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THE CHEMISTRY OF MANGANESE DEPOSITS

by

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MINERAL DRESSING AND PROCESS METALLURGY DIVISION

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FOREWORD

Recently, Professor W. R. Trost of Dalhousie University became interested in tracing the origins of Canadian manganese deposits and has spent the past year on sabbatical leave, working on this problem in the Mines Branch laboratories.

Over a period of years, the Mines Branch has been requested to do beneficiation and leaching studies on Canadian manganese ores of many grades and types. Some basic similarities in the ores have become obvious during the testing, but sufficient information was not available to create an integrated picture of the reasons for the similarities and differences in the ores.

Basing his work on geological information and well known chemical principles, Dr. Trost has evolved a reasonable explanation for the formation of primary sedimentary manganese deposits which involves the natural erosion and dissolution of igneous rocks and the precipitation of manganese compounds, according to solution equilibria consideration. The arguments are extensive, the approach new, and the results unexpectedly accurate and interesting.

John Convey,
Director,
Mines Branch.

ACKNOWLEDGMENTS

It is a pleasure to acknowledge my indebtedness to the many people at the Mines Branch who have so cheerfully assisted me. My thanks must first go to Dr. T. R. Ingraham for his friendly and continued interest and for his help in many important and detailed ways. Dr. A. T. Prince has been most kind, and has suggested many valuable improvements in the manuscript.

It is agreeable as well to remark here on the benefits received from a presentation of the material, while it was still only roughly prepared, to a seminar at the Mines Branch. As a result, many individuals made suggestions that were helpful to me. For these, the author's thanks are extended to Dr. G. Thomas, who was particularly helpful in connection with an oxidation problem, to Drs. N. F. H. Bright and B. J. P. Whalley, Mr. Dan Pickett, and others. A special appreciation is due Dr. E. H. Nickel, whose extensive mineralogical reports appear in the Appendix, for his professional assistance and for many clarifying discussions on the mineralogy of these deposits. There is, as well, a debt to Mr. A. Peacock and to Mrs. D. Varette for their care and attention in preparing the figures and the manuscript.

I wish to thank Mr. K. O. J. Sidwell, of Strategic Manganese Corporation Limited, for his permission to quote at length from his paper on the geology of the Woodstock manganese ores. Mr. W. F. Take, of the Nova Scotia Museum of Science, was also kind enough to permit a quotation from him on the mineralogy of a manganese deposit in Nova Scotia. Then, for many interesting talks and field trips, the author would like to thank Mr. G. P. MacKay of Halifax.

Finally, it is a pleasant duty to recognize the beneficence of the two institutions, Dalhousie University and the Department of Mines and Technical Surveys, Ottawa, that together provided the support, the space and the time which made the work possible. Dr. Convey, Director of the Mines Branch, and Dr. Downes, Chief of the Mineral Dressing and Process Metallurgy Division, were at all times most helpful. I am grateful to Dalhousie University for the year of sabbatical leave which in the first place made the work possible.

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Mines Branch Research Report R 8

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ABSTRACT

A new geochemical approach has been developed for relating the chemical composition of North American manganese deposits to the igneous rock from which they originated. The approach consists of specifying the nature and composition of amenable source rocks; of devising a leaching cycle during which certain constituents of the rock are solubilized; of specifying the conditions under which the solubility products of carbonate, oxide and related compounds are exceeded; of specifying the order and association in which the compounds would be precipitated; and of specifying the changes to be expected in aging of the deposit. The theoretical predictions agree well with observations on known deposits.

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PART I

THE SOURCE ROCK

INTRODUCTION

Three steps occur in the history of a sedimentary ore body as the source rock passes through water to give a primary deposit and as this deposit ages. The source rock itself has a definite life and composition. Then, through diverse chemical agencies, the material is dissassembled and transformed to be deposited in new locations. At any point the primary deposit also has a definite composition in its new location. As it ages, however, through thermal, pressure and other effects, changes occur in composition, association and orientation. Finally, the contemporary condition is achieved.

To describe the development of a manganese ore body, it is first necessary to specify the source rock. Then, those processes which can lead to concentration and separation of the manganese from it, must be followed, to obtain the primary sediment. Finally, the effect of metamorphic processes on the sediment must be considered before contemporary material is produced.

In this paper, the development of the primary sediment from a source rock will be described. Subsequently, the aging of the sediment will be considered, and comparison with known deposits will be made. Among known deposits, those in the Woodstock region of New Brunswick, and along the eastern shore of Nova Scotia, will be used as examples. The Woodstock deposit has been only slightly metamorphosed and thus is close to a primary sediment. The Eastern Shore spessartites, on the other hand, have been exposed to higher temperatures and provide an example of a more fully metamorphosed deposit.

THE CHOICE OF A SOURCE ROCK

The chemical transformation to be considered for the source rock is a single pass from the source rock to a sediment. It is evident that further concentrations and changes can occur in subsequent passages from sediment to sediment. These would be double-pass, triple-pass, etc. sediments. Here, only a single-pass sediment will be considered. Therefore the source rock to be chosen is an igneous one.

To obtain a manganese deposit it is necessary that manganese occur in the source rock. The universal average for manganese in igneous rocks is given as 0.08%(1). It is known, however, that in the cooling of magmas the manganese crystallizes out with the ferromagnesian silicates rather than with the feldspar or quartz. This is shown in Table 1. As the ferromagnesian silicates, the pyroxenes, constitute about 17% of igneous rocks, as shown in Table 2, the average manganese content in them becomes about 0.5%.

TABLE 1

The Average Atom Composition of Igneous Rocks

Atoms per 1000 atoms (Si + Al)

Igneous Rock	Si	Al	Fe^{+2}	Fe^{+3}	Mg	Ca	Mn	M^{++} [**]
Average Igneous Rock	770	230	69[*]		65	69	1.3	204
Quartz	1000	0	0	0	0	0	0	0
Feldspar (plagioclase)	605	395	0	0	0	145	0	145
Amphibole (gabbro)	780	220	145	61	331	226	1.3	703
Pyroxenes (gabbro)	930	70	232	18	585	111	6	934
Olivines (gabbro)	952	48	866	48	984	10	3	1863

[*] Total iron

[**] M = Fe + Mg + Ca + Mn

TABLE 2

The Average Mineral Composition of Igneous Rocks[*]

Feldspar	Quartz	Pyroxene	Others	Given by
67.5	9.0	17.7	5.8	Clarke & Washington
59.5	12.0	16.8	11.7	Clarke
67.0	17.6	11.8	3.6	Vogt

[*] Data assembled from Rankama and Sahama(1)

The ferromagnesian silicates may be orthosilicates like the olivines (M_2SiO_4), or metasilicates like the pyroxenes ($M_2Si_2O_6$) and amphiboles ($M_7Si_8O_{22}$). Manganese can occur in any of them. However, partly because the olivines tend to form first and sink in a cooling magma, while the pyroxenes and amphiboles come out later in the main stage of magmatic crystallization, a measure of natural separation occurs in these components. However, even if olivines do begin to appear in a rock that has the average composition of a pyroxene, which is possible, the $\frac{M}{Si}$ values determine that an $\frac{\text{amphibole}}{\text{olivine}}$ ratio of 8 to 1 be maintained. The pyroxene-amphibole components remain predominant. In any case, from composition analyses, the pyroxenes are known to be the dominant representatives of the ferromagnesian silicates among the igneous rocks in the accessible regions of the world. (Table 2)

According to Shand(2), and as has been observed by others (1,3), the pyroxenes frequently constitute the whole of very large and also smaller rock masses, though in such cases it appears that the pyroxene has not been derived from a magma of its own composition. When association occurs, lime-feldspars and iron ores are to be expected, as these separate out with the pyroxenes in a common stage during the cooling of the magma.

In brief, the pyroxenes contain the manganese and can occur as large intrusions. They therefore have the properties that identify them as the igneous source rock for manganese deposits.

THE PYROXENES

In the pyroxenes, the divalent ions of magnesium, calcium and iron quite freely replace one another so that the general formula $(Mg, Ca, Fe)_2\ Si_2O_6$ shows very considerable variations in metal atom ratios up to and including pure end members like $Mg_2Si_2O_6$. A universal average composition for pyroxenes, calculated from the data of Vogt, is however $(Fe_{0.53}\ Mg_{1.23}\ Ca_{0.23})\ Si_2O_6$.

The scarcity of manganese makes its occurrence as a pure, or even a substantially enriched, manganese silicate rock statistically rare. Moreover, as divalent manganese is able to replace the relatively much more abundant divalent metals calcium, magnesium and iron in these silicates, it is all the more likely that manganese occurs principally as a more or less minor replacement among the major metals in the structures of these silicates. According to Clarke and Washington, the universal average composition for pyroxenes including manganese is:

$$(Fe_{0.51}\ Mg_{1.13}\ Ca_{0.34}\ Mn_{0.018})\ Si_2O_6.$$

Rather large local deviations do occur, as shown in Table 3. They depend, in part, on the rocks with which the pyroxene is associated and on the specific pyroxene that is present. Consequently, two choices are open: either to assume magmas to have been universally homogeneous, and thus accept a universal average rock as the source material, or to attempt to specify a local deviant that could give rise to a manganese deposit.

Manganese has unequal resemblances to iron, magnesium, and calcium. Accordingly, it will be able to replace some of these more readily than others in the silicate framework of pyroxene rocks. With respect to ionic radii, and the d sub-shell wherein reside the possibilities for multiple bonds and a higher valence, it resembles iron the more closely. This is shown, for example, in the following radius ratios of the divalent ions, taken from Goldschmidt's table of ionic radii:

$$\frac{Fe}{Mn} = 0.912,\quad \frac{Mg}{Mn} = 0.86, \text{and } \frac{Mn}{Ca} = 0.86$$

Here manganese is, by ratio, as much larger than magnesium as it is smaller than calcium. However, the values of the ratios are such

TABLE 3

Metal Ratios in Different Average Pyroxenes

Metal Ratios	Pyroxene taken from	Ultra basic rock		Gabbros and Norite	Alkali Pyroxene Nepheline Syenites	
					Fe++	Total Fe
Pyroxene	$\frac{\text{Fe}}{\text{Mg}}$	0.15		0.426	2.1	9.7
	$\frac{\text{Fe}}{\text{Mn}}$	115		38.4	9.7	45.8
Amphiboles		Amphiboles Calc-Alkali		Granites	Alkali Syenites	
		Gabbros	Diorite			Total Fe
	$\frac{\text{Fe}}{\text{Mg}}$	0.425	0.436	0.43	4.12	5.35
	$\frac{\text{Fe}}{\text{Mn}}$	113	70	45	26	35

that manganese can substitute for any one of the ions, other factors being agreeable, so that only a tendency to follow iron is suggested by these ratios. In addition, to the extent that the d sub-shell is effective, as for example certainly when multiple bonds can form, the resemblance to iron is emphasized. This may be of some slight importance in the silicates, for it is noticed, particularly in the hypersthenes, that iron-rich ferro-magnesian silicates $(Fe,Mg)_2\ Si_2O_6$ always contain more than the average amount of manganese $^{(1,4)}$. By contrast, manganese does not seem to stabilize ferro-calcium silicates, although this would be expected if the sizes of the ions were the only factors. Both hedenbergite $(Fe,Ca)_2\ Si_2O_6$ and manganhedenbergite $(Fe,Ca,Mn)_2\ Si_2O_6$ occur naturally$^{(4)}$. Consequently, a rather closer following of the iron, by manganese, is to be expected than the radius ratios themselves indicate.

As well, the position of equivalence that manganese possesses between magnesium and calcium, through radius ratios, is also apt to be distorted by secondary considerations. For example, though the four divalent ions can all, under some circumstances, employ octahedral coordination, this is true in pyroxenes only for Mn, Mg and Fe. Calcium shows a coordination number of eight, rather than six, in the pyroxenes, making its replacement by Mn presumably more difficult than in the other cases$^{(3)}$. Indeed, if Ca is in fact rigorously restricted to a coordination number of eight in the pyroxenes, which is not definitely known, then manganese could not replace it at all without a structural change. There would then be no tendency for Mn to follow Ca, though both could, of course, still occur in the same deposit.

Consequently, summing up the foregoing, a mixed silicate containing Mg, Fe, Ca and Mn is expected to be the principal manganese-bearing rock. In the relative amounts of Mg, Fe and Ca present, if the manganese content were to be above average, in accordance with the above arguments it would be expected that the material would be substantially enriched in iron, and that the Ca/Mg ratio would be considerably smaller than in the universal average pyroxene. With $(Fe_{0.51}\ Mg_{1.13}\ Ca_{0.34}\ Mn_{0.018})\ Si_2O_6$ as the composition of the universal average, a specific rock with the formula $(Fe_{0.8}\ Mg_{1.0}\ Ca_{0.16}\ Mn_{0.04})\ Si_2O_6$ will be chosen to specify the enriched manganese source rock. This is to be understood as a representation of the composition of the average of all the diverse ferro-magnesian constituents present in the rock, and not as a specification of any one of them.

The formula provides a 0.95% manganese rock. Such a rock has, therefore, about twice the manganese content of the universal average pyroxene, but it is only slightly richer than the richest rocks in Table 3, where the manganese content varies from 0.06 to 0.85%(1). The $\frac{Fe}{Mn}$ ratio of 20 in the source rock is also just below the upper range for this ratio, values from 26 to 200, centering around 50, being the average values. The ratio $\frac{Ca}{Mg} = 0.16$ which was selected is appreciably smaller than the value of 0.30 in the universal average, and somewhat smaller than the value 0.19 shown by pyroxenes from gabbro (Table 1). The metallic components add up to two, as in the general formula for a pyroxene, $M_2\ Si_2O_6$. Consequently, the ratios of metal to silica are also defined in the source rock. The effect of deviations from the formula, which of course are to be expected, and of the presence of associated non-pyroxenous rocks in the source material, will be considered in later sections.

PART II

THE FORMATION OF THE SEDIMENTARY DEPOSIT

INTRODUCTION

The weathering of igneous rock leads to the formation of a new assemblage of compounds, many of which are soluble to some extent in water. Transportation and precipitation of the dissolved substances, followed by their consolidation, leads to the formation of new deposits. The resistance of different kinds of rocks to weathering agents shows a considerable variation. In a general way, as shown by Goldich's Reactivity Series(5), the ferro-magnesian pyroxenes are among the most susceptible to these disintegrative processes. In addition, the components in the rock are also extracted at different rates, so that the breakdown of the rock is not simply a steady dissolution.

In a general consideration of the transfer of an igneous rock through water to form a sedimentary deposit, numerous combinations of conditions arise. The waters may be acidic or basic, with or without oxidative powers, and with or without dissolved CO_2. In addition, the physical conditions surrounding the exposure, such as flow rates, depth of immersion, the fate of sediments, etc., can have important effects on the newly forming deposit. Here the problem is to follow the manganese and establish conditions which can lead to a concentration of this component. Two physical processes will be described, one leading directly to a manganese deposit, the other not.

PROCESSES NOT LEADING TO A MANGANESE DEPOSIT

Igneous Rock not Exposed to Water

Air weathering of an exposed igneous rock can lead to disintegration, working from the surface down and depending on temperature and humidity. Ferric and manganese oxides would appear on exposures, and in cracks and crevices, leaving a crumbly rock behind. Unless the eroded surfaces were worn away by wind or water, the process would slow down with time, and in the end, be confined to the surface regions. Here some oxide enrichment would occur, particularly in cracks and fissures and on surfaces. However, a sedimentary deposit would not arise, nor would any substantial concentration of the Mn component be effected from its 1% presence in the source rock, unless a mechanical separation of the chemically distinct oxidic and rock residues were made. Here the Fe and Mn oxides are the smaller looser particles, the rock remnants tending to be micaceous and sand-like if no further chemical decomposition has occurred.

Igneous Rock Exposed to Water

The properties of natural waters that have importance to the present problem are its pH, its oxidation potential, and its content of dissolved potent gases, like CO_2, O_2 and H_2S. The effect on pyroxene rocks of acid waters with no dissolved gases will be considered first of all. Other combinations will be considered later.

(a) Acid waters, no valence change

In general, the susceptibility of the silicate rocks to weathering decompositions increases uniformly as the silicate structure becomes less prominent(5). Thus, olivine decomposes most rapidly, pyroxenes next, etc., down to quartz which is the most resistant to weathering.

Furthermore, in considering a particular rock, different components in it may be extracted first. In general, in the ferromagnesian silicates the metallic components are lost first, and then the framework elements, silica and alumina.

These general considerations seem valid, more or less, without regard to the acidity or oxidizing strength of the solution. However, the manner in which the rock breaks down (and possibly the order in which the various metals are withdrawn) and the extent to which the framework constituents are transformed, probably have a considerable dependence on pH, oxidation potential and other conditions in the encroaching waters.

Here the source rock is of a type that weathers rapidly. In acid waters, under the condition that oxidation does not occur, the preliminary step becomes substantially an ion-exchange process, with H^+ going into the rock and Ca^{++}, Mg^{++}, Fe^{++} and Mn^{++} coming out into solution; that is, the divalent ions holding the silicate chains together are replaced by H^+, with the result that the chains tend to separate, become hydrated, and are brought into solution. If the process is complete, soluble polysilicic acids are produced, along with solutions of the metal ions. This has been shown to happen in the acid solution of $Ca_2Si_2O_6$ (6). It is possible that some chain ruptures occur in the polysilicic acid units. In acid solutions these are more likely to occur in mid-portions of the chain, leaving a polymeric though heterogeneous silicic acid in solution(6).

Returning to the extraction of the metallic components, the Mg, Ca, Fe and Mn will come out at different rates, depending on their properties in the lattice and including their different abundances. Experimentally, for an amphibole the observed rates were in the order Ca$>$, Mg$>$, Fe. The rate of solution of manganese was not investigated(5). From its ionic radius and electron structure the rate would be close to that for Fe, and probably between those of Mg and Fe. Consequently, the order of specific extraction rates becomes Ca$>$, Mg$>$, Mn$>$, Fe. As a result, in the preliminary stages the waters become relatively enriched in the Ca and Mg components, while the residual material in the rocks, and the colloidal silicates themselves, become relatively enriched in the Fe, Mn components.

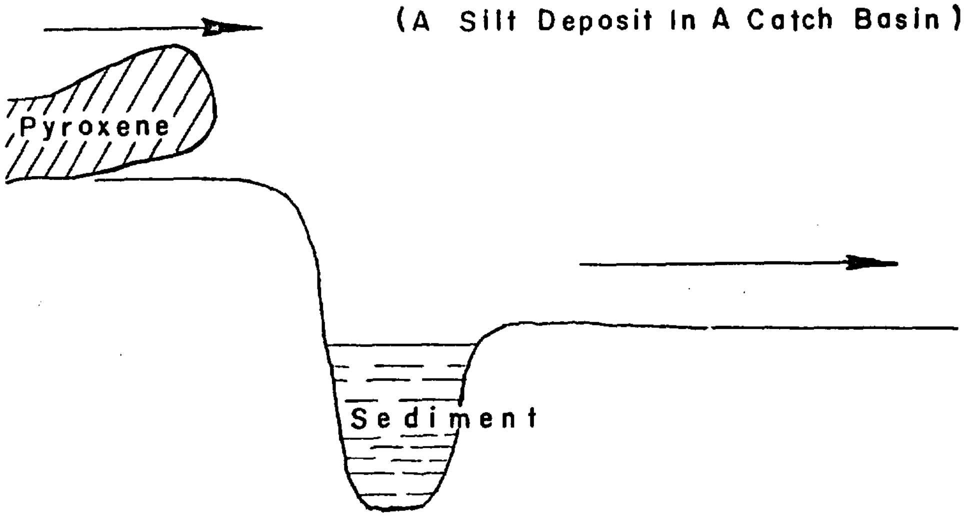
It is to be borne in mind that, although the attack of acid waters will give a complete decomposition of the rock over a period of time with the material in solution as metal ions and colloidal polysilicic acid, the preliminary stages constitute concentrating processes that can lead to partial separations if conditions are correct. Though the relative magnitudes of the rates for metal ion extractions are not exactly known, nevertheless two separations do occur:

1. A partial separation of the Ca and Mg from the Mn and Fe.
2. A partial separation of the metallic ions from the silicate framework.

The extent to which these fractionations are successful depends not only on the chemistry of the system, but also on mechanical factors. For example, if the acid waters, in rapid motion over the pyroxene rock, then move over a pool and on to exit, as in Figure 1, a steady state representing a preliminary stage in the decomposition of the rock would be established.

Figure 1

(A Silt Deposit In A Catch Basin)



In solution, metallic ions enriched by ratio in Ca and Mg components would pass through the pool, leaving a coherent and particulate residue behind, enriched in Mn and Fe, so far as the metal components are concerned. These colloidal silts and grits would tend to settle out in the pool, liberating their remaining ions at ever slower rates as further sediments accumulated. The deposit, as it formed, would be a Fe-Mn siliceous material, retaining less Ca than Mg, but losing both. Through its loss in metal relative to the source rock, it would have a composition corresponding to something like biotite or clay or quartz, depending on the amounts of metals removed, and on the aluminum content of the source rock or in the background.

It can be shown, however, that such a process does not lead to a manganese deposit. For, as some manganese is lost to the solution, its ratio to the silicate is lower in the sediment than in the source rock, though a gain has been made for manganese in the metal ion ratios. For example, if metals extraction in the single-pass exposure has changed the pyroxene to a micaceous type deposit, the composition change has been from a $M_2Si_2O_6$ to a $M_6Si_8O_{22}$ material. As 1/4 of the total metal content has been lost to the solution, rather more than 1/4 of the Ca and rather less than 1/4 of the Fe will be lost to the solution. Taking Ca as 1/2, Mg as 1/3, Mn as 1/4, and balancing with Fe, something like

$(Fe_{0.69}\ Mg_{0.70}\ Ca_{0.08}\ Mn_{0.03})_4\ Si_8O_{22}$ is obtained

for the sediment from the source rock $(Fe_{0.8}\ Mg_{1.0}\ Ca_{0.16}\ Mn_{0.04})\ Si_2O_6$. From these compositions, the Fe and Mn contents fall slightly, from 19.7% and 0.87% in the source rock to 19.5% and 0.80% in the sediment, respectively. The deposit therefore is, or could become, a ferruginous clay, slate or shale, but it is in no way a manganese deposit.

(b) Basic waters, no valence change

When pyroxene-type rocks break down in water, the net result is the liberation of basic components, whether the mechanism be hydrolytic or through ion exchange.

$$R_2\ Si_2O_6 + H_2O \longrightarrow 2R^{++} + 2OH^- + H_4Si_2O_6.$$

The metallic hydroxides are dissociated bases, and the silicic acid is weak enough so that its acid property is effective only at high pH (above 10.8). Consequently, the previous assumption of acid waters constitutes the special case where sufficient acidity is present to more than neutralize the basic ingredients liberated by the decomposing rock. That is, a substantial acid source, prior to and apart from the rock, was implied for the water.

Apart from such a special case the natural expectation is that basic rocks, as for example the pyroxenes, will, either at once or shortly, produce basic waters. At once, in such a particular circumstance, the participation of CO_2 must be considered.

The solubility of CO_2 in water changes abruptly from amounts less than 10^{-6}M in neutral or acid waters under normal conditions, to concentrations somewhat in excess of that of the metal ion, in basic solutions. This corresponds to a change in solubility of CO_2 by a factor of 10,000, when the concentration of the basic metallic ion is taken to be 0.01 molar. Consequently, the absorption of appreciable amounts of CO_2 can hardly be avoided if the atmosphere contains it and if the waters are basic. Moreover, in basic solutions the concentrations of the dissolved forms of CO_2 become less dependent on temperature and partial pressure variations, the concentration of the cation becoming the principal determining factor, as shown in Table 4.

TABLE 4

Solubility of CO_2 in $Na_2B_4O_7$ Solutions(7)

$pCO_2 = 1$ atm

$Na_2B_4O_7$	Molarity of CO_2
0.025 N	0.061
0.125 N	0.161
0.250 N	0.256

i. Basic Waters with no CO_2

It is known that carbonated waters attack rocks more rapidly than do waters with no carbon dioxide, a phenomenon apparently associated with the pH control shown by the dissolved CO_2. As carbonic acid, it acts to dissipate the alkalinity resulting from the hydrolysis of the basic rock. In the absence of carbon dioxide, as has been shown in closed systems(1,4), the alkalinity builds up until the polysilicic acids and the metallic hydroxides begin to recombine, the new sediments essentially reversing the original hydrolytic decomposition.

$$R_2Si_2O_6 + 4\ H_2O \rightleftharpoons 2\ R\ (OH)_2 + H_4Si_2O_6$$

It should be noted that in a suitable flow system such a series of reactions could lead to a transportation of material, with a partial separation of components. Judging by the solubilities of the hydroxides (K_{sp} $Mn(OH)_2 = 10^{-14}$; $Fe(OH)_2 = 10^{-15}$; $Mg(OH)_2 = 10^{-13}$), basic, carbonic-acid-free waters would produce a sedimentary (Fe,Mg,Mn) silicate deposit, with the more soluble $Ca(OH)_2$ and (K_{sp} 10^{-5}) remaining in solution. If all the calcium were lost, the metal/Si ratio would be lowered from 1 to about 0.9. The material would not, therefore, be reconverted as a pyroxene. No appreciable enrichment in the manganese component would, however, have occurred.

ii. Carbon dioxide in basic waters

For practical purposes it is probably unavoidable that basic surface waters do have CO_2 in solution. Besides neutralizing the alkalinity, the CO_2 also complexes with the metal ions, as in the equation

$$R_2Si_2O_6 + 4\ H_2O + 4\ CO_2 \longrightarrow 2R\ (HCO_3)^+ + H_4Si_2O_6 + 2\ HCO_3^-.$$

There are several points to be made with regard to this overall reaction:

1. The bicarbonate complex ions, $M(HCO_3)^+$, increase the total solubilities of the metallic species, as the concentrations of

the uncomplexed divalent ions, M^{++}, are thereby reduced according to the equilibrium:

$$M(HCO_3)^+ \rightleftharpoons M^{++} + HCO_3^-$$

2. The bicarbonate acts to control the pH of the solution. Slightly alkaline solutions, with a pH of about 8, are associated with the Ca, Mg and Fe bicarbonates. pH control operates both for dilution type changes and for acid-base ratio changes.

3. The form of and opportunity for precipitation are affected, because on the one hand the M^{++} concentration depends on the stability of the complex, and on the other, precipitation can result from such diverse, though partly interdependent, equilibria as:

$$M^{++} + CO_3 \rightleftharpoons MCO_3 \downarrow$$

$$M^{++} + 2OH \rightleftharpoons M(OH)_2 \downarrow$$

$$2\ M^{++} + H_4Si_2O_6 \rightleftharpoons M_2Si_2O_6 \downarrow + 4H^+$$

4. At pH 8, neither the acid property of breaking polysilicic acid chains in the middle, nor the basic property of breaking them at the ends to form silicate ions, can become predominant. The polysilicic acid chains derived from the rock may therefore be expected to have a substantial persistence in the bicarbonate solutions. Moreover, it is known that the agglomeration of polysilicic acids leading to sediments and gel formation is most rapid in the pH range 5 to 8, although above a pH of about 7 the particles begin to bear a negative charge that stabilizes the colloid(6). Hence, at a pH of 8, a tendency towards agglomeration as chains condense together, rather than to the further breakdown of the chains, is to be expected.

5. The possibility that neutral or acid waters attack the rock, with the CO_2 absorbed only as the waters become basic, seems to be indicated. From this point of view, the metal ions are extracted by the hydrolysis of the rock-- or what is in effect the same process, by ion-exchange--although HCO_3^- ions might help by complexing with exposed metal ions not yet removed from the lattice. It appears, therefore, that CO_2 and its related species are important not so much in the breakdown of the rock, as in the solution equilibria that follow.

CONDITIONS LEADING TO A MANGANESE DEPOSIT

Before the physical properties of the primary sediment, and the processes leading to its development, are considered, some preliminary data will be obtained from the more general aspects of the bicarbonate equilibria system. These data will then be used to calculate such properties as distribution, composition, mineral type, etc., in the sediment. Finally, the role of oxygen and the influence it may exert under these conditions will also be included.

The Bicarbonate System

(a) Preliminary considerations about the equilibria

Whether the rock materials are brought into solution by originally acidic, basic carbonic, or neutral waters, a basic carbonic solution is ultimately established through absorption of CO_2. For the metallic components, as long as oxidation is not occurring, five equilibria seem sufficient to describe the system.

$$M^{++} + CO_3^{=} \rightleftharpoons MCO_{3(s)} \qquad (1)$$

$$HCO_3^{-} \rightleftharpoons H^{+} + CO_3^{=} \qquad (2)$$

$$M^{++} + HCO_3^{-} \rightleftharpoons M(HCO_3)^{+} \qquad (3)$$

$$M^{++} + 2OH^{-} \rightleftharpoons M(OH)_{2(s)} \qquad (4)$$

$$2M^{++} + H_4Si_2O_6 \rightleftharpoons M_2Si_2O_6 + 4H^{+} \qquad (5)$$

The metal ion concentrations, derived solely from the rock, are controlled in solution by the concentrations of OH^-, $CO_3^=$, HCO_3^- and polysilicic acids. Of the five reactions, three remove the metallic ions as precipitates, which, as sediments, constitute an irreversible withdrawal in a flow system. In reaction 3, where the bicarbonate complex forms, the metal remains in solution although the concentration of the M^{++} ion is lowered.

The equilibrium in reaction 3, therefore, acts to increase the total solubility of the metal, providing a reservoir for M^{++} ions, which are permanently withdrawn as precipitates by reactions 1, 5, and 4. Consequently, the specific fates of the various metals depend on the properties of the four equilibria in an interrelated way.

The equilibrium constants for the hydroxide and carbonate precipitations of Fe, Mn, Mg and Ca are known(8). The constants for the silicate precipitation (reaction 5) and the bicarbonate complex ion dissociation (reaction 3) are not. It is known, however, that the silicates tend to precipitate at a pH just above that required to precipitate the hydroxides(6). This generalization will be used in subsequent arguments. The K_3 values for the bicarbonate complex can be calculated from the carbonate system, using solubility data.

$$\text{Taking } MCO_3 \rightleftarrows M^{++} + CO_3^{=} \qquad K_1$$

$$HCO_3^- \rightleftarrows H^+ + CO_3^{=} \qquad K_2$$

$$M(HCO_3)^+ \rightleftarrows M^{++} + HCO_3^- \qquad K_3$$

$$C = M(HCO_3)^+ + M^{++}$$

Here C is the total concentration of the soluble species of M in a carbonate system. The solubility data were taken from Seidell(7), under the conditions, 20°C., $P_{CO_2} = 0.1$ atm.

$$\text{Then, for } K_3 = \frac{(M^{++})\ (HCO_3^-)}{(M\ (HCO_3)^+)},$$

$$\text{since } (M^{++}) = \frac{K_1}{(CO_3^{=})}$$

$$\text{and } (CO_3^{=}) = \frac{K_2\ (HCO_3^-)}{(H^+)},$$

$$\text{then } (M^{++}) = \frac{K_1}{K_2}\ \frac{(H^+)}{(HCO_3)}$$

$$\text{and } \therefore K_3 = \frac{K_1}{K_2}\ \frac{(H^+)}{(M\ (HCO_3)^+)}$$

$$\text{as } (M(HCO_3)^+) = C - M^{++} = C - \frac{K_1}{K_2}\ \frac{(H^+)}{(HCO_3^-)}$$

$$\therefore K_3 = \frac{K_1}{K_2} \cdot (H^+)\ \frac{1}{C-(M^{++})}$$

The (H^+), which in the bicarbonate system is buffered in the vicinity of 10^{-8} molar and at any rate equally affects the K_3 values for each metal, will therefore be specified at 10^{-8} with no relative error but the possibility of some absolute error.

In the term, $C - (M^{++})$, the value is substantially that of C alone if $(M\ (HCO_3)^+)$ greatly exceeds M^{++}, that is, if K_3 is small. The data (Seidell) show this to be the case, e.g. in $CaCO_3$ solutions where $(CaHCO_3^+)$ is 10^{-4} (Ca^{++}). It is not so markedly the case in Mg carbonates.

Accordingly, K_3 becomes

$$K_3 = \frac{K_1}{4.7 \times 10^{-11}} \cdot \frac{10^{-8}}{C} = \frac{K_1}{4.7 \times 10^{-3} \times C}.$$

The values for K_3, calculated from this expression, are given in Table 5.

TABLE 5

Bicarbonate Equilibrium Constants

K_1	C	K_3	$M(HCO_3)^+$
1×10^{-5}	0.21	10^{-2}	$Mg\ (HCO_3)^+$
4.8×10^{-9}	0.53×10^{-2}	2×10^{-4}	$Ca\ (HCO_3)^+$
2.1×10^{-11}	0.24×10^{-2}	2×10^{-6}	$Fe\ (HCO_3)^+$
8.8×10^{-11}	0.28×10^{-2}	6×10^{-6}	$Mn\ (HCO_3)^+$

From Table 5 it is evident that although $Mg(HCO_3)^+$ is the least stable bicarbonate complex, as shown in the K_3 column, the total solubility of magnesium species exceeds that of the other metals. This follows from the greater solubility of $MgCO_3$ itself, so that rather greater concentrations of $Mg(HCO_3)^+$ and much greater concentrations of Mg^{++} can remain in solution than for the respective ions of the other elements. Mn and Fe, on the other hand, have the smaller saturated values for the M^{++} species, but they have the larger $\frac{M(HCO_3)^+}{M^{++}}$ ratios. That is, a larger percentage of Fe and Mn is in solution as $M(HCO_3)^+$ than is the case for Mg and Ca, though the total solubilities of Mg and Ca are greater.

A further question concerns the relative effectiveness of the precipitating reactions 1, 4, and 5. A comparison of the solubilities of the carbonate and hydroxides shows that Ca, Fe and Mn have a tendency to precipitate out as carbonates, even though the $\frac{OH^-}{CO_3^=}$ ratio be as large as 10^4 or 10^5, though this depends on the concentration of the metal ion. This is shown in Table 6.

TABLE 6

$\frac{(OH^-)}{(CO_3^=)}$ Ratios Required for Co-precipitation of Hydroxide and Carbonate

M^{++}	K_{sp} MCO_3	K_{sp} $M(OH)_2$	$^*\frac{(OH^-)}{(CO_3^=)} = \frac{K_4^{**}}{K_2 \cdot (M^{++})}$	
			$M^{++} = 0.01$	$M^{++} = 0.0001$
Mg	1×10^{-5}	5.5×10^{-12}	2.4	24
Ca	4.8×10^{-9}	7.9×10^{-6}	6×10^5	6×10^4
Fe	2.1×10^{-11}	1.6×10^{-15}	2×10^5	2×10^4
Mn	8.8×10^{-11}	7.1×10^{-15}	1×10^5	1×10^4

$^{**}K_4$ is the equilibrium constant for $M^{++} + 2OH^- \rightleftarrows M(OH)_{2(s)}$

Mg, in contrast to the other elements, has its $\frac{OH^-}{CO3^=}$ ratio for co-precipitation close to unity. Thus in general, the expectation would be for carbonate precipitates of Mn, Fe and Ca from a wide variety of basic waters, if any precipitation were to occur, while Mg^{++} could come down as either carbonate or hydroxide, with slight changes in the hydroxyl/carbonate ratio in the basic carbonate solution. This is confirmed, perhaps, in the natural occurrence of basic Mg carbonate and Mg hydroxide deposits.

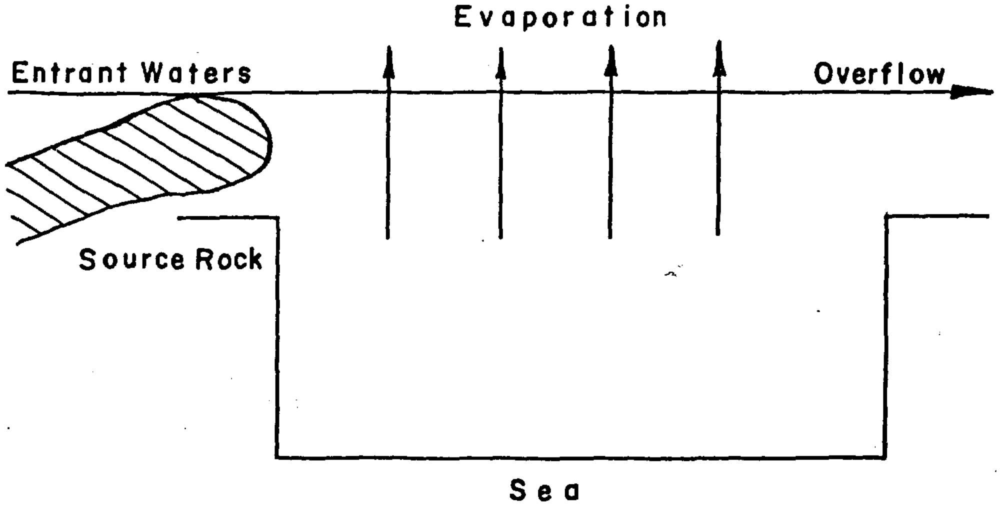
(b) The Formation of the primary sediment

i. Physical conditions

It will be assumed that the sediments are being set down in a flat inland sea having one entry and one outlet, as in a river with an extraordinary bulge. The entrant waters have passed over the source rocks. These waters carry the soluble components in at one end of the fresh-water sea. At the other, effluent waters take the overflow to undetermined regions. A schematic representation is shown in Figure 2. The fresh-water sea is to be understood as a body of water intermediate to contemporary fresh-water lakes and salt-water seas. The problem is to define the chemical occurrences in the fresh-water sea.

Figure 2

The Flat Inland Sea



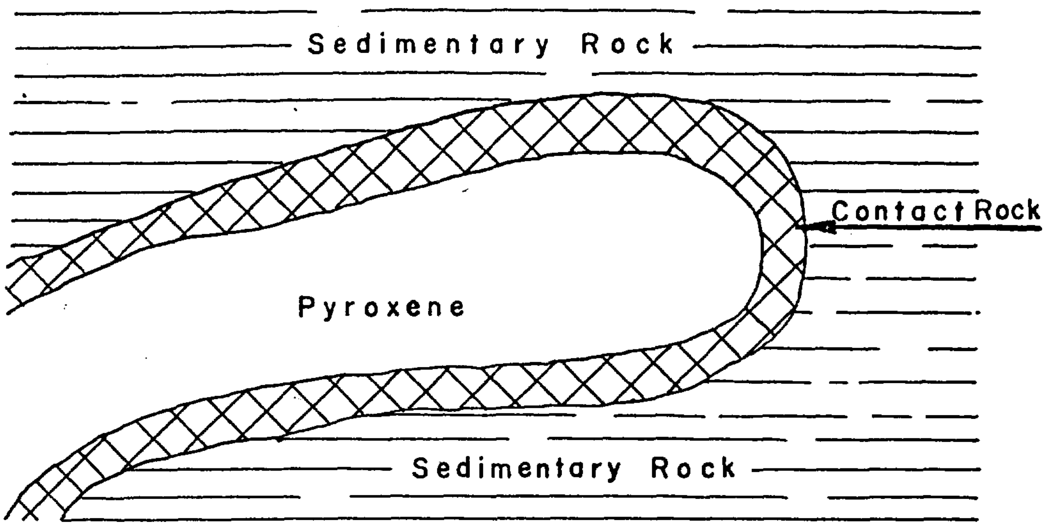
Evaporation from the sea will cause a loss of water from the flow system. This will lower the flow rates of, and increase concentrations in, the effluent waters as compared with those at the entry end. Assuming uniform mixing to depth and across the breadth of the inland sea, a concentration gradient in the soluble species will be set up, the concentrations steadily increasing from the entry to the exit end. If evaporation losses are high enough, concentrations will begin to exceed solubilities before the waters leave the sea. Then precipitation will occur. On the other hand, if evaporation is less than this, the effluent waters will still retain all components, and no sediment will appear. The implication, therefore, is that the sea must have a certain minimal area if deposition is to precede the overflow.

As rates of evaporation depend on temperature and humidity as well as surface area, and the volume of water to be evaporated depends on flow rates, concentrations and solubilities, estimates of sea/river ratios under sets of assumed conditions are possible. None is given here.

The entrant waters have passed over the source rock before they reach the sea. Consequently, all extractive processes occur prior to the concentrations leading to deposition. However, differences in the physical environment do affect the nature of the deposits. Therefore, to make the example clear, the source will be more closely defined as an igneous intrusion into sediments, the pyroxenious material coming in as an off-shoot from a distant magma. Consequently, as in Figure 3, the source rock will be surrounded by contact-metamorphic rocks, which in turn are surrounded by the sedimentary rocks of the district. In this case, material from the pyroxene source begins to appear in the entrant waters only after the ancient sediments and contact-metamorphic rocks surrounding it have been worn away.

Figure 3

The Source Rock



Once the pyroxene source has been exposed, the relatively reactive silicate is able to dominate the entrant waters, providing metal ions, present principally as bicarbonates in the basic carbonated waters, and providing silica as polysilicic acid chains, and as colloidal agglomerates of these polymeric units, as long as the pyroxene source remains.

The relative concentrations of the dissolved species must, however, vary during the life of the igneous source, as the calcium and magnesium are extracted more rapidly, and the siliceous materials more slowly, than the iron and manganese components. Consequently, the entrant waters will at first have Ca and Mg in excess ratios, and at the end will be poor in Ca and Mg but enriched in polysilicic material, as compared with the source rock. Presumably, during the middle life of the source the entrant waters will carry over solution concentrations in ratios similar to the composition of the source. These three epochs will be called

Stage 1, Stage 2 and Stage 3, in the life of the source rock.

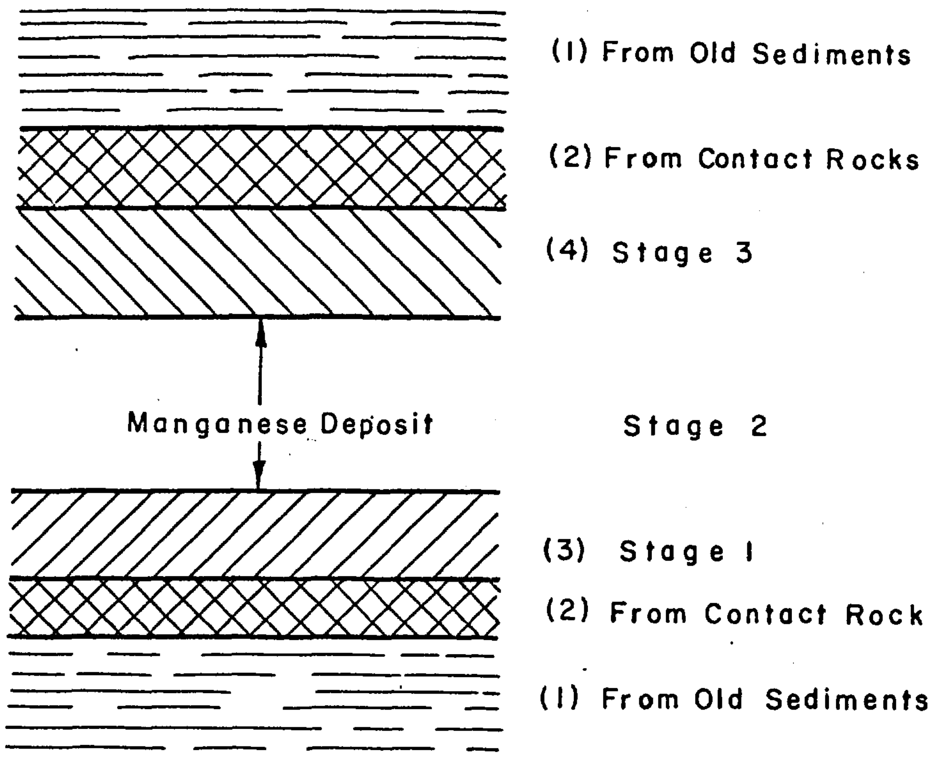
ii. (Stages 1 and 3). Deposits are laid down that contain no manganese

In the first stage, as principally calcium and magnesium are extracted from the source and mixed with material from earlier rocks still in solution, manganese is deficient--at any rate as compared with its presence in the source rock. The deposit formed at this stage is calcareous. Carbonates could be present in it, but there should be no manganese. The Stage 1 deposit is laid down on the sediments from contact-metamorphic rocks, which in turn overlay the sediments derived from the old rocks surrounding the source material.

It might be noted that Stage 1 and Stage 3 have a common relationship to the contact-metamorphic and to the old sedimentary zones. That is, Stage 1 is preceded and Stage 3 is followed by the same series of events, the deposition of sediments derived from the contact zone and from the country rock respectively. As a result, the main stage in the deposition of the manganese deposit has the schematic relationship shown in Figure 4.

Figure 4

Strata in the Sediments



iii. (Stage 2) The formation of the manganese deposit

Manganese begins to appear in the entrant waters as soon as the pyroxene rock is exposed. Its concentration, at first small as compared with the Ca, Mg components, then builds up as a debris of partially decomposed material accumulates on the surface. During the steady breakdown of the rock, the mixture exposed to contact with the water remains sensibly unchanged, as long as unaltered pyroxene remains the major component. Through this period, therefore, and though the extraction is a complicated summing up of different rates from products at different stages of degradation, the overall effect is to put all components into solution in concentration ratios like those in the pyroxene itself. The Fe, Mn enrichment in Stage 2, implied by the Ca, Mg enrichment in Stage 1 and the siliceous residue of Stage 3, cannot reasonably be appreciable if the pyroxene source is of any size. Consequently, Stage 2 constitutes the major episode in the erosion-life of the igneous source; but it acts only to put all components of the rock into the eroding waters in molar ratios like those in the source itself. Once in solution, however, separations and concentrations can begin. In these waters, bicarbonate equilibria, oxidation and colloidal settling provide the mechanisms for the formation of the sediment. The paths taken by the metal ions, through reducing and through oxidizing waters, will be discussed first. Then the route taken by the siliceous components will be considered.

The Precipitation of the Metallic Components

(a) In the absence of oxygen but with dissolved CO_2.

On passing from the entry to the exit end, evaporation losses increase the concentrations of all the species until one of them becomes insoluble. Precipitation then begins, as evaporation continues, with the concentration of the precipitating ion remaining constant but the others still increasing. Then a second material becomes insoluble, and so on. The mole ratios of the ions remaining in solution change only during these selective precipitations. Consequently, mole ratios in the sediments become equal to the change in mole ratios in the solutions above the sediments.

When the bicarbonate system includes only the divalent ions of Mg, Ca, Fe and Mn, the equilibria involved in the precipitation of the carbonates are:

$$M(HCO_3)^+ \rightleftharpoons M^{++} + HCO_3^- \qquad K_3$$

$$HCO_3^- \rightleftharpoons H^+ + CO_3^= \qquad K_2$$

$$M^{++} + CO_3^= \rightleftharpoons MCO_3 \downarrow \qquad K_1$$

From these equations and equilibrium constants, it is possible to calculate the concentration ratios for which co-precipitation of the carbonates of any pair of ions will occur. Where M', M'' and K', K'' stand for the concentrations and equilibrium constants of the M ions (Fe, Mn, etc.), the co-precipitation ratios are

$$\frac{M'}{M''} = \frac{K_1' \cdot K_3''}{K_1'' \cdot K_3'} \cdot \frac{K_3' + (HCO_3^-)}{K_3'' + (HCO_3^-)} \qquad (1)$$

In the special circumstance that $(HCO_3^-) \gg K_3$, the simpler expression

$$\frac{M'}{M''} = \frac{K_1' \cdot K_3''}{K_1'' \cdot K_3'}$$ is obtained.

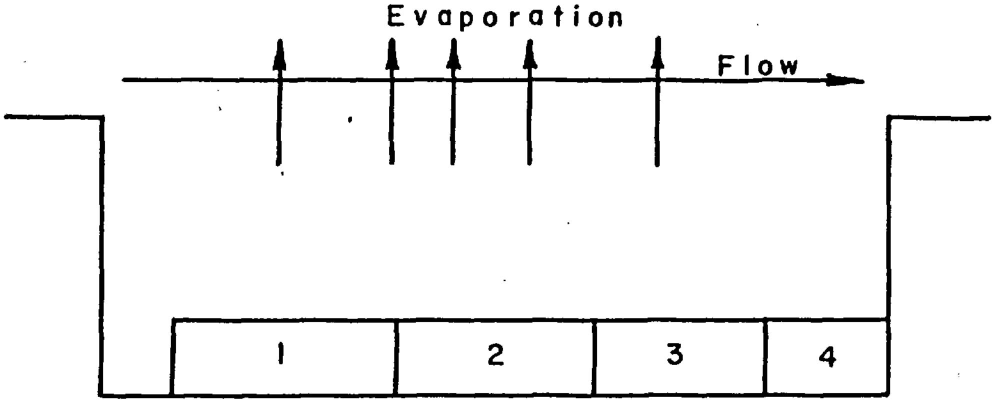
The assumption is valid without specifying concentrations, inasmuch as if (HCO_3^-) is not greater than K_3 in these instances, a carbonate solution does not exist.

From the equation (1), the ratios at which the co-precipitation of carbonates occur are $\frac{Ca}{Mg} = 2.4 \times 10^{-2}$, $\frac{Ca}{Fe} = 2.2$, $\frac{Ca}{Mn} = 1.6$, or $Mg_{1.00}\ Ca_{0.024}\ Fe_{0.011}\ Mn_{0.0133}$ for co-precipitation of all four. Consequently, as the absolute concentrations increase, $FeCO_3$ will precipitate first, coming down until the $\frac{Ca}{Fe}$ ratio is 2.2. The ions in solution then have the mole ratios $Mg_{1.0}\ Ca_{0.16}\ Fe_{0.072}\ Mn_{0.04}$. Next, Ca and Fe carbonates come down together, until the Ca/Mn ratio in solution has changed to Ca/Mn = 1.8. The residual concentrations then are in the ratios $Mg_{1.0}\ Ca_{0.064}\ Fe_{0.033}\ Mn_{0.040}$. Then calcium, iron and manganese co-precipitate until the $\frac{Ca}{Mg}$ ratio in solution is 2.4×10^{-2}. At this stage the ions are in solution in the ratios of $Mg_{1.0}\ Ca_{0.024}\ Fe_{0.011}\ Mn_{0.015}$, and presumably all precipitate together, if evaporation continues and if the waters have not yet reached the effluent end.

If we now consider the precipitated sediments, it is apparent that four zones appear, as shown in Figure 5, on going from the entrant to the exit ends of the sea. The chemical sediments begin at an unknown distance from the entrant end. The relative amount and kind of material in each zone can be calculated from the changes in solution molar ratios, going from zone to zone. The manganese deposit is in the third zone.

Figure 5

<u>Zones in the Carbonate Deposit</u>



Zone 1 = $0.73\ FeCO_3$

Zone 2 = $0.04\ FeCO_3$
$0.096\ CaCO_3$

Zone 3 = $0.04\ CaCO_3$
$0.022\ FeCO_3$
$0.025\ MnCO_3$

Zone 4 = The Residue

A little more than half of the manganese (0.025 of 0.04) comes down in Zone 3, as the solution phase passes from mole ratios of $Mg_{1.0}\ Ca_{0.064}\ Fe_{0.033}\ Mn_{0.04}$ to $Mg_{1.0}\ Ca_{0.024}\ Fe_{0.011}\ Mn_{0.015}$. In the carbonate deposit, a composition of 0.04 $CaCO_3$, 0.033 $FeCO_3$ and 0.025 $MnCO_3$ is obtained. The manganese has been upgraded from 0.9% in the igneous rock to 16% in the mixed carbonate. The concentration results from the precipitation of the larger part of the Fe and Ca prior to Zone 3, and from the retention in solution of the magnesium beyond Zone 3.

Three points are to be made about the manganese deposit in Zone 3 before oxidation is considered. First of all, since calcite is not isomorphous with siderite and rhodochrosite, whereas the last two are with each other, two carbonates should be present, the one a calcite with a small amount of Fe and Mn, the other a mixed Fe, Mn carbonate, with small amounts of Ca. The average manganese content of the second carbonate, a rhodochrosite, is 27% Mn. Since the calcium, unlike the iron, is an irregular replacement in pyroxene rocks enriched in manganese, the 27% value in the mixed carbonate is a better diagnostic feature for manganese content than the 16% in the carbonates in the overall.

The second point has reference to the magnesium in solution. The solubilities of mixed carbonates need not be the same as those of the pure compounds. This is particularly relevant when co-precipitation can occur. A particular result of mixed carbonate formation would be to bring Mg into the carbonates in the third zone. Whether this occurred by making additional carbonate, or as a replacement of Mg for say Mn in carbonates already there, the result would be to lower Mn percentages in this zone. On the other hand, the assumption that $(HCO_3^-) \gg K_3$ is least likely to be valid when magnesium is involved. The result here, calculated in terms of $\frac{Mg}{Mn}$ ratios, would be to keep Mg out of the carbonates in Zone 3. As the two deviations tend to compensate for each other, it seems best to accept an uncorrected picture.

Finally the third point. As the manganese deposit occurs in Zone 3 under solution concentration ratios defined by equilibrium constants, the original composition of the source rock can have quite considerable variations without affecting the composition of the deposit in Zone 3. The manganese deposit is laid down from a solution of composition $Mg_{1.0}\ Ca_{0.064}\ Fe_{0.033}\ Mn_{0.04}$. Ca and Fe in excess of these relative amounts is precipitated earlier. Therefore, the amount in which they exceed these ratios in the source rock has no effect on the manganese deposit. So far as the calculations are concerned, the composition of the deposit is affected only if Ca and Fe are present in the source rocks in lesser relative amounts than $Ca_{0.064}\ Fe_{0.033}\ Mn_{0.04}$.

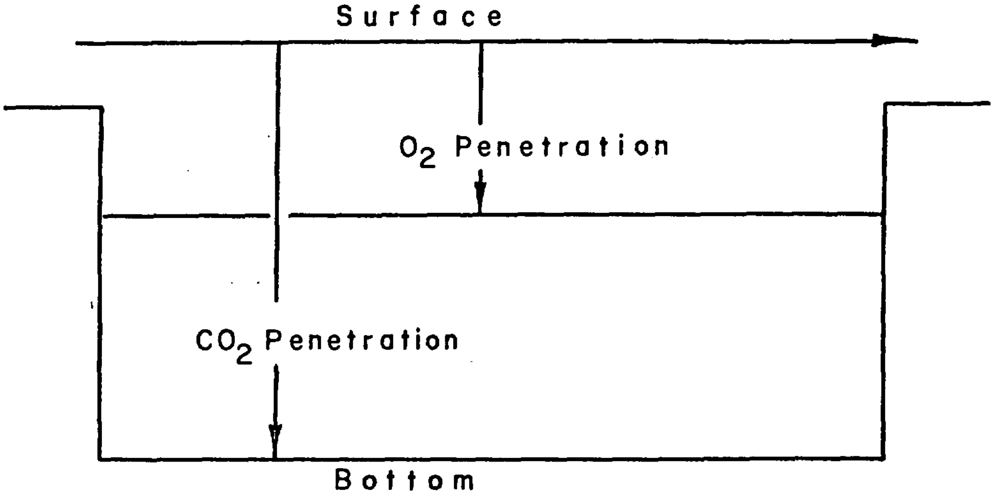
The composition of the zones referred to above may be used to support the assumptions used earlier on the relative manganese content of the source rock. Manganese remains in solution after Zone 3 in the composition ratio $Mg_{1.0}\ Ca_{0.024}\ Fe_{0.011}\ Mn_{0.015}$. That is, the manganese deposited in Zone 3 is very nearly just the manganese in excess of the manganese in an average pyroxene. The conclusion then is that the source rock must have more than average manganese for a manganese carbonate deposit to form. This confirms the assumption used in defining the source rock.

(b) The effect of oxygen and CO_2 on the precipitation

The assumption that CO_2 is absorbed from the air to set up a bicarbonate system, carries with it the necessary corollary that oxygen may also appear in the solution. Assuming that the CO_2 penetrates to the bottom of the sea while oxygen is confined to a superficial layer, as in Figure 6, calculations and conclusions can be drawn on the effects of oxidation on the deposit. The assumption is partly justified by the chemical equilibria that involve CO_2 and take it to the depths. Oxygen is not so involved, and may, therefore, more reasonably be confined to an upper layer.

Figure 6

CO_2 and O_2 in the Waters



Two extreme cases, a deep sea and a shallow one, will be taken for examples.

Example 1. Deep Sea. (Incomplete oxidation)

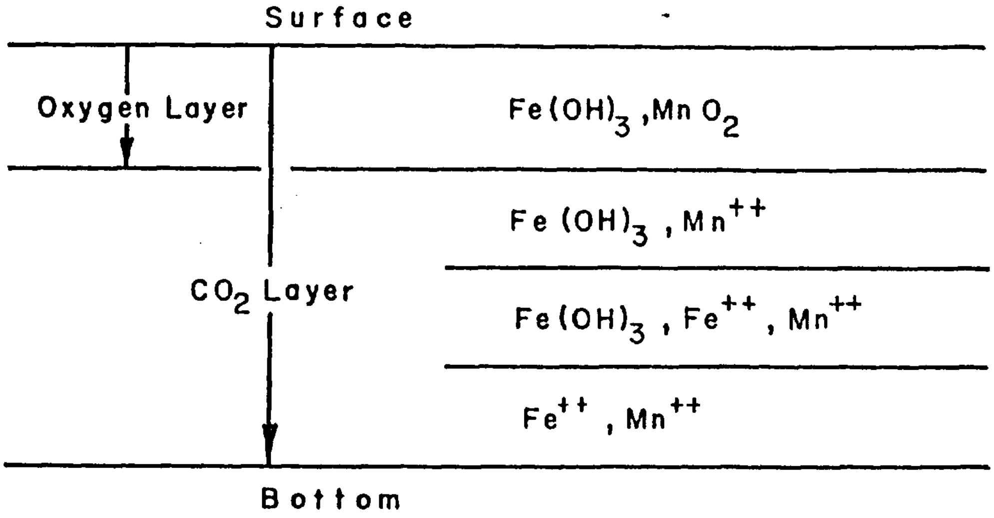
In the bicarbonate system, oxidation can affect the Fe and Mn components, but not the Ca, Mg, and polysilicic acids. Ferrous ion is oxidized more readily than manganous. In addition, ferrous ion can reduce MnO_2 to manganous ion(9), as in the reaction

$$MnO_2 + 2\ Fe^{++} + 4\ H_2O \rightleftarrows 2\ Fe(OH)_3 + Mn^{++} + 2H^+$$

In the particular case where the depth of the solution exceeds the depth of the oxygenated layer, as in Figures 5 and 6, these oxidation-reduction reactions lead to a depth-dependent distribution of iron and manganese compounds in the waters. This is shown in Figure 7.

Figure 7

The Oxidation States of Mn and Fe at Different Depths in the Inland Sea



Both $Fe(OH)_3$ and MnO_2 may form in the upper layer, the $Fe(OH)_3$ to a greater depth. By consuming oxygen, these reactions tend to restrict the deeper penetration of the oxygen and to sharpen the delineation between the oxidizing and non-oxidizing zones. Both $Fe(OH)_3$ and MnO_2 are insoluble and unprotected. They, therefore, settle out as rapidly as they form. At lower levels, the $Fe(OH)_3$ persists, but the MnO_2 is reduced to manganous ion by the ferrous ion found below the oxidizing zone. Consequently, though MnO_2 may appear as particles in the upper levels, it will not appear as a precipitate until the Fe at all levels has been oxidized. The net result of incomplete oxidation is, therefore, to add a ferric hydroxide (or a ferric silicate, see later) ingredient to the sediments below.

When oxidation is incomplete, the $Fe(OH)_3$ component mixes with the carbonate precipitates in the zones. In the water phase, the oxidation to $Fe(OH)_3$ lowers the concentration of ferrous ion but is otherwise independent of the carbonate equilibria. Consequently, the $\frac{Fe^{+3}}{Fe^{+2}}$ ratio in the water phase can have values ranging from infinity at the surface, where oxidation is complete, to zero at the lowest levels, where oxygen is absent. In the deposit, however, where ferric compounds replace on the average, rather than add to, the ferrous carbonate, the $\frac{Fe^{+3}}{Fe^{+2}}$ ratio should sum up the effects. The ratio in the deposit then becomes a measure of the relative depths of the carbonated and oxygenated layers.

Example 2. Shallow Sea. (Complete oxidation)

In the previous section it was seen that surface oxidation had an effect on the materials associated with manganese in the manganese deposit, but had none on the manganese itself. Complete oxidation, however, has more drastic results. They also vary with the zone in which the oxidation is occurring.

If complete oxidation occurs in any zone, an occurrence corresponding to a shallowness in that region, complete precipitation of the iron and the manganese in solution in that zone takes place. As the solution concentrations change from zone to zone, due to the precipitation of the carbonates, different mixtures of $Fe(OH)_3$ and MnO_2 will come down. The composition of the deposits from the different zones, assuming complete oxidation in that zone, with no preceding oxidation, is shown in Table 7, for the four zones.

For example, with complete oxidation occurring prior to zone 1, a solution containing $Mg_{1.0}$ $Fe_{0.8}$ $Ca_{0.16}$ $Mn_{0.04}$ yields a manganiferous hematite deposit of the composition 0.4 Fe_2O_3, 0.04 MnO_2. The deposit, which has 3.3% Mn, contains no carbonate, as carbonate precipitation has not yet begun. It is to be noted that the oxidation can have two effects. It can separate (as will be shown later) the oxides of manganese and iron from the carbonates of Ca and perhaps Mg. It also creates the possibility that manganiferous hematites of quite different composition may be built up. Complete oxidation in Zone 3, with no prior oxidation, precipitates the Fe and Mn from a $Mg_{1.0}$ $Fe_{0.033}$ $Ca_{0.064}$ $Mn_{0.040}$ solution. The deposit has the composition of 0.01 Fe_2O_3, 0.04 MnO_2, with 0.04 $CaCO_3$ as well, since calcium carbonate is coming down in this zone. The mixed carbonate-oxide has 25% Mn. When oxidation has not been quite complete, the MnO_2 is diminished before the Fe_2O_3, then $MnCO_3$ comes down. When it does, however, some Mn must also remain in solution. Hence, a mixed MnO_2, $MnCO_3$ is possible in Zone 3 if something less than 100% oxidation occurs. If so, a net loss of manganese to the solution must also occur, according to the scheme, with manganese percentages less than 25% in the deposit.

In summary, the result of complete oxidation in one zone is to shift the manganese to that zone, and to change it from a

TABLE 7

Deposits from Complete Oxidation

Complete Oxidation in Zone	Composition	% Mn	Fe/Mn
Zone 1	0.4 Fe_2O_3, 0.04 MnO_2	3.4	20
Zone 2	0.035 Fe_2O_3, 0.04 MnO_2, 0.1 $CaCO_3$	11.5	1.8
Zone 3	0.01 Fe_2O_3, 0.04 MnO_2, 0.04 $CaCO_3$	25	0.5
Zone 4	0.005 Fe_2O_3, 0.015 MnO_2, 0.024 $CaCO_3$ 1.0 $MgCO_3$	0.93	0.7

low-grade manganiferous hematite (3% Mn), through a medium grade manganiferous hematite (11.5% Mn) carrying lime, to a manganese oxide deposit (25% Mn) carrying iron oxides and carbonates, depending on the zone in which oxidation occurs. As in the case of the bicarbonate system, oxidation also puts the highest grade manganese deposit in Zone 3.

The Deposition of the Silicates

The siliceous portion of the pyroxene source-rock is taken to be present in the waters as linear or coiled polysilicic acid chains, with a greater tendency to agglomerate than to break down into monomeric units. Two possibilities are to be considered:

1. Through agglomeration and colloidal settling, essentially an amorphous silica deposit is obtained.

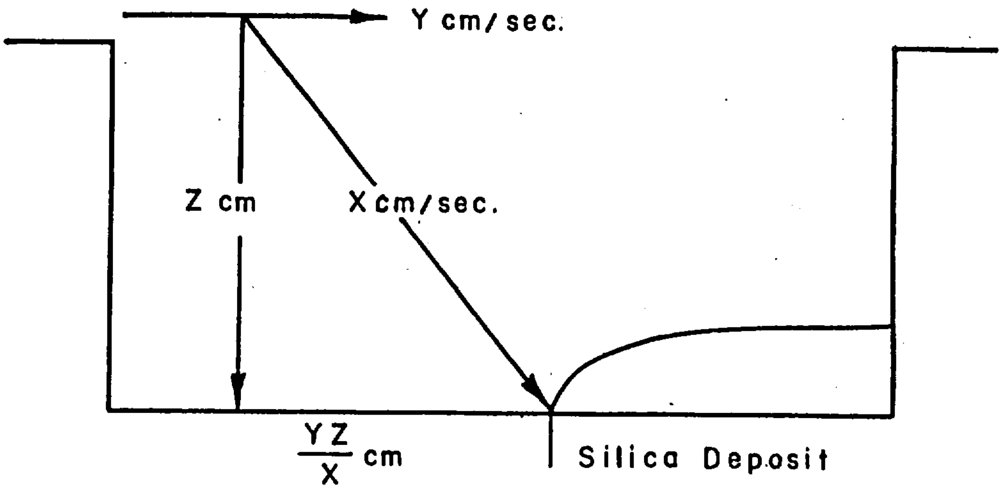
2. The polysilicic acids may combine with metal ions in solution to form new insoluble metal silicates.

Factors involved in the precipitation of amorphous silica are: the rates of agglomeration, of sedimentation, and of linear flow within the precipitating waters. Since pH is roughly constant in the bicarbonate system, changes in the rate of agglomeration depend largely on changes in the concentration of the polysilicic acid. Since the formation of insoluble metal silicate also depends on this concentration, as will be seen later, these two rates for the siliceous components are partly competitive.

During the formation of the silica deposit, the concentration of the silicic acids is being lowered by the precipitation. At the same time, evaporation losses tend to increase all concentrations, including that of the colloidal particles. As agglomeration rates increase with concentration, three possibilities exist. The rate of silica sedimentation can increase, decrease or remain unchanged with increasing distance from the entrant end of the sea.

Figure 8

The Settling of Silica in the Inland Sea



In the general scheme, shown in Figure 8, the particles are moving forward with the water at a speed of Y cm/sec. With a settling rate of X cm/sec, and a water depth of Z cm, the particles can first appear as a deposit at $\frac{YZ}{X}$ cm from the entrant mouth of the sea. Once started, the deposit will be of even thickness going towards the exit end, if the sediment loss just balances the evaporation gain, thus keeping the concentration constant. However, the deposit can become either thinner or thicker, going towards the exit end, if the concentration falls or rises, as sedimentation respectively falls behind or gets ahead of the evaporation gain. When metal silicates begin to add siliceous material to the deposit, and this, as will be seen, is more likely towards Zone 4, the sedimentary loss is most apt to exceed the evaporation gain. Consequently, whatever the variation in the deposit of amphorous silica in the earlier zones, it is expected that the silica is diminished when the silicates come down.

The Formation of Insoluble Metal Silicates

(a) In the absence of oxidation

The concentration of the polysilicic acids is not controlled by the bicarbonate equilibria. It is, therefore, not possible to say, without specifying concentrations, just when the metal ions begin to precipitate the dissolved polysilicic acid chains and colloids. It is possible, however, using the observation that di- and tri-valent cations tend to precipitate out the polysilicic acid units just before the cations would come down as hydroxides, to decide which cation, if any, will be the precipitant.

The ratios of the concentrations of the ions in solution are given by

$$\frac{M'^{++}}{M''^{++}} = \frac{K_3'}{K_3''} \cdot \frac{M' - M'^{++}}{M'' - M''^{++}}$$

where M' and M" are total concentrations, taken from the mole ratios remaining in solution in the respective zones. The ratios in which ion pairs co-precipitate hydroxides can be obtained from the solubility products. By combining these two ratios, the factor by which the ion concentration of a particular species exceeds all others for hydroxide precipitation directly appears. As the silicates come down just before or concurrently with the hydroxides, the values apply, it will be assumed, to silicate precipitations. The factors by which (Mg^{++}) exceeds the various (M^{++}) in the different zones are shown in Table 8.

TABLE 8

Ratios by which (Mg^{++}) exceeds (M^{++}) for silicate precipitation

	Zone 1	Zone 2	Zone 3
$\frac{Mg}{Fe}$	1.3	15	36
$\frac{Mg}{Mn}$	400	400	400
$\frac{Mg}{Ca}$	4×10^6	4×10^6	10^7

From Table 8 it can be seen that Mg^{++} is everywhere preferred for silicate formation, and that this preference increases from zone to zone as carbonate precipitation brings down the other ions. At the same time, the absolute value of (Mg^{++}) increases; possibly, also, that of the silicic acids. Consequently, the likelihood that metal silicate precipitation occurs, and that the silicate will be specifically a Mg silicate, increases from zone to zone.

Once Mg silicates do come down, the (Mg^{++}) is lessened. From Table 8, only Fe^{++} would seem to have a chance to become competitive, particularly in the first zone before $FeCO_3$ has been withdrawn. Consequently, co-precipitation of Fe and Mg silicates is a possibility, which becomes less likely in the later zones.

The type of silicate to be expected can be partly defined. There are present in solution roughly equimolar amounts of Mg^{++}, M^{++}, $Si_2O_6^{4-}$ at the beginning. Carbonate precipitation removes the M^{++}, amorphous silica deposition diminishes the $Si_2O_6^{4-}$. The $\frac{Mg^{++}}{Si_2O_6^{=}}$ ratios that can result lead to the expectation that a magnesium silicate in composition intermediate to $Mg\ Si_2O_6$ and $Mg_2\ Si_2O_6$ will form.

Structurally, the condensation of linear $(Si_2O_6)_\infty$ chains to $(Si_4O_{11})_\infty$ chain pairs and $(Si_4O_{10})_\infty$ layer networks, with the simultaneous interposition of $Mg(OH)_2$ layers, builds up a specific insoluble magnesium silicate of the chlorite type, that provides a plausible solution to the problem(10). The particular merit is that the insoluble particles are built up by simple progressive condensations that presumably depend on concentrations rather than on energetics. Both structural requirements, construction from available entities and construction towards a specific mineral, seem to be satisfied by the specification of a chlorite as the product.

Consequently, when oxidation does not occur, the polysilicic acids may be expected to come down as a mixture of amorphous silica and a magnesium chlorite, the former predominating in the early zones, the latter in the later. As Fe^{++} can replace Mg^{++} in the chlorites, and as Fe^{++} is the most likely co-precipitant, the chlorite is likely to contain some iron with the magnesium.

It is not possible to apply the present argument to determine the relative amounts of silica and chlorite in the manganese deposit of Zone 3. However, upper and lower limits may be set by an independent argument. Assuming that all the polysilicic acid comes down as chlorite ($\sim 5\ Mg(OH)_2 \cdot Si_4O_{10}$) and amorphous silica, SiO_2, the relative amounts of each to be expected can be determined from the magnesium composition. If the SiO_2 is evenly spread over the first two zones and the chlorite over the last two, the manganese deposit gains the composition

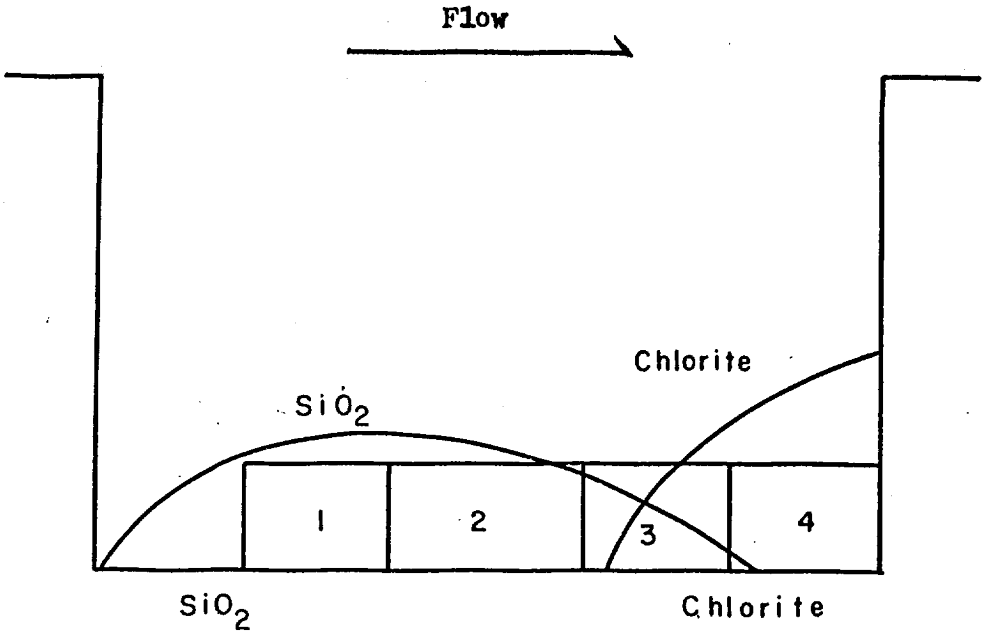
$$0.5\ Mg(OH)_2 \cdot 0.1\ Si_4O_{10};\ 0.04\ CaCO_3;\ 0.02\ FeCO_3;$$
$$0.025\ MnCO_3.$$

This is a 2.1% Mn deposit. With no chlorite, the percentage would be 16%. See Figure 9.

The 2.1% figure is taken to be the least manganese the deposit could have, for the following reasons: First of all, chlorite precipitation is apt to be heavier in Zone 4 than in Zone 3, as the (Mg^{++}) needed for hydroxide and carbonate precipitation are not too different, under these conditions, and $MgCO_3$ precipitation begins for the first time in Zone 4. This will tend to skew the chlorite distribution, moving it from Zone 3 to Zone 4. At the same

Figure 9

Distribution of Silica and Chlorite in the Deposit



time, as chlorite is withdrawn, an amorphous silica deposition will invade Zone 3. The silica is, however, now spread over a larger area, thereby becoming a lighter deposit. Moreover, total chlorite exceeds total silica in weight terms. Consequently, though both silica and chlorite now appear in Zone 3, the result will be to raise Mn percentages to higher values in the range 2.1 to 16%. The question of grade is discussed again, from another point of view, in a later section.

(b) From oxidized solutions

An important change, resulting from oxidation, is the appearance of ferric ion, with the possibility that Fe^{+3} will replace Mg^{++} in the metal silicate deposit. This would be expected at once, as the $Fe(OH)_3$ is so much more insoluble than $Mg(OH)_2$. The K_{sp}'s are 4×10^{-38} for $Fe(OH)_3$ and 3×10^{-11} for $Mg(OH)_2$.

Moreover, any reasonable assumption as to the complexing of Fe^{+++} in solution, the pH, or the total concentration of soluble ferric and divalent Mg species, still leaves Fe^{+++} favored over Mg^{++} by a very large factor ($\sim 10^{11}$) as the precipitating ion for the silicates in regions where oxidation occurs. The data are shown in Table 9.

TABIE 9

Fe^{+++} vs Mg^{++} as a Precipitating Agent for the Polysilicic Acids

Zone	Ratio in Solution $\frac{Mg^{++}}{Fe^{+++}}$	Ratio for co-precipitation, pH=8 Mg^{++}/Fe^{+++}	Factor favoring Fe^{+3} silicate
1	5×10^{7}	1.2×10^{20}	2.4×10^{12}
2	55×10^{7}	1.2×10^{20}	2.4×10^{11}
3	1.3×10^{9}	1.2×10^{20}	1×10^{11}
4	4×10^{9}	1.2×10^{20}	3×10^{10}

The values for the $\frac{Mg^{++}}{Fe^{+++}}$ ratios depend on the stability constants K_3, as before, but the HCO_3^- concentration is also involved. It was taken to be 0.1 molar. At lower concentrations Fe^{+++} becomes still more favored.

Consequently, as the factor favoring Fe^{+3} over Mg^{++} for the silicate precipitator is so very large, the Mg chlorite must be ruled out as a deposited material from a fully oxidized zone, as long as any Fe^{+3} remains. Moreover, as Fe^{+3} condenses with the silicates at much lower polysilicic acid concentrations, the Fe^{+3} silicates can come down in earlier zones than the chlorite could.

A second problem concerns the effect of the silicate deposition on the hydroxides and the oxides. Once again, equilibrium principles can be applied, but now because they are violated, rather than obeyed.

Through oxidation the divalent Fe^{++} and Mn^{++} are rather abruptly changed into Fe^{+3} and Mn^{+4} entities under conditions that are, for them, widely removed from equilibrium. They are at once able to react in diverse ways to give, irreversibly, diverse solid products. By contrast, the divalent ions gradually approach, slowly adjust, and are, in the end, nicely though only partially separated through closely balanced equilibrium reactions. It is because the Fe^{+3} and Mn^{+4} appear in a system with which they are not at equilibrium, that mixed products can be expected. As a simplification, both $Fe(OH)_3$ and ferric silicates may be expected as separate species, or distinguishable intergrowths. The conclusion comes from structural and kinetic, rather than equilibrium, considerations. It may be possible to conclude, nevertheless, that the ratio of $Fe(OH)_3$ to ferric silicates in deposits from oxidized zones should bear a relation to the polysilicic and hydroxyl concentrations. As the solution is buffered, this may have the consequence that the silicates increase with respect to the hydroxides, from zone to zone.

In some ways, the fate of the oxidized Mn^{+4} ions may be analogous to the ferric ion. However, MnO_2 is itself acidic and would not be expected to condense with the polysilicic acids. Indeed, the precipitation of the metal silicates is, properly speaking, an acid-base reaction.

However, in its lower oxidized states, as for example Mn^{+3}, or in approximations to it, manganese forms poorly resolved, highly insoluble hydroxides with more basic properties than MnO_2. Consequently, some manganese silicates may co-precipitate with MnO_2. The condition would seem to be that the manganese in the silicate be intermediate to Mn^{+2} and Mn^{+4} in its oxidation state. An example is the mineral Braunite; $3\ MnMnO_3 \cdot MnSiO_3$.

A final point remains. In stage 3 of the erosion life of the igneous rock, a siliceous remnant containing Fe (and perhaps some Mn) still remains. The sediments from it, if put down under oxidizing conditions, should retain the ferric silicate in the sediment, making a continuous gangue from barren hanging wall to central mineralized regions of the deposit. The siliceous content should be high, however, as the basic components by this time have largely been extracted. The Fe and Mn contents should be less as compared with the central zones, and should fall quickly through this stage.

THE STRUCTURE AND COMPOSITION OF THE PRIMARY DEPOSIT

The previous discussions have dealt with the distribution and the composition of the sediments along horizons extending from the entrant to the exit ends of the inland sea. To reproduce the deposit at any point along a horizon, it is, of course, necessary to add up all the components that have come out there, including both the metallic and siliceous parts. In this way, many substantially different deposits can be specified.

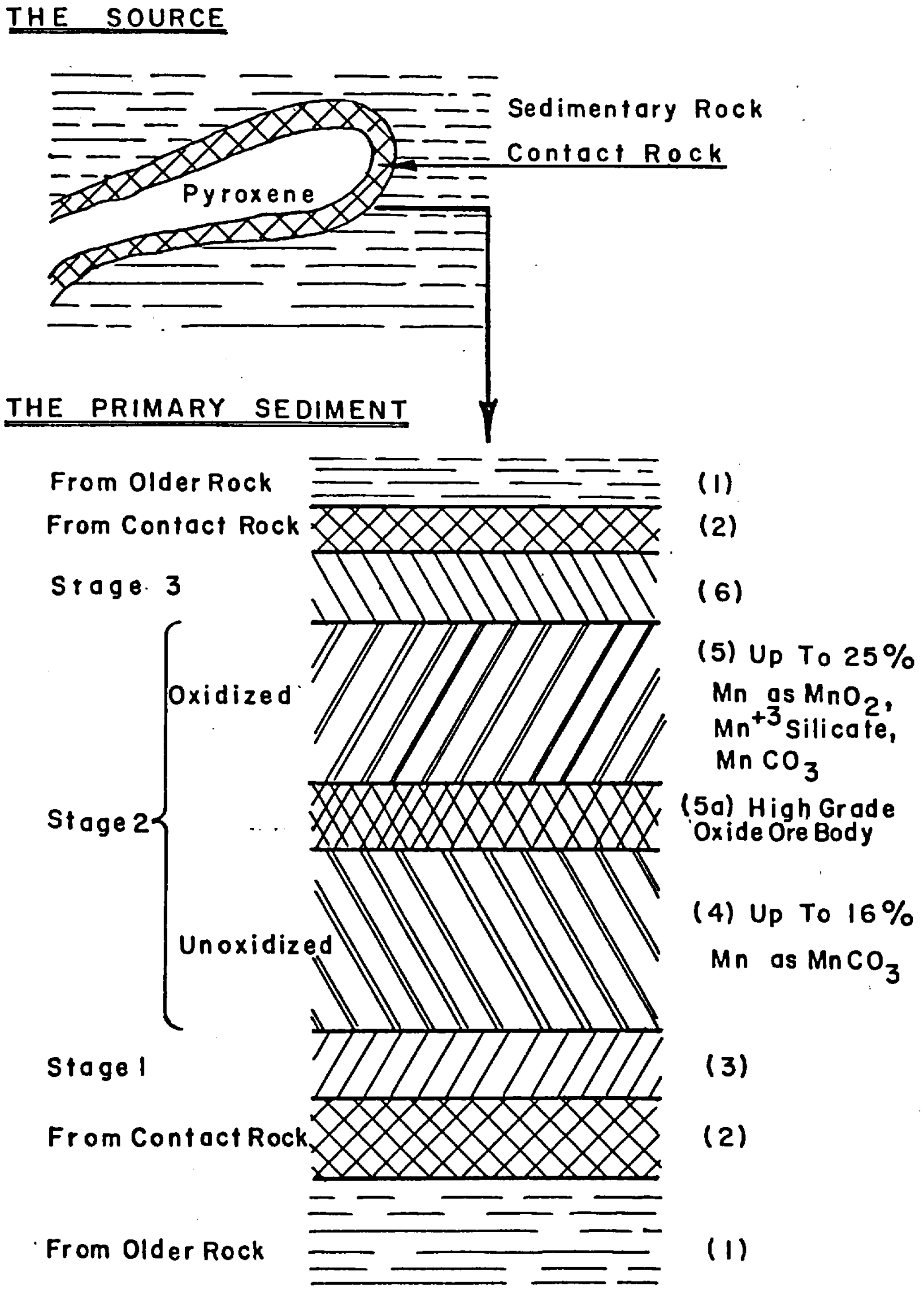
First of all, sediments from oxidizing and non-oxidizing solutions are found to be substantially different in association, composition, and horizontal location. Moreover, the oxidizing property in the solutions may vary vertically, horizontally, and with geologic time. Consequently, a vertical section through a deposit can in principle reveal many changes or combinations of changes, including alternations, depending on conditions during the time the deposit was laid down. One vertical section through a deposit will be classified, under simple conditions, as an illustration of the possible combinations. See Figure 10.

It will be assumed, as before, that the deposit is being laid down in a flat inland sea, with the O_2 penetration superficial, and CO_2 penetration to the depths. The relative contributions from oxidizing and non-oxidizing waters, therefore, vary with the depth of sea. In the beginning, for example, when the sea should be the deepest, oxidation will be least important. Then the iron and manganese carbonates, along with (Mg Fe) chlorites, dominate in the deposit. As time passes and the sediments accumulate, the sea becomes more shallow. At a certain point, only the depth of the oxidizing layer is left. The deposit reverts to an oxide type. This condition then persists until the source rock has been worn away. To estimate the time involved: if the sediment is laid down at the rate of half-an-inch a year, about 10,000 years are required for a thickness in the deposit of 300 feet.

The source rock will be taken, as before, to be an igneous pyroxene intrusion into older sedimentary rocks. The whole cycle of deposition will be followed, from the beginning to the end of the erosion life of the deposit. A stratification emerges that describes the deposit itself, as well as its relation to post and prior

Figure 10

The Structure of the Deposit



(Vertical Section Through Zone 3)

sediments. The stratification will be followed in a vertical section taken through Zone 3, to locate the manganese deposit.

The older sedimentary rocks and the contact-metamorphosed rocks are first eroded before the source rock can be exposed. Then the first erosive stage in the life of the source begins, providing a calcareous feed to the waters. Sediments from these three steps provide three distinguishable strata (1, 2, 3 in Figure 10) that precede the manganese deposit.

At its commencement, the manganese deposit is almost entirely of the carbonate type. Manganese is present in mixed Mn,Fe carbonates, along with calcite. Mg chlorite, perhaps containing Fe^{++}, and amorphous silica are also present. The Mn content can vary within the limits 3 to 16%, with an upper median value indicated (see later for a closer estimate). Traces of Fe^{+3}, but not of oxidized manganese, can be expected, the ferric iron disappearing into the quartz and chlorite, as far as the silicates are concerned, and otherwise, appearing as hematite. This is stratum 4 in Figure 10.

The thickness of the sediments containing the manganese deposit should be many times those of the two preceding layers. The relative proportion of the deposit found as the carbonate type, however, depends on the depth of the waters. It may be either the whole of the deposit, or, in fact, none of it. The transition from the carbonate to the oxide deposit may be sharp in some regards, but not in others. For example, the $\frac{Fe^{+3}}{Fe^{+2}}$ ratio could increase consistently through the transition zone, and also the $Fe(OH)_3$ to $FeCO_3$ ratio in products. The siliceous material may, however, show a sharper change from dark grey and green Mg chlorites to the red ferric silicates, for at certain $\frac{Fe^{+++}}{Mg^{++}}$ ratios, one ion will dominate and the other accommodate itself to the determined structure. In the manganese component, a rather definite chain of change occurs between the two extremes. The manganese is found only as $MnCO_3$, until the Fe has all been oxidized. That is, $MnCO_3$ will extend from the unoxidized well into the oxidized regions, although the admixture with it of $FeCO_3$ should then be decreasing. Later, when MnO_2 and perhaps oxidized Mn silicates like braunite appear, some $MnCO_3$ can still remain. Only when oxidation has been complete will the $MnCO_3$ entirely disappear.

Consequently, the transition zone may have the appearance of a sharp transition, for the silicate change from chlorite to a ferric silicate may be abrupt. This will provide what amounts to a sharp colour change, but the texture will not alter, as both components are fine grained and micaceous. Within these coloured layers, changes in the mineral components are continuous, rather than abrupt.

In the region of complete oxidation, in the simplest case only $Fe(OH)_3$, MnO_2, Fe^{+3} and Mn^{+3} silicates, SiO_2 and calcite are expected, with up to 27% Mn. However, oxidations prior to Zone 3 can sharply affect these compositions. Moreover, as the oxidized and non-oxidized deposits are widely separated in time, and shifts in oxidation zones move the iron and manganese about, considerable and even abrupt changes in Fe and Mn percentages and ratios are to be expected. The upper limit is 27% Mn, in the form of MnO_2 and perhaps a Mn^{+3} silicate. The lower limits are 11%, 3%, down to calcareous layers barren in manganese and iron. The conclusion is that the deposit from oxidizing waters may have richer regions, but in the overall will be far more varied, than the carbonate deposit.

Passing from stage 2 to stage 3 in the erosive life of the source rock, the waters become impoverished in Ca, Mg, then in Mn, Fe, until finally only siliceous materials remain. That is, the polysilicic acid concentrations show a steady relative increase through stage 3. Under oxidizing conditions, the sediments reflect these changes by becoming themselves more siliceous, with Mn and Fe decreasing percentage wise, and the Fe^{+3} silicates persisting at the expense of the hematite. Finally, the contact metamorphic rocks below the source are reached, and in the next step, the older rocks that, in the first place, were invaded. Visually, therefore, because of the continuity provided by the red Fe^{+3} silicates, the oxidized deposit of stage 2 seems to persist through stage 3 towards the hanging wall of the deposit. The layer from stage 3 (#6 in Figure 10) is, however, low in Mn and high in silica, compared with the main deposit.

In the scheme as outlined, the hanging and the foot walls are recapitulations above and below the manganese deposit. This small point arises from the assumption that the connection to the parent magma has a small cross-section compared with the area of the source. The result is that the deposit appears as a regular and continuous, though finite, occurrence within the sediments of the region.

THE GRADE AND TONNAGE OF THE PRIMARY DEPOSIT

The Size of the Deposit

It has been shown that the composition of the Mn carbonate deposit is independent of the composition of the source within certain limits. Thus, if $\frac{Mn}{M} > 0.01$ (M = total metals), $\frac{Fe}{Mn} > 0.75$, $\frac{Ca}{Mn} > 1.6$, and $\frac{Mg}{Mn} < 66$ in the source rock, a carbonate deposit with the composition prescribed for Zone 3 should presumably precipitate.

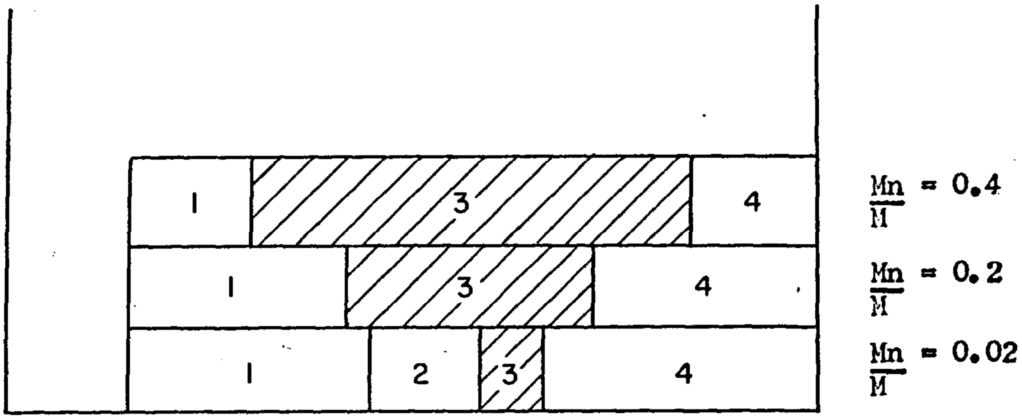
The relative amounts of carbonate material in the four zones, on the other hand, is a direct reflection of the composition of the source. For example, a $Mg_{1.0}\ Fe_{0.8}\ Ca_{0.16}\ Mn_{0.04}$ source gives 0.73 carbonate units in Zone 1, 0.14 in Zone 2, 0.085 in Zone 3, and 1.045 in Zone 4. As these relative amounts have been put down on a sedimentary horizon, they signify the relative surface areas of the four deposits. It is evident from the figures, which are also shown graphically in Figure 10, that in this case the area of the manganese deposit (Zone 3) is a small fraction of the area of the whole. This results from the selection of a source with just a bit more than the average amount of manganese in it.

If the source rock had been richer in manganese, the first result would be an increase in the area of Zone 3 relative to the other areas. This is shown in Figure 11, for specific source rock manganese to total metal ratios of 0.02, 0.2 and 0.4, respectively.

Besides an increase in its relative area, the calcite content of Zone 3 is also subject to alteration as the igneous source becomes richer in manganese. This follows because calcium is, in the first place, a minor ingredient in the pyroxenes, compared with manganese and iron. Moreover, with manganese enrichment, the remaining metals must diminish to retain a balance. Calcium is more apt than the others to be lost. If, for example, the manganese

Figure 11

Dependence of the Areas of the Sedimentary Zones on the Manganese Content of the Source Rock



Legend
1 = $FeCO_3$
2 = $FeCO_3$, $CaCO_3$
3 = $MnCO_3$, $FeCO_3$ ($CaCO_3$)
4 = $MgCO_3$ etc.

The manganese deposit is shaded. The manganese content of the source rock is given in terms of the $\frac{Mn}{M}$ atom ratio. $M = Mg + Fe + Ca + Mn$.

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content doubles, from $Fe_{0.8}\ Mg_{1.0}\ Ca_{0.16}\ Mn_{0.04}$ to $Fe_{0.8}\ Mg_{1.0}\ Ca_{0.12}\ Mn_{0.08}$, the $\frac{Ca}{Mn}$ ratio already is as low as 1.5. This is below the lower limit, 1.6, for the $\frac{Ca}{Mn}$ ratio, in the deposits. Consequently, not only has Zone 2 vanished for want of calcite co-precipitation with $FeCO_3$, but $CaCO_3$ has also begun to disappear from Zone 3. At manganese-to-metal ratios of 0.2 and 0.4, corresponding to source rocks of $Fe_{0.8}\ Mg_{0.8}\ Mn_{0.4}$ and $Fe_{0.8}\ Mg_{0.4}\ Mn_{0.8}$ respectively, the manganese content is so high that calcium has become unimportant, according to the argument. Based on the carbonates alone, the Mn content has thereby increased from 16% (in (Mn,Fe,Ca) CO_3) to 27% in (Fe, Mn) CO_3.

The conclusion to be drawn relates the calcite content to the area of the manganese deposit, as both of these reflect the composition of the source. In brief, large areas are associated with small values for the $\frac{Ca}{Mn}$ ratio in the deposit. $\frac{Ca}{Mn}$ ratios of 1.6 indicate small areas. Values below 1.6 indicate intermediate areas of increasing size. Absence of calcite becomes a diagnostic feature for the largest areas the method can predict.

Finally, some conclusions as to the probabilities of large tonnage manganese carbonate deposits can be drawn. Two factors are involved. The first of these is the area of the deposit, which depends on the factor by which manganese in the source rock exceeds average for a pyroxene. Secondly, the thickness of the deposit, which depends on the volume of the source.

Deposits of small area may occur frequently, as they are derived from near average source rocks. However, substantial enrichment factors, in the range 10 to 40, are needed before deposits with substantial relative areas begin to appear. This is shown in Figure 11. The chances for such an occurrence become correspondingly small.

As the composition and the volume of the igneous source are independent parameters, the area and the depth of sediments are also independent. That is, small area deposits of great thickness, and large area deposits that are very thin, are both possible. For tonnage, the factors must be combined, a large area of great thickness being desired. The probability of such an occurrence becomes the product of the probabilities for Mn enrichment and for volume, in the source rock. The chances for large tonnage, therefore, become again reduced.

The Grade of the Deposits

(a) The carbonate deposit

This is also the best place to recalculate the grade of the deposit, as more definite answers are possible than have as yet been given. Recalling the factors that control silica precipitation, it is evident that this component will be unevenly distributed throughout the sediments. If the manganese zone is large, however, an overall average reflecting the composition of the source rock is a reasonable expectation. Then the $(Fe,Mn,Ca)CO_3$ deposit would contain equal molar amounts of metal and of SiO_2, giving the composition 0.8 $FeCO_3$, 1.0 $MnCO_3$, 1.6 $CaCO_3$, 3.4 SiO_2. The percent of manganese in this deposit is 9.7.

Taking the 10% manganese in the complex small deposit above, it is further evident that this value must

a) become smaller as chlorite replaces SiO_2 ;

b) become smaller as the pyroxene source rock becomes containinated with non-manganiferous rocks;

c) become larger as the area of the deposit increases, for then the calcium value goes down.

Reasonable estimates of these three factors are possible. Chlorite roughly doubles the weight of the silica it replaces; 5 to 15% impurity in the source rock is the order observed in related pyroxenous intrusions; variations in area can raise the Mn value from 9.7 to 17.5 as in 0.8 $FeCO_3$, 1.0 $MnCO_3$, 1.8 SiO_2. From these considerations it can at once be shown that a very large variety of carbonate deposits may be expected to have manganese values between 8 and 12%.

(b) The oxide deposit

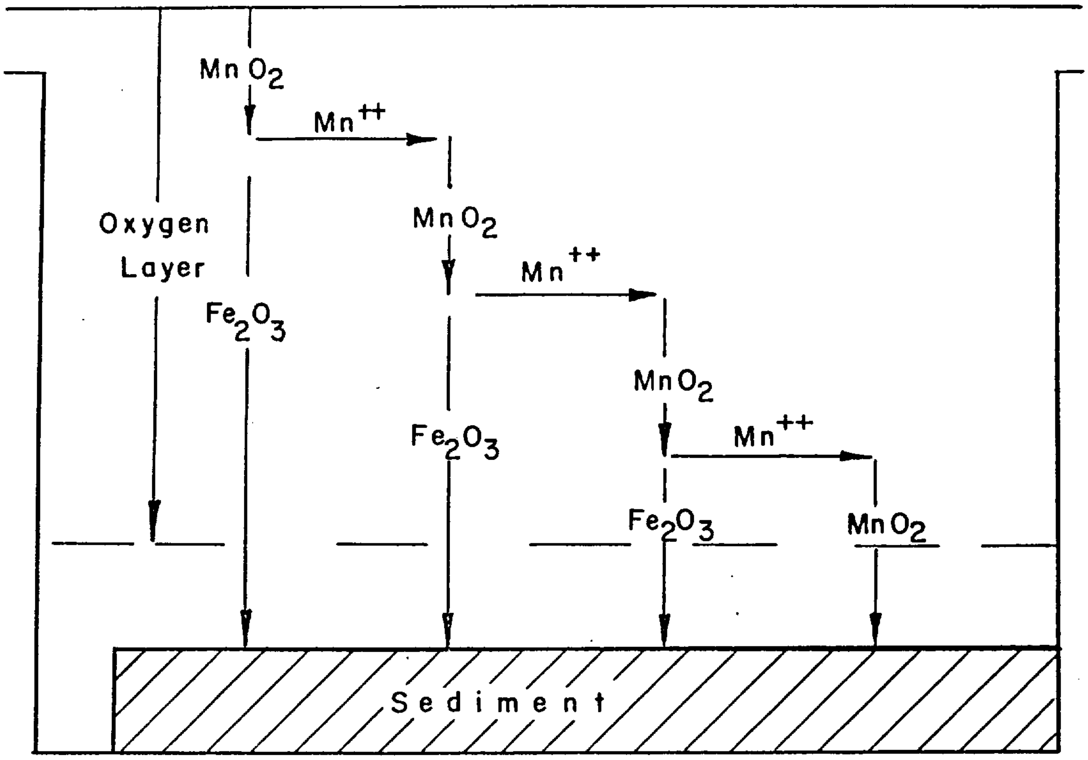
The precipitation of iron and manganese oxides from bicarbonate solutions occurs when the oxides can form before the carbonates do. Moreover, manganese can act to catalyze the oxidation of the ferrous ion, further increasing the rate of oxide precipitation. Assuming that the rate of silica deposition is unchanged, these factors combine to make the oxide of a higher grade than the carbonate deposit under conditions that can be specified. The argument follows.

In the oxygen layer, Figure 11, both ferrous and manganous ions are oxidized, thereby becoming insoluble and settling out. The MnO_2, however, can react with ferrous ion as it descends. This reconverts manganous ion, while ferric oxide is made. If the manganous ion so produced is still in the oxygen layer, it can be oxidized again. The insoluble manganese dioxide again begins to settle out until it reacts once more with ferrous ion at the lower level, and the reactions repeat themselves. In this way, a cyclic event is involved, in which manganese is alternately oxidized by oxygen and reduced by ferrous ion. The number of cyclic events each manganous ion undergoes is determined by the depth of the oxygen layer, the rate of settling of the manganese dioxide, and the speed of the reaction between MnO_2 and ferrous ion.

An example can be made from Figure 12. When the depth of the oxygen layer is d cm, and the settling speed of the manganese

Figure 12

The Catalyzed Precipitation of Ferric Oxide



dioxide particles is s cm/sec, each particle will remain in the oxygen layer for d/s sec. During this interval, the reaction cycle

$$Mn^{++} + 1/2\ O_2 + 2\ OH^- \longrightarrow MnO_2\downarrow + H_2O \qquad (1)$$

$$MnO_2 + 2Fe^{++} + H_2O \longrightarrow Mn^{++} + Fe_2O_3\downarrow + 2H^+ \qquad (2)$$

can occur $(d/s)r_2$ times, where r_2 is the rate of reaction (2). It is assumed that the manganous ion retains its own level. These reactions supplement the oxide formed independently in reaction (3).

$$2\ Fe^{++} + O_2 + 4\ OH^- \longrightarrow Fe_2O_3\downarrow + 2\ H_2O \qquad (3)$$

The ratio of the rates of oxide precipitation, with and without the participation of manganese becomes, therefore,

$$\frac{r_3 + (d/s)r_2}{r_2} = 1 + C$$

where $C = n\, r_2/r_3 = (d/s) \cdot r_2/r_3$.

As reaction (3) competes with reaction (4)

$$Fe^{++} + CO_3^{=} \qquad FeCO_3 \tag{4}$$

for ferrous ion, r_3 must be larger than r_4 when the oxide deposit forms. If the rate of silica deposition has not changed, the oxide deposit must be enriched, as compared with the carbonate deposit, by the minimum factor, 1+C. That is, the oxide/silica mole ratio in the oxide deposit becomes 1+C times the carbonate/silica mole ratio in the carbonate deposit. The effect this would have on the grade of the oxide deposit is shown graphically for different values of C in Figure 13 and Table 10.

Figure 13

Composition of Oxide Deposit as a Function of the Enrichment Factor

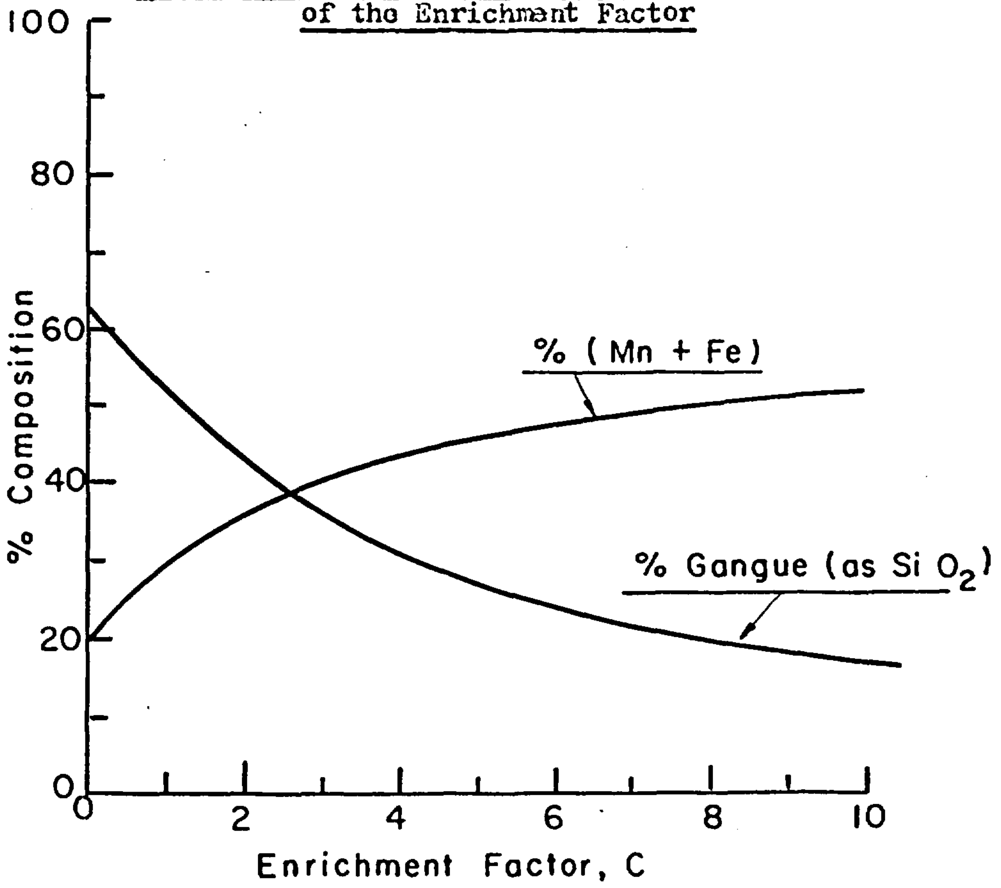


TABLE 10

Composition of the Oxide Deposit as a Function of the Enrichment Factor

Enrichment Factor		Composition of Deposit (gangue shown as SiO_2)	%(Mn + Fe)	% Gangue
C	1+C			
0	1	1.0 $MnCO_3$, 0.8 $FeCO_3$, 5.7 SiO_2	18.1	62.3
0	1	1.0 MnO_2 , 0.4 Fe_2O_3, 5.7 SiO_2	19.4	69.5
1	2	" " 2.8 SiO_2	30.0	53.0
2	3	" " 1.9 SiO_2	36.0	43.2
3	4	" " 1.42 SiO_2	40.4	36.2
4	5	" " 1.14 SiO_2	43.5	31.3
5	6	" " 0.95 SiO_2	46.0	27.5
6	7	" " 0.81 SiO_2	47.7	24.2
10	11	" " 0.52 SiO_2	52.5	17.2

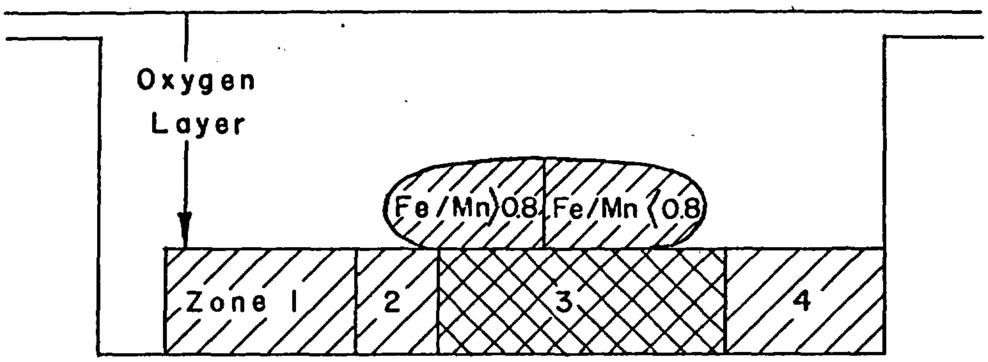
The value of the quantity, C, depends on both constant and variable factors. The specific rate constants, k_2 and k_3, and the settling speed, s, presumably do not change. Such factors, however, as the depth of the oxygen layer and the concentrations of manganese and iron in the oxygen layer do vary under the range of conditions in which the oxide deposit is formed. As a result, the enrichment factor 1+C has different values at different points in the oxide deposit. Corresponding variations in the grade must also occur. These can be of two sorts.

The variations in C that follow from changes in the depth of the oxygen layer and changes in the manganese concentration will be considered first. From the expression, $C = (d/s).r_2/r_3$, it is evident that C varies directly with the depth of the oxygen layer and with the manganese concentration. Consequently, the enrichment factor will have its greatest value just where the carbonate turns into the oxide deposit (in the vertical ascension through the ore body, Figures 9 to 13), and will decrease to zero as the waters become more shallow. It is to be recalled that $MnCO_3$ continues for some distance into the ferric silicate slates. That is, the horizon that separates the manganese oxides from the manganese carbonates does not coincide with the horizon of colour change, which is determined by the nature of the gangue (see page 51). As a result, the high grade body will be bounded above and below by red slates (Fe^{+3}), for the same reason, that it marks the transition from $MnCO_3$ to MnO_2.

On the horizontal contour extending over the four zones, enrichment will be greatest where the (Mn^{++}) has been highest, and will fall to zero at either end. This is in the waters just prior to and in zone 3. Combining the vertical and horizontal factors, a lens-like or band-like 'high-grade' oxide ore body can be located just where the zone 3 carbonate transforms into the oxide deposit, as shown in Figure 14.

Figure 14

The Location of the 'High-Grade' Oxide Deposit



A second conclusion refers to the Fe/Mn ratio to be found in the oxide deposit at different parts of the lens-like body. Manganese dioxide appears in the deposit only when the oxygen layer extends nearly to the sediment, as in Figure 11. By then, each MnO_2 unit has caused the precipitation of n Fe_2O_3 units, where n is the 'chain length'. In the first parts of the oxide lens, therefore, the Fe/Mn ratio in the deposit will exceed that in the solution. In later portions, when Fe has been more fully precipitated and Mn still remains, the Fe/Mn ratio will be lower than in the solution. The rate expression that evaluates these changing ratios is

$$\frac{Fe}{Mn} = \frac{r_3 + (d/s)\, r_2}{r_1},$$

from which it appears that when d and (Fe^{++}) are large, Fe/Mn is large, and vice versa. The regions of large and small values for the Fe/Mn ratio are shown in Figure 14.

SUMMARY

As a summary, (Mn,Fe,Ca) CO_3 deposits carrying 8 to 12% manganese may be expected to occur not infrequently. Large tonnages, however, combining area and depth, will be relatively rare. The Fe/Mn ratios of the various deposits should not vary, and some consistencies should remain in the siliceous components. The Ca/Mn values, however, do vary. They become a diagnostic feature for surface areal extent. Tonnages are not thereby necessarily indicated.

The oxide deposit is more complex than the carbonate. It consists of three distinguishable bodies. The high-grade, with high combined Fe and Mn as compared with the carbonate, shows wide variations in the Fe/Mn ratio within the body. The low-grade is poorer in manganese than in iron, though poor in both. The third oxide body has intermediate properties. Taking the hematitic gangue as the common feature, this body could also include the mixed MnO_2, $MnCO_3$ region in which the carbonate becomes an oxide deposit.

In conclusion, some points will be discussed that have a bearing on the validity of the argument.

Variations in the Composition of the Source Rock

Manganese will not come down in carbonate deposits, according to the argument, unless the $\frac{Mn}{Mg}$ ratio exceeds about $\frac{0.015}{1.00}$ in the source rock. This is the ratio in which the respective ions pass in solution from Zone 3 to Zone 4. The manganese percentage in Zone 4 is about 0.9%. A principal condition in the source rock, therefore, is that it contain more manganese than average ferromagnesians. It is just this excess that appears in the carbonate.

Apart from this condition, the source rock can have a fairly wide composition variation, without much effect on the carbonate deposit, as the Fe and Ca are largely laid down before, and the Mg after, the manganese itself comes down. Moreover, variations in the $\frac{M}{SiO_2}$ values in the source rock, that is, whether it is more basic or acidic than the pyroxene, will tend to be reflected only in the siliceous component of the deposit. The effect will be to vary the abundance of Mn in the deposit in a minor way, without affecting its essential properties.

The connections between the oxide deposits and the source rock are not so clear cut. For example, manganese can be concentrated, by oxidation, even if its presence in the source is less than average. In general, however, the arguments remain valid for both kinds of deposits for source rocks showing a considerable composition range.

Contamination by Aluminum

The assumption of the specific composition for the source rock has one result, however, that almost certainly leads to error; that is, the exclusion of aluminum. Not only from feldspathic rocks that could occur as minor or major entities contaminating the source, but even in pyroxenous materials like augite, and also in the amphiboles, aluminum does appear.

Most other common elements that could be derived from non-pyroxenous rocks associated with the source are either already present in the pyroxene, like Ca, Mg, Fe, SiO_2, or, like Na and K, would largely remain in solution above the deposits.

$Al(OH)_3$, like $Fe(OH)_3$, is highly insoluble. Unlike Fe^{+++}, however, Al^{+++} approaches its precipitation under the foregoing circumstances in a system in which it is at equilibrium. Consequently, Al^{+3} silicates and not $Al(OH)_3$ will form. Moreover, whether there is oxidation or not, the Al^{+++} can combine with the silicate, to an extent depending on its concentration and the equilibria involved. Consequently, if it is found in either, it should be found in both the Mg chlorite and the ferric silicate components as well as in the silica. Its percentage presence should in either case be small, compared with the silica.

Besides its appearance in the waters as Al^{+3}, aluminum may in principle also be introduced as a constituent part of the colloidal silica. As long as total Al is low the general conclusions remain valid. The variety and type of specific minerals that are formed, may, however, be affected.

Variations in the Equilibrium Constants

The composition of the manganese carbonate deposit depends more closely on the equilibrium constants for the bicarbonate system than on any other factor, in the argument presented. These constants certainly vary with temperature, and doubtless, with the form and composition of the precipitate. It may be that such variations are similar for the different divalent ions involved, so that some consistency could perhaps be hoped for as conditions change. But this is not known.

The calculations invariably involve the ratios of constants, so that concentrations (for the most part)cancel out. Assuming a fivefold error in the ratio of constants that define the $\frac{Ca}{Mn}$ concentrations, a 27.5% manganese deposit, made up of 0.039 $MnCO_3$, 0.021 $FeCO_3$, appears in Zone 3. This compares with the 16% Mn in the manganese carbonate (see Figure 9). That is, a fivefold variation in equilibrium constant ratios less than doubles the Mn content of the deposit. Apart from the quantitative change, the qualitative features of the deposit remain unaltered. Zones of sediments still appear, with manganese among mixed carbonates in the third zone as before. Consequently, within such limits, many of the essential features of the synthetic deposit are retained, even though the bicarbonate equilibrium constants varied widely from the values used.

Variations in CO_2 Concentrations

Preliminary calculations show that, as the (HCO_3^-) concentrations fall, the sharpness of the separation of the Ca, Mn and Fe from the $MgCO_3$ increases. At the same time it becomes less likely that any carbonate precipitation occurs at all, or at any rate, not until the concentrations of the divalent ions reach higher values than before. Then formation of insoluble metal silicates becomes more likely. Fe and Mg silicate precipitation is, in this case, at first preferred. In brief, the indications are that a carbonate precipitate changes steadily to a silicate precipitate, through equilibrium reactions, as the HCO_3^- concentration falls. There is insufficient data to press the conclusion further than this.

Finally, another point about the silicates should perhaps be made here. The identification of the silicate precipitation with hydroxide formation for the di- and trivalent cations, as was done in the body of the work, will almost certainly prove to be too crude an approximation. It was adopted, failing more specific data. The silicates, particularly in structure and replacement properties, are many degrees more complex than the hydroxides. Consequently, such conclusions as have been reached with respect to silicate formation are to be regarded as tentative and directional only.

CONCLUSIONS

Hypothetical manganese deposits can be deduced from nearly average igneous rocks by the application of chemical principles to idealized erosion systems. The sediment built up, from a single pass, is given quantitative as well as qualitative properties. Tonnages can not be known, as they depend on the size and the extent of the above average manganese content of the source rock. Percentages, ratios, associations, and to some extent, mineral type, can be specified. These become the diagnostic features through which comparisons can be made with natural deposits.

The calculations are made for a primary deposit. On aging, and by exposure to changing pressures and temperatures, some aspects of the deposit may change and others not. The metamorphic phenomena become a part of the comparison of the synthetic with real deposits.

In principle, the method seems to have that combination of uniqueness and generality that would enable it to be a common route for the development of the kind of manganese deposits found in North America. Higher grade deposits then arise from double-pass or triple-pass systems.

PART III

AGING OF THE PRIMARY SEDIMENT

INTRODUCTION

Two temperature levels seem important in the metamorphosis of single-pass manganese deposits. The first occurs when the manganese oxides or carbonates decompose. At this stage the manganese, present in a crumbling oxide lattice, becomes reactive and disappears into the gangue material. At higher temperatures, the siliceous material, in which the manganese is by then found, becomes mobile enough to permit the formation and segregation of stable manganese minerals. The model becomes a chemically isolated slab of the primary deposit, heated step-wise to successively higher temperatures. Descriptions of the deposit will be made to correspond with these temperature horizons. Then such features as seem pertinent to discovery and utilization will be discussed.

THE MANGANESE CARBONATE DEPOSIT

The manganese carbonate zone consists of a mixture of carbonates spread out in a siliceous gangue. Among the carbonates, iron and manganese are present in fixed ratios, while calcium is variable as it depends on the area of the zone. Magnesium may also be present, though only in small amounts. The siliceous material consists of amorphous silica and a (Mg,Fe) chlorite. Each of these may have a minor content of alumina. A sample ore is specified in Table 11, for a large deposit that contains 10% Mn. It was further assumed, to obtain the composition shown in Table 11, that SiO_2 was evenly distributed between amorphous silica and the chlorite.

TABLE 11

Composition of a Carbonate Deposit containing 10% Mn

	Weight, %	Formula Ratio
$MnCO_3$	20.9	1.00
$FeCO_3$	16.9	0.80
SiO_2	15.2	1.40
*$H_4(Fe,Mg)_3\ Si_2O_9$	37.7	0.75
*Al_2O_3	5.2	0.14
$CaCO_3$, etc.	4.1	

*If the Al_2O_3 is evenly distributed between the silica and the chlorite, the latter becomes
$0.61\ H_4\ (Fe,Mg)_3\ Si_2O_9,\ 0.14\ H_4\ (Fe,Mg)_2\ Al_2SiO_9$, making it a penninite member of the chlorite group(3).

These materials are thermally stable at the temperatures at which they form. At higher temperatures, however, certain of the minerals decompose. Also, reactions may begin between adjacent minerals. The transportation of material over only the shortest distances is envisaged, with no movement of material into or out of the deposit, except for the gases which are evolved.

Discriminations between the two kinds of solid state reactions that are provided here can be made from both thermodynamic and kinetic considerations. In the decomposition of a single lattice system, such as a carbonate or hydrate, the gas is given off without appreciable mechanistic hindrance. Consequently, the response to rising temperature is smooth and continuous, as determined by the free energy change. For two solid species, however, interaction depends not only on the temperature through the free energy connection, but also in a specific way on the achievement of mobility by one of the reacting species. Such a mobility, in principle and in practice, can be associated with the breakdown of a solid lattice, as in melting or decomposition. For example, two solids in contact may show little or no chemical response to rising temperatures until one of the solid phases begins to deteriorate. Then, quite abruptly, a reaction may begin. This is only to say that besides energy requirements, mechanistic features must also be fulfilled in these solid state systems.

As it happens, manganese carbonate is distinctly less stable than the other carbonates in the sediment. This appears both from the heats of decomposition, Table 12, where $MnCO_3$ is the least endothermic, and, more directly, from observation of the temperatures at which the carbonates maintain a pressure of one atmosphere of CO_2. These temperatures are about 390°C for $MnCO_3$, 490°C for $FeCO_3$, 540°C for $MgCO_3$ and 900°C for $CaCO_3$. It has also been observed that the decomposition of $MnCO_3$ begins at about 100°C(9).

TABLE 12

The Heats of Decomposition of the Carbonates*

	ΔH
$MnCO_3 = MnO + CO_2$	-16.9
$FeCO_3 = FeO + CO_2$	-21.3
$MgCO_3 = MgO + CO_2$	-27.5
$CaCO_3 = CaO + CO_2$	-42.9

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*Calculated from the data of Berthelot, as quoted in Bichowski and Rossini(11).

The Low Temperature Horizon

From the above data it is to be concluded that, so far as the carbonates are concerned, the first response to rising temperature is the decomposition of $MnCO_3$ (Footnote 1). The evolution of CO_2 from this compound, as it increases the concentration of the gas in the sediment, to some extent further retards the breakdown of the other carbonates. The two factors combine to imply a step-wise attack on the carbonates, with manganese carbonates going first, particularly if equilibrium conditions are approached.

Footnote (1): It should be mentioned that data obtained from the differential thermal analysis of Mn and Fe carbonates(13) do not unambiguously support this assumption. The temperatures at which the decompositions begin and at which they reach their peak, as measured in a DTA apparatus, are shown in Table 13.

TABLE 13

Decomposition Temperatures of Fe and Mn Carbonates in an Atmosphere of CO_2

	Reaction begins	Peak of reaction curve
$MnCO_3$ (crystalline)	430°C	620°C
$MnCO_3$ (precipitate)	383	460
$FeCO_3$	440 - 500	580 to 620

These data imply that, although the $MnCO_3$ has a tendency to begin to decompose at somewhat lower temperatures, the two carbonates are not clearly distinguished from each other throughout their decomposition cycle. The result would be, under suitable circumstances, that some iron would follow manganese at the low temperature horizon. These data do not include the effect of water or amorphous silica on the decompositions.

As well as decompositions, the two-phase reactions, carbonates-silica, are to be considered. In the particular reaction

$$MnCO_3 + SiO_2 = MnSiO_3 + CO_2$$

the endothermicity is 14.6 kcal, close to the 16.9 kcal value for the decomposition of $MnCO_3$. Consequently, a direct reaction between the carbonate and silica can hardly begin until temperatures are reached at which some of the carbonate has decomposed. The latter is an equilibrium process with a regular dependence on temperature, whereas, in the carbonate-silica system, phase separations must first be overcome. The decomposition of $MnCO_3$ introduces MnO, which must exist, at least momentarily, in an open active lattice. The reaction between MnO and SiO_2 is slightly exothermic, at 2.3 kcal/mole. Therefore, as manganous carbonate decomposes, a spontaneous reaction between MnO and SiO_2 can begin. This is taken to be the interphase reaction characterizing the low temperature horizon.

At the temperatures that seem to be involved, somewhat above 100° and increasing with the pressure, the sediment cannot be wet, although chemically bound water must still remain. Such traces and films of water, which have been shown to catalyze solid state reactions in a remarkable way, are presumably influential in the oxide-silica reaction. As a simplification, it will be assumed that mobility arises from the combination of the open MnO lattice and the water films or hydrations. Diverse products are possible from the reaction.

Two points can be made. Either the manganese or the silica can be carried to the reaction zone. If the manganese is mobile, reactions that are all spontaneous occur on contact with the silica and alumina silicates. Once the specific mineral is formed it then remains. That is, a simple equilibrium product can not be expected, but rather a mixture of manganese silicates and alumina silicates that may be hydrated or anhydrous, depending on specific largely mechanistic considerations. If, on the other hand, the siliceous component is mobile it must be as a monomeric unit, like H_4SiO_4. The chains and layers could not move. Again, on contact with the manganese, spontaneous reactions fix the components as they meet. Now, ortho·silicates may be formed whereas, before, chain and layer silicates were the simpler expectation.

As for the chlorites, only replacement type reactions, if any, occur. The chlorite is already a (Mg, Fe) silicate. The formation of an ultra-basic silicate from this material by a net absorption of MnO, likely endothermic, can not be defended.

The overall picture at this first temperature horizon shows the formation of various manganese silicates and alumino silicates containing no metal other than the manganese. Also, a manganous chlorite may be found, in which manganese is a minor element along with iron and magnesium. The manganese silicates and alumino silicates are in proportion to the silica and alumino silica originally in the deposit. The proportion of manganese in the chlorite is presumably small.

This stage corresponds to a low grade metamorphosis. At its end, with all the $MnCO_3$ decomposed, a manganese silicate deposit has formed, with the composition shown in Table 14. Carbonates are still retained in the Fe and Ca components. These have not yet decomposed.

TABLE 14

Formula Composition of the Manganese Zone after Low Grade Metamorphosis

$FeCO_3$	0.80
SiO_2	0.40
(Fe,Mg,Mn) Chlorite	0.75
$Mn\ SiO_3$	0.93
$MnO.Al_2O_3.SiO_2$	0.07
Al_2O_3	0.07
$CaCO_3$, etc.	

The High Temperature Horizon

The conversion of the mixed manganese silicates and alumino silicates into equilibrium species requires ionic mobilities both within and between the particles. Temperatures must be high enough to permit the chain, layer and three-dimensional structures to seek out their stablest form. This corresponds to the achievement of a considerable mobility, at least by the SiO_4 tetrahedral units, which in turn implies an approach to a melting point transition. One-half the absolute melting point is sometimes used as a rough rule of thumb in cases of this sort, which would place the high temperature horizon in the neighborhood of 800°C. Water need not be involved in these internal rearrangements and crystal growths. Indeed, at such temperatures, it is unlikely to remain. A substantial distinction is, therefore, to be inferred between the low and high temperature horizons, both in the temperatures themselves and in the reactions that occur.

There is a very general agreement that the specific mineral, Spessartite, a manganese alumino silicate with the composition, $3MnO.Al_2O_3.3SiO_2$, is the substance to which the manganese turns, at high temperatures(1,4,12). Spessartite is an ortho-silicate that is not ultra basic and thus combines the stability features of alumino-silicates with the close ionic packing possible around SiO_4 islands. Thermal data and compositional analyses to confirm and give detail to the selection have not been found, but by analogy with other systems and because of its appearance in nature under the correct conditions, the selection seems a good one.

In so far as the composition will permit, it is concluded that spessartite forms from the manganese silicates and alumino-silicates at the high temperature horizon. After such a conversion, assuming the simplest conditions, the 10% deposit of Tables 11 and 13 has the manganese present as 0.42 part in manganese garnet and 0.58 part in a manganese silicate. The minerals are, at this approximation, pure species. But such factors as alumina or manganese in the chlorite, or reactions with residues from the Fe and Ca carbonates, could introduce mixed (Mn,Fe,Ca) garnets and shift the proportion between spessartite and silicate. Moreover, spessartite can only become the sole manganese-bearing mineral if the alumina content is relatively high. For example, even with 10% Al_2O_3 in the exemplary deposit, the manganese is at the most, 84% in spessartite.

Such ratios as $\frac{SiO_2}{\text{chlorite}}$ and $\frac{Al_2O_3}{SiO_2}$ are relevant, not only in determining purity and proportion of spessartite formed in the deposit, but also in giving a measure of the amount of inter-particle

A response of the Fe (and Ca) carbonates to these high temperatures can be the introduction of new garnet species, such as almandite, $Fe_3Al_2\ (SiO_4)_3$, putting additional claims on the gangue components. However, the argument as developed gives manganese the prior claim. The field observation, that garnetization of manganese precedes general garnetization on a temperature scale, confirms the increase in separation. To the extent that the gangue is deficient, therefore, the $FeCO_3$ will emerge as an oxide, with magnetite preferred. Here use is made of the observation$^{(9)}$ that, at high temperatures, CO_2 oxidizes iron. The composition of the exemplary deposit after high grade metamorphoses is given in Table 15.

In summary, the manganese produced from high grade metamorphoses is to be found both in garnets and in silicates. The specific garnet, spessartite, is always an important constituent. It dominates, however, only as the overall Mn/Al atom ratio approaches 1.5.

TABLE 15

Composition of the Deposit after High Grade Metamorphoses

	Formula Ratios
$Mn_3Si_2(SiO_4)_3$	0.14
$MnSiO_3$	0.58
Chlorite	0.75
Fe_3O_4	0.13
$FeSiO_3$	0.40

THE OXIDE DEPOSITS

Manganous carbonate and the higher oxides of manganese are both relatively unstable compared with the other materials with which they are associated in their respective deposits. Their decompositions, both tending towards manganous oxide, are, in each case, the first step in the transformation of the deposit. As a result, increasing temperatures tend to make the two deposits rather more alike.

The Low Temperature Horizon

A comparison of the heats of decomposition, Table 16, suggests a temperature sequence in which ascending steps are the decomposition of MnO_2, Mn_2O_3, Mn_3O_4, $MnCO_3$, ending with MnO. The intermediate oxides, Mn_2O_3 and Mn_3O_4, are separated, however, by a wide thermal step from the end product, MnO. Associating the onset of chemical reaction between two solids with the first appearance of a weakened lattice, as before, it may be concluded that, in the absence of CO_2 and oxygen, reactions between these intermediate oxides and adjacent siliceous material will precede the appearance of manganese silicates in the carbonate zone. Furthermore, these first products of metamorphoses in the oxide zone will contain manganese in a valence state between two and four. Consequently, though manganese silicates appear in both the oxide and carbonate zones at low temperatures, the manganese silicates in the two zones differ in temperature levels at which they appear, and in the specific kind of silicate mineral that is achieved. In the oxide zone, silicate minerals like braunite, $3Mn_2O_3 \cdot MnSiO_3$, and alumino-silicates like piedmontite, $HCa_2(Al,Mn)_3Si_3O_{13}$, are examples of the two types to be

TABLE 16

The Heats of Decomposition of Manganese Oxides and Carbonates

	Heats of Decomposition*, kcal/mole Mn	
	(a) MnO_2 crystalline	(b) MnO_2 amorphous
$MnO_2 \rightarrow \frac{Mn_2O_3}{2}$	-6.5 kcal.	+1 kcal
$MnO_2 \rightarrow \frac{Mn_3O_4}{3}$	-8.0	+0.7
$MnCO_3 \rightarrow MnO$	-16.9	-16.9
$MnO_2 \rightarrow MnO$	-26.5	-19.0

*From Bichowski and Rossini(11)

expected. Braunite is an example of silica invading a decomposing higher oxide of manganese; piedmontite, of mobile tri-valent manganese moving into an alumino-silicate. Both are to occur at temperatures at which water facilitates the transport mechanism.

An earlier conclusion, that minerals like braunite containing high valent manganese could also appear in the primary sediment, is to be recalled. The relatively slight, or perhaps just ambiguous, temperature separation between the higher oxides of manganese is also confirmed by the fact that MnO_2 does not occur in nature without the admixture of somewhat lower oxides. Such an equilibrium is in turn confirmed by the quite small heats involved in the conversions. Consequently, though the appearance of silicates and alumino-silicates like braunite and piedmontite can be unambiguously related to the oxide deposit, their presence does not necessarily prove that a temperature metamorphosis has occurred.

The High Temperature Horizon

At temperatures above the horizon for carbonate decomposition, the intermediate oxides are further reduced, disappearing in the divalent form during high grade metamorphoses into garnets and silicates. At this stage, compositions otherwise permitting, the manganese minerals in what were originally oxide and carbonate zones have become the same. Differences that still remain depend in part on the gangue material with, for example, chlorite or chloritic remnants in what had been the carbonate, and remnants from a ferric silicate, perhaps a biotite or silica and an iron oxide, in the oxide zone. The large variations possible in the $\frac{Fe}{Mn}$ and oxide/gangue ratios in the oxide deposits, compared with the relatively constant values for similar ratios in the carbonate zone, also remain as distinctions. In extreme cases, for example in the 'high grade' band in the oxide deposit, either total oxides can be so high, or the manganese oxide fraction so low, that reaction with the gangue is incomplete, or not selective of the manganese. Then oxides like magnetite and, in the first case, hausmannite, may still remain.

EXPLORATION AND EXPLOITATION

Some new features can be developed, that may have relevance to the discovery and the use of the deposits, when the physical and chemical properties of the several kinds of deposits are put in contrast with one another. The new features deal with the gross appearance of the deposits, and the response of the deposits to agents involved in metallurgical processes.

Classification of the Deposits

The response of the manganese minerals to temperature exposures is summarized in Figure 15. As carbonate and oxide type deposits can coexist, and as each travels a different path on the way to garnetization, a measure of variety exists even within the three main classes, the carbonate-oxide, the silicate-oxidized silicate and the garnet. The oxide-carbonate deposits may have been put down in any proportion, and the thermal horizons for the oxide and for the carbonate zones are not identical, particularly in the first transition. Each class of deposit can, therefore, within such limits, have variant members. Examples are a carbonate-oxidized silicate deposit, and a carbonate with no oxide whatever.

Apart from such a general classification of deposits, a single deposit may also show certain variations. Depending on whether the temperature condition was quite local or more widespread, and depending on whether the deposit was large or small, a single deposit may contain successive zones of garnet, silicates and carbonate-oxides at increasing distances from the heat source, or the deposit may exist throughout at a uniform temperature horizon. In general, greater variations may be expected in deposits that contain the high temperature modification, as such a heat source is more apt to be local, and is rapidly cooled by distance.

Figure 15

Distribution of Manganese Minerals with Distance from a Heat Source

	Contact Zone	
Garnets	↑ Temperature	Garnets
Silicates		
		Oxidized Silicates
Carbonate		Oxide (MnO_2)

Slates, Quartzites and Chlorite-Schists

The gangue material in the primary carbonate sediment is a mixture of amorphous silica and chlorite. Thermal metamorphoses will affect these components as well as the manganese-bearing minerals, when the deposit passes through suitable temperature horizons. Moreover, the form in which the deposit finally emerges, whether as a quartzite, slate, shale, chlorite-schist, etc., depends for the most part on the gangue material. Two factors combine to imply the presence of more than one form in a deposit that has been thoroughly heated. The argument is covered in the illustrations 16a and 16b.

Two variations are involved. First of all, the area of the manganese zone is a variable fraction of the area of the whole deposit, depending on the manganese-to-metal ratio in the igneous source rock, as was shown before. Also, the $\frac{SiO_2}{\text{chlorite}}$ ratio changes along the length of the overall deposit. In general, the silica predominates in the first lengths, and the chlorite in the last lengths along the sediment, as shown in Figure 16a, for a deposit in which the manganese zone is small.

Combining the two effects, the $\frac{SiO_2}{\text{chlorite}}$ ratio will have many values within the manganese zone, particularly when the relative area is large as in Figure 16b. Then gangue variations for pure SiO_2 to pure chlorite can be contemplated. It has separately been shown that the relative area is expected to increase as the calcium content falls.

The conclusion follows that gangue variations from pure silica to pure chlorite are to be anticipated when calcium is low in the manganese zone.

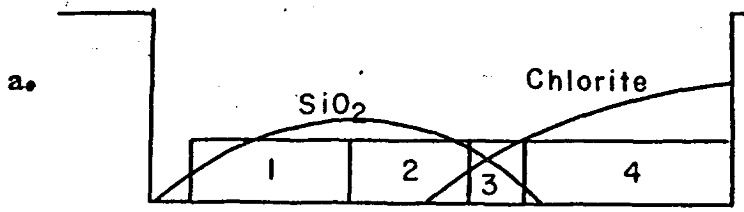
At temperature horizons high enough for the spessartite conversion, excess silica in the gangue grows in a three-dimensional sense, while the chlorite retains its layer-like properties. The siliceous gangue, therefore, gives rise to quartzite-like deposits, and the chlorite to chloritic slates and schists. Intermediate areas presumably consist of quartzites containing chlorite, and slates or schists with fine-grained quartz.

In the foregoing, the presence of alumina was ignored. This was not important in the chlorites, for its presence there does not alter the layer-like properties of these particles. In silica, however, it may in principal convert three-dimensional quartz to two-dimensional alumino-silicates and micas. As it happens, manganese acts against this trend, by using alumina in the formation of the spessartite. These are three-dimensional particles, like quartz. It is unlikely that the alumina content ever appreciably exceeds that needed to make spessartite in these deposits. Therefore, the presence of alumina tends to facilitate, or at least is compatible with, the appearance of both quartzites and chlorite-schists at high temperature horizons.

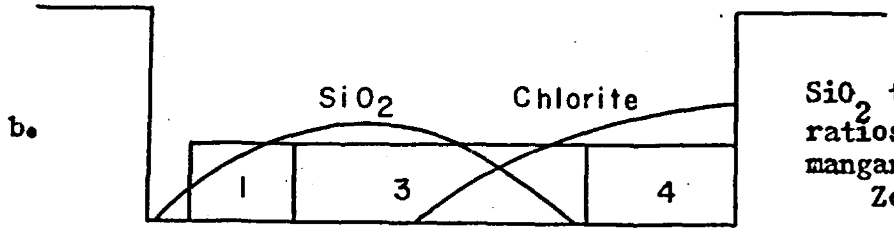
The inference to be made is that a manganese deposit may be essentially continuous through sedimentary rocks of diverse types such as slates, quartzites and schists.

Figure 16

Variations in Relative Areas and in Quartz to Chlorite Ratios



SiO_2 to chlorite ratios in a small manganese deposit, Zone 3.



SiO_2 to chlorite ratios in a large manganese deposit, Zone 3.

Secondary Enrichment

Secondary enrichment can occur in a single-pass sediment, either when the deposit is laid down or during the aging period. This may be entirely fortuitous. On the other hand, it is possible that in some instances a significant connection does exist between a secondary mineral and the leading constituent, or some other, in the deposit. The co-occurrence of limited groups of elements and minerals, which is frequently observed and often remarked upon, suggests that the possibility may have substance.

The occurrence of an additional element in the primary sediment can be given significance under two conditions. It is necessary, first of all, that the secondary element have the property of appearing in rocks like the igneous source. Further, it is necessary that the oxide or the carbonate have the solubility properties that precipitate it out in the manganese zone, or in some relation to it. Then the new element becomes included in the system on the same terms as iron, magnesium, calcium and manganese. Divalent metals like nickel and zinc at once come to mind for co-precipitation in the carbonate zone, and metals of variable valence like titanium, chromium, and perhaps cobalt for the oxide zone. The co-occurrence of these elements in the source rock will, of course, tax the odds somewhat, or the new element may displace manganese (or iron, etc.) in the source. In either case, those secondary elements that thoroughly satisfy the two conditions have a good chance to be found in some part, if not throughout, the larger manganese deposits.

A second way in which new material can be introduced is through external encroachment during the aging period. For this to be not wholly fortuitous, again some significant connection must be established with the deposit. For example, the redox property of manganese may be cited as a property of the ore. Then those elements taken out of mobile systems percolating through the deposit, by redox reactions with the manganese, can be said to be fixed in significant association with manganese. Through oxidation by a manganese oxide, for example, tungsten could be raised to the tungstate state and fixed in the deposit as the calcium, iron or manganese tungstate salt. This association is in fact known in deposits where scheelite coexists with spessartite along the Eastern Shore of Nova Scotia. Gold is also found in certain areas of this region. Here, the manganese must act to reduce the gold, presumably from the auric state, if its deposition as the noble metal is to have a specific connection with the redox property of the manganese deposit.

It is, of course, an accident if any invasion, particularly one containing a specified material, does in fact occur. Moreover, in each case the facts of fixation must be confirmed. Nevertheless, it is evident in a general way that specific connections may exist between minerals in a deposit and minerals later fixed in that deposit by invasion from the outside. The formation of iron pyrites through sulphurous invasions is possibly the best known example relevant to the deposit. These extra details have a measure of significance for exploration and utilization.

Metallurgical Aspects

Changes in mineral type and association occur during the life of the deposit, and the grade alters. Extractive techniques depend on these features. The question then arises as to which class of deposit is best suited to metallurgical purposes.

In the cold primary sediments, the carbonates and oxides are chemically and physically distinct from the gangue material. They are themselves, however, mixtures of iron, manganese and calcium components. At the first temperature horizon, a selective reaction converts the manganese to silicates and oxidized silicates, while the iron and calcium components are unchanged. A measure of separation from the metallic components is thereby achieved, but the manganese minerals have become more similar to the gangue. These two trends continue through the high temperature horizon, with spessartite becoming the principal carrier of manganese. This completes the separation of manganese from the other metals, but increases the similarity of its mineral to the quartz and chlorite gangue. In brief, therefore, the metallic components (Fe,Mn) can be more easily separated from the siliceous gangue in unheated deposits, whereas manganese can be more easily separated from the iron in deposits that have been heated. This refers to mechanical separations. In application, the simplest implication is that ferro-manganese products be sought from unheated deposits and unalloyed manganese metal from heat-aged ores.

Heat aging not only causes consistent trends. Considering the variety of manganese minerals, for example, the two species in the carbonate-oxide deposit abruptly become the very many oxidized and unoxidized silicates and alumino-silicates of the first horizon. Then a unique species is achieved at the spessartite level; that is, the variety is greatest at the middle, and least at either end, of the temperature range. In general, however, these changes merely represent progressive simplifications in an ambivalent carbonate-oxide deposit, moving towards a less ambiguous end, spessartite.

Beside changes in the distribution of the manganese minerals among the metallic and the siliceous gangue components during heat-aging, a noticeable up-grading also occurs due to the evolution of gas during dehydration and decomposition. At the first horizon, where only $MnCO_3$ decomposes, manganese increases from 10.0 to 10.9%. At the garnet level, where the decompositions and dehydrations are presumably complete, the manganese is 12.5%. The overall up-grading, by 25%, is, on the other hand, diminished if material has been added from external sources.

A final comparison has relevance to the power requirements in metallurgical processes. The heats needed to liberate a similar product (MnO) from the different kinds of deposits are as follows:

$$MnO_2 = MnO + \frac{1}{2} O_2 \qquad - 19.0 \text{ kcal} \qquad (1)$$

$$MnCO_3 = MnO + CO_2 \qquad - 16.9 \text{ kcal} \qquad (2)$$

$$MnSiO_3 = MnO + SiO_2 \qquad - 2.6 \text{ kcal} \qquad (3)$$

It is evidently more costly to convert the carbonate and dioxide than the silicate in these endothermic reactions. The heat of the reaction

$$\text{Spessartite} = 3\ MnO + Al_2O_3 \cdot 3SiO_2 \qquad (4)$$

is unknown. It is likely to be somewhat more endothermic, on a comparable basis, than reaction 3. Ideally, therefore, the silicates and spessartites appear to have a distinct thermal advantage for metallurgical purposes. Quite obviously, however, the comparison is too simple. For though the CO_2 and O_2 can be automatically removed during the heating process, the silica is not so separated even above the melting point of the silicate or spessartite. There is a problem, therefore, in devising a method that makes use of the thermal advantage and at the same time copes with the disadvantageous condensed phase equilibria.

From the foregoing, five trends can be listed that cover the passage from the unheated carbonate-oxide to the high temperature spessartite deposit.

1. The purity of the manganese minerals improves.
2. The variety of manganese minerals first increases, then decreases.

3. The grade of manganese increases, though by no more than 25%.

4. The mechanical separation of the manganese is more difficult from the metallic components in the first deposits, and from the gangue components in the latter.

5. The manganese minerals are, at the first, chemically more reactive, and, at the end, have smaller heats of decomposition.

In general, the metallurgical problem is to take advantage of favorable features in such a way as to overcome the difficult properties of the ore.

(a) The Metallurgy of the Carbonate-Oxide Deposit

In the carbonate-oxide deposit, the favorable features are the possibility of a mechanical up-grading, and the reactivity of the minerals. Because of the fine-grained texture of the sediments, and of the likelihood that the metallic components will separate together, the degree of up-grading that can be achieved is, however, limited.

The difficulties to be overcome include the mineralogical complexity and the problem of separating the manganese from the iron. Both carbonate and oxide species, together with related variations in the gangue, may occur in the deposit. This difficulty can be met, in part, by heating the mixed deposit to temperatures at which both oxides and carbonates have decomposed to MnO. At the same time, it is necessary that a base, e.g. CaO, be added. Its function is to react with the silica and thus prevent the formation of manganese silicates and spessartite. For the diversion to be successful, it is also necessary that the MnO be suppressed separately, for example, through reduction by the use of coke. Because of oxidation potentials the iron will also be reduced at this time. Finally, as temperatures high enough to melt the mixture will be needed to push the reactions to completion, separation can be effected by withdrawing the molten metal (Mn,Fe,C) which underlies the liquid slag ($CaSiO_3$). That is to say, a smelting operation in which coke and lime are added to a mechanically up-graded carbonate-oxide ore, represents a sensible solution to the problems of the ore, but only under the condition that the product can contain both Fe and Mn. The product here appears as an (Mn,Fe,C) alloy. In practice, the Udy process, which is a smelting process somewhat like that outlined above, yields a (Mn,Fe,C,Si) alloy as a product.

It might be noted that the smelting process takes the material from the deposit to temperatures well above those at which the manganese silicates and spessartite begin to form. On the face of it, it might therefore seem that the silicate and spessartite deposits would also yield to a smelting operation. However, in the case of the carbonate-oxide ore, the CaO and the coke attack the distinct and separate phases, SiO_2 and MnO respectively. These reactions no doubt begin even before the mixture becomes fluid. In the molten spessartite ore, on the other hand, the lime and the coke must first break down the single phase, $Mn_3Al_2(SiO_4)_3$, before an analogous situation can begin to be established. It is evident from this that the two smelting operations will by no means operate under the same set of controls.

An alternative process is, in principle, attractive.

In it, more emphasis is placed on the reactivity property of the carbonates and oxides. The carbonates react with sulphuric acid, whereas MnO_2 does not unless a reducing agent is present. As, however, the acid solution of the carbonates yields ferrous ion, and as ferrous ion reduces MnO_2 to manganous ion rather quickly in acid solution, it becomes possible in principle to dissolve the complex carbonate-oxide deposit by a straight forward sulphuric acid leach. Some control of the $\frac{\text{oxide}}{\text{carbonate}}$ ratio in the ore feed would be required, so that enough ferrous ion be present for the MnO_2 reduction. The product of the leaching process is $MnSO_4$. Ferric sulphate is also present in the spent liquor. Acid conservation would require that the iron be precipitated as $Fe(OH)_3$, and the manganese removed, electrolytically, as the pure manganese metal. Presumably the process could be worked out on a cyclic basis. Much work has been done at the Mines Branch(14) on individual reactions mentioned above. The overall process has not yet been tested.

(b) Metallurgy of the Spessartite Deposits

In the metamorphosed deposits, however, the spessartites present a different set of advantages and obstacles. It is possible to remove the magnetitic and sulphidic iron, but apart from this the processes must apparently be made to work in the presence of the siliceous gangue. The combination of the fine grain size in the sediments, and the close physical and chemical similarity of the manganese silicates to the siliceous gangue, offers little reason to hope for a separation between these components.

The first problem becomes how to lift the manganese out of the spessartite, in which it is chemically bound, at temperatures below smelting temperatures. The smelting process has already been considered.

For such a chemical transformation, it is in general necessary to destroy or alter the spessartite lattice, while a new and separable chemical species is formed from the manganese. This can, in principle, be done in two ways: either by replacing the manganese in the alumino-silicate, or by removing the alumino-silicate from about the manganese.

(a) Chemical agents that can affect the fit of the manganese in the spessartite lattice, and thus provide a basis for chemical separation, fall into two categories: those that can substitute for the manganese, and those that can change the valence state of the manganese. If both processes can be combined, the manganese can in principle be lifted out of the spessartite lattice, through oxidation, at the same time that it is pushed out of the lattice by substitution. As a specific example, a lye roast would enable Na to substitute for the Mn while the manganese is being oxidized, by atmospheric oxygen, from the divalent to the tetravalent (or higher) state. The product would be a manganese oxide (say MnO_2), with a sodium alumino-silicate as the second phase. The lye roast would have to be done in air at temperatures high enough to make the Na ions mobile. These are relatively low temperatures, in the range 400 to 800°C. Such a process has been investigated, with satisfactory results(15). To make the process attractive, the lye would have to be recovered from the sodium alumino-silicate, either in the by-product of this material, or by the treatment of it, for example, with lime.

(b) If the problem is reversed, so that substitution for the alumino-silicate about the manganese becomes the formal objective, it is evident that a more pervasive degradation of the lattice is required. An acid constituent, like SO_3, is required to invade the lattice until, by continuous replacement of the ligands about the manganese, a manganese sulphate product is obtained. To facilitate the decrepitation of the alumino-silicate framework which must be effected before the reaction can go to completion, the ability of water at high temperatures and pressures to open up the lattice by forming acidic silicas and alumino-silicates, should also be employed. At the same time, advantage may still be taken of the redox properties of the Mn, which in this case partly depend on the considerable thermal stability of the $MnSO_4$. That is, because the temperatures can be high enough to maintain a mixture of SO_3, SO_2 and O_2, the oxygen may assist in the formation of MnO_2 from the spessartite, while reduction of SO_2 facilitates the solution of this oxide as $MnSO_4$.

Either high pressure, high temperature autoclaving or what might be called wet SO_3 fluidization, is the sort of technique called for. Neither has yet been tried in detail on these ores, nor is the role of water sufficiently well known to hazard a guess as to whether or not such an extraction would have a reasonable chance of success. The final product, in view of the need for acid conservation, would probably be electrolytic manganese.

In summary, the carbonate-oxide deposits have the advantage of a greater low temperature reactivity and an easier separation from the siliceous gangue. The silicate and spessartite deposits, conversely, show somewhat higher grades with a cleaner separation of the manganese from the iron and calcium components; they enjoy as well, in an ideal sense, a distinct thermal advantage.

Metallurgical investigation of these deposits is a relatively new study, with a history of perhaps twenty years. As yet, no methods have been developed for a large scale production.

It is of interest to note that all North American deposits, with the exception of minor bogs and recent erosions, are single-pass deposits. In other continents, however, double-pass, perhaps even triple-pass, deposits of huge dimensions are also found. These, in their derivation from single-pass sediments, have been vigorously upgraded by a disentanglement of the manganese from alumina and silica and, in some cases, by a further separation of the manganese from the iron(16,17). As a result, high grade surface deposits of the oxides, pyrolusite and psilomelane, have been found on other continents. These second and third pass stages are absent in North America--swept off by the glaciers, it has often been said. Consequently, on this continent the problem for the metallurgist is the treatment of single-pass deposits.

The intensive laboratory work of the past twenty years has revealed many methods for extraction. Processes with different merits and at different stages of development are now known for each class of deposit, and also for specific variants(18). There is still much work being done.

There is, of course, the obvious practical question of competition from the high grade ores. Though obvious, this is a complex question, involving sociological as well as technological features. It may be pointed out, however, that a 10 to 15% deposit is by no means a hopelessly impoverished raw material. The prospects are good that more than one method can be proven up to see these ores through to a useful production.

PART IV

APPENDIX

1. INTRODUCTION

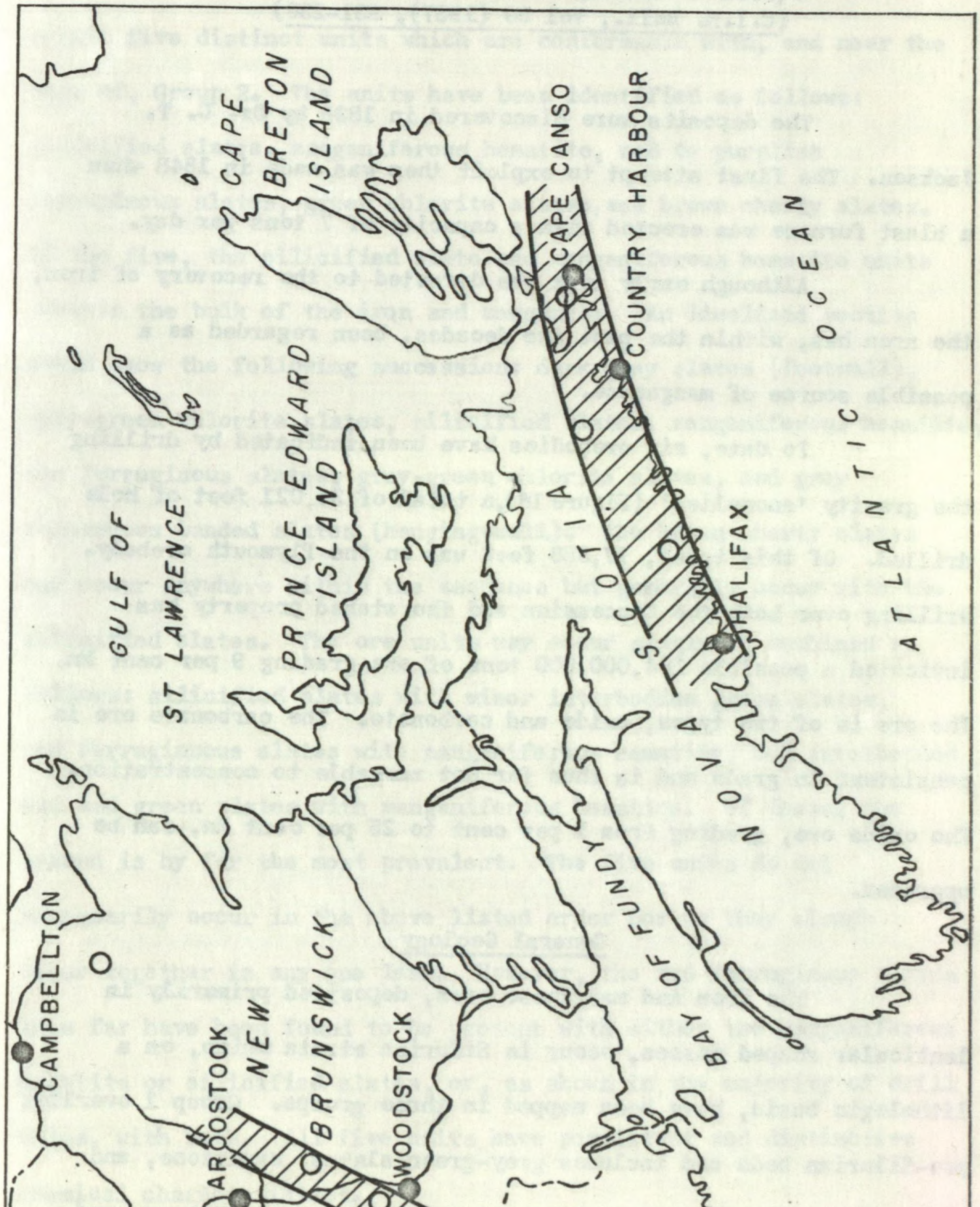
The two areas of interest are shown in Figure 17. For further information on the Maine part of the New Brunswick-Maine region, an article on "Manganese Deposits of Aroostook County, Maine" by R. L. Miller, can be recommended(19). The extensive quotations appended below on the Woodstock, New Brunswick deposits are extracts from "The Woodstock N. B. Iron-Manganese Deposits" by K. O. J. Sidwell(20). A report by E. Nickel(21) on the mineralogy of located samples from the Plymouth deposit is also appended, together with a chemical analyses of these samples and some of their component parts.

The deposits of the Eastern Shore of Nova Scotia are much less well known. Two reports on the mineralogy of different specimens from the Canso area are appended(22,23).

The manganese deposits of Conception Bay and Trinity Bay, Newfoundland, not shown on the map, have been described by G. F. Carr(24).

Figure 17

The New Brunswick-Maine and the Eastern Shore, N. S. Areas



2. THE WOODSTOCK, N. B., IRON-MANGANESE DEPOSITS

(From article by K.O.J. Sidwell in)
(C.I.M. Bull., Vol 50 (1957), 231-236)

The deposits were discovered in 1836 by Dr. C. T. Jackson. The first attempt to exploit them was made in 1848 when a blast furnace was erected with a capacity of 7 tons per day.

Although early work was directed to the recovery of iron, the area has, within the past two decades, been regarded as a possible source of manganese.

To date, six orebodies have been indicated by drilling the gravity 'anomalies' (Figure 18), a total of 34,021 feet of hole drilled. Of this total, 17,388 feet was on the Plymouth orebody. Drilling over both the Concession and the staked property has indicated a possible 194,000,000 tons of ore grading 9 per cent Mn. The ore is of two types, oxide and carbonate. The carbonate ore is consistent in grade and is thus far not amenable to concentration. The oxide ore, grading from 1 per cent to 25 per cent Mn, can be upgraded.

General Geology

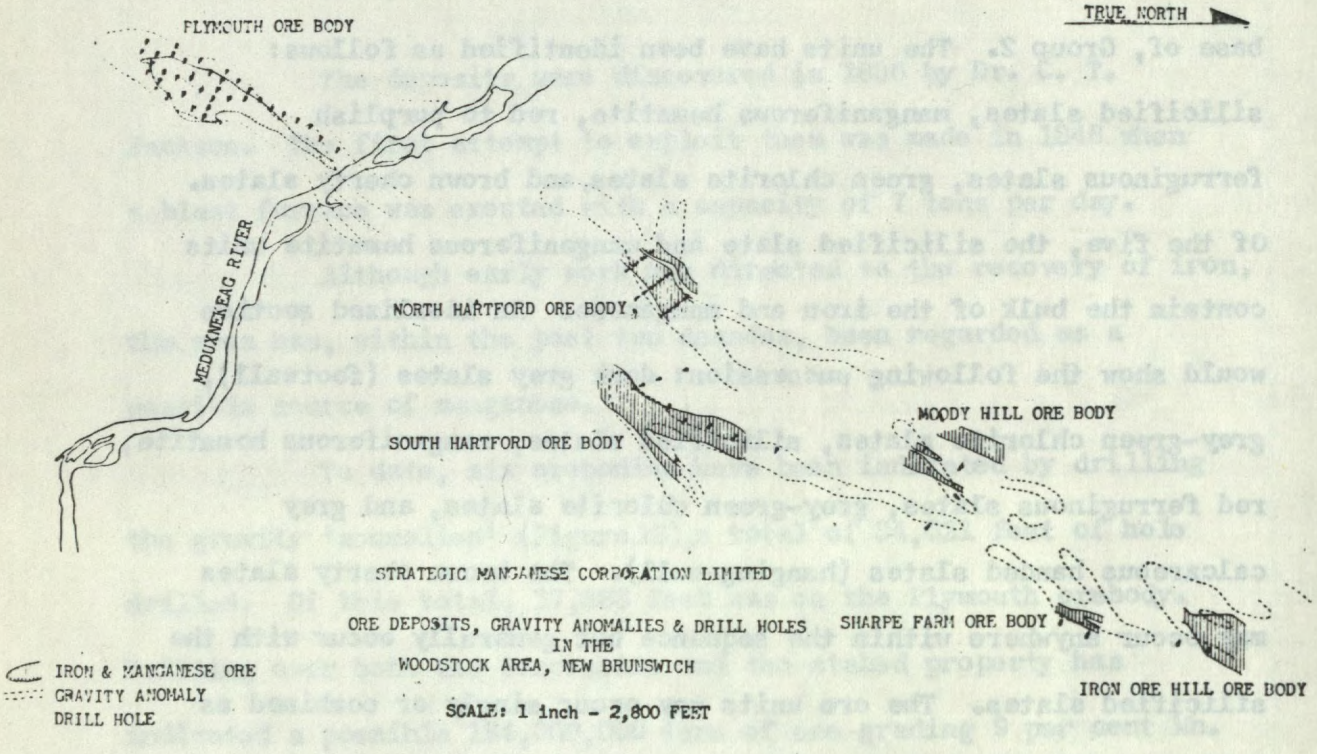
The iron and manganese ores, deposited primarily in lenticular shaped masses, occur in Silurian strata which, on a lithologic basis, have been mapped in three groups. Group 1 overlies pre-Silurian beds and includes grey-green slates, sandstone, and greywacke. The rocks of Group 2 are grey-green, grey, green, and red slates, and those of Group 3 are dark grey, contorted, calcareous slates(2). The slates are all steeply folded, are predominantly thinly bedded, and trend in a general northeasterly direction.

The iron and manganese minerals have been deposited within five distinct units which are conformable with, and near the base of, Group 2. The units have been identified as follows: silicified slates, manganiferous hematite, red to purplish ferruginous slates, green chlorite slates, and brown cherty slates. Of the five, the silicified slate and manganiferous hematite units contain the bulk of the iron and manganese. An idealized section would show the following succession: dark grey slates (footwall), grey-green chlorite slates, silicified slates, manganiferous hematite, red ferruginous slates, grey-green chlorite slates, and grey calcareous banded slates (hanging-wall). The brown cherty slates may occur anywhere within the sequence but generally occur with the silicified slates. The ore units may occur singly or combined as follows: silicified slates with minor interbedded green slates, red ferruginuous slates with manganiferous hematite, and interbedded red and green slates with manganiferous hematite. Of these, the second is by far the most prevalent. The five units do not necessarily occur in the above listed order nor do they always occur together in any one lens. However, the red ferruginous slates thus far have been found to be present with either the manganiferous hematite or silicified slates, or, as shown in the majority of drill holes, with both. All five units have persistent and distinctive chemical characteristics.

The manganiferous hematite, the highest grade unit, is a dark red to black, finely banded rock with, occasionally,

Figure 18

Ore Deposits, Gravity Anomalies and Drill Holes in the Woodstock Area, New Brunswick



alternating red and black or dark red laminae. It has a blocky fracture and is frequently replaced with quartz. It is believed that this quartz replacement is predominant on the crests or troughs of folds. The unit is also cut by narrow quartz stringers and by veinlets of pink granular rhodochrosite and quartz which occasionally carry minute specks of chalcopyrite, galena and sphalerite. Pyrite is a more prominent sulphide and is found particularly near the base of the unit. The unit is also cut by narrow, deep red stringers of the manganese silicate piedmontite and contains occasional blebs of pale yellow to brown manganese-bearing axinite.

The original manganese minerals in the manganiferous hematite are too finely divided to be identified microscopically, and the X-ray method of mineral determination has been used. The predominant manganese mineral has been identified as braunite, $3(Mn,Fe)_2O_3 \cdot MnSiO_3$, which is intimately intergrown with the hematite. Apatite is commonly associated with the hematite. The principal gangue minerals are quartz, chlorite, and feldspar.

The weathered surfaces of this rock are heavily stained with a coating of manganese oxide, which adds appreciably to the grade. Below the weathering zone, the grade is uniform at all intersected depths. There are, however, distinct changes in grade of the unit along the strike. This feature is noted in comparing analyses of samples taken from the Plymouth deposit and the Iron Ore Hill-Moody Hill deposits. The latter are higher in iron and lower in manganese than the Plymouth deposit, and there is a corresponding increase in the percentage of phosphorus with the increase in iron. This relationship is shown in the following table of analyses:

	Moody Hill	Plymouth
Fe%	29.50	18.25
Mn%	12.30	16.71
SiO_2%	20.80	21.50
P%	0.98	0.65

The manganiferous hematite has a specific gravity of 3.8 and contains up to 45 per cent combined metal with iron and manganese in the ratio of 5 to 4, although occasionally this ratio may be reversed. It occurs both in the form of definite beds in widths up to 100 feet and as narrow lenses (up to 5 feet in width) in the red ferruginous slates, although it is not presently known whether some of these wide beds are indicative of a true thickness or represent the combined width of closely folded lenses.

The silicified slate unit is a thinly bedded slaty rock consisting of alternating bands of silica and carbonate. It varies in colour from light grey to dark grey to dark green to black, and is dense and hard. This rock is coarser grained than the manganiferous hematite and consists largely of rhodochrosite, manganous chlorite, and hematite. Subordinate silicates are manganous axinite, piedmontite, rhodonite, with accessory quartz, pyrite and magnetite. These slates are locally feebly magnetic and are cut by numerous narrow quartz stringers. The pyrite occurs as pods and thin laminae throughout the unit but is predominant near the top and base of the slate band.

These slates have a specific gravity of 3.5 and contain approximately 35 per cent combined iron and manganese in the ratio of 5 to 4. The percentage of manganese is remarkably constant, habitually between 12 and 16 per cent, with the dark green phase carrying about 15 per cent. In places, the unit attains a maximum width of 470 feet. It is most prevalent in the staked property south of the Concession. The slates are considered to be metamorphosed grey and green slates which originally had a high content of iron and manganese. The weathered surface of the rock is heavily stained with a coating of manganese oxide. Below the weathering zone the grade is uniform at all intersected depths. A typical composite analysis of the ore from one 326-foot intersection is as follows:

Fe	16.49 per cent
Mn	13.52 "
CaO	2.65 "
MgO	5.57 "
SiO_2	30.06 "
P	0.61 "

The red ferruginous slate unit usually has a width greater than the combined width of the other four units of the iron-manganese formation. This is especially so on the Concession, where the silicified slates do not occur in appreciable widths. The ferruginous slates have a well defined cleavage and vary in colour from bright red near the base of the unit to purplish-red near the top. They generally carry manganiferous hematite interbeds which increase, both in width and frequency, from the top to the base of the unit. The average iron and manganese contents are estimated, respectively, as 7 and 3 per cent. In places these slates attain a thickness of 500 feet but it is suspected that this width is due to folding. However, the unit will probably average 250 to 350 feet. It is to be noted that the percentages given above for average iron and manganese content in the red slates are applicable only to the red slates proper and not to the combination of red slates and manganiferous hematite interbeds, which average 12 per cent iron and 7 per cent manganese.

The green slate unit, although occurring at the top and usually also at the bottom of the deposits, is considered as an ore unit because of its additional occurrence as interbeds with both the red slates and the silicified slates. It is a chlorite slate with a well developed cleavage and it contains minor amounts of iron and manganese. Locally, the interbeds may approach a sericite-chlorite schist. The manganese content of the green slate unit ranges from 2 per cent to 7 per cent with an estimated average of 4 per cent.

The brown cherty slates, the least important unit, occur in widths up to 10 feet, predominantly as interbeds in the silicified slate unit. They contain up to 9 per cent Mn.

Table 17 gives the minimum, maximum and estimated averages of iron and manganese content in each of the five units, as determined from drill core analyses.

TABLE 17

Analyses of Ore from Each of the Five Zones

Unit	Iron Min. %	Iron Max. %	Manganese Min. %	Manganese Max. %	Fe Av. (Est) %	Mn Av. (Est) %
Manganiferous hem	11	30	12	25	22	14-16
Silicified slates	10	25	9	20	16	12-14
Red ferrug. slates	5	9	1	6	6	2-3
Green slates	3	11	2	7	7	4
Brown cherty slates	2	12	2	9	8	6

The occurrence of at least two or more units interbedded in a particular zone will, of course, alter the figures for manganese given in Table 17. Such is the case where the manganiferous hematite occurs as interbeds in the red slates, with a resultant increase in manganese grade across the unit. Since the location, frequency, and thickness of these interbeds cannot be predicted, the entire zone of red slates must be considered as potential ore.

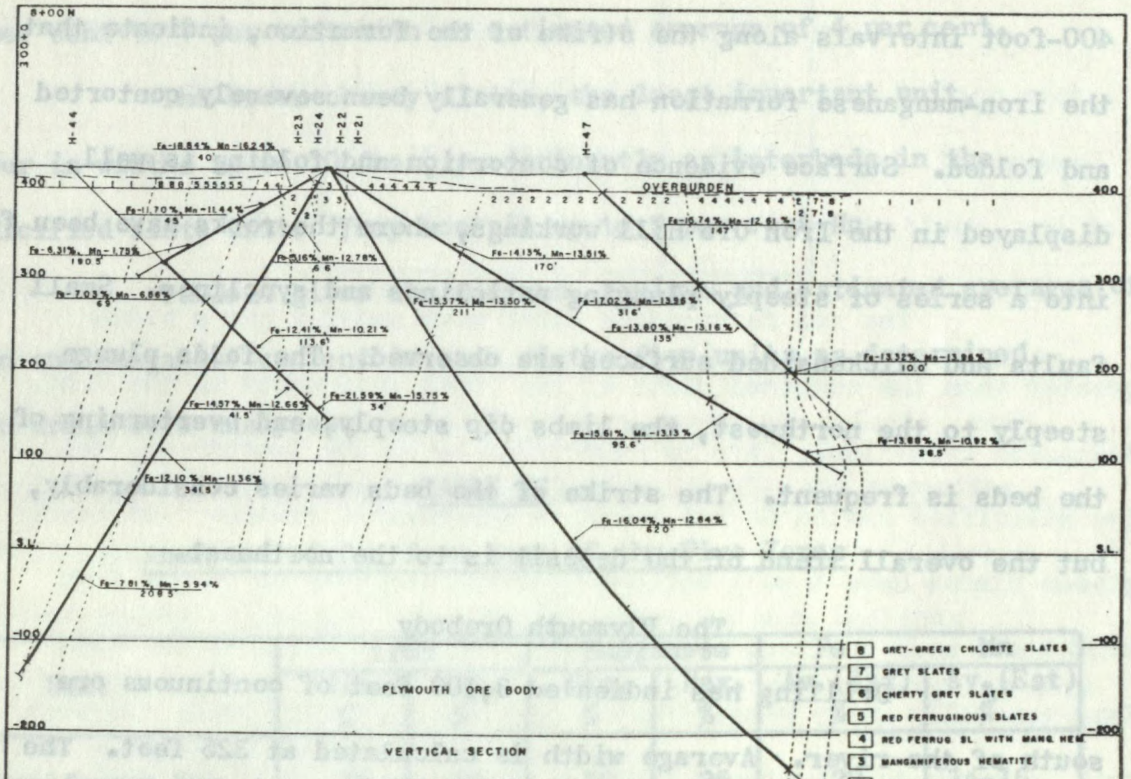
Minor drag-folds, fracture cleavage, and banding as displayed in drill cores, as well as the differing relative position and thickness of each unit and the sequence of the units in holes at 400-foot intervals along the strike of the formation, indicate that the iron-manganese formation has generally been severely contorted and folded. Surface evidence of contortion and folding is well displayed in the Iron Ore Hill workings, where the rocks have been folded into a series of steeply plunging anticlines and synclines. Small faults and slickensided surfaces are observed. The folds plunge steeply to the northwest, the limbs dip steeply, and overturning of the beds is frequent. The strike of the beds varies considerably, but the overall trend of the deposit is to the northeast.

The Plymouth Orebody

Drilling has indicated 3,100 feet of continuous ore south of the river. Average width is calculated at 325 feet. The depth of deposit is not known but one drill hole intersected continuous ore to a depth of 700 feet. The orebody is lenticular, with a maximum width of 740 feet and a minimum width of 55 feet. It strikes approximately N.30°E. and dips about 75° to the west. However, individual beds within the ore-bearing units may vary from flat to vertical. The footwall of the ore-body is predominantly green slates, which overlie either grey calcareous banded slates or grey slates. Overlying the green slates with an abrupt demarcation is a band of silicified slates which in places attains a width of 470 feet (Figure 19). This silicified slate unit encloses a red slate lens which has a maximum width of 130 feet at the surface but which appears to pinch out at a depth of 400 feet. Overlying the silicified

Figure 19

Plymouth Ore Body



slates is a wide band of red slates with manganiferous hematite in narrow lenses and occasional beds up to 100 feet in width. The manganiferous hematite beds occur principally toward the bottom of the red slate band. The top of the band is primarily barren red slates, the width of which is usually proportionate to that of the entire red slate section. Conformably overlying the red slate band are green slates which are in turn overlain by grey calcareous banded slates. In addition to these definite units there are several interbedded units. One zone, across a width of 50 feet near the contact of the red and silicified slate units, has interbedded silicified slates, red slates, manganiferous hematite, green slates, and brown cherty slates.

In the tabulation below, the tonnage is calculated to a depth of 215 feet at the southern end of the orebody, using a tonnage-volume factor of 10. Allowing a 1 per cent gradient for pit floor from north to south, the north end of the pit would be on the south bank of Meduxnekeag river at a point 25 feet above the mean summer low.

Ore Type	Short Tons	Tenor %	
		Fe	Mn
Red	12,417,400	12.70	12.12
Grey	7,402,820	14.11	11.97
Total	19,820,220	13.23	10.81

Origin

The iron-manganese deposits in the Woodstock area are of sedimentary origin. Occasional ripple marks in the hematite beds indicate that deposition took place in shallow marine water.

Caley[2] regards the iron and manganese concentration in the rocks as due to chemical precipitation accompanying volcanic activity. Although volcanic rocks do not occur directly associated with the deposits, such rocks are found within a radius of ten miles of them.

Miller[3], in discussing similar manganese deposits in Maine, is inclined to regard the manganese and iron as being derived from subaerial weathering and erosion of volcanic rocks.

The present writer leans toward the latter view, and also is of opinion that the iron and manganese were precipitated from solution in a shallow lagoon or sea in basin-shaped depressions.

It is further believed that iron and manganese were carried in sluggish streams with gradients too low to permit abundant suspended matter to be carried. It is probable, however, that minor uplifts did occur, thus allowing temporary increase in suspended matter which would account for the lean ore or high-silica zones within the orebody and especially for the high-silica, low-manganese-bearing red slates.

The immediate conditions that controlled precipitation of the ore are thought to have been much varied. Here, vulcanism may have effected the deposition of the ores by influencing temperature changes and bacteria growth in the water. The occurrence of pyrite in the silicified slates indicates a reducing condition during deposition, and it is thought possible that manganese was carried in solution as a bicarbonate, with carbon dioxide being liberated from the bicarbonate by bacterial action and thus allowing the manganese to be deposited as a carbonate.

With regard to the manganiferous hematite, it would appear that the manganese was precipitated as an oxide from a carbonate in solution and that the oxide combined with excess silica during metamorphism accompanying folding to form braunite.

The iron is believed to have been carried in solution as a bicarbonate and to have been deposited directly as hematite in the silicified slates and manganiferous hematite.

References

(1) CALEY, J. F., Geology of the Woodstock Area, Carleton and York Counties, New Brunswick; Geol. Surv. Can., Mem. 198, 1936, pp. 18-19.

(2) ANDERSON, F. D., Preliminary Map, Woodstock, Carleton County, New Brunswick; Geol. Surv. Can., Paper 53-33, 1954.

(3) MILLER, Ralph L., Manganese Deposits of Aroostook County, Maine; Maine Geol. Surv., Bull. 4, 1947, pp.33-36.

3. THE MINERALOGY OF EIGHT SAMPLES OF MANGANESE ORE FROM STRATMAT LTD., WOODSTOCK, N. B.

(From Mineragraphic Report M-1537-S, by E. H. Nickel,)
(Ore Mineralogy Laboratory, Mineral Dressing and Process)
(Metallurgy Division, Mines Branch, Ottawa, Canada, 1957)

Introduction:

On August 14, 1957, Mr. K. O. J. Sidwell, Regional Manager of Stratmat Limited, shipped to the Mines Branch, Ottawa, eight samples said to be representative of the principal rock type of the "Plymouth Orebody". The descriptions of the samples, as provided by Mr. Sidwell, are given in Table 18.

TABLE 18

Information Provided on Samples

*Sample No.	Drill Hole No.	Distance from collar	Description
1	29	50'	Grey calcareous banded slates
2	(22	750'	Green silicified slates
	(38	250'	Grey silicified slates
3	34	350'	Manganiferous hematite
4	16	50'	Red ferruginous slates, with manganiferous hematite
5	23	165'	Red ferruginous slates
6	38	225'	Cherty grey slates
7	25	880'	Grey footwall slates
8	31	90'	Grey-green chlorite slates from hanging wall

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* As in Figure 19.

Procedure:

At least one polished section and one thin section were made from each of the eight samples, for examination under ore and petrographic microscopes, respectively.

The remainder of the samples were crushed to -65 mesh for separation and concentration of the individual mineral components wherever possible. The separations were carried out with heavy liquids ranging in specific gravity from 3.0 to 3.6, followed by separation of the Frantz Isodynamic separator.

The minerals were identified by X-ray diffraction analysis and by their optical properties under ore and petrographic microscopes. Spectrographic and chemical analyses were employed in individual cases (see Tables 19 and 20).

Mineralogical Description of Individual Samples:

No. 1 -

This sample consists primarily of fine-grained quartz and mica (sericite) in which are suspended larger aggregates of calcite averaging about 0.15 mm in diameter. The calcite, in turn, contains quartz and sericite inclusions. Fine-grained pyroxene, magnetite, and pyrite were also observed. No manganese minerals were detected.

No. 2 -

The grey sample consists predominantly of quartz and a carbonate mineral. The X-ray diffraction pattern of the carbonate matches that of siderite. Manganese, however, can replace the iron in siderite in any proportion, and considerable manganese may be present in siderite without an appreciable change in the spacings of the

X-ray diffraction lines. Chemical analyses of the carbonate in this sample revealed the presence of 8 to 9 percent Mn, so the carbonate can probably be referred to as a manganoan siderite. The manganoan siderite occurs as tiny inclusions in the quartz, but also as lenticular masses in the quartz. Some of the lenses exhibit zonal structure, probably due to microscopic inclusions in the siderite. The quartz is mainly coarse-grained, although some fine-grained cherty areas were observed, particularly in association with the siderite.

The green sample consists principally of a dark green silicate mineral interbanded with carbonate. The silicate mineral has not yet been identified. It is somewhat similar to chlorite in appearance, yet it has inclined extinction in contrast to the parallel extinction of chlorite, the X-ray pattern does not match that of the common chlorites, and it seems to be too hard. For want of a positive identification, and until a complete chemical analysis is available, this mineral will be designated as "chlorite". The X-ray pattern of the carbonate matches that of rhodochrosite fairly closely. Rhodochrosite can have a considerable amount of calcium and iron substituting for manganese and this seems to be the case here. The rhodochrosite varies in colour from pink to white to light green. Some of it contains a great many sub-microscopic inclusions, giving it a dusty appearance in transmitted light.

Magnetite is abundant as inclusions in some of the "chlorite".

No. 3 -

This entire sample is stained a deep red by hematitic material, much of which appears to be amorphous, although some tiny hematite laths were observed in polished section. Some quartz and some rhodochrosite were identified as inclusions and narrow bands and veinlets in the rock.

No. 4 -

The principal minerals in this sample are quartz, sericite, hematite, and braunite. The rock is prominently banded, with braunite-rich layers alternating with hematite-stained quartz and sericite. The braunite is extremely fine-grained and contains abundant intergrown gangue. Some of the larger grains are rounded and have a nodular appearance. A small amount of dolomite was observed in this sample.

No. 5 -

This sample consists almost entirely of fine-grained quartz and sericite heavily indurated with amorphous hematite. No manganese minerals were observed.

No. 6 -

The chief minerals in this sample are quartz, sericite, and siderite. The quartz and sericite are extremely fine-grained and contain dusty nodules of siderite. A tiny veinlet of chalcopyrite was observed in one polished section.

No. 7 -

This rock consists almost entirely of extremely fine-grained quartz and sericite.

No. 8 -

This sample is quite similar to No. 7, except that it contains some calcite. The calcite is coarser than the quartz and sericite.

Summary of Mineralogy:

The minerals identified in each sample are tabulated below. The letter X below the sample number indicates the presence of the mineral listed in the left-hand column.

Sample No.	1	2	3	4	5	6	7	8
Calcite	X							X
Dolomite				X				
Siderite (manganiferous)		X				X		
Rhodochrosite		X	X					
Braunite				X				
Hematite			X	X	X			
Quartz	X	X	X	X	X	X	X	X
Sericite	X			X	X	X	X	X
Pyroxene	X							
Magnetite	X	X						
"Chlorite"		X						

TABLE 19

The Chemical Analysis of the Eight Samples

Product	Percentage Composition						
	Mn	Fe	Mg	CaO	SiO_2	Al_2O_3	L.O.I.
#1	0.056	3.76	n.d.	11.2	38.0	15.2	21.4
#2A	7.67	13.9	n.d.	2.25	40.6	4.8	25.7
#2B	12.2	27.8	0.25	3.86	17.0	6.4	23.4
#3	9.14	29.5	n.d.	3.57	22.0	5.2	26.8
#4	15.2	13.6	0.22	3.63	26.0	9.6	19.0
#5	1.21	6.05	n.d.	0.23	56.2	20.2	10.0
#6	3.04	6.10	n.d.	0.17	44.6	18.8	16.8
#7	0.54	6.86	n.d.	0.06	57.3	19.8	7.4
#8	2.81	4.72	n.d.	17.3	39.8	12.3	20.7

TABLE 20

Analysis of Carbonate and "Chlorite" Components in Samples 2 and 3

From Sample 2	Percentage Composition										
Unit	S.G.	Fe	Mn	Ca	Mg	Si	Al	CO_2	H_2O	Na_2O	K_2O
"Chlorite"	3.0-3.2	27.0	5.16	3.20	0.25	14.0	2.73		7.63	0.06	0.08
Siderite	3.3-3.7	22.9	8.25	2.03				24.6			
Siderite	3.7	27.7	9.18	0.56	0.22			26.5			
Rhodochrosite	3.4-3.5	10.0	31.4	2.86				28.8			
From Sample 3											
Carbonate	3.3-3.4	7.28	4.93	15.3				27.1			

Comparison of Samples Taken in Mid-19th Century with Channel Samples Taken in 1939:

The following six samples were taken during the operations of the mid-19th century and were assayed in England(15):

TABLE 21A

	1.	2.	3.	4.	5.	6.
Perox. iron	47.858	39.285	67.857	42.587	27.143	50.000
Prot. iron	2.140	1.140	1.070	----	trace	2.400
Alumina	3.924	3.116	2.004	6.412	10.742	6.114
Oxide. mang.	6.110	5.872	0.976	2.140	5.172	3.742
Perox. mang.	----	----	----	8.740	----	----
Lime	1.004	1.120	0.887	1.074	5.964	1.146
Magnesia	5.016	4.602	2.940	5.107	2.057	4.072
Potash	0.972	0.702	0.744	0.217	0.884	0.214
Soda	0.671	0.512	0.631	0.202	0.772	0.216
Sulf. acid	0.596	1.274	0.588	0.977	0.842	0.572
Phos. acid	0.977	1.389	0.064	0.680	1.924	1.062
Silica	16.842	25.964	5.630	22.420	34.214	19.842
Car. acid & water	13.890	14.964	5.609	8.974	10.286	10.630
	100.000	100.000	100.000	100.000	100.000	100.000
Metal iron	35.147	28.377	48.323	30.000	19.000	36.848

Mean of the six ... 32.949

The following channel samples were taken in 1939 by officials of the Department of Lands and Mines, Fredericton, N. B.(21):

TABLE 21B
Iron Ore Hill

Width of Sample	Iron	Manganese	Sulphur	Phosphorus	Insoluble	Gold
Feet	%	%	%	%	%	Oz Per Ton
6	33.73	13.38	---	---	---	---
10	20.91	18.53	Trace	1.28	---	---
10	15.05	14.10	0.25	0.56	---	---
12	30.00	9.30	0.02	1.02	---	---
11.5	27.47	10.80	0.03	0.89	---	---
8	11.31	7.50	0.02	0.21	---	---
9	20.60	11.40	0.01	0.68	---	---
7	---	13.50	0.13	0.66	---	None detected
10	25.43	14.69	0.09	0.96	21.76	---
16	27.57	11.78	0.42	1.09	---	---
7	24.95	10.28	0.13	0.86	---	---
12	26.97	17.10	0.00	0.86	---	---

It will be noted that the samples of the mid-19th Century representing the typical ore feed to the furnace were higher in iron and lower in manganese than the samples taken in 1939.

4. THE NOVA SCOTIA EASTERN SHORE MANGANESE DEPOSITS: Manganese Silicate Rock from Lazy Point, Guysborough County, N. S.

By W. F. Take, Nova Scotia Museum
of Science, Halifax, N. S.

- -

Macroscopic Character:

A strongly banded and laminated, dense, fine grained, metasedimentary rock. The rock is composed of alternating layers of a buff to a dark greenish grey colour. These layers represent, or are, relics of bedding in the original sediment.

Composition:

The rock is almost wholly composed of spessartite, chlorite, and quartz. Minor amounts of feldspar, magnetite, hematite, zircon, apatite, and possibly rhodonite, occur. There also is some secondary carbonate. (Est. vol.%: 40%sp., 25%qtz., 25%cl., 10%others)

Texture:

The rock has a distinct crystalloblastic texture. It consists of strongly idioblastic spessartite grains and clusters of grains set in a zenoblastic aggregate of quartz or chlorite. Veinlets of carbonate, and sutured carbonate replacements are present.

Bands or Layers:

The buff coloured layers are composed almost entirely of fine grained (.03 m) sub-idioblastic spessartite set in a zenoblastic mosaic of quartz.

The dark greenish grey layers are composed almost entirely of coarser grained (.06 m) idioblastic spessartite set in a xenoblastic decussate matrix of chlorite.

There are layers intermediate in composition between these two extremes.

Most of the magnetite occurs in the spessartite-chlorite layers, while most of the zircon (?) occurs in the spessartite-quartz layers.

Classification:

Rocks of this type are known as gondites. They are rather rare rocks.

Origin:

Rocks of this type are believed to have formed through medium to low grade metamorphism of manganiferous sedimentary rocks. These might have had the form of rhodochrosite chert rocks, or rhodochrosite shale-slate. The latter two rocks are known in the Meguma Series of Nova Scotia, i.e. Lake Charlotte region.

Mode of Occurrence:

Manganiferous sediments of this type, occurring in the greywacke assemblage of the Meguma Series, may be expected to be quite persistent and extensive in their range. Because their field characters are not distinctive, they are very easily overlooked in field investigations, being mistaken for ordinary impure quartzites or greywacke.

5. A MINERALOGICAL INVESTIGATION OF MANGANESE SILICATE ROCK FROM LAZY POINT, GUYSBOROUGH COUNTY, N. S.

(From Mineragraphic Report M-1567-S, by E. H. Nickel,)
(Ore Mineralogy Laboratory, Mineral Dressing and Process)
(Metallurgy Division, Mines Branch, Ottawa, Canada, 1957)

Introduction:

Several pounds of rock, reported to be from Lazy Point, Guysborough County, N. S., were submitted for mineralogical examination late in 1957. The rock was sampled by breaking a chip from each of the fragments received, and the chips were then crushed to -65 mesh. The mineral components were concentrated by heavy liquids and magnetic separator.

Mineralogical Description:

The rock is prominently banded and consists of alternating layers of fine-grained light and dark grey materials. A heavy liquid separation of the -65+325 mesh portion, using liquids with specific gravities of 2.96, 3.32 and 3.60, resulted in the mineral distribution shown in Table 22.

TABLE 22

Heavy Liquid Separation of Manganese Rock

Crushed to -65+325 Mesh

Specific Gravity	Weight %	Minerals Present
Less than 2.96	2.8	Quartz, biotite
2.96 to 3.32	6.9	Quartz, biotite, garnet, fluorite
3.32-3.60	21.1	Quartz, garnet
Greater than 3.60	69.2	Garnet, arsenopyrite, magnetite.

The majority of the minerals are very fine-grained and therefore a considerable proportion of the -65+325 mesh grains are combined ones consisting of two or more minerals. This is especially true of the intermediate fractions (2.96 to 3.60), which consist largely of combined quartz-garnet grains.

Two types of garnet are present in the rock, and these are closely intergrown and therefore not readily amenable to separation. They also contain tiny dark inclusions of other minerals. Since the garnets are the only minerals in the rock likely to contain appreciable amounts of manganese, they will be considered in detail.

The specific gravity of the combined garnet concentrate is 4.0. Both garnets are colourless and have similar magnetic susceptibilities, as indicated by their response to high intensity magnetic separation. The cell constants of the two garnets, as determined by X-ray powder diffraction, are 11.60A and 11.67A and the refractive indices are 1.77 and 1.79, although it is not known to which cell constants the refractive indices correspond. In Table 23 are listed the common garnet end members and their corresponding cell constants and refractive indices.

The more abundant garnet in the sample under study has a cell constant of 11.60A, which is quite close to that of spessartite (11.62A). The refractive index of spessartite is 1.80 and, since the refractive index of one of the garnets is 1.79, this may be the index of the garnet under consideration. If so, a garnet with these properties is approximated by a garnet solid solution composed of 88% of the spessartite end-member and 12% of the pyrope end-member; i.e. a manganese-aluminum garnet containing a small amount of magnesium. This is not an unequivocal result, however, since several other combinations of the pyrope, almandine, grossularite, and

TABLE 23

Compositions, Cell Constants, and Refractive Indices of Garnet End-members

Garnet	Composition	Cell Constant (A)	Refractive Index
Pyrope	$Mg_3Al_2Si_3O_{12}$	11.46	1.71
Almandine	$Fe_3Al_2Si_3O_{12}$	11.53	1.83
Spessartite	$Mn_3Al_2Si_3O_{12}$	11.62	1.80
Grossularite	$Ca_3Al_2Si_3O_{12}$	11.85	1.73
Andradite	$Ca_3Fe_2Si_3O_{12}$	12.05	1.89

andradite end-members also result in cell edge and refractive index values close to those measured. These other possibilities are less likely, however, since all of them require either grossularite or andradite to be combined with the other end-members, and analyses of numerous garnets in the past indicate such a combination to be rather unusual.

If the refractive index of 1.79 is considered to belong to the garnet with a cell edge of 11.60A as noted above, then the 1.77 refractive index is that of the garnet with a cell edge of 11.67A. These values correspond fairly closely to a 70% spessartite-30% grossularite garnet, and the specific gravity of the garnet concentrate tends to substantiate this. There are several other combinations of garnet end-members with the required cell edge and refractive index, but the only one with a specific gravity close to the measured specific gravity is a garnet with the following composition: 45% grossularite, 40% almandine, and 15% pyrope.

In summary, it may be said that the properties of the two garnets in the sample permit of a number of solutions, but that the most probable compositions are an 88% spessartite-12% pyrope garnet and either a 70% spessartite-30% grossularite garnet or a 45% grossularite-40% almandine-15% pyrope garnet. A chemical analysis ought to establish which of these compositions, if any, are the correct ones (see Table 24).

TABLE 24

Chemical Analysis of the Garnet Mixture

	%
Al_2O_3	24.26
CaO	6.16
FeO	9.42
MnO	24.15
SiO_2	36.50
MgO	n.d.

Anal.: $M_{2.84}Al_{1.96}Si_3O_{12}$ Theor.: $M_3Al_2Si_3O_{12}$

M = Mn - Fe - Ca - Mg

From the chemical and mineralogical analyses, a probable identification of the garnet mixture as 60 parts Spessartite ($Mn_3Al_2Si_3O_{12}$) and 40 parts Grossularite-Almandine ($Fe_{1.77}Ca_{1.23}Al_2Si_3O_{12}$) is indicated.

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