit in March 1974 under the supervision of W. H. Hamilton and A. Bosman, Alberta Research Council. The sample site (Section 1, Tp 91, R 5, W 6th Mer) was about 182 m west of Rambling Creek, in the midst of closely spaced (400 m) test drilling, and at a point where the overburden is 15 m thick. The overburden was excavated with a bulldozer, and a trench 9 m deep was cut into the oolitic ironstone bed. Six samples of minus 15 cm material, representing a vertical cross section through the deposit, arrived at CANMET, Ottawa on April 18, 1974 in 115 barrels (Table 3).

CHEMICAL AND THERMOGRAVIMETRIC ANALYSES

Chemical analytical results can vary greatly for the same sample because this material expels water on exposure to dry atmospheric con-

TABLE 4. CHEMICAL COMPOSITION OF ORE

wt.%	From Hamilton (1974) Sample 1	2	3	4	5	6	From Krupp (1975) 0-1.5 m	1.5-3 m	3-4.5 m	4.5-6 m	6-7.5 m	From Nickel *et al.* (1960) NE	OP
Fe_2O_3	39.2	29.6	28.2	26.3	33.1	28.8	50.4	48.2	47.7	43.8	29.7	48.0	47.0
FeO	9.6	17.6	20.6	21.9	10.8	13.8	4.5	5.3	5.1	6.7	13.4	1.3	0.7
SiO_2	16.6	17.4	17.8	17.3	17.9	19.3	21.4	23.7	24.6	27.6	31.5	16.6	22.0
Al_2O_3	5.7	5.3	5.3	4.9	4.7	4.7	5.0	5.0	5.1	5.2	5.8	8.3	8.4
CaO	2.0	1.6	1.4	1.6	1.9	2.0	1.8	1.7	1.5	1.3	2.1	4.3	4.7
MgO	1.0	0.9	0.9	1.0	1.1	1.3	1.0	1.0	1.0	0.9	1.4	2.7	1.8
P_2O_5	1.6	1.8	1.3	1.4	1.4	1.4	1.9	1.8	1.7	1.5	1.6	0.8	0.8
S	0.03	0.02	0.02	0.03	0.03	0.07	0.04	0.03	0.03	0.03	0.14	0.11	0.11
Na_2O							0.2	0.2	0.2	0.2	0.2	0.1	0.1
K_2O							0.5	0.4	0.5	0.5	0.6	0.6	0.7
MnO	0.7	0.6	0.7	1.1	0.9	0.8						0.1	0.1
TiO_2												0.3	0.4
V	0.2	0.2	0.2	0.2	0.2	0.2							
CO_2												3.3	2.9
H_2O												13.7	10.4
L.O.I.	24.3	24.3	24.1	24.0	25.1	28.9	13.2	12.8	12.6	12.4	13.6		
Total	100.7	99.3	100.5	99.6	97.1	101.3	99.9	100.1	100.0	100.1	100.0	100.2	99.1
Fe	33.8	32.2	33.3	32.7	30.15	28.0	38.7	37.8	37.4	35.9	31.2	34.6	32.7

L.O.I. = loss on ignition NE & OP = sample nos.

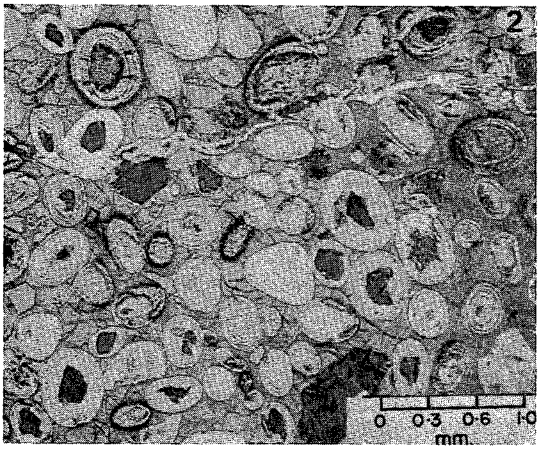


FIG. 2. Ooliths and minor siderite (light grey) embedded in a matrix of clasts and ferruginous opal. The ooliths contain variable quantities of goethite (white) and some have quartz cores (dark grey). The ferruginous opal shows shrinkage cracks, and a goethite veinlet (white) is in the middle of the photograph.

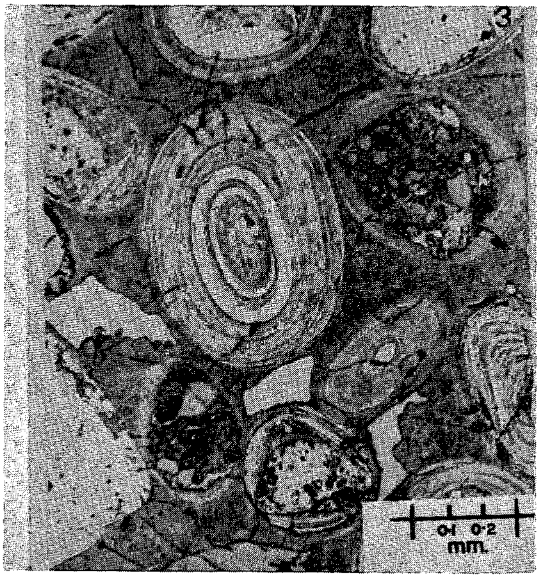


FIG. 3. Ooliths composed of concentric layers around cores. The matrix material with shrinkage cracks is ferruginous opal, and irregular-shaped, light grey material is siderite. Two ooliths have cores of clastic fragments.

ditions and re-absorbs it under humid conditions. One sample from barrel 38, as received in a sealed plastic bag, contained 22 wt. % water and 31.9 wt. % Fe. After drying for 5 hours at 150°C, 15.5 wt. % was lost and the sample assayed 37.5 wt. % Fe.

One set of chemical analyses was performed by Alberta Research Council for material as received in plastic bags and considered representative of Samples 1 to 6 inclusive (Hamilton 1974), and another set was analyzed by Krupp Industries Limited for partly dried samples taken from the same site at depth intervals (in metres) of 0 to 1.5, 1.5 to 3, 3 to 4.5, 4.5 to 6, and 6 to 7.5 (Table 4). The results show higher water and FeO contents, and lower amounts of all other elements for samples as received in plastic bags. Analyses for two unlocated, highly oxidized samples (Nickel *et al.* 1960) are included.

A thermogravimetric analysis was performed by W. S. Bowman, Physical Sciences Laboratory, on a sample from barrel 38, as received. The results show a weight loss of 16.5% from 20 to 175°C (adsorbed water), another weight loss of 4.5% at 385°C (OH in goethite), a further loss of 3.8 wt. % between 385 and 600°C (CO_2 and H_2O) and a loss of 1.2 wt. % from 600 to 1060°C for a total loss of 26 wt. %.

GENERAL MINERALOGY

The samples are brownish, earthy, friable, and composed of ooliths, siderite, and earthy fragments embedded in a clastic matrix and ferruginous cement (Fig. 2). The clastic matrix, described in detail by Mellon (1962), consists of illite and nontronite embedded in ferruginous opal, and the ferruginous cement is ferruginous opal.

The ooliths vary in shape from spheroidal to ellipsoidal, are 50 to 1,000 microns in diameter (Table 5), and consist of concentric layers of goethite, nontronite, and an amorphous phosphate in variable quantities around cores (Fig. 3). The cores are quartz, amorphous phosphate, massive goethite, parts of broken ooliths, clastic fragments and magnetite. An average oolith consists of about 45 wt. % goethite, 45 wt. % nontronite, 5 wt. % quartz, and 5 wt. % amorphous phosphate, but large variations are present. The concentric layers in some ooliths are largely goethite, whereas in others they are almost wholly nontronite. In this paper, ooliths with predominantly goethite layers will be referred to as goethite ooliths, those with nontronite layers as nontronite ooliths, and ooliths with interlayered goethite and nontronite will be referred to as layered ooliths. Goethite ooliths represent about 10% of the ooliths in the ironstone horizon but are most abundant in the top section. Nontronite ooliths were found only in Sample 6 (7 to 8 m section), whereas layered ooliths are abundant throughout the horizon. An electron microprobe trace across a layered oolith shows variable

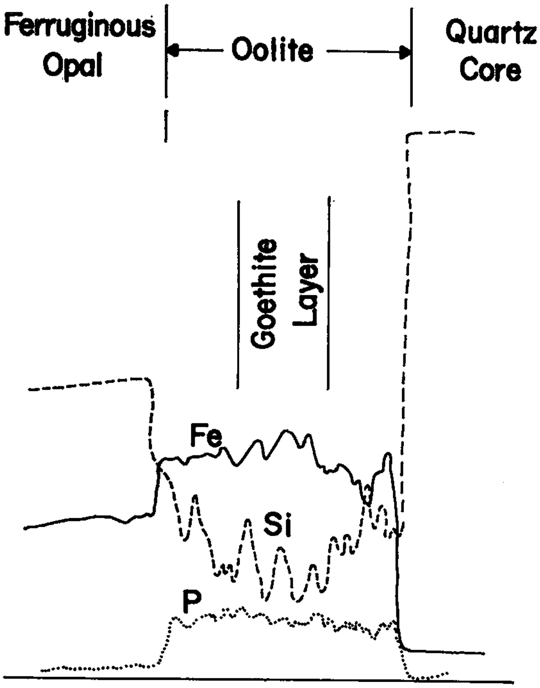


FIG. 4. Electron microprobe scan for Fe, Si, and P across the layered oolith of Figure 7.

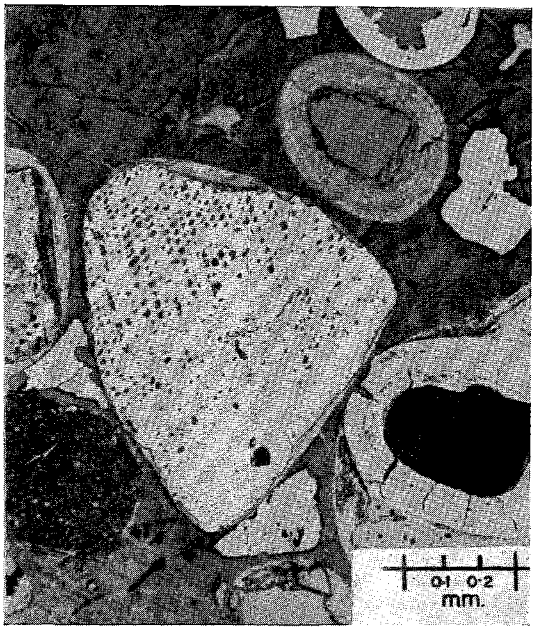


FIG. 5. Ooliths, and goethite with the cellular appearance of a fossil, in matrix material. The matrix is mainly ferruginous opal, but the pitted matrix in the upper and lower left-hand corner is clastic.

quantities of Fe and Si and nearly uniform P (Fig. 4). The highest amount of Fe is in the goethite layer, and the highest amount of Si is in the nontronite layer. It is significant that in addition to the nearly uniform phosphorus content in the ooliths, a few isolated phosphorus-rich zones occur near some oolith cores and interstitial to some goethite and nontronite layers (see section on amorphous phosphate).

Mineral contents of Samples 1 to 6, crushed to minus 14 mesh and blended, were determined by Quantimet image analysis of polished sections and the data converted to wt. % (Table 6). Table 6 shows that the goethite content decreases with depth, whereas siderite, quartz, and ferruginous opal increase. Mellon (1962) reported compositions, determined by grain count, for samples of material from the Swift Creek deposit. His data, converted to wt. %, give

TABLE 5. SIZE ANALYSIS OF OOLITHS AND MINERALS**

Size (in microns)	Ooliths (Sample 2)wt.%	Goethite* Sample 2 wt.%	Goethite* Samples 1-6 wt.%	Quartz wt.%	Siderite wt.%
plus 823	15				
833 to 580	7	4	3	6	
580 to 417	26	6	2	10	
417 to 295	10	4	2	10	3
295 to 209	14	4	1	13	5
209 to 147	10	3	2	10	7
147 to 104	7	6	3	10	10
104 to 74	7	11	2	12	10
74 to 52	3	7	5	10	15
52 to 44	1	0	10	6	9
44 to 37		2	8	6	9
37 to 26		11	17	7	16
26 to 18.5		5	14		16
18.5 to 13.1		5	10		
13.1 to 7.8		9	10		
7.8 to 2.3		13	9		
minus 2.3		10	2		
TOTAL	100	100	100	100	100

*All goethite larger than 100 microns is as massive ooliths. The rest occurs as geothite layers in ooliths. The size refers to diameters of ooliths or widths of geothite layers. For Sample 2, 27% of the goethite occurs as ooliths and 73% as goethite layers; for the Samples 1-6, 13% occurs as ooliths and 87% as goethite layers.
**From Petruk et al. (1974), and Petruk (1976).

TABLE 6. QUANTITIES OF MINERALS AND OOLITHS IN SAMPLES 1 to 6

Sample No.	1 wt.%	2 wt.%	3 wt.%	4 wt.%	5 wt.%	6 wt.%	Av. 1-6 wt.%
Ooliths	78	78	68	68	63	58	75
Geothite	30	33	32	27	27	13	31
Nontronite-goethite	28	27	25	33	18	10	37
Nontronite	14	11	7	4	11	28	
Opal	8	10	15	16	15	21	14
Siderite	8	8	7	6	10	12	7
Quartz	6	5	8	8	13	10	5
Phosphate (est.)	3	3	3	3	3	3	3
Illite (est.)	3	3	3	3	3	3	3
Total	100	100	100	100	100	100	100

TABLE 7. PARTIAL COMPOSITIONS OF MINERALS

Element	Goethite			Nontronite-Goethite	Nontronite	Opal	Phosphate				Illite		Siderite
wt.%	Massive m.c.	Spongy m	Layer in Oolith m	m	m.c.	m.c.	1 m	2 m	3 m	4 m	1 m	2 m	m
FeO					3.0								59.6
Fe_2O_3	80.1	71.3	65.9.	56.9	48.3	34.1	6.1	11.2	13.9	32.8	36.5	40.7	
SiO_2	2.0	12.2	9.7	19.5	21.0	35.3	---	8.1	2.8	9.3	34.8	34.1	
Al_2O_3	2.0	4.6	5.3	5.4	4.9	5.2	---	3.0	2.0	5.1	10.1	11.8	
CaO	0.1	0.4	0.5	0.2	0.2	2.1	44.6	42.9	38.8	21.2	1.9	0.6	0.9
MgO	---	---	---	---	---	---	---				---	---	
P_2O_5	1.6	1.7	1.5	0.9	0.8	---	35.0	29.2	27.1	15.4	---	---	
K_2O	---	0.3	---	---	---	---	---	1.0	0.3	0.6	0.5	0.8	
H_2O	14.1	---	---	---	3.5	6.9	---						
H_2O^+	---	---	---	---	15.8	10.0							
Total	99.9	90.5	82.9	82.9	97.9	93.6	85.7	95.4	84.9	84.4	83.8	88.0	60.5
Fe	56	49.9	46.1	39.8	36.7	23.9	4.3	7.8	9.7	22.9	25.5	28.5	46.3

H_2O - water driven off above 175°C

H_2O^+ - water driven off between 20 and 175°C

* nontronite should contain about 29 wt.% Fe_2O_3 (Isophording 1975)

m - microprobe analyses

m.c. - combination of microprobe and chemical analyses

68 wt.% oolites at the top of the ironstone horizon, and 47 wt.% for the bottom 1.5 m section of the horizon.

DETAILED MINERALOGY

Goethite

Goethite occurs as concentric layers 1 to 75 microns wide in layered ooliths, and as goethite ooliths larger than 100 microns in diameter. Goethite proportions and size distributions are included in Table 5. Some of the goethite is massive, some is disseminated in nontronite, some has inclusions of nontronite and quartz and has a spongy appearance (Fig. 6), and traces occur in the form of fossils (Fig. 5). The goethite contains several elements, but the quantities vary (Table 7). An average goethite from this deposit contains about 49 wt.% Fe. The goethite gives distinct X-ray diffraction and infrared patterns. Its specific gravity, determined with heavy liquids, ranges from 3.65 (spongy goethite) to 3.95 (massive goethite), with the mean being near 3.8.

TABLE 8. DISTRIBUTION OF ELEMENTS IN SAMPLE 3

MINERALS	Elements or oxides (wt.%)							
	Fe	SiO_2	Al_2O_3	CaO	P_2O_5	MnO	K_2O	MgO
goethite	16.0	3.9	1.5	0.13	0.54	0.06	0.10	---
nontronite-goethite	10.0	4.9	1.4	0.05	0.23	?	?	?
P.R. nontronite	2.6	1.5	0.3	0.01	0.06	?	?	?
ferruginous opal	3.6	5.3	0.8	0.32	---	---	---	---
siderite	3.2	---	---	0.06	---	?	?	?
quartz	---	8.0	---	---	---	---	---	---
illite	0.9	1.0	0.4	0.02	---	---	0.02	?
phosphate	0.2	0.2	0.1	1.29	0.88		0.03	---
calcite	---	---	---	tr	---	---	---	---
calculated chemical composition (Total)	36.5	24.8	4.5	1.88	1.71	0.06	0.15	?
analyzed chemical comp. (Table 4 - Krupp 1975)	37.4	24.6	5.1	1.5	1.7	0.7	0.5	1.0

FIGS. 6-10. Photographs, electron backscatter diagrams (EBS), and X-ray scanning diagrams for Ca, and P. Fig. 6: spongy goethite. Fig. 7: part of a layered oolith with a quartz core. Note that the goethite layer (white) has uniform Ca and P contents. The grey areas in the oolith are P.R. nontronite. The black line represents the position for the scan shown in Figure 4. Fig. 8: a nontronite oolith with a quartz core. Fig. 9: an oolith with a phosphate core. The wide layer in the centre of the oolith is mainly nontronite-goethite. Fig. 10: an oolith containing phosphate interstitial to the concentric layers in ooliths. The arrow indicates oolith analyzed.

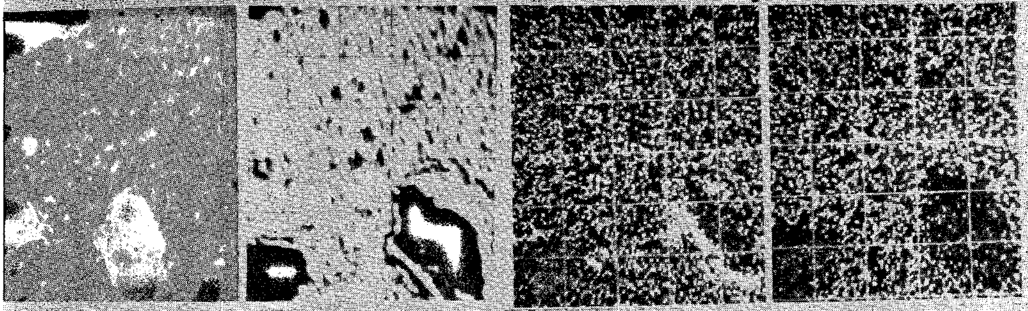
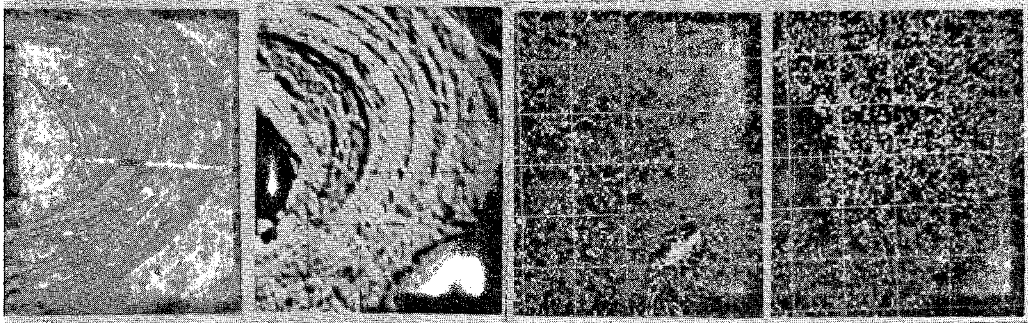


Fig. 6



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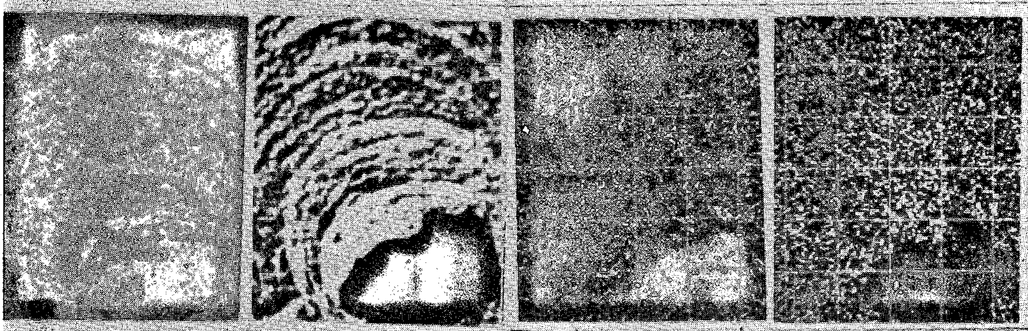

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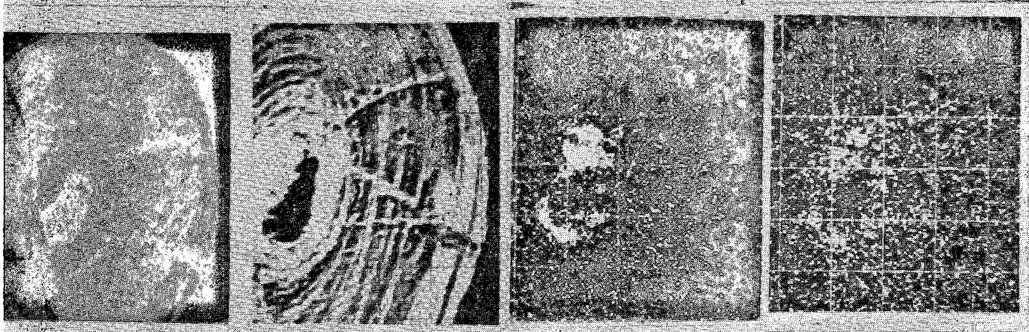

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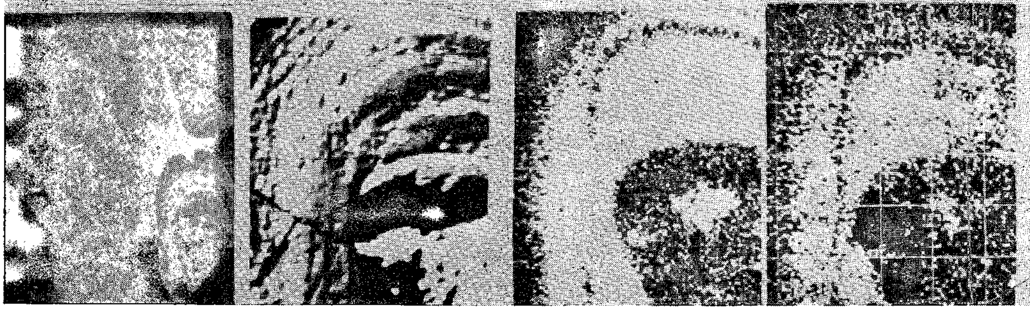

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Peace River nontronite (P.R. nontronite)

The material that is interlayered with goethite in layered ooliths (Fig. 7), and is the main constituent of nontronite ooliths (Fig. 8), will be referred to in the remainder of this paper as Peace River nontronite. It is amorphous to X-ray diffraction but gives a nontronite-like infrared pattern, and a fraction of the crystallites examined by transmission electron microscopy gave nontronite diffraction patterns. Electron microprobe analyses (Table 7) gave anomalously high Fe values attributable to goethite contamination as confirmed by X-ray diffraction studies. The goethite is so fine-grained that it could not be seen at 100× with oil immersion. This indicates that the P.R. nontronite is a mixture of sub-microscopic goethite and amorphous nontronite-like material. The specific gravity of the P.R. nontronite was determined with heavy liquids as 2.5 to 2.7 (mean 2.6). Electron microscope photographs show that the material has a basal cleavage. Mössbauer studies indicate that ~92% of the Fe in partly dried P.R. nontronite is Fe^{3+}, that much of it occurs as goethite, and that ~8% of the Fe is Fe^{2+} in octahedral coordination. P.R. nontronite heated to 1,000°C and cooled slowly gave a residue of hematite and amorphous material. Details of the mineral are reported in another paper (Petruk *et al.* 1977).

Nontronite-goethite

Some material that has a reflectivity between goethite and P.R. nontronite occurs as concentric layers in ooliths. This material consists of P.R. nontronite and submicroscopic goethite. The material is referred to in this paper as nontronite–goethite. Its composition varies from that of P.R. nontronite to that of goethite; average nontronite–goethite contains about 39 wt. % Fe. A partial microprobe analysis of one nontronite–goethite layer is included in Table 7.

Amorphous phosphate (apatite)

Diffuse phosphorus-rich zones, 1 to 50 microns in diameter, occur near oolith cores (Fig. 9), interstitial to the concentric goethite and P.R. nontronite layers, and as fragments (Fig. 10). These zones contain variable amounts of CaO and P_2O_5 (Table 7) and are mixtures of a Ca-rich phosphate, goethite and silicates. The phosphate is largely amorphous but one grain gave a weak X-ray diffraction pattern of apatite. Furthermore, phosphate fragments have a Ca:P ratio similar to that of apatite. Goethite and P.R. nontronite contain 1.6 and 0.8 wt. % P_2O_5 respectively, and every gradation between 0.8 and 35.0 wt. % P_2O_5 is present in the ooliths.

Ferruginous opal

The main matrix material is ferruginous opal which occurs as a cement between the ooliths and in the clastic matrix. The ferruginous opal is pale yellowish material that is isotropic in transmitted light and amorphous to X-ray diffraction, but gives the infrared pattern of opal. The mineral absorbs water in humid conditions, and expels it upon drying, producing shrinkage cracks. Its specific gravity, determined by heavy liquids, is about 2.0, and its approximate composition is given in Table 7. Mössbauer studies show that the Fe is largely in the ferric state. Details of the mineral are reported in another paper (Petruk *et al.* this issue).

Unidentified silicates

Grains of silicate phases, about 3 vol.% of the ore, are present in the clastic matrix. The grains consist of the following elements, in approximate order of abundance (each group refers to elements found in individual grains) SiAlK, SiFeAlK, SiAlFeKCa, SiFeAlMgK, SiFeMgAlKCa, SiFeMgAl, and SiFeAlMg. Electron probe compositions of two grains are included in Table 7. X-ray diffraction shows that the grains are largely amorphous but a very weak peak was observed at 9.6Å. Transmission electron microscopy shows interplanar spacings of 4.46, 3.9, 2.84, 2.55 and 2.24Å for a grain that contains SiFeAlCa. This diffraction pattern corresponds to that of illite.

Other minerals

Siderite occurs as irregular grains in ferruginous opal outside the ooliths (Figs. 2 and 3). A partial electron microprobe composition is included in Table 7. Semi-quantitative electron microscope analyses show that the mineral contains a trace of Mn, but this element was not analyzed for with the electron microprobe. The size distribution of siderite grains in Sample 2 is included in Table 5.

Trace amounts of *calcite* were detected by X-ray diffraction of ground material, and calcite grains were observed at the cores of ooliths.

Quartz occurs mainly as large grains (Table 5) at cores of ooliths, but some is present as minute grains in the earthy matrix.

Clumps of minute framboidal *pyrite* grains (1–5 microns in diameter) occur in the ferruginous opal. The grains form a circular pattern and have the appearance of a cross section of a coral about 10 microns in diameter. It is likely that all the sulfur reported in Table 4 can be accounted for by pyrite.

Mellon (1962) reported *feldspar* as large and minute grains but none was found in this study.

DISTRIBUTION OF ELEMENTS

Distribution of elements among the minerals was calculated for Sample 3 (3 to 4.5 m section) from the mineral quantities in the sample and chemical compositions of the minerals, using the spongy goethite composition of Table 7 for goethite, and the composition of phosphate No. 2 for the phosphate. The results (Table 8), show that the chemical composition determined by adding the quantities of each element or oxide attributed to each mineral compares well with the analyzed values for all elements except the trace elements Mn, K, and Mg. These trace elements could not be properly allocated to minerals due to insufficient data. Mn is a minor constituent of goethite and siderite, but only goethite was analyzed for the element; K was determined in several silicate and spongy goethite grains, but not in other minerals; Mg was detected in the illite grains with an electron microscope but the quantities were not determined. Na, V, and Ti were detected by chemical analysis of the ore but the distribution among minerals was not determined.

Table 8 shows that iron is in all minerals except quartz, i.e. of 36.5 wt.% Fe in the sample, 16 wt. % occurs as goethite, 10 wt. % as nontronite–goethite, 2.6 wt.% as P.R. nontronite, 3.6 wt.% as ferruginous opal, 3.2 wt.% as siderite, and 1.1 wt.% as the unidentified silicates and phosphate. It was also calculated that 79% of the iron is in ooliths, 12% in matrix, and 9% in siderite.

SiO_2 is a constituent of quartz, opal, nontronite, goethite, and the unidentified silicate. Al_2O_5 occurs in nontronite, opal, goethite, unidentified silicate, and phosphate.

Nearly all the phosphorus is in ooliths, about half being in goethite and nontronite, and half as impure phosphate grains. CaO is associated with the phosphate, but a small amount is in opal, siderite, and calcite.

OXIDATION OF IRON

Mössbauer studies of a sample exposed to atmospheric conditions indicate that the iron in goethite, ferruginous opal, and 92% of that in P.R. nontronite is ferric, whereas the iron in siderite and 8% of that in P.R. nontronite is ferrous. Using this distribution of ferrous iron, FeO in Sample 3 was calculated as 4.2 wt.%. This value is comparable to the analyzed FeO content of 5.1 wt. % reported by Krupp (1975) for material that is equivalent to Sample 3 (3 to 4.5 m, Table 4). On the other hand, analytical FeO is 20.5 wt.% for Sample 3 (Table 4) as received in sealed plastic bags. Such a high ferrous iron content can be accounted for by considering the octahedrally coordinated iron in P.R. nontronite as Fe^{2+}. It is, therefore, interpreted that P.R. nontronite *in situ* contains ferrous iron, but upon exposure to atmospheric conditions the iron oxidizes to the ferric state. For the samples studied, the oxidation stabilized when the iron in P.R. nontronite was 92% Fe^{3+}, but for samples studied by Nickel *et al.* (1960) all the iron in P.R. nontronite was oxidized.

The oxidation of iron in P.R. nontronite coincides with the high loss of water from the material upon exposure to atmospheric conditions. This suggests that the mechanism for the oxidation of ferrous iron in P.R. nontronite octahedral sites is one that involves a loss of protons from the OH^- group according to the formula $2Fe^{2+}+2OH+\frac{1}{2}O_2 \rightarrow 2Fe^{3+}+2O^{2-}+H_2O$. Such a mechanism is used to explain the oxidation of iron in clays by weathering (Coey 1975). This mechanism is likely related to the adsorbed water in P.R. nontronite but not to the adsorbed water in ferruginous opal. Therefore, it is suggested that the water content in Samples 5 and 6, as received, is due largely to adsorbed water in ferruginous opal; this would explain why the water loss upon exposure to atmospheric conditions was not accompanied by a large change in the oxidation state of the iron (compare Samples 5 and 6 with Sample 6 — 7.5 m — Table 4).

The chemical analyses for material in sealed plastic bags (Table 4) show increased FeO contents from Sample 1 to Sample 4 and much lower FeO in Samples 5 and 6. This indicates decreasing oxidation of the material *in situ* with depth to 5.8 m, and higher oxidation at the base of the horizon than in the middle. Mellon (1962) suggested that the higher oxidation state at the base took place either before or immediately after deposition, but prior to cementation of the rock by ferruginous opal. On the other hand, the present author interprets that the highly oxidized material at the top of the horizon is due to surficial oxidation (either recent, or prior to deposition of the overburden). Intense surficial oxidation causes the material to be brown and friable, whereas the unoxidized

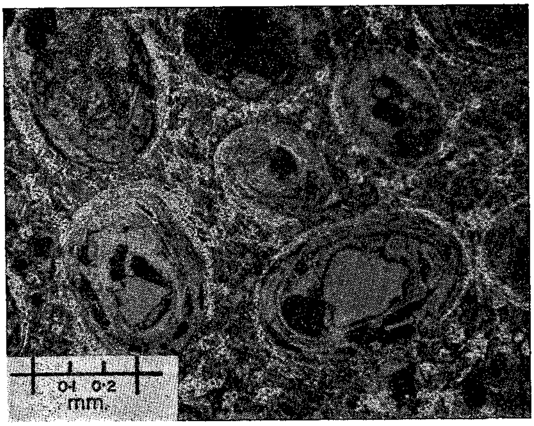

FIG. 11. Oolith in a matrix with goethite (white) expelled from the matrix (photograph from Nickel *et al.* 1960).

material is greenish black and difficult to break (Table 2).

The loss of adsorbed water from ferruginous opal, upon exposure to atmospheric conditions, causes shrinkage cracks and this may account for the lack of strength of the material. The material is crumbly from 0 to 0.6 m, can be ripped with bulldozer to 3.4 m, but cannot be ripped below this depth. Thus surficial oxidation extends to 3.4 m at the sample site of the Swift Creek deposit, but is intense only at 0 to 0.6 m.

Photographs recorded by Nickel *et al.* (1960) of completely oxidized samples show that the ferruginous opal contains minute disseminated goethite grains (Fig. 11). This suggests that very intense oxidation of the ore causes the ferric iron to be expelled from the ferruginous opal as goethite.

ORIGIN

The Peace River iron deposits are sedimentary ironstone beds composed of ooliths and clastic material in a ferruginous cement. The ooliths are ellipsoidal and rounded, which indicate that they were formed in open space near the sediment-water interface by accretion of FeO, SiO_2, Al_2O_3, P_2O_5, CaO and minor amounts of other oxides around solid particles such as quartz, magnetite, calcite, goethite, and parts of broken ooliths. The most likely process for the deposition of ooliths was given by Bubenicek (1968), who suggested that the ooliths formed by precipitation of material around grains. Local currents broke some ooliths before they were buried in the sediment and some oolith pieces served as nuclei for deposition of other ooliths. The present author suggests that the fairly uniform size of the ooliths reflects sorting due to current action. The clastic matrix, which consists of unidentified silicates in ferruginous opal, probably represents partly solidified material that was disturbed by local currents and redeposited, as well as material that the ooliths settled into. Ferruginous opal represents the SiO_2, FeO, Al_2O_3, CaO, and other minor elements that were deposited between and around the ooliths and clastic matrix. The siderite, in the ferruginous opal, is probably authigenic.

The Peace River iron deposits have textures and chemistry (including high P_2O_5) similar to other minette-type deposits throughout the world (Rohrlich 1974). However, the Peace River deposits contain nontronite and opal as the main silicate minerals, whereas chamosite, chlorite, kaolinite, etc. predominate in other worldwide deposits such as Ramin, Israel (Boscovitz-Rohrlich *et al.* 1963); Hussigny, Lorraine (Bubenicek 1963); Raasay, Scotland (Wilson 1966); Loch Etive, Scotland (Rohrlich *et al.* 1969); and Northhampton (Taylor 1951). On the other hand, nontronite is the major silicate in recent iron-formation at the bottom of Lake Malawi, Africa (Müller & Förstner 1973), in the Djebel Ank, Tunisia oolitic iron deposit (Nicolini 1967), and in the iron-manganese concretions of the Pacific Ocean (Skornyakova & Andrushchenko 1974). Müller & Förstner (1973) interpreted, from the stability relations of iron oxides proposed by Garrels & Christ (1965), that the Lake Malawi iron-formation was deposited within a very narrow range of pH and Eh values during changes from reducing to oxidizing conditions. It is possible that similar conditions prevailed during deposition of the Peace River iron deposits.

The stratigraphy of the rocks in the Peace River area suggests that the iron beds were deposited between marine and brackish water environments (Kidd 1959; Mellon 1962). These conditions are consistent with the proposed near-shore environments for the deposition of minette-type deposits (Gross 1965; Nicolini 1967; Bubenicek 1963).

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