METAMORPHISM OF SEDIMENTARY MANGANESE DEPOSITS

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ABSTRACT: Metamorphosed sedimentary deposits of manganese occur extensively in India, Brazil, U. S. A., Australia, New Zealand, U. S. S. R., West and South West Africa, Madagascar and Japan. Different mineral-assemblages have been recorded from these deposits which may be classified into oxide, carbonate, silicate and silicate-carbonate formations. The oxide formations are represented by lower oxides (braunite, bixbyite, hollandite, hausmannite, jacobsite, vredenburgite etc.), the carbonate formations by rhodochrosite, kutnahorite, manganoan calcite etc., the silicate formations by spessartite, rhodonite, manganiferous amphiboles and pyroxenes, manganophyllite, piedmontite etc. and the silicate-carbonate formations by rhodochrosite, rhodonite, tephroite, spessartite etc. Petrographic and phase-equilibia data indicate that the original bulk composition in the sediments, the reactions during metamorphism (contact and regional and the variations and effect of O_2, CO_2, etc. with rise of temperature, control the mineralogy of the metamorphosed manganese formations. The general trend of formation and transformation of mineral phases in oxide, carbonate, silicate and silicate-carbonate formations during regional and contact metamorphism has, thus, been established.

Sedimentary manganese formations, later modified by regional or contact metamorphism, have been reported from different parts of the world. The most important among such deposits occur in India, Brazil, U.S.A., U.S.S.R., Ghana, South and South West Africa, Madagascar, Australia, New Zealand, Great Britain, Japan etc. An attempt will be made to summarize the pertinent data on these metamorphosed sedimentary formations so as to establish the role of original bulk composition of the sediments, transformation and reaction of phases at elevated temperature and varying oxygen and carbon dioxide fugacities in determining the mineral assemblages in these deposits.

DEPOSITS OF SEDIMENTARY AND DIAGENETIC MANGANESE FORMATIONS

Unmetamorphosed volcanogenic-sedimentary manganese deposits have been described from Taratana, Pompo and Sabanill deposits (Cuba), Kokko, Pirika and Kinjo mine areas (Hokkaido, Japan), Coquimbo deposits (Chile), Artillery Peak (Arizona, U.S.A.), Lucifer area (Baja California, Mexico), Glib en Nam (Morocco) etc. Sedimentary deposits of non-volcanogenic source have been described from Chiatura, Nikopol, Babinsk, Usinsk, Ulu-Telyaksk (U.S.S.R.), Timna Dome (Israel), Urkut (Hungary), Imini-Tasdrent (Morocco), Western Mato Grosso (Brazil) and eastern Bolivia. The details of most of these deposits have been summarized by HEWETT and FLEISCHER [1960], HEWETT [1966] and ROY [1968, 1970]. The mineralogy of these unmetamorphosed sedimentary deposits, volcanogenic or non-volcanogenic, is very similar and is characterized by the presence of higher oxides or hydroxides (cryptomelane, psilomelane, pyrolusite, todorokite,

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birnessite, manganite, vernadite etc.) or by carbonates (rhodochrosite, manganoan calcite) often with varying silica content. Only in very rare cases, braunite has been reported from volcanogenic sedimentary deposits (Glib en Nam, Morocco and Coquimbo, Chile) [HEWETT, 1966]. At Tiaratine L'Ayat, Morocco, hausmannite and jacobsite have been reported, which are however, clastic materials derived from older deposits [POUIT, 1964]. The deposition of manganese as higher oxide, hydroxide, or carbonate is controlled by the Eh and pH of the medium [BRICKER, 1965]. The manganese sulfide, alabandite, has not been reported from any sedimentary ore-body excepting from the recent depositions in the Black Sea [SOREM and GUNN, 1967] as it is precipitated only in very reducing condition.

In western Mato Grosso, Brazil and eastern Bolivia, unmetamorphosed oxide-facies iron formation is interstratified with primary manganese oxide in a non-volcanogenic environment [DORR, 1970]. Similar interstratification of manganese oxide beds with iron formation is found in the Kuruman District, South Africa.

Recent deposits of manganese nodules in deep sea and shallow waters, are consituted of 10 Å manganite and 7 Å manganite having the empirical formulas $3 MnO_2.Mn(OH)_2.nH_2O$ and $4 MnO_2.Mn(OH)_2.nH_2O$ respectively, birnessite (δ-MnO_2), todorokite and rancieite [MANHEIM, 1965; PRICE, 1967; SOREM, 1967, 1967 etc.]. Very often these nodules have a high iron content and unless iron is diagenetically separated, ferro-manganese nodules are common.

The pyrolusite-psilomelane-manganite-rhodocrosite-manganocalcite assemblage of Chiatura and Nikopol are considered by BETEKHTIN [1937] to be gradational due to deposition from near-shore condition (oxidizing) to deeper zones (reducing) of the basin. STRAKHOV [1966], on the other hand, considered that the manganese carbonates have formed by diagenesis of oxidic sediments as indicated by the transition of higher oxides to carbonates with manganite (Mn^{3+}) as intermediate member. STRAKHOV [1966] mainly attributed the concentration of manganese in sedimentary ores of recent and ancient deposits to diagenesis and accordingly recognized different types: lacustrine sedimentary-diagentic, lacustrine-diagenetic, shallow-water diagenetic, shallow-water sedimentary-diagenetic and marine and sedimentary-diagenetic ores.

Diagenetic redistribution and reconstitution in deep-sea and shallow water manganese and ferro-manganese nodules have been reported by a number of workers including LYNN and BONATTI [1965], MANHEIM [1965], STRAKHOV [1966], BOSTRÖM [1967], PRICE [1967], SEVAST'YANOV [1968], CALVERT and PRICE [1970] and this is of considerable importance in the separation of iron and the formation of manganese carbonates. BOSTRÖM explained LYNN and BONATTI's find of diagenetic manganese carbonate by the following reaction:
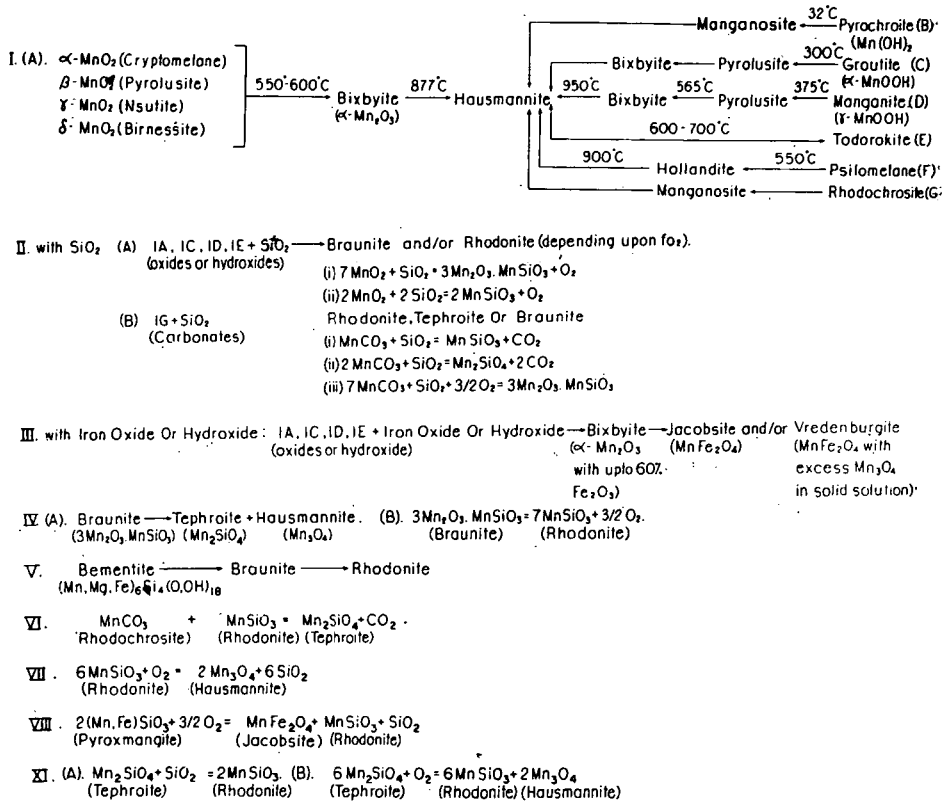
$$xCaCO_3 + yMn^{2+} = (Ca_{x-y}Mn_y)CO_3 + yCa^{2+}.$$
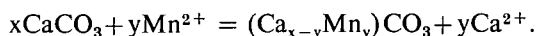
Studies on behavior of manganese minerals in elevated temperature

Considerable work on the behavior of low temperature manganese minerals when subjected to elevated temperature, has been done in the laboratory. Consequently a fairly good idea about the formation and transformation of manganese minerals in rising temperature has been obtained. These data, mainly derived from phase equilibria studies and differential thermal analysis, may be effectively utilized in explaining the mineral assemblages of metamorphosed manganese formations and are summarized in Table 1.

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TABLE - I

TRANSFORMATION OF MANGANESE MINERALS IN RISING TEMPERATURE

I. (A). α-MnO_2 (Cryptomelane)
β-MnO_2 (Pyrolusite)
γ-MnO_2 (Nsutite)
δ-MnO_2 (Birnessite)

550-600°C → Bixbyite (α-Mn_2O_3) — 877°C → Hausmannite

Manganosite — 32°C → Pyrochroile (B) (Mn(OH)$_2$)
Bixbyite — Pyrolusite — 300°C → Groutite (C) (α-MnOOH)
950°C → Bixbyite — 565°C → Pyrolusite — 375°C → Manganite (D) (γ-MnOOH)
600-700°C → Todorokite (E)
900°C → Hollandite — 550°C → Psilomelane (F)
Manganosite ← Rhodochrosite (G)

II. with SiO_2 (A) IA, IC, ID, IE + SiO_2 → Braunite and/or Rhodonite (depending upon f_{O_2}).
(oxides or hydroxides)
(i) $7 MnO_2 + SiO_2 = 3Mn_2O_3 . MnSiO_3 + O_2$
(ii) $2 MnO_2 + 2 SiO_2 = 2 MnSiO_3 + O_2$

(B) IG + SiO_2 Rhodonite, Tephroite Or Braunite
(Carbonates)
(i) $MnCO_3 + SiO_2 = MnSiO_3 + CO_2$
(ii) $2 MnCO_3 + SiO_2 = Mn_2SiO_4 + 2 CO_2$
(iii) $7 MnCO_3 + SiO_2 + 3/2 O_2 = 3Mn_2O_3 . MnSiO_3$

III. with Iron Oxide Or Hydroxide: IA, IC, ID, IE + Iron Oxide Or Hydroxide → Bixbyite → Jacobsite and/or Vredenburgite
(oxides or hydroxide)   (α-Mn_2O_3 (MnFe_2O_4) (MnFe_2O_4 with
with upto 60%   excess Mn_3O_4
Fe_2O_3)   in solid solution)

IV (A). Braunite → Tephroite + Hausmannite. (B). $3Mn_2O_3 . MnSiO_3 = 7MnSiO_3 + 3/2 O_2$.
($3Mn_2O_3 . MnSiO_3$) (Mn_2SiO_4) (Mn_3O_4)   (Braunite)   (Rhodonite)

V. Bementite → Braunite → Rhodonite
(Mn,Mg,Fe)$_6$Si$_4$(O,OH)$_{18}$

VI. $MnCO_3$ + $MnSiO_3 = Mn_2SiO_4 + CO_2$.
(Rhodochrosite) (Rhodonite) (Tephroite)

VII. $6MnSiO_3 + O_2 = 2 Mn_3O_4 + 6 SiO_2$
(Rhodonite) (Hausmannite)

VIII. $2(Mn,Fe)SiO_3 + 3/2 O_2 = Mn Fe_2O_4 + MnSiO_3 + SiO_2$
(Pyroxmangite) (Jacobsite) (Rhodonite)

XI. (A). $Mn_2SiO_4 + SiO_2 = 2MnSiO_3$. (B). $6 Mn_2SiO_4 + O_2 = 6 Mn SiO_3 + 2 Mn_3O_4$
(Tephroite) (Rhodonite) (Tephroite) (Rhodonite) (Hausmannite)

REFERENCES TO TABLE 1

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II. B. (iii) Huebner, 1967.
III. Roy, 1970.
IV. A. Pavlovitch, 1931. IV. B. Huebner, 1967.
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VIII. Roy, 1970.
IX. A. & B. Huebner, 1967.

(In Table 1 instead of XI read IX)

The regionally metamorphosed sedimentary manganese formations may broadly be divided into three types according to their mineral assemblages.

(i) Deposits consisting of metamorphic oxide and silicate assemblages and devoid of carbonates

The geology and mineralogy of the regionally metamorphosed Precambrian sedimentary manganese formations of India in the Sauser, Aravalli, Champaner and Khondalite Groups were discussed at considerable length by FERMOR [1909], ROY [1966, 1970], ROY and MITRA [1964], ROY and PURKAIT [1968] and others. These non-volcanogenic sedimentary deposits, subjected to different grades of regional metamorphism from quartz-albite-muscovite-chlorite subfacies (greenschist facies) to granulite facies in different parts [ROY, 1970], are characterized by oxidic manganese ores, sharply interbanded with manganese silicate rocks (gondite). In the oxidic ore beds, braunite is the first metamorphic mineral to appear in the quartz-albite-muscovite-chlorite subfacies and the mineral is stable throughout the greenschitc, almandine-amphibolite and granulite facies. Bixbyite appears in the quartz-albite-epidote-biotite subfacies in association with hollandite, jacobsite (with high Fe_3O_4 content) and braunite and persists in the higher grades. Hausmannite, jacobsite (with high Mn_3O_4 content) and vredenburgite appear in the staurolite-almandine subfacies and continue to granulite facies in association with braunite. The texture of the ore exhibits a remarkable change with the degree of metamorphism [ROY, 1970]. In low-grade facies, fine grained and relict colloform textures are exhibited by manganese oxide minerals constituting the ore-bodies. Braunite and hollandite are stretched and elongated, showing preferential dimensional orientation parallel to the banding. A schistosity is thus imparted on the ores perpendicular to the direction of maximum compression. Braunite-bixbyite-hollandite ores of greenschist facies often show microfolding and translation twin is developed in hollandite. In high-grade metamorphism, the texture of the oxidic minerals in the ores is characteristically granoblastic. In these ores exsolution of hausmannite in the octahedral plaine of jacobsite and rhodonite are characteristic.

The manganese silicate rocks (gondite are essentially constituted of spessartite and quartz, very often with rhodonite (and/or pyroxmangite, bustamite) and sometimes manganiferous aegirine, aegirine-augite (blanfordite, brown manganiferous pyroxene), diopside, manganiferous magnesioriebeckite (juddite) and richterite-tremolite (winchite, tirodite), manganiferous micas and piedmontite. Rhodochrosite and tephroite are characteristically absent. The field and laboratory studies confirm that the oxidic ore-bands and the sharply interbanded manganese silicate rocks are separate entities. Both were laid down as carbonate-free syngenetic sediments in separate beds and were regionally metamorphosed.

Regionally metamorphosed manganese formations of Otjosondu, S.W. Africa [ROPER, 1956] occur in three stratigraphic zones in the Precambrian Damara System, associated with itabirite-schist and quartzite. Interbanded oxidic and manganese-silicate layers; metamorphosed to almandine- amphibolite facies, are represented by braunite-bixbyite-hollandite-jacobsite-hausmannite-vredenburgite assemblage and by spessartite-rhodonite-diopside-acmite-quartz assemblage, respectively. These manganese formations are, thus, similar to those in India, although the association of the former with metamorphosed bedded iron formation (itabirite schist) differentiates them from the latter.

The manganese formations of S. Ural [BETEKHTIN in ZVEREFF, 1953] of Paleozoic age, have been regionally metamorphosed and the oxidic and silicate formations contain braunite and spessartite-rhodonite-bustamite-piedmontite assemblages respectively.

The deposit at Tierre, W. Africa, regionally metamorphosed to the chlorite zone, exhibits only manganese silicate (spessartite-quartz) assemblage [SERVANT, 1956] and is devoid of metamorphic oxides. This deposit, therefore, represents only admixed manganiferous sediments with manganese oxide, clay, silica etc.

Manganese deposits of volcanogenic-sedimentary spilite-keratophyric type, later metamorphosed regionally, are found in Japan [WATANABE *et al*, 1970a]. At Shiromaru mine near Tokyo, such deposits metamorphosed in low-temperature high-pressure condition (as shown by the presence of cymrite), consist of braunite-rhodonite assemblage. At Muramatsu mine, Hagashaki Prefecture, similar manganese formations metamorphosed to amphibolite facies, exhibit a mineral assemblage: braunite-rhodonite-piedmontite-spessartite.

(ii) Deposits exhibiting manganese silicate-carbonate assemblage

The manganese silicate-carbonate formation of Precambrian Minas Series at Minas Gerais, Brazil, metamorphosed to quartz-albite-epidote-almandine sub-facies, consist of rhodochrosite-manganoan calcite-rhodonite-pyroxmangite-te-phroit-spessartite-kupfferite-bementite-neotocite-alabandite-graphite-quartz assemblage. The local manganese oxide concentrations are supergene higher oxides, but for the minor hausmannite formed by the dissociation of rhodochrosite during metamorphism [HOREN, 1953]. The widespread presence of graphite and alabandite ensures the original depositional condition of the sediments of negative Eh and pH around 7 in an euxinic environment and as such manganese oxides and hydroxides could not form [DORR *et al,* 1956]. PARK (pers. com.), however, considers that alabandite formed entirely due to later contact metamorphism. In fact, PARK *et al* [1951] and others concluded that this manganese-silicate-carbonate formation is a product of contact metamorphism of syngenetic sediments.

At Serra do Navio deposit, Brazil, impure manganese carbonate, with concentration of silica and alumina at places, were originally deposited in an environment of low redox potential in a basin of restricted circulation (NAGELL, 1962). These were later regionally metamorphosed to give rise to recrystallized rhodochrosite bodies with rhodonite, spessartite and picrotephroite. Metamorphic manganese oxides are absent.

Metamorphosed manganese formations of Sierra Nevada, U.S.A., have undergone a higher degree of metamorphism than that of the Coast Ranges of California [HEWETT *et al*, 1961]. Some of the more important deposits in Sierra Nevada exhibit the following mineral assemblages: rhodochrosite-tephroite-rhodonite-spessartite (Big Indian Deposit, Korn County: Precambrian); rhodochrosite-tephroite-rho-donite-spessartite and minor bementite and neotocite (Calaverous Formations: Late Paleozoic); hausmannite: tephroite-rhodonite-spessartite-alleghanyite-piedmon-tite-bementite-rhodochrosite (Smith Prospect, Amador Group: Jurassic).

The Buckeye deposits (late Jurassic to early Cretaceous) of California Coast Range has been metamorphosed to blueschist facies [HUEBNER, 1967], with the following mineral assemblages: oxide — hausmannite, braunite; silicate — carbonate — rhodochrosite, bementite, 7 & 12 silicates. Hausmannite and braunite are associated with rhodochrosite, as euhedral crystals. Braunite also exhibits fine to coarse laminations which might have been sedimentary in origin. According

to HUEBNER [1967], the Buckeye deposit originally formed by precipitation from thermal waters on ocean floor and was later regionally metamorphosed.

The Manganese Shale Group of the Harlock Dome, Merionethshire, Great Britain, has been metamorphosed to chlorite zone and exhibits an assemblage of rhodochrosite-spessartite-quartz [WOODLAND, 1939]. Tephroite is absent. The higher oxides present are all supergene.

Rhodochrosite-rhodonite-spessartite assemblage has been recorded in meta-sedimentary lenses and beds in basic lava and tuff regionally metamorphosed to chlorite zone in western Otago, New Zealand [HUTTON, 1957]. Metamorphic oxides of manganese as well as tephroite are absent.

At Kiuragi mine, Saga Prefecture, Japan [WATANABE et al, 1970a], manganese silicate-carbonate formations of volcanogenic Jasperoid Formation type have been metamorphosed regionally to amphibolite facies, with the following mineral assemblage: tephroite-rhodonite-spessartite-rhodochrosite-jacobsite (with exsolved galaxite).

Around Tamworth, New South Wales, Australia, sedimentary manganese deposits regionally metamorphosed to low grade [SEGNIT, 1962] occur enclosed in phyllites and siliceous rocks. The only metamorphic oxides present are hausmannite and jacobsite with a silicate-carbonate assemblage tephroite-knebelite-mangan-dolomite-spessartite. At Danglemah deposit, tephroite-mangandolomite, rhodo-nite-tephroite-spessartite-hausmannite and quartz-knebelite assemblages occur.

(iii) Deposits exhibiting both metamorphic oxides and silicate-carbonate assemblages

The regionally metamorphosed manganese deposits of S. Khingan [CHEBO-TAREV, 1960] and the Karadzhal deposit, Central Kazakhstan [MAKSIMOV, 1960; KALININ, 1965; NOVOKHATSKY, 1970], U.S.S.R., constitute a distinct type as they contain both metamorphic low oxide and silicate-carbonate assemblages. The S. Khingan deposits exhibit braunite-hausmannite-hematite-magnetite and rhodoch-rosite-tephroite-rhodonite-bustamite assemblages. The Karadzhal deposit (vol-canogenic-sedimentary; NOVOKHATSKY, 1970) exhibits assemblages of braunite-hausmannite-jacobsite and manganocalcite-rhodochrosite-rhodonite-tephroite. According to KALININ [1965], however, the Karadzhal deposits first underwent regional metamorphism of low grade when oxidic ore bands were converted to braunite and the carbonate manganese formations (with siliceous material) were recrystallized into rhodochrosite-manganocalcite-quartz-chalcedony. This was followed by contact metamorphism when braunite-hausmannite-jacobsite assemblage formed in the oxidic bands and the silicate-carbonate bands were reconstituted to mangano-calcite-rhodochrosite-rhodonite-tephroite assemblage. Thus, in different parts of these deposits, a sedimentary facies change from manganese oxide to carbonate was present which were reconstituted on metamorphism. Another characteristic feature of these deposits is that the oxidic manganese ore bands are interlayered with iron formation similar to that at Otjosondu, S.W. Africa and western Mato Grosso (Brazil).

SEDIMENTARY MANGANESE FORMATIONS AFFECTED BY CONTACT METAMORPHISM

Sedimentary manganese formations later modified by contact metamorphism have been described principally from Japan [WATANABE, 1959, 1960; WATANABE, YUI and KATO, 1970a, 1970b], Sweden [KOARK, 1970] and India [ROY, 1966, 1970].

Bedded volcanogenic manganese and iron-manganese formations of Jasperoid type occur mainly in the Paleozoic Chichibu geosyncline in Japan. Deposits of Mesozoic (S. Shikoku) and Miocene age (Fossa Magna region and Hokkaido) are also found. Many of these deposits have later been modified by contact metamorphism, among which those at Kaso Mine (Tochigi Prefecture), Noda Tamagawa (Iwate Prefecture), and Kanoiri-Yokoneyama are important.

The manganese deposits of Kaso Mine were metamorphosed thermally to hornblende-hornfels facies as shown by the development of cordierite-biotite hornfels in the enclosing rocks [WATANABE et al, 1970a]. YOSHIMURA [1939] described as many as forty different minerals from this mine-area. Abundant occurence of tephroite, rhodonite, rhodochrosite, alabandite, jacobsite etc. has been reported. Later pyrometasomatism and boron metasomatism gave rise to huebnerite, jimboite, wiserite, pyrosmalite and manganpyrosmalite, caused by later granitic intrusions.

At Noda-Tamagawa mine, manganese orebodies of Paleozoic (Chichibu Complex) age occur as roof-pendant on the Tanchata granite (Cretaceous). According to WATANABE [1959] et al [1970b] the manganese formation here has suffered a higher grade of contact metamorphism (hornblende-hornfels to pyroxene-hornfels facies) than that in the Kaso Mine, as shown by the presence of sillimanite, andalusite and cordierite in pelitic hornfelses enclosing the orebody. The sharply banded manganese formations are characterized by different mineral assemblages. Rhodochrosite (major)-tephroite-galaxite-maganosite assemblage is most common and is often in contact with hausmannite-rich lenses. Manganese-bearing pyroxenes and amphiboles occur in hornfelses on the footwall side. Interbanded braunite-rich (braunite-hausmannite-tephroite-barite) and braunite-poor (rhodonite-quartz-alkali pyroxene-alkali amphibole) assemblages also occur in this part. Tephroite and rhodonite-rich assemblages (with rhodochrosite and spessartite) are considered to have formed as reaction skarns. Pyrochroite, in pyrochroite-manganosite-tephroite-galaxite-rhodochrosite-barite-alabandite assemblage, has formed by hydration (by residual magmatic water) of manganosite which again formed by thermal dissociation of rhodochrosite, hausmannite and possibly hydrous manganese silicates constituted the original sedimentary manganese deposits at Noda Tamagawa.

The manganese deposits of Kanoiri and Yokneyama mines, Ashio Mountainland, have been thermally metamorphosed to orthopyroxene-cordierite-biotite hornfels (pyroxene-hornfels facies) by later granitic bodies [WATANABE et al, 1970a]. Tephroite, rhodonite, bustamite and spessartite are principal minerals in the assemblage with minor pyroxmangite and Mn—Ca pyroxene. No rhodochrosite is left after contact metamorphism.

The manganese formations at Nyberget, Långban and Ultevis, Sweden, are of volcanogenic-sedimentary type associated with jaspilitic iron formation. All these deposits show polymetamorphic history and in the deposits at Nyberget and Långban, the latest progressive facies is equivalent to albite-epidote hornfels facies, whereas that of Ultevis is equivalent to albite-epidote hornfels facies [KOARK, 1970]. The mineral assemblages in these deposits are as follows:

Nyberget: (oxide) braunite, hematite, jacobsite; (silicate) spessartite, rhodonite, urbanite, richterite, manganophyllite, piedmontite, schefferite, and barite, calcite.

Långban: (oxide) braunite, hausmannite, manganosite; (silicate) rhodonite, schefferite, richterite, spessartite, tephroite, manganophyllite and numerous minerals with Pb, As, Sb, Be, Ba, Ti etc.

Ultevis: (oxide) braunite, hollandite, bixbyite, hematite: (silicate) spessartite, piedmontite, viridine, mica.

The Precambrian Champaner Group or rocks (including bedded manganese formations, pure and impure limestone, quartzite and pelitic rocks) in Gujarat, India, show a low grade regional metamorphism to quartz-albite-muscovite-chlorite subfacies. A small patch of these rocks, at Jothvad, has been invaded and enclosed by later porphyritic biotite-granite (Erimpura Granite) which has thermally metamorphosed the manganese formation and the country rocks to hornblende-hornfels facies grading into pyroxene-hornfels facies near the aureole. The thermally metamorphosed manganese oxide assemblage (braunite-hollandite-bixbyite-hausmannite) is sharply interbanded with manganese silicate rocks (spandite-rhodonite-bustamite-blanfordite-brown manganese pyroxene-winchite-tirodite-piedmontite-manganophyllite-alurgite). The manganese formation is characteristically devoid of rhodochrosite and tephroite indicating an original bulk composition free of manganese carbonates.

DISCUSSION

Manganese sediments, formed by chemical precipitation, may be constituted of higher oxides of manganese (with dominant Mn^{4+}), manganese hydroxides (manganite in particular) and manganese carbonate (rhodochrosite, manganocalcite etc.). Braunite is also rarely detected in unmetamorphosed volcanogenic sediments. Alabandite is practically absent in the sediments.

Primary deposition of manganese only as higher oxides and hydroxides (cryptomelane, todorokite, birnessite, 7Å and 10Å manganites etc.), generally in association with iron, has been demonstrated by recent nodular deposits in shallow water and deep sea as well as in the bog manganese ores of Sweden and Norway [LJUNGGREN, 1955]. These deposits also demonstrated that the formation of manganese carbonate and the separation of iron took place by diagenesis. STRAKHOV [1966] considered most of the ancient manganese carbonate deposits as sedimentary-diagenetic. Rhodochrosite may, however, be also directly precipitated as a primary mineral.

Metamorphism of manganese formation leads to reconstitution of minerals due to rising temperature, pressure and the effect of f_{O_2}, f_{CO_2}, etc. The initial chemical and mineralogical composition of the sediments largely controls the metamorphic mineral assemblages. In case of oxidic sediments, a progressive reduction is observed in rising temperature during metamorphism (I. A. to I. F. Table 1), giving rise to lower oxides such as bixbyite, hollandite and hausmannite. The hydroxides, groutite and manganite, are first dehydrated in rising temperature to pyrolusite and then reduced to hausmannite through bixbyite (I. C. & I. D.; Table 1).

Admixture of oxides and hydroxides of manganese and iron in the sediments convert, during metamorphism, to iron-rich bixbyite and jacobsite (and/or vredenburgite). With silica present in the sediment, the manganese oxides and hydroxides react with it during metamorphism giving rise to braunite or rhodonite depending upon the oxygen fugacity [HUEBNER, 1967]. Thus, a sediment, predominantly rich in manganese oxide and/or hydroxide, and admixed with limited iron and silica, will be reconstituted to braunite-bixbyite-hollandite-jacobsite-hausmannite-vredenburgite assemblage when subjected to high grade metamorphism (almandine-amphibolite or pyroxene-hornfels facies). The relative abundance of Mn, Fe, Si, Ba etc. in the sediments controls the presence or absence of the different phases to a great extent. In greenschist or albite-epidote hornfels facies, hausmannite, jacobsite (high-iron type) and vredenburgite are generally absent.

Where oxides and/or hydroxides of manganese are admixed with silica and argillaceous matter in high proportions, an assemblage of spessartite-rhodonite-quartz, often with manganiferous pyroxenes and amphiboles, is formed during metamorphism.* The resulting manganese silicate rocks are generally interbanded with oxidic bands (India; Otjosondu; Ultevis, Nyberget, Sweden) where metamorphic reactions where confined to the bands themselves, controlled by the original bulk composition. In some cases, mixed manganese oxide-silicate assemblages are also found (Shiromaru, Japan: Braunite-rhodonite; Muramatsu, Japan: Braunite-rhodonite; Nuramatsu, Japan: Braunite-rhodonite-piedmontite-spessartite). In these volcanogenic sedimentary (Jasperoid type) deposits of Japan, braunite formed as primary mineral in the sediment [WATANABE et al, 1970a], which perhaps was reduced to form rhodonite (IV. B., Table 1) and by reaction with admixed Ca, Al etc., gave rise to spessartite and piedmontite. Rhodonite may be oxidized to hausmannite and silica [HUEBNER, 1967] and pyroxmangite has been demonstrated [ROY, 1970] to have oxidized to rhodonite and jacobsite (VII & VII, Table 1) in manganese silicate rocks. Deposits of manganese silicate rocks without any association of metamorphic oxides (Tiere, W. Africa) may be explained by the relative paucity of manganese oxides in the original sediments.

Manganese carbonate sediments without admixture are recrystallized without change of mineral phases in low grade metamorphism. In high grade metamorphism, rhodochrosite dissociates to MnO (manganosite) and CO_2 and the manganosite is readily oxidized to hausmannite [CUTHBERT and ROWLAND, 1947; KULP et al, 1949]. When silica and argillaceous matter are associated with manganese carbonate sediment, an assemblage of rhodochrosite (and/or manganoan calcite) -rhodonite-pyroxmangite-tephroite-spessartite is formed during metamorphism (Minas Gerais, Brazil; Sierra Nevada, U. S. A.,; Kiuragi, Noda Tamagawa, Japan etc.). The formation of rhodonite and tephroite may be explained by the reactions shown in Table 1 (II. B. i & ii) and their formation is controled by Mn:Si ratio in the sediment. The formation of tephroite is further controlled by f_{O_2} and f_{CO_2} in rising temperature and, therefore, its formation cannot be predicted by the grade of metamorphism. Tephroite is also characteristic of silicate-carbonate assemblage only and cannot form in carbonate-free silicate rocks (India, Otjosondu, S. Ural etc.) even in high grade metamorphism as explained by ROY and PURKAIT [1968].

The metamorphosed carbonate-silicate rocks are characteristically poor in or devoid of metamorphic manganese oxides which is explained as due to absence of higher oxides in the sediments. However, hausmannite is sometimes reported from these assemblages (Minas Gerais, Smith Prospect, Buckeye, Tamworth, Noda Tamagawa etc.) which apparently formed by the dissociation of rhodochrosite. The presence of braunite at Buckeye and Noda Tamagawa may be explained either by recrystallization of sedimentary braunite in volcanogenic formation (WATANABE et al, 1970b] or by the reaction II. B. *(iii)* in Table 1 [HUEBNER, 1967] which is a rare phenomenon in natural deposits.

It may, therefore, be concluded that abundance of lower oxides in metamorphosed manganese assemblages with total absence of rhodochrosite and tephroite is an unequivocal evidence of an original carbonate-free oxidic sediment. On the other hand, the presenc eof tephroite and/or rhodochrosite, with absence or minor pre-

* Alternatively a bulk composition rich in low temperature manganese silicates (bementite, neotocite etc.) might also give a similar assemblage on metamorphism. But this possibility demands that manganese oxides and manganese silicates were deposited as thin interbands with a sharp and alternate change of Eh and pH which is rather unlikely.

sence of lower oxides (as dissociation or reaction product of rhodochrosite), is indicative of an original carbonatic sediment. The question, however, remains whether these oxidic manganese sediments (which are also generally iron-rich) escaped diagenetic reconstitution before metamorphism and also whether the carbonatic manganese sediments (generally iron-poor) were all diagenetic products. Studies on recent manganese nodules show that iron separates out at the first stage of diagenesis followed by change of manganese oxide to manganese carbonate. But this process depends on the extent of burial, presence of organic matter, pressure of dissolved carbonate in pore waters etc. When some of these agencies fail to act, the diagenesis is not complete and if followed closely by contact or regional metamorphism, the primary sediments may be directly metamorphosed. All manganese carbonate in sedimentary manganese deposits, however, may not be diagenetic and direct precipitation of manganese as carbonate rhodochrosite, depending on Eh, pH and activity of dissolved CO_2 in the medium, is also probable [BRICKER, 1965].

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