O T T A W A June 17th, 1942.

R E P O R T

of the

ORE DRESSING AND METALLURGICAL LABORATORIES.

Investigation No. 1249.

Flotation Concentration of Manganese Ore from Manuels Manganese Deposits of Conception Bay, Newfoundland.

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Shipment:

Four bulk samples were received on March 26th, 1942, from the Manuels manganese deposits of Conception Bay, Newfoundland. The samples were submitted by Claude K. Howse, Associate Government Geologist, Geological Survey, St. John's, Newfoundland, at the request of Dr. G. A. Young, Chief Geologist, Mines and Geology Branch, Department of Mines and Resources, Ottawa,

(Shipment, cont'd) -

Ontario.

The bulk samples were channel samples taken across the beds of the deposit where it outcrops on the south side of the Manuels River valley.

Bulk Sample No. 1. - 481 pounds - a channel, 1 foot 11 inches long, taken across the manganese beds from the uppermost section of the deposit.

Bulk Sample No. 2. - 1134 pounds - the next 4 foot 8 inch section of the beds.

Bulk Sample No. 3. - 1063 pounds - bottom 5 foot section of the beds.

Bulk Sample No. 4. - 226 pounds - consisted of the section of Bulk Sample No. 2 and the uppermost 14 inch section of Bulk Sample No. 3.

Sampling and Analysis:

The samples were crushed, ground, and sampled by standard methods. Analysis showed the following:

	Bulk Sample No. 1	Bulk Sample No. 2	Bulk Sample No. 3	Bulk Sample No. 4
Manganese, per cent	5.68	10.69	9.27	10.35
Iron, "	9.26	5.67	5.21	5.37
CaO (acid soluble)"	3.09	2.96	2.50	2.81
MgO " " "	1.84	1.22	1.16	1.19
Phosphorus "	0.09	0.07	0.10	0.06
Sulphur "	0.36	0.13	0.12	0.10

Characteristics of the Ore:

Polished sections prepared from specimens of the samples were examined under the reflecting microscope to determine the metallic minerals in the ore. The examination showed that the metallic mineralization was rather sparse and represented almost entirely by pyrite. This mineral is disseminated through gangue as small masses and coarse to fine grains and crystals which contain numerous tiny inclusions of gangue. Occasional small grains of chalcopyrite are visible in gangue

(Characteristics of the Ore, cont'd) -

and in pyrite.

Thin sections were prepared and examined under a microscope, for the purpose of determining the character of the ore, by Dr. J. D. Bateman, Bureau of Geology and Topography, Ottawa, who reports as follows:

REPORT ON MANGANESE SAMPLES FROM MANUELS, NEWFOUNDLAND.

Summary

Examination of one thin section of material from each of the four samples submitted by the Bureau of Mines failed to disclose any pertinent information on the mineral association. This is because it was not possible to resolve the minerals under the microscope owing to the extreme fineness of grain of most of the material. The samples were then investigated by microchemical methods and staining procedure, and the information gained in this way is correlated with the geological and chemical work of Dale (1). The results of this investigation indicate that most of the manganese occurs as a carbonate associated with a complex carbonate group in red and green argillaceous carbonate rocks. The manganiferous carbonates are finely disseminated throughout the rocks, and are also concentrated in (a) carbonate nodules, (b) pale green cherty lenticles and (c) red iron oxide laminae. These manganese-rich structures are not easily amenable to mechanical methods of concentration, but most of the manganese content of the specimens is soluble in acids without difficulty.

Geology.

Manganese occurs at Topsail, Manuels, Long Pond,

(Characteristics of the Ore, cont'd) -

Chapel Cove, and Brigus on Conception Bay, at Smith Point on Trinity Bay, and at Ships Cove, Placentia Bay. The different occurrences are apparently at the same stratigraphic horizon in green and red shales of late Lower Cambrian age. The manganese-bearing zone is overlain by green shales containing Paradoxides and is underlain by green shale containing Protolenus harveyi. At Manuels, this zone is 13.7 feet thick and consists essentially of green and red argillaceous carbonate rocks containing manganese carbonates, and with hematite, barite, and tricalcium phosphate as accessories. The manganese is contained in thin, jasper-like green and brown bands, in nodular beds, and in argillaceous and calcareous beds. The following section is confined to the manganese-bearing zone near the locality where the samples were taken. The beds strike roughly east-west and dip 10 degrees north.

Manuels Brook.

Thickness, in feet	Lithology
1.0	Shaly phosphatic pebble bed
1.4	Black nodular green shale
0.5	Red manganiferous shale
3.5	Jaspery manganiferous lenticular shale
0.5	Red and green jaspery manganiferous shale
0.3	Red slate
0.7	Red and green manganiferous shale
0.5	Red shale
0.2	Red manganiferous shale
5.1	Manganiferous nodular shale.

Examination of Thin Sections.

Each of the four samples submitted consisted of a number of rock types and, of these, four thin sections from representative specimens were studied. A few mineral areas could be determined as relatively large clusters of carbonate, but it was of course not possible to distinguish the species. Hematite, particularly in the red beds, occurs as evenly distributed reddish-brown flecks in a light coloured extremely fine-grained groundmass, but no manganese oxides were seen. A blade of barite was observed in one section. Nodular and concretionary structures are prominent, but the material is indeterminable because, as Dale said, "of the impalpable fineness of grain."

Chemical Investigation of Samples.

Dale made a number of analyses of different materials in the manganese zone, and these are shown in Table I correlated with the geological section. In the present investigation, material from 19 specimens was powdered, treated with cold HCL, heated, and then tested for manganese by the standard sodium bismuthate method. The resulting permanganate precipitate was pale pink to deep carmine depending upon the relative

(Characteristics of the Ore, cont'd) -

amount of manganese present. The results of this investigation are tabulated in Table II, and indicate that the manganese content is roughly proportional to the carbonate content. There is also a suggestion of considerable variation in the species of carbonate present.

Polished surfaces of 13 specimens were then stained in order to distinguish calcite from any other carbonates present. The copper nitrate method with fixation in ammonia according to Rodgers[2] was used. Only one of the specimens was found to contain calcite which occurred with other carbonates in an irregular, nodular-like form in green shale. Following this procedure the surfaces of the specimens were then re-polished and stained in such a way as to produce brown manganese protoxide on the manganese-bearing minerals (see photographs). The staining tests are tabulated in Table III. It was found that the pink and grey carbonates stained deep-brown, indicating a relatively high manganese content; the white carbonates stained pale-brown; and the green cherty layers and red laminae stained an intermediate brown. Most of the megascopically visible carbonate is in the form of nodules, but the staining tests showed that fine-grained manganese-bearing carbonates are disseminated throughout most of the specimens.

In the manganese deposits at Batesville, Arkansas, which are in many respects similar to the Newfoundland occurrences, Miser[3] found four groups of carbonates as follows:

		Per cent Mn
(1)	Pink carbonate (rhodochrosite)	33.8 - 36.8
(2)	White carbonate	Low
(3)	Grey carbonate	32.6 - 38.5
(4)	Red or reddish-brown carbonate	20 - 30

These figures compare with about 47 per cent manganese in pure rhodochrosite. There is, in addition, at Batesville another group of manganese-bearing carbonates that consists of a mottled mixture of red and black carbonates, generally with some pink and white carbonates.

A study of the chemical analyses shown in Table I suggests that the manganese at Manuels occurs largely as carbonate, and recalculations of the analyses show that the $MnCO_3$ content would vary from 10.23 per cent in the red band to 44.39 per cent in the green band. These calculations, however, do not allow for any of the ferrous iron to occur as a carbonate and, as $MnCO_3$ may contain up to 40 per cent $FeCO_3$ in solid solution, it is probable that the manganese-bearing carbonates also contain ferrous iron. On the other hand, the only specimen that stained positively for calcite also stained positively for manganese, indicating a low manganese variety of manganocalcite. Krieger[4] finds that manganocalcite is not a definite mineral like dolomite, but that there is a relationship between the physical and structural (X-ray) properties and per cent manganese content, and that there is a solid solution series between calcite and rhodochrosite. The recasts of the analyses indicate a considerable content of $CaCO_3$, but the staining tests indicate

(Characteristics of the Ore, cont'd) -

that there is almost no free calcite. It is evident that the $CaCO_3$ is associated with a complex group of carbonates that contains iron, manganese, and magnesium.

Dale noted that Cl_2 was evolved by the action of HCl on some of his specimens, indicating that some manganese in excess of that amount necessary to form carbonates is present as a peroxide. No manganese oxides were observed in the hand specimen or microscopically, but the recasts of the analyses show some manganese oxide left over. In the green band there is an excess of ferric over ferrous iron and in the green shale there is almost as much ferric as ferrous iron. As these beds are green the ferric iron is probably present in some other mineral than hematite, and it may be contained in a silicate. Such a silicate might also contain the excess manganese. On the other hand, the red laminae stain positively for manganese, and it is possible that some manganese oxides are present, but are masked by the colour of the hematite.

Conclusions.

Most of the manganese in the specimens from Manuels, Newfoundland, occurs in complex carbonates that are solid solutions of $MnCO_3$ with $FeCO_3$ on one hand and with $CaCO_3$ on the other. The carbonates are finely disseminated throughout red and green shales, but the manganese is limited to a definite horizon that varies from place to place. Within this horizon there are local concentrations of manganese in concretionary nodules, cherty lenticles, and some hematite-rich laminae. The accompanying photographs show typical specimens of nodular and laminated material before and after staining for manganese. The areas that, by comparison, are darkened on the stained specimens, indicate the localization of the manganese. The local concentration, as well as the dissemination of manganese carbonates, is to be considered a primary occurrence. In the specimens examined from Manuels there is little evidence of any alteration that has resulted in a reconcentration of the manganese.

The primary carbonates at Brigus have been oxidized to psilomelane that forms a small deposit of commercial manganese ore. Elsewhere at this horizon conditions may exist that have favoured a reconcentration or residual enrichment of manganese.

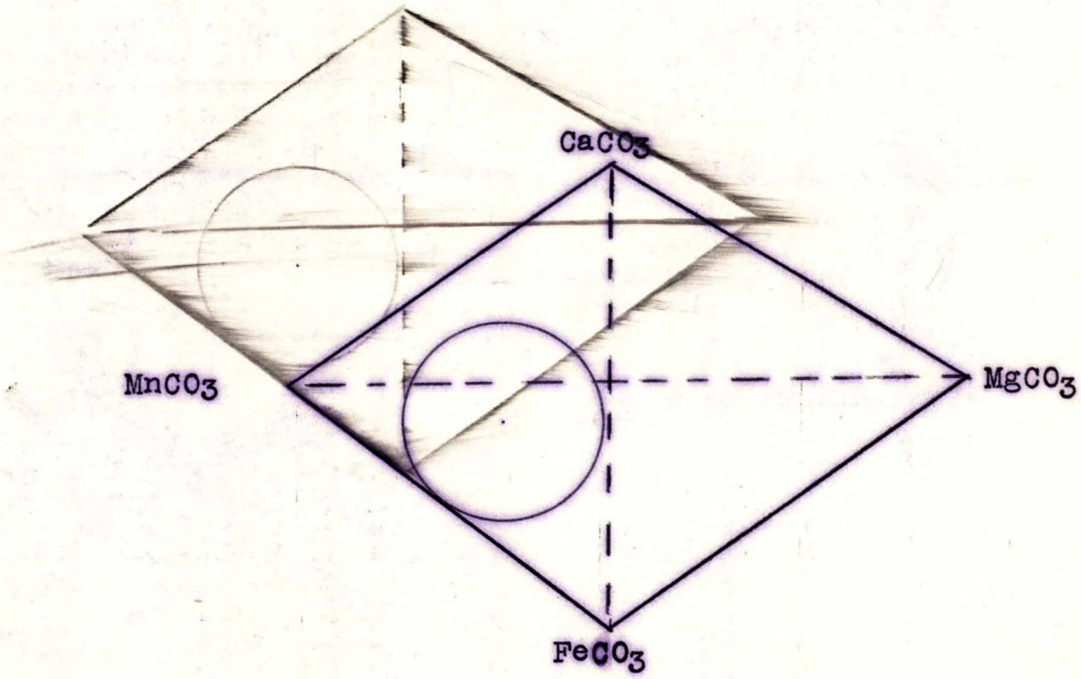
REFERENCES

(1) Dale, N.C., Proc. Amer. Phil. Soc., vol. 54, 1915, pp. 371-456.
(2) Rodgers, J., Amer. Jour. Sci., vol. 238, 1940, pp. 788-798.
(3) Miser, H.D., U.S. Geol. Surv., Bull. 921-A, P. 13.
(4) Krieger, P., Amer. Min., vol. 15, 1930, p. 23.

(Tables and Figures follow)

Figure 1.

Carbonate Relationships

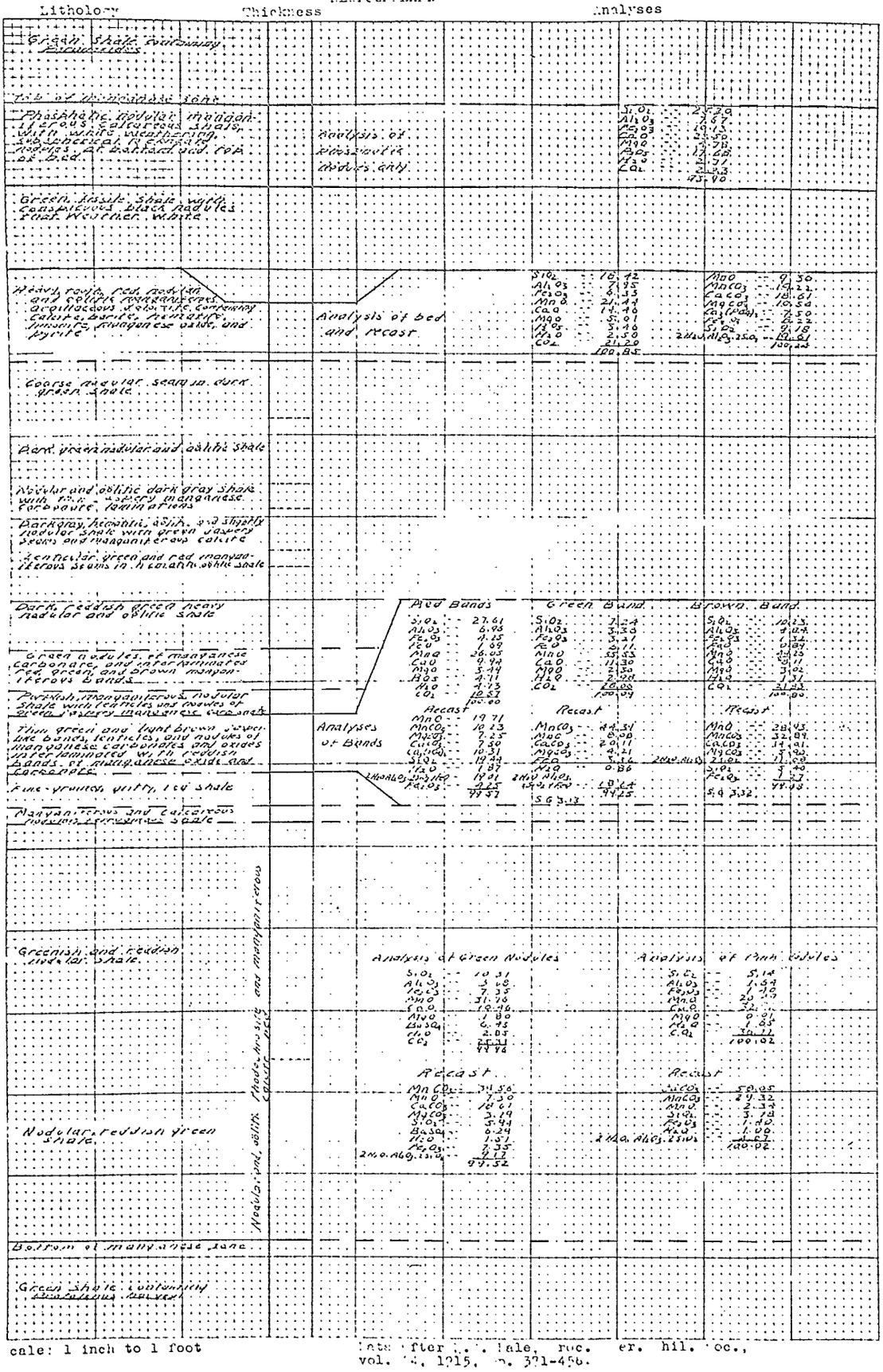


Carbonate Tetrahedron.

The pink carbonates, which are highest in manganese, probably lie in the northwest quarter of the tetrahedron; whereas the grey carbonates, also of high manganese content, lie in the southwest quarter. The relatively low magnesium content of Dale's analyses suggests that most of the carbonates occur in the western half of the tetrahedron. The absence of calcite, as indicated by staining, probably means that most of the carbonates lie closer to the south pole than the north pole of the tetrahedron. This suggestion is supported by the relatively large ferrous iron content. On the basis of available information, most of the high manganese carbonates lie within the circle.

TABLE I

SECTION ACROSS MANGANESE ZONE IN LOWER CUTHBIN AT MANUEL'S BROOK, NEWFOUNDLAND



Scale: 1 inch to 1 foot

Interpreter's Sale, Proc. Amer. Phil. Soc., vol. 54, 1915, pp. 391-456.

TABLE II.

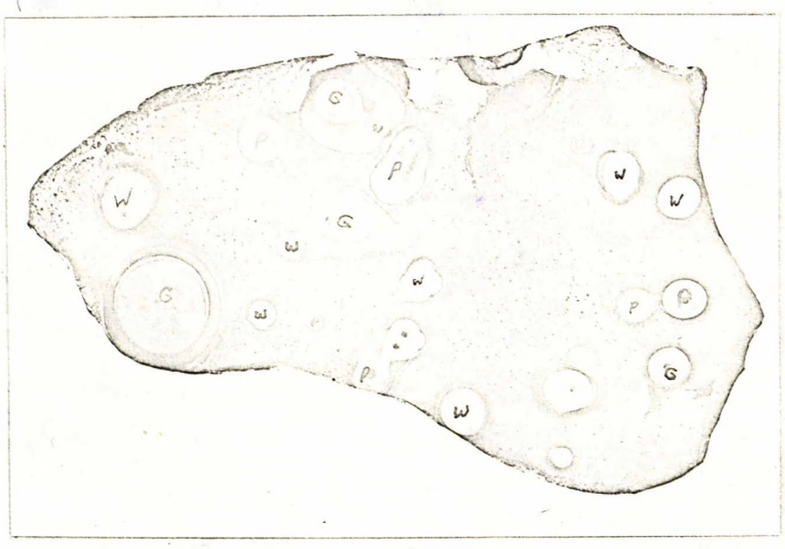
Sample	Specimen	Lithology	Efferves-cence in cold HCl	Efferves-cence in hot HCl	Relative Mn content
4	b	green pyritiferous material	minor	moderate	very high
1	b	pinkish carbonate material	vigorous	moderate	very high
1	b	pinkish carbonate material	vigorous	vigorous	high
2	d	pyritiferous green cherty and red zone	moderate	vigorous	high
2	a	pyritiferous red shale	moderate	vigorous	high
3	c	nodular red and green shale	moderate	vigorous	high
4	a	cherty material	moderate	vigorous	high
4	d	green and red shale	minor	vigorous	high
3	b	red and green shale	minor	vigorous	high
3	d	red and green shale	very minor	vigorous	moderate
2	c	green shale	very minor	minor	moderate
2	b	cherty lenticles in red shale	very minor	minor	moderate
1	d	cherty material	minor	moderate	low
1	c	pyritiferous black material	minor	moderate	low
1	c	pyritiferous black material	very minor	moderate	very low
1	a	green shale	very minor	very minor	very low
1	a	green shale	very minor	very minor	trace
4	c	red shale	negative	negative	trace
3	a	green shale	negative	negative	trace

TABLE III.

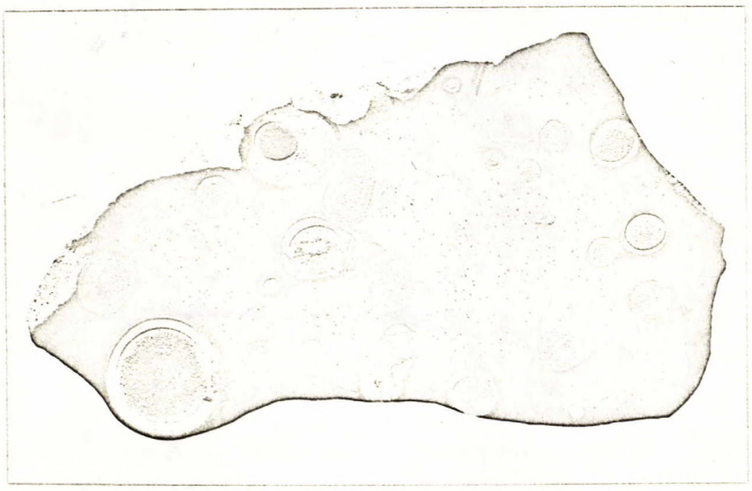
Sample	Specimen	Lithology	Calcite Stain	Localization of Mn Stain
4	b	green pyritiferous material	neg.	dissem. and streaks
2	a	pyritiferous red shale	neg.	dissem. and red laminae
3	c	nodular red and green shale	neg.	carbonate nodules
4	a	cherty carbonate material	neg.	part of carb., and part of cherty material
3	b	red and green shale	neg.	dissem.
2	b	cherty lenticles in red shale	neg.	dissem. and lenticles
2	e	laminated red and green shale	neg.	red laminae
2	f	carbonate nodule	neg.	completely stained
3	e	cherty green and red shale	neg.	streaks
4	e	green shale with red laminae	neg.	neg. for Mn.
4	f	red and green shale	neg.	dissem.
2	10	red carbonate and black material	neg.	completely stained
3	10	carbonate nodule in green shale	part of nodule positive	nodule only stained

PLATE I.

Manganiferous Nodular Shale.



A. - Before staining.



B. - After staining.

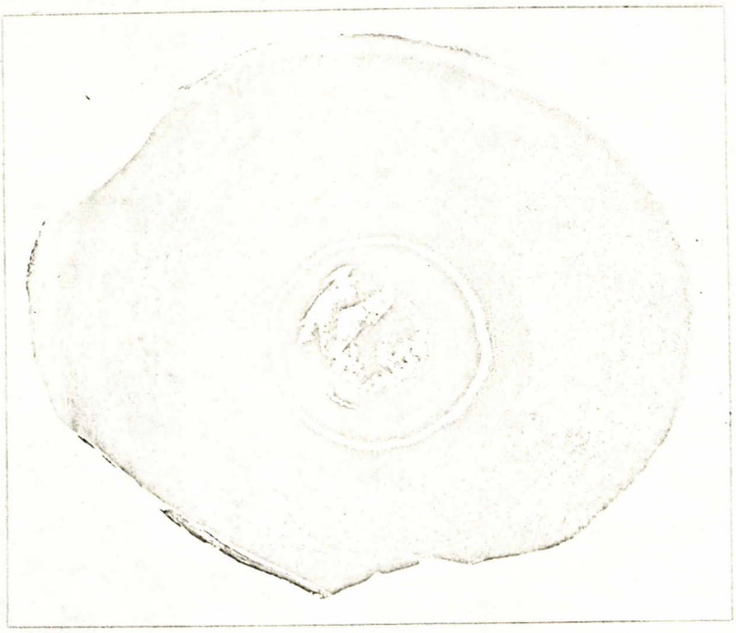
Showing localization of manganese in the concretionary carbonate nodules, which are etched after staining. The relative density of colour in the stained specimen indicates the relative amount of manganese.

About twice natural size.
P = pink carbonate
G = grey carbonate
W = white carbonate.

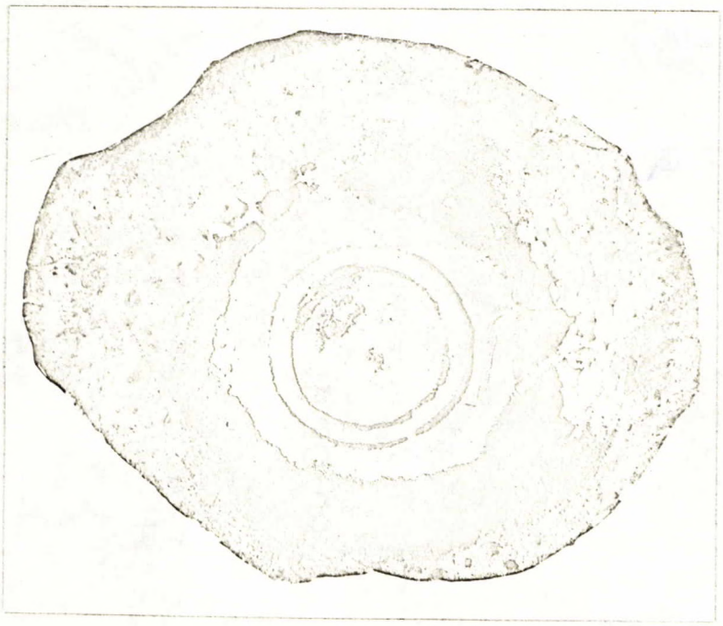
The different varieties of carbonate are, in part, indicated by differential etching.

PLATE II.

Carbonate Nodule.



A. - Before staining.



B. - After staining.

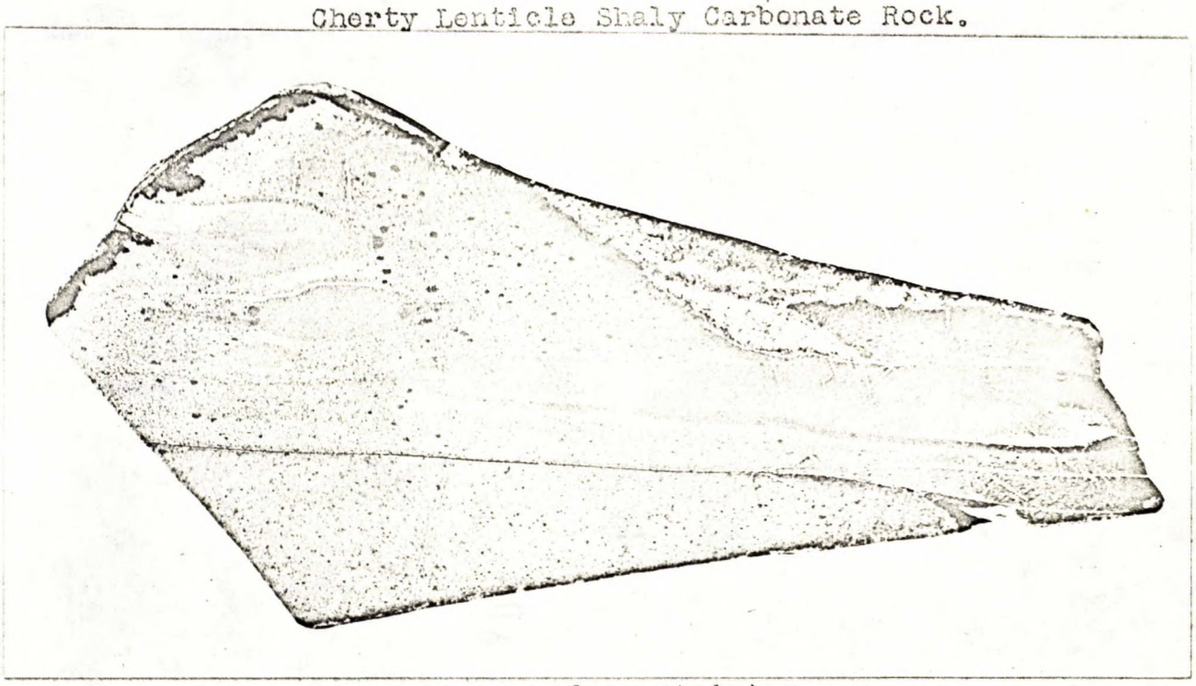
The stained specimen was completely coated with dark manganese oxide film, which was in part removed by rubbing on chamois to indicate the differential etching of the carbonates of different composition.

The unstained nodule is brown-pink in colour.

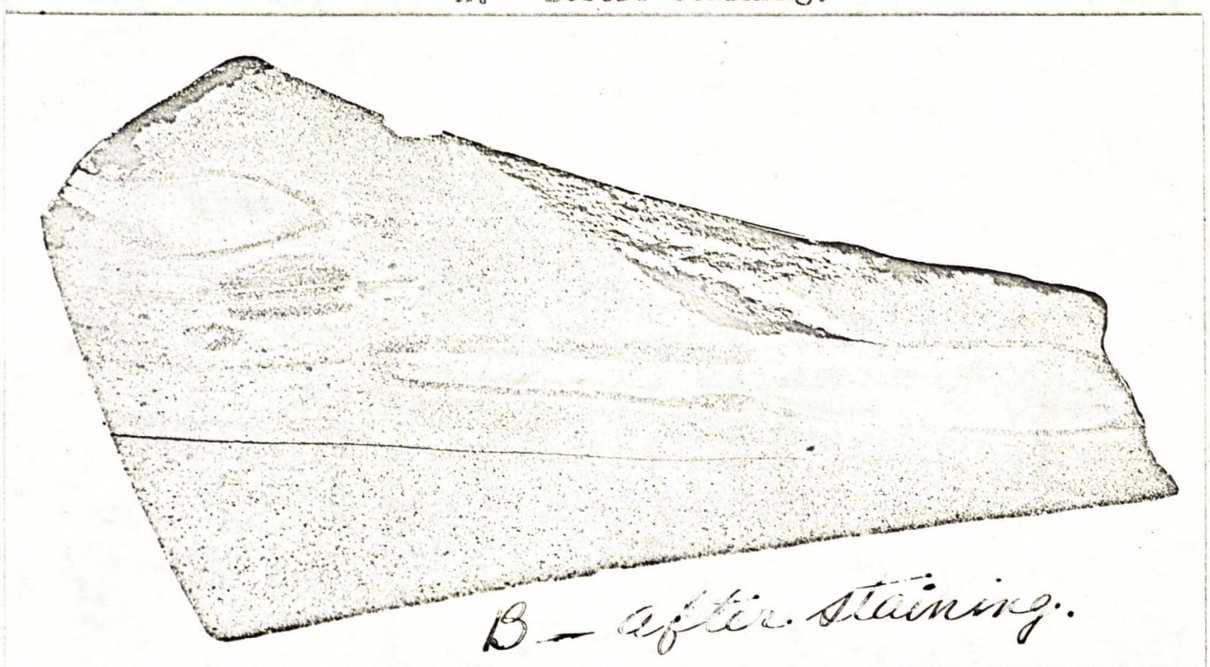
Four times natural size.

PLATE III.

Cherty Lenticle Shaly Carbonate Rock.



A. - Before staining.

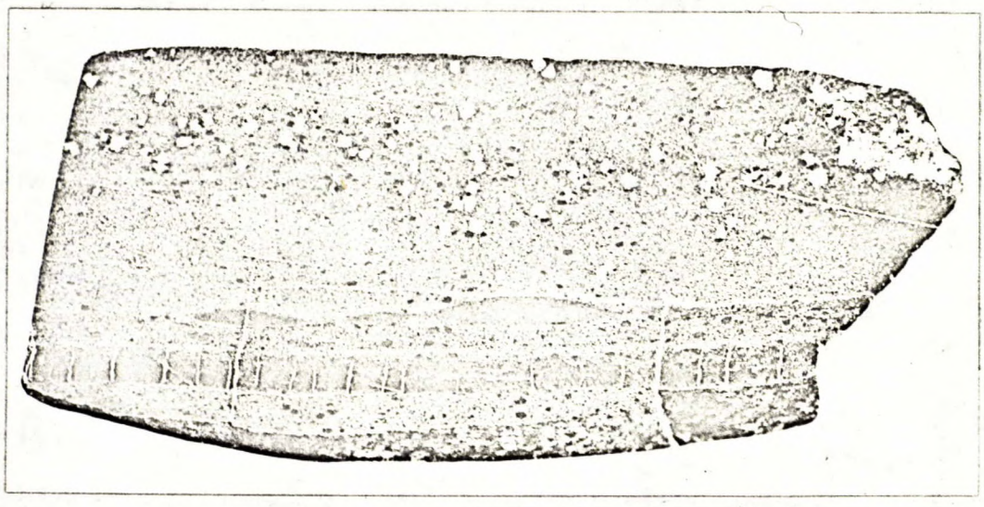


The cherty lenticles in the unstained specimen show as the darker lenses. In the stained specimen the localization of manganese is indicated by the darker portion of the lenticles.

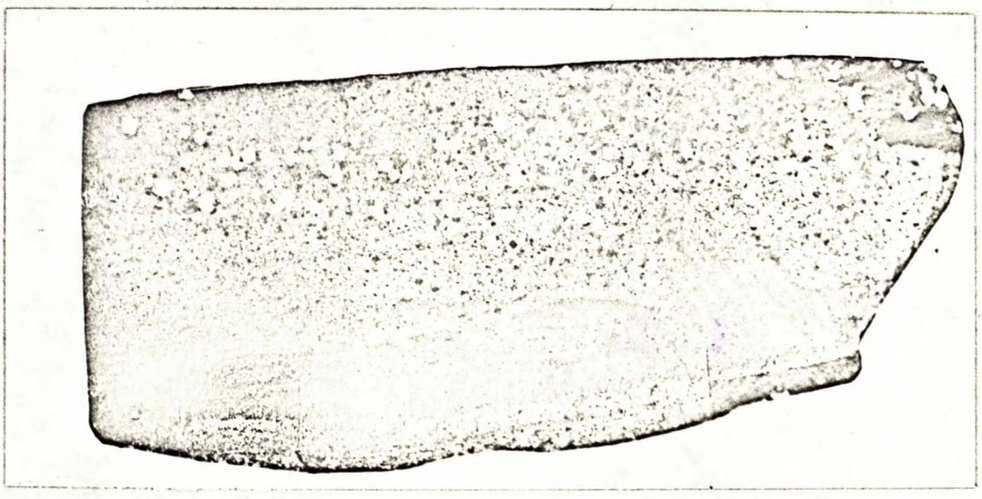
Three times natural size.

PLATE IV.

Reddish Banded Pyritiferous Shale.



A. - Before staining.



B. - After staining.

Manganese oxide stain in B is localized in two reddish bands near bottom of specimen. As in Plates II and III the disseminated manganiferous carbonates are too fine-grained to observe.

About four times natural size.

Experimental Tests:

The experimental tests were conducted on Sample No. 4 ore.

The results of the investigation show that the ore is not amenable to flotation concentration for the recovery of manganese. The concentrates obtained contained about 30 per cent of the manganese in the ore and were low grade, analysing from 24 to 26 per cent manganese.

Desliming the pulp prior to flotation did not improve the grade of concentrate. (Test No. 6).

Calcining the ore prior to flotation treatment gave a concentrate analysing 20.24 per cent Mn; the flotation tailing assayed 9.94 per cent Mn and contained 61.9 per cent of the manganese in the ore. (Test No. 7).

Details of Tests:

FLOTATION.

Test No. 1.

A series of tests were carried out mainly to determine the effect of fineness of grind on the recovery of manganese.

Samples of ore were ground in water to about 75, 85 and 90 per cent minus 200 mesh, with 1.0 pound of sodium silicate per ton of ore. The pulp from each grind was transferred to a flotation cell and the manganese was floated using 2.0 pounds of sodium oleate and 0.13 pound of cresylic acid per ton of ore.

The rougher concentrates were cleaned by refloating, using 1.0 pound of sodium silicate per ton of ore.

Test 1-A,	ground	to	about	75	per cent	minus	200	mesh.
1-B,	"	"	"	85	"	"	200	"
1-C,	"	"	"	90	"	"	200	"

(Continued on next page)

(Test No. 1, cont'd) -

Results of Flotation:

Test No.	Product	Weight, per cent	Manganese, per cent		Ratio of concentration
			Analysis	Distribution	
1-A	Feed	100.00	10.20⊕	100.0	
	Concentrate	7.77	20.78	15.8	12.87:1.
	Middling	24.92	13.01	31.8	
	Tailing	67.31	7.94	52.4	
1-B	Feed	100.00	10.64⊕	100.0	
	Concentrate	6.67	19.95	12.5	14.99:1.
	Middling	27.02	12.26	31.1	
	Tailing	66.31	9.04	56.4	
1-C	Feed	100.00	10.41⊕	100.0	
	Concentrate	4.09	20.78	8.2	24.45:1.
	Middling	26.63	10.81	27.7	
	Tailing	69.28	9.64	64.1	

⊕ Calculated values.

Screen Analysis of Flotation Tailing, Test No. 1-A.

Mesh	Weight, per cent	Manganese, per cent
+100	6.9	10.62
-100+200	31.3	10.62
-200	61.8	6.28

The results of screen analysis indicate that fine grinding is necessary to lower the manganese content in the flotation tailing.

The results of the flotation tests show that the manganese content in the flotation tailing increases with the increase of fineness of grind. This is due to the fact that by increasing the fineness of grind the surface area of the pulp particles is increased; thus, a larger amount of collecting reagent will be necessary to coat the manganese minerals. Hence, when the amount of collecting reagent is constant but the fineness of grind is increased, the amount

(Test No. 1, cont'd) -

of manganese minerals coated will be less and the recovery will be lower.

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Tests Nos. 2, 3, and 4.

In these tests various collecting reagents, such as "Orso," "Copacol" and oleic acid, were tried. "Copacol" showed a slightly adverse effect as a collector for manganese carbonate. When oleic acid was used the recovery of manganese was low. The recovery was about the same when "Orso" was used as that obtained with sodium oleate as collector.

—

Test No. 5.

A sample of ore was ground to about 90 per cent minus 200 mesh with 1.0 pound of sodium silicate per ton of ore. The pulp was transferred to a flotation cell and the manganese was floated using 4.0 pounds of sodium oleate and 0.06 pound of cresylic acid per ton. The rougher concentrate was cleaned three times, using 1.0 pound of sodium silicate in the first and second cleaning treatments and 0.50 pound of sodium silicate per ton of ore in the third cleaning operation.

Results of Flotation:

Product	Weight, per cent	Manganese, per cent		Ratio of concentration
		Analysis	Distribution	
Feed	100.00	10.79*	100.0	
Concentrate	14.08	26.08	34.0	7.10:1.
1st cleaner tailing	29.42	8.41	22.9	
2nd " "	15.86	11.84	17.4	
3rd " "	6.22	19.39	11.2	
Rougher flotation tailing	34.42	4.53	14.5	

* Calculated value.

(Continued on next page)

(Test No. 5, cont'd) -

Manganese Content of Flotation Concentrates.

		Manganese, per cent
Rougher concentrate (calculated)	-	14.07
1st cleaner " "	-	18.68
2nd " " "	-	24.03
3rd " " (analysed)	-	26.08

The third cleaning increased the manganese in the concentrate by 2.05 per cent only.

—

Test No. 6.

On some non-metallic ores a high-grade concentrate cannot be obtained without desliming the pulp prior to flotation.

A sample of ore was ground to about 90 per cent minus 200 mesh. The ground pulp was deslimed and the deslimed product was treated by flotation, using 1.10 pound of sodium silicate, 3.55 pounds of sodium oleate and 0.07 pound of cresylic acid per ton of flotation feed. The rougher concentrate was cleaned twice, using 1.10 pound of sodium silicate per ton of rougher flotation feed in each cleaning operation.

Results of Flotation:

Product	Weight, per cent	Manganese, per cent		Ratio of concentration
		Analysis	Distribution	
Feed	100.00	9.97*	100.0	
Concentrate	10.84	24.87	27.0	9.23:1.
1st cleaner tailing	19.08	8.32	15.9	
2nd " "	12.88	18.22	23.6	
Rougher flotation tailing	32.38	3.99	13.0	
Slimes	24.82	8.24	20.5	

* Calculated value.

(Continued on next page)

(Test No. 6, cont'd) -

Desliming did not improve the grade of concentrate. The analysis of the concentrates was as follows:

		Per cent
Manganese (Mn)	-	24.87
Lime (CaO), acid soluble	-	7.24
Magnesia (MgO), "	-	1.00
Iron (Fe)	-	3.79

As the ore is practically free of calcite the CaO in the concentrate is mainly that which is in the manganocalcite.

CALCINATION AND FLOTATION OF CALCINE.

A test was carried out to determine whether the grade of concentrate could be improved by converting the carbonates to oxides by calcination followed by flotation of the calcine.

Test No. 7.

A sample of ore was calcined in a retort furnace under reducing atmosphere. The initial temperature of 500° F. was raised to 1600° F. and kept at that temperature for two hours.

The calcine analysed 0.25 per cent CO_2.

A sample of calcine was ground to about 90 per cent minus 200 mesh with 1.0 pound of soda ash and 0.30 pound of kerosene per ton of calcine. The pulp was transferred to a flotation cell and manganese was floated, using 4.0 pounds of sodium oleate and 0.19 pound of cresylic acid per ton.

The rougher concentrate was cleaned twice by refloating. No reagents were used in the cleaning treatment.

(Continued on next page)

(Test No. 7, cont'd) -

Results of Flotation of Calcine:

Product	Weight, per cent	Analysis, per cent Mn	Analysis, per cent Fe	Distribution of Mn, per cent	Ratio of concentration
Feed	100.00	11.72◆		100.0	
Concentrate	5.04	20.24	7.30	8.7	19.84:1.
1st cleaner tailing	16.05	14.75		20.2	
2nd " "	5.95	18.18		9.2	
Rougher flot. tailing	72.96	9.94		61.9	

◆ Calculated value.

Calcining the ore prior to flotation treatment did not improve the grade of the concentrate nor increase the recovery.

CONCLUSIONS:

The results of the investigation show that the ore is not amenable to flotation concentration; the grade of concentrate is low, analysing about 25 per cent manganese, and the recovery is poor.

Microscopic examination of thin sections prepared from the ore specimens show that the mineral grains are extremely fine and the manganiferous carbonates are finely disseminated throughout the rock. Microchemical and staining methods of determination indicate that most of the manganese occurs in complex carbonates that are solid solutions of $MnCO_3$ with $FeCO_3$ on one hand and with $CaCO_3$ on the other. This mode of mineral association will account for the low-grade concentrates and low recoveries obtained.

It therefore is apparent that this manganese deposit cannot be exploited by any known means of concentration short of chemical treatment.

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