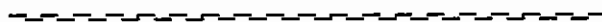


GEOLOGY AND TRACE ELEMENT STUDIES
OF NOVA SCOTIA MANGANESE OCCURRENCES



CHAPTER I

INTRODUCTION

Manganese oxides have been used since ancient times as agents for decolorizing glass and coloring glass and pottery; but whereas the ancients had no metallurgical use for the ore, it is at present indispensable in the manufacture of steel and no acceptable or adequate substitute has yet been discovered, nor is any in prospect.

Manganese ores occur widely distributed throughout the world and most countries have some resources which might be used in an emergency. Large scale production is confined to Russia, India, Brazil, Cuba, Egypt and Africa with important contributions from Japan, Czechoslovakia, China and the Malay States. It is also noted that many of the great iron and steel producing countries of Europe as well as the United States and Canada, have to rely almost entirely upon imports from distant countries for their essential supplies of manganese ore of metallurgical grade. Many of the industrial countries of the world have small amounts of manganese ore of battery or chemical grade.

The mining of manganese ore in Canada attained an annual production ranging from around 1,000 tons to 1,700 tons from 1879 to 1890; since that time

the production has been much smaller, with many blank years.

Manganese ores have been reported and worked on a small scale at many localities in Nova Scotia, but no deposits of commercial grade capable of maintaining a large continuous output have yet been discovered. In Nova Scotia, manganese ores have been mined in Richmond County, Cape Breton Island and on the mainland in the adjoining counties of Colchester, Hants and Lunenburg. Most of the production in the last century came from New Ross, Lunenburg County. The principal manganese areas in Nova Scotia are indicated in figure 2.

During the field season of 1967 through 1970, over fifty manganese occurrences were investigated in the field and samples collected for laboratory studies, both chemically and under the microscope (Fig. 1, in Pocket). The purpose of this study of the manganese deposits is to obtain and record information relative to the deposits with a view of establishing geological and other criteria of value in judging the possible extension of ore occurrences.

ORES OF MANGANESE

The affinity of manganese for oxygen is very great, and the metal is, consequently, nowhere found in the free or uncombined state. Its ores, of which metallurgically, the oxides are the most important are very widely distributed. They are even found in the form of nodules, thickly strewn over the ocean beds for hundreds of miles and often at great depths, as well as at the bottom of many lakes. Manganese ores are invariably associated with iron ores. At the same time, iron is not found in any important quantity with the major manganese occurrence in Nova Scotia.

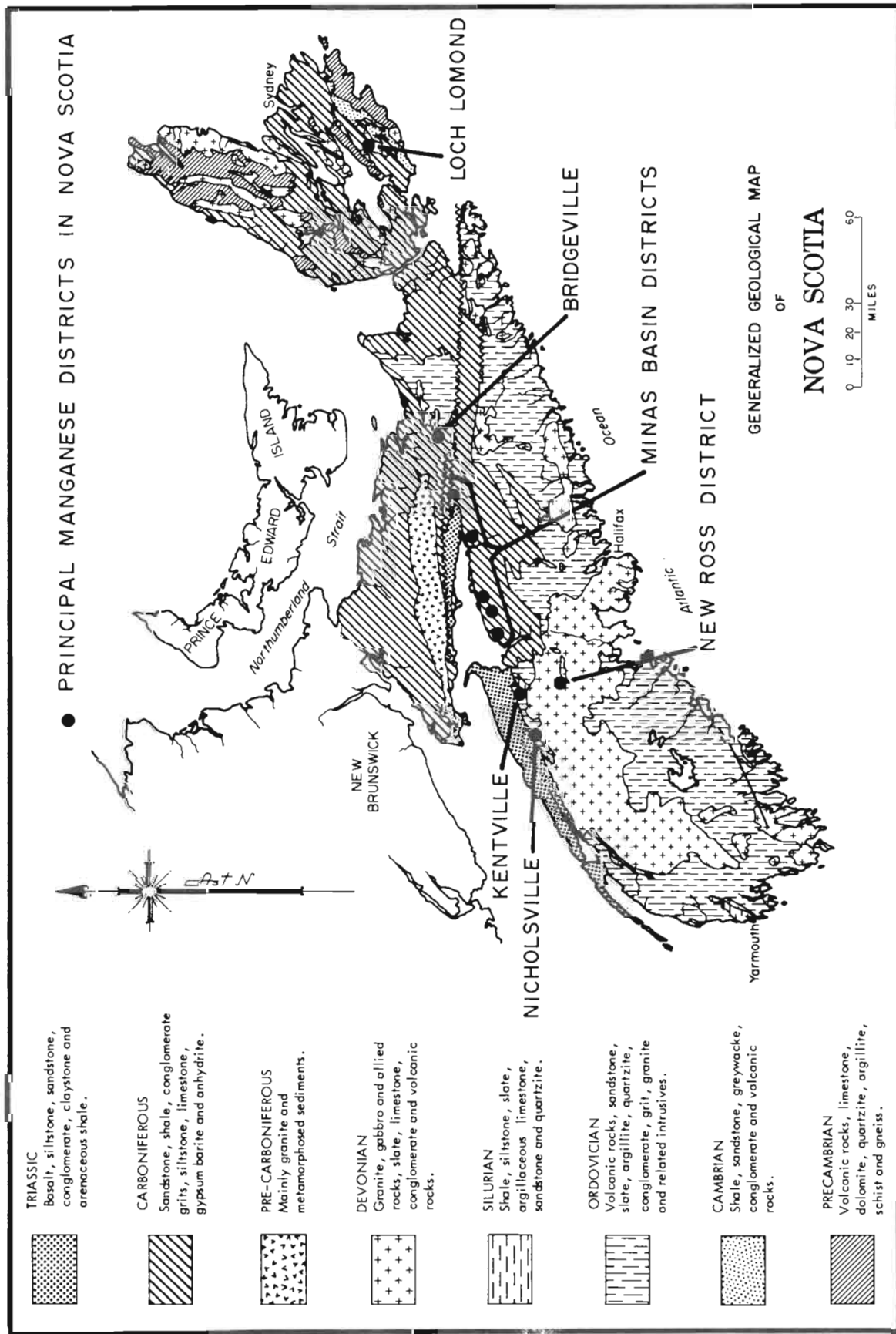


FIGURE 2

Common Manganese Minerals

<u>Ore Minerals</u>	<u>Composition</u>	<u>Percent Manganese</u>
<u>Oxides</u>		
Pyrolusite	MnO_2	63.2
Manganite	Mn_2O_3, H_2O	62.4
Psilomelane	$MnO_2 \cdot 2H_2O$	45.6
Wad	Chiefly hydrous manganese oxides	47.56
Hausmannite	Mn_3O_4	47.6
<u>Carbonate</u>		
Rhodochrosite	$MnCO_3$	47.6
<u>Silicates</u>		
Rhodonite	$MnSiO_3$	31.0
Braunite	$3Mn_2O_3, MnSiO_3$	69.0

The ores of manganese, that have proved of some commercial value in Nova Scotia, consist of pyrolusite, manganite, psilomelane, wad and minor amounts of hausmannite.

Pyrolusite (MnO_2) containing 63.2 percent of manganese is a greyish black to black mineral soft enough to soil the fingers when handled. It occurs in well-crystallized form, but more commonly has a columnar habit or is granular massive. It forms at or near the surface of the earth at ordinary temperatures and pressures under strongly oxidizing conditions.

Manganite ($\text{Mn}_2\text{O}_3, \text{H}_2\text{O}$) is a black mineral with a hardness of 4. It occurs in prismatic crystals in columnar forms and in granular condition. It forms at or near the surface of the earth. It is not as stable under oxidizing conditions as pyrolusite and under such conditions is replaced by the latter.

Psilomelane ($\text{MnO}_2, 2\text{H}_2\text{O}, \text{Mn}$) is a bluish to greyish black mineral of variable composition. If subjected to oxidizing conditions it will, eventually, be transformed to pyrolusite and in the process may pass through an intermediate stage of manganite.

Wad or bog manganese is a soft, earthy mixture consisting mainly of oxide of manganese and water, with some oxide of iron. Wad cannot be considered as a true manganese ore. It results from the decomposition of other manganese minerals. It is not so valuable as pyrolusite or psilomelane, but it sometimes is used in the manufacture of chlorine.

Hausmannite (Mn_3O_4) is a brownish-black mineral, very low in oxygen. A minor amount has been identified in the manganese mineralization at New Ross, Lunenburg County.

Rhodo-chrosite (MnCO_3) is a carbonate of manganese, often with carbonates of iron, calcium, and magnesium in varying quantities. It must be roasted for removal of carbon dioxide before being charged into the smelting furnaces.

Rhodonite (MnSiO_3) is a pink mineral. It is a pyroxene belonging to the triclinic system, and is one of the less important ores. Rhodonite forms by ascending thermal solutions of igneous origin and also in the process of metamorphism.

Braunite ($3\text{Mn}_2\text{O}_3, \text{MnSiO}_3$) is a brownish to greyish black mineral with a hardness of 6. It forms under ordinary conditions of temperature and pressure at or near the surface of the earth. It generally contains from 8 to 10 percent silica.

IMPURITIES ASSOCIATED WITH MANGANESE MINERALS

Iron is the most abundant of the metallic impurities, but on account of its occurrence in the form of oxides, it is usually difficult to remove by ore-dressing methods. The type of alloy that can be made from a manganese ore depends on the iron content. Ores or concentrates containing more than one part of iron to nine of manganese are usually unsuitable for the manufacture of ferro-manganese.

Small amounts of copper, lead, zinc or silver may be present, but appreciable quantities are objectionable.

Manganese ores frequently contain silica, alumina, lime, magnesia and barite, which are slag forming constituents and must be kept within definite limits if the metallurgical treatment is to remain economical. Although a certain amount of slag is essential for the removal of injurious impurities such as sulphur, a large volume is undesirable. A high gangue content entails a higher consumption of coke. Ferro-grade ores with more than 8 percent of silica are generally considered undesirable and higher silica than this is usually penalized. Alumina in excess of 10 percent is very objectionable, especially when silica is also high.

Phosphorus and sulphur are objectionable in manganese ore intended for metallurgical use. Sulphur usually passes into the slag in the course of metallurgical operations, hence its effects are not so harmful as those of phosphorus. The phosphorus

passes almost entirely into the ferro-alloy for which the ore is used, and, since low-phosphorus alloys are essential, an ore with a high phosphorus content cannot be used in the manufacture of ferro-manganese or spiegeleisen. The steel manufacturer must keep the phosphorus in the steel below 0.05 percent. The maximum phosphorus content allowed in ferro-grade ores is 0.20 to 0.25 percent. Since phosphorus generally occurs in chemical combination with the manganese minerals or else as a constituent of some other mineral in intimate mechanical admixture with the ore its elimination by ore-dressing methods is impracticable.

Water and carbon dioxide are the principal volatile impurities. The former is not only a diluent, it lowers the metallurgical efficiency of a blast furnace. Carbon dioxide is present in objectionable amounts only in rhodochrosite ores. The carbon dioxide content of pure rhodochrosite is 38.3 percent.

USES OF MANGANESE

Manganese ores having a minimum content of 45 percent of manganese are required for most commercial purposes. The iron and steel industry uses ore of uniform composition, lacking those impurities which are deleterious to the finished product. In the blast furnace, the ore is objectionable if it is too soft and friable. Ferro-grade ore (34 percent plus of manganese) is used in making ferro-manganese (75 to 82 percent of manganese, 5 or 7 percent of carbon); ferruginous manganese ore (10 to 35 percent of manganese) is used in making

spiegeleisen (15 to 30 percent of manganese); manganiferous iron ore (5 to 6 percent of manganese) is used in the manufacture of pig iron where a small manganese content is desired.

The chemical industry requires manganese for the purpose of liberating oxygen easily. The most valuable manganese mineral for this purpose is pyrolusite, which has the highest content of available oxygen. For chemical use, ore having a minimum of impurities is required. Metallurgical ore accounts for about 90 percent of world consumption, the remainder being of chemical grade.

Larger quantities of manganese ore are required than of any other strategic mineral commodity except iron and coal. There is no substitute for manganese in deoxidizing, desulphurizing and recarbonizing steel. High-grade manganese is used for these purposes, at the rate of 11 to 14 percent of the steel produced. Standard ferro-grades, the form in which manganese is generally added in steel manufacture, are manufactured from high-grade ore having a minimum content of 48 percent of manganese.

Manganese steel, tough and resistant to abrasion, is used extensively in the electrical industry. Compared with ordinary steel, it is a much poorer conductor of heat and electricity. Manganin, a copper-manganese-nickel alloy, is widely used in heating coils and electric furnaces, owing to its high resistance to electricity. In steel rails, manganese increases the life of ordinary carbon steel five to six times.

The chemical industry uses 5 to 10 percent of the manganese produced, the remainder being employed in metallurgy. It is employed as a coloring material

in the manufacture of dyes, paints, and varnishes and as a decolorizer in making glass, grey and black brick, pottery, and tile. Chemical grade ores are used largely in the manufacture of dry batteries, battery ore containing a minimum of 75 percent of MnO_2 . Various impurities modify the value of the ores for the various chemical uses.

TYPES OF MANGANESE DEPOSITS

The commercially valuable manganese deposits are local concentrations of manganese, included in 3 principal types of deposits as follows:

1. Sedimentary deposits
 - (a) oxide type
 - (b) carbonate type
 - (c) bog type
2. Replacement and residual deposits
3. Vein deposits

Apart from bog manganese, the majority of the manganese ores of Nova Scotia belong to the second and third classes noted above. The ores won from bedrock sources in Nova Scotia are all replacements or fissure fillings.

The manganese deposits include a variety of types of which the more important are ores associated with Carboniferous strata, particularly the Windsor limestone, ores filling fissures in pre-Carboniferous rocks and surface bog deposits.

There are in Hants County veins and replacement deposits of the disseminated type in conglomerates and sandstones, but the most extensive and complete replacement are bodies occur in limestone, which is of the calcium variety in some places and dolomitic in others. These replacement ore bodies in limestone have been the source of the most profitable mining of manganese in Nova Scotia and this type of occurrence holds the promise for any future production. Such replacement ore bodies have been mined at Cheverie, Pembroke, Walton and Tennycape.

The Tennycape mine was the largest replacement deposit in the Minas Basin area. About 4,000 tons of manganese oxides were produced. Manganese oxides occurred as fissure fillings and replacement in the lowermost Windsor Formation, the Macumber shaly limestone and as nodules and replacement in the Pembroke limestone conglomerate which overlies the Macumber. Within 10 miles of Tennycape mine are no less than 15 manganese occurrences, many of which had a production of at least several hundredweights of oxide. The manganese oxide won from these deposits was of exceptionally high grade and classed as chemical ore, thereby commanding a much higher price than ordinary ores.

Vein Type

The third type of deposit, those filling fissures in pre-Carboniferous rocks is represented in the New Ross area. The manganese mines at New Ross are in the northern part of Lunenburg County, Nova Scotia, about 8 miles from the village of New Ross. Manganese was discovered in this district about 1891

and three mines were operated sporadically until 1921. The ore-bodies lie in lenticular masses occupying fault and crushed zones in Devonian granite. The north walls of the ore bodies are in general sharp and lie against undeformed granite. On the south the lenticular masses of manganese oxide are bordered by an extensive zone of crushed and altered granite containing much hematite, limonite and some calcite.

Bog Manganese Deposits

Deposits of bog manganese are common in Nova Scotia. Most of the deposits of this type have a small areal extent and contain a great deal of limonite mixed with peat and vegetation. Bog deposits have supplied some of the world's manganese but so little that when compared with deposits of a different kind they are quite insignificant.

Bog deposits are precipitated from springs issuing at the surface and consequently consist of manganese oxides and iron hydroxides. The precipitation is effected by escape of CO_2 from the bicarbonate solution and oxidation of the manganese carbonate.

One of the best known deposits of bog manganese is located along the south shore of Boularderie Island, in Cape Breton and Victoria Counties. The deposit is on a gently sloping hillside and was formed from springs issuing at its upper margin. The material of the bog contains around 20 percent manganese.

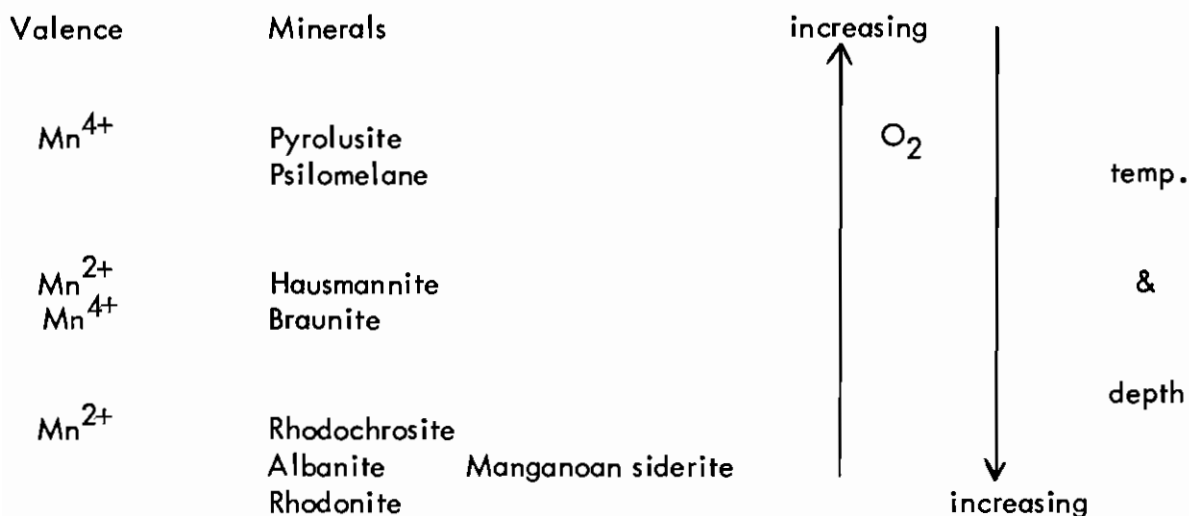
ORIGIN OF MANGANESE DEPOSITS

The element manganese is widely distributed over the crust of the earth. Small amounts are present in almost all of the rocks but only rarely does the content exceed 1.0 percent. On the other hand, manganese is an essential constituent of at least 200 minerals and the content ranges from several percent to as much as 70 percent. From 1967 to 1971, the Nova Scotia Department of Mines has been engaged in the study of the manganese minerals and trace elements in order to determine the various geologic environments in which they occur and thereby suggest the chemical and physical conditions under which they were formed.

For several years it has been known that some manganese minerals are found in certain geologic environments. Some manganese oxides are only found near the surface in a shallow zone in which waters of surface origin circulate; other oxides are deposited in surface basins on the continents or in marine basins; most of the other manganese minerals, carbonates, silicates and sulphides occur in veins that have formed by hot or warm waters that have risen from depths. Until recent years it has been widely believed that most of the accumulations of the common oxides of manganese have been deposited by cool waters of surficial origin circulating in a shallow zone.

Recent studies, using several kinds of data, especially the content of minor elements indicated by spectrographic analyses and the assemblages of minerals associated with the manganese oxides, indicate that many deposits of some of the oxides are not derived from local surficial sources but were deposited by hydrothermal waters rising from depth.

In some metal-mining districts in the western United States bodies of manganese oxides are explored near the surface but exploration in depth shows that they are derived from local concentrated masses of such other manganese minerals as rhodochrosite, rhodonite and alabandite. The bodies of manganese oxides near the surface are obviously derived from these minerals as illustrated below.



Hewett and Fleisher (1959) studied two hundred and fifty samples of manganese oxide by x-ray analysis and put forth conclusions as to the geological environment in which they were deposited. From this paper they defined criteria that could be used to differentiate deposits of supergene origin from those of hypogene origin.

Until the era of x-ray analysis, manganese oxides as a group of minerals were widely misunderstood and names were loosely applied. It was not until 1940 that the United States Geological Survey began a study of manganese oxides using x-ray and chemical analyses. By 1960, nearly five hundred x-ray analyses had been carried out. In 1955, D. F. Hewett began a review of the recorded deposits of each

state. It was then realized that the original thinking on the origin of manganese oxides needed revision.

The source of the manganese is the basic problem and it has to be determined whether the manganese is derived from above, supergene, or from below, hypogene. In the majority of districts, manganese oxides above ground water level change in depth to carbonate, silicates or sulphides and manganese. In the eastern Bisbee, Arizona district, oxides of manganese are found one thousand feet below the water level. At Philipsburg, Montana where the deposits are known in great detail, it has been proven that the oxides of manganese are derived from rhodochrosite. It is here that the oxides are found below the water level to several hundred feet.

In the metalliferous districts of the southwestern United States common non-metallic minerals found associated with the manganese oxides are black (manganiferous) calcite, opal, barite, fluorite, zeolites, quartz and chalcedony. The presence of zeolites, fluorite, barite and opal indicate a hydrothermal origin. It was originally indicated by Hewett in 1959 that the amounts of certain trace elements present in hypogene oxides versus supergene oxides are significant. He listed the following elements as being indicators of a hypogene origin.

- | | | |
|-----------|--------------|-------------|
| 1. Nickel | 4. Copper | 7. Zinc |
| 2. Cobalt | 5. Strontium | 8. Arsenic |
| 3. Lead | 6. Tungsten | 9. Vanadium |

It is known that in some base metal mining districts, the primary manganese minerals are found in a central core associated with base metals, especially copper.

Examples in the United States are Bisbee, Tombstone, Butte in Montana and the Ely district in Nevada. Manganese oxides are found as veins in Tertiary volcanics. It is known that they are found in belts that border areas of zinc and lead deposits. Examples are found in the Luis Lopez district in New Mexico in which oxides are found southeast of the Magdalena zinc mines. In the Little Florida Mountains of New Mexico there are three mineral belts; one of lead deposits, veins of manganese oxides and veins with considerable fluorite and minor barite.

Most of the deposits are veins which have only been explored from 100 to 200 feet in depth. Luna mine in New Mexico has been explored to a depth of 500 feet. Another occurrence in the area (manganese valley) has been mined to 350 feet with no change in the mineralogy of the manganese oxides. The host rocks are for the most part Tertiary volcanics.

Studies on the manganese deposits in the Socorro district, New Mexico show that the surface zones of the veins contain psilomelane, pyrolusite, ballandite and crypomelane, associated with a black calcite. The manganese is present as arborescent growths of psilomelane around which calcite has grown (Hewett). Miesch and Jicha concluded that the black calcite and the oxides of manganese are hypogene in origin.

Ore from Socorro County, New Mexico, contained one to four percent lead and the most persistent minor metal is tungsten. Tungstic oxide occurs in many manganese oxides from the American Southwest ranging from .24 percent to 2 percent.

From data on hot spring waters that contain .10 parts per million or more manganese, it has been noted that they contain noteworthy amounts of boron, fluorine,

strontium and lithium. The traventine aprons that contain manganese oxides persistently contain fluorite and barite, the manganese oxides in the aprons contain tungsten and strontium.

The most abundant oxide minerals in the veins are psilomelane, cryptomelane, hollandite with abundant fluorite and barite.

Table

The Common Manganese Minerals of Hypogene and Supergene Deposits¹

<u>Mineral</u>	<u>Composition</u>	<u>Hypogene</u>	<u>Supergene</u>	<u>Hypogene Mineral group</u>
Alabandite	MnS	x	-	Carb-Sili-Sulf
Manganosite	MnO	x	-	Hausmannite
Hausmannite	MnMn ₂ O ₄	x	-	
Franklinite	(Zn,Mn)(Fe,Mn) ₂ O ₄	x	-	
Jacobsite	MnFe ₂ O ₄	x	-	
Bixbyite	(Mn,Fe) ₂ O ₃	x	-	
Braunite	3Mn ₂ O ₃ MnSiO ₃	x	x	
Pyrolusite	MnO ₂	x	x	
Hollandite	BaMn ₈ O ₁₆	x	x?	
Manganite	Mn ₂ O ₃ H ₂ O	x	x	
Cryptomelane	KMn ₈ O ₁₆	x	x	
Psilomelane	BaMn ₉ O ₁₈ 2H ₂ O	x	x	
Rancieite	CaMn ₄ O ₉ 3H ₂ O(?)	-	x	
Lithiophorite	Li ₂ Mn ₂ Al ₈ Mn ₁₀ O ₃₅ .14H ₂ O(?)	-	x	
Rhodochrosite	MnCO ₃	x	x	Carb-Sili-Sulf
Manganooan calcite	(Ca,Mn)CO ₃	x	-	Carb-Sili-Sulf
Manganooan dolomite	Ca(Mg,Mn)(Co ₃) ₂	x	-	Carb-Sili-Sulf
Manganooan siderite	(Fe,Mn)CO ₃	x	-	Carb-Sili-Sulf
Rhodonite	MnSiO ₃	x	-	Carb-Sili-Sulf
Bustamite	(Ca,Mn)SiO ₃	x	-	Carb-Sili-Sulf
Pyroxmangite	(Mn,Fe)SiO ₃			
Johannsenite	CaMn(SiO ₃) ₂	x	-	
Helvite	(Mn,Fe) ₄ Be ₃ (SiO ₄) ₃ S	x	-	Carb-Sili-Sulf
Spessartite	Mn ₃ Al ₂ (SiO ₄) ₃		-	Pegmatite-Silicate
Piedmontite	Ca ₂ (Al,Mn) ₃ (SiO ₄)(OH)	x	-	
Tephroite	Mn ₂ SiO ₄	x	-	Silicate
Alleghanyite	Mn ₅ (SiO ₄) ₂ (OH,F) ₂	x	-	Silicate
Inesite	Ca ₂ Mn ₇ Si ₁₀ O ₂₈ (OH) ₂ .5H ₂ O	x	-	Hausmannite
Bementite	8MnO.7SiO ₂ .5H ₂ O	x	-	Hausmannite
Neotocite	(Mn,Fe)SiO ₃ .nH ₂ O	x?	x	
Mangantantalite	MnTa ₂ O ₆	x	-	Pegmatite
Triphylite-Lithiophilite	Li(Mn,Fe)PO ₄	x	-	Pegmatite
Triplite	(Mn,Fe) ₂ PO ₄ F	x	-	Pegmatite
Huebnerite	MnWO ₄	x	-	Carb-Sili-Sulf

¹ Hewett and others (1959)

CLASSIFICATION OF MANGANIFEROUS ORES

In commercial nomenclature the term "manganese ore" is used for ores from which high-grade ferro-manganese can be made and "manganiferous iron ore" for ores only suitable for making low-grade ferro-manganese and spiegeleisen.

Manganiferous ores are commonly divided into: (1) iron ores, containing less than 5 percent of manganese; (2) manganiferous iron ores containing 5 to 35 percent of manganese; and (3) manganese ores, containing not less than 45 percent of manganese. Ores containing less than 45 percent of manganese are not considered to be true ferro-grade. Manganiferous iron ores are used for making manganiferous pig-iron. Ferruginuous manganese ores, also known as spiegel ores are those used for making spiegeleisen. For the manufacture of 20 percent spiegeleisen, the iron content of the ore must not be more than about 2.7 times that of manganese.

In this report the classification of manganese ores outlined by Johnson and McCartney is followed.

CLASSIFICATION OF MANGANESE ORES AND USES
(After Johnson and McCartney)

CLASS OF ORE	PERCENT Mn IN ORE	METALLURGICAL PRODUCT	PERCENT Mn IN PRODUCT	USE
Manganiferous Ore (5-35 percent Mn)	5 - 10	Manganiferous pig iron		
	20 - 35	Spiegeleisen	26 - 28	
	Greater than 35	Silicospiegeleisen	25 - 30	
		Silicomanganese	50 - 75	Metallurgy of steel
	Greater than 48	Ferromanganese	75 - 85	
	May be low grade	Manganese metal	90 - 95	Alloy and foundry work
			95 - 99.9	
Manganese Ore 35 percent	Greater than 70 percent MnO ₂			Dry batteries
	Usually greater than 75 percent MnO ₂			Drier for paint and varnish Coloring agent in ceramics Decolorizer in glass making Manufacture of manganese chemicals including manganese sulphate fertilizer

PRODUCTION OF MANGANESE

The production of manganese ore in Nova Scotia from 1878 to 1930 is given as 8,630 tons. These figures are incomplete. Hanson's report credits the year 1865 with a 300 ton production. Dawson's Acadian Geology mentions that in the two years prior to 1866 about 1,000 tons of ore had been taken out at the Tenny-cape Mine in Hants County, a property which continued to product until about 4,000 tons production was won from it alone. The greatest production of manganese ore from Nova Scotia was 1,256 tons for the year 1870.

The Canadian production of manganese ore has always been small, never amounting to more than 1,800 tons annually. Until 1918 deposits in the Maritime Provinces had furnished the entire output.

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