*A Thermodynamic Interretation of the Zonal Arrangement of Minerals in the Bedded Manganese Deposits of the Noda-Tamagawa Mine, Japan

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ABSTRACT

Calculated phase relations in the system MnO-SiO_2-CO_2-O_2 were used to propose a thermodynamic explanation for the thermal metamorphism of rhodochrosite beds lying between chert strata. The metamorphic MnO-SiO_2 minerals are arranged in order quartz(chert), rhodonite, tephroite and manganosite-hausmannite-pyrochroite rhodonite across the ore bed. The calculation covered temperatures up to 1000 K and pressures up to 5 kb. The zoning was interpreted as the result of a continuous rise in metamorphic temperature. The equilibrium partner of rhodochrosite changed from rhodonite through manganosite. Across the ore bed there are gradients in the chemical potential of MnO and SiO_2 but fugacities of volatile components such as CO_2, O_2 and H_2O were probably uniform at any given time and location during formation of the zones. Assuming that the total pressure and the fugacity of CO_2 were at 1.4 kb and 1.01 b, respectively, rhodonite, tephroite and manganosite would have formed at 472, 478 and 629 K.

INTRODUCTION

An interesting zonal arrangement of minerals in the system MnO-SiO_2 is observed in the thermally metamorphosed bedded manganese deposits of the Noda-Tamagawa mine, one of the most representative manganese mines in Japan. Ore beds lie between chert strata. A traverse away from chert toward the center of the ore bed encounters successively a rhodonite zone, a tephroite zone and finally a manganosite-pyrochroite-hausmannite-rhodochrosite zone /1-3/.

From a geological point of view, the zoning is thought to have resulted from the thermal metamorphism of rhodochrosite beds /2-5/, but it has not been satisfactorily explained from a thermodynamic point of view.

This paper aims at inferring the thermodynamic basis of the zoning and a probable explanation of its genesis. In order to obtain quantitative knowledge of phase relations in the system MnO-SiO_2-CO_2-O_2, equilibrium calculations were carried out up to 1000 K and 5 kb. It will be shown that the zoning is easily explained by a series of decarbonation reactions that occur with an increase in temperature.

OUTLINE OF THE ZONING

The Noda-Tamagawa district in the outer belt of the Kitakami mountain land is a roof pendant area lying on Cretaceous granitic rock. Jurassic slate, sandstone, chert and limestone in the area are highly metamorphosed by granitic-rock intrusion and they are turned into hornfels. Silimanite, andulsite and cordierite are found in pelitic rocks of the area /5,6/. Ore-bearing zones are actually ore beds intervening conformably between Jurassic thin-bedded and massive chert strate (Fig. 1). They have a general strike of N10°-20°E and almost vertical dip. The largest ore bed named Misago continues for about 1200 m along the strike and more than 450 m along the dip, with varying thickness between one half and two meters.

Ore beds are essentially composed of minerals belonging to the system MnO-SiO_2-CO_2-

O_2-H_2, including tephroite (Mn_2SiO_4), rhodonite ($MnSiO_3$), rhodochrosite($MnCO_3$), manganosite (MnO), hausmannite(Mn_3O_4) and pyrochroite [$Mn(OH)_2$]; but they also contain lesser amounts of galaxite ($MnAl_2O_4$), spessartine ($Mn_3Al_2Si_3O_{12}$), bustamite [$(Mn,Ca)_3Si_3O_9$], penwithite ($MnSiO_3 \cdot 2H_2O$), alabandiate, braunite and manganoan mica, pyroxene and amnophibole. The ores show a mosaic texture which indicates their metamorphic origin.

Ore minerals are zoned in parallel to the overlying and underlying chert strata (Fig. 1).

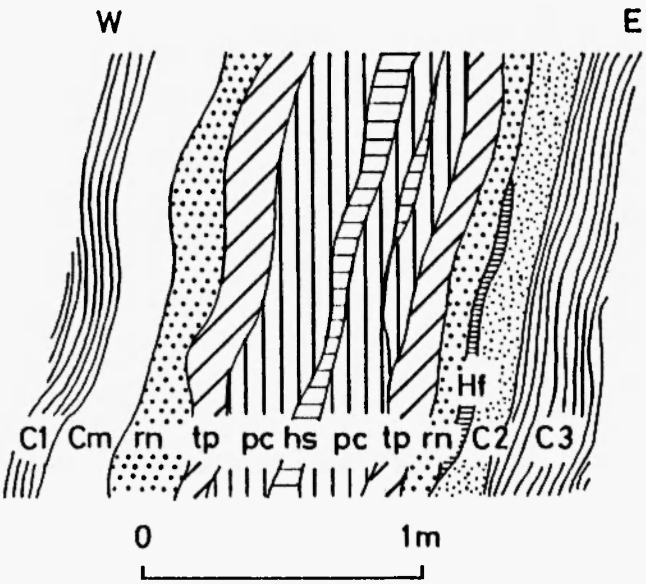

Fig. 1 Idealized cross section of the manganese ore zone of the Noda-Tamagawa mine, showing the bedded arrangement of manganese ores and country rocks. hs:hausmannite, pc:pyrochroite, tp:tephroite, rn:rhodonite, hf:hornfers, C1-Cm:chert.

Three zones are identified. Rhodonite forms the outermost layer of the ore bed and makes immediate contact with the chert strata. Next to the rhodonite zone, toward the center of the ore bed, is the tephroite zone. The central zone, which is sandwiched between tephroite layers, is made up of an assemblage of pyrochroite-manganosite-hausmannite-rhodochrosite. Pyrochroite was formed from manganosite through retrogressive metamorphism. Two kinds of rhodochrosite seem to occur in the deposits: one is a survivor of decarbonation reactions and is concentrated in the central zone, and the other is of retrogressive metamorphic origin and fills fissures in the deposits and in the surrounding rocks.

Locally, as the ore bed becomes narrower, the central zone and then the tephroite zone pinches out and the bed becomes entirely composed of the rhodonite zone. The boundaries between ore zones are sharp. Neither the tephroite nor the central zones make immediate contact with chert strate. There is always an intervening tephroite zone between the central and the rhodonite zones. The zoning is schematically shown in Fig. 2.

ANALYTICAL METHODS

The zoning in the Noda-Tamagawa deposits is closely related to the fact that the ore deposits were rhodochrosite strate sandwiched between chert strate before thermal metamorphism occurred. When existence of small amounts of minerals containing such components as Al_2O_3, CaO, FeO, MgO and S_2 are ignored, this kind of metamorphism can be treated as primarily belonging to the system MnO-SiO_2-CO_2-O_2-H_2O. The zoning may, therefore, be explained with the aid of the chemical potentials of MnO, SiO_2, CO_2, O_2 and H_2O as well as temperature and total pressure.

The deposit actually contains small amounts

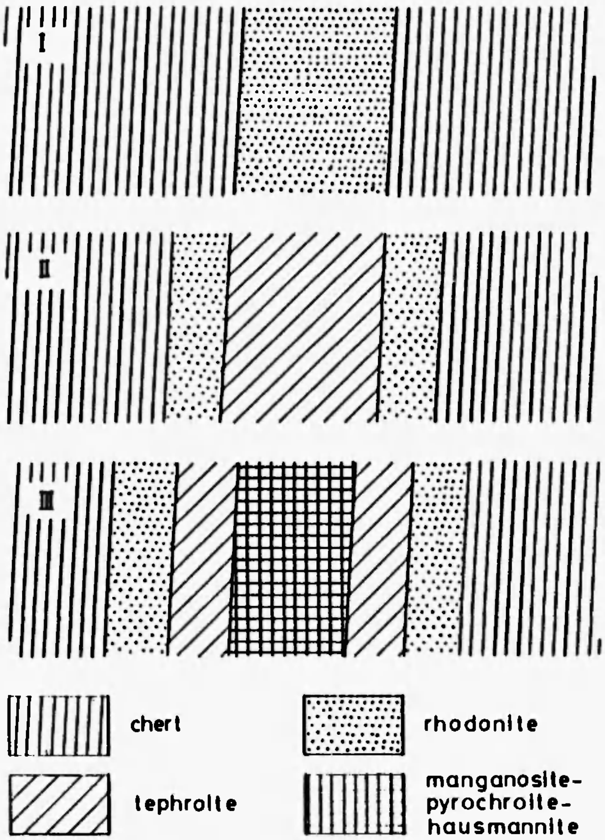

Fig. 2 Three types of mineral arrangements n the Noda-Tamagawa manganese deposit.

of braunite locally /5/, but his mineral has been omitted from present discussion because there is no reliable thermodynamic data on it. The $MnSiO_3$ phase was treated as rhodonite for convenience though its other polymorph, pyroxmangite /7/, is known.

Potential-temperature diagrams were constructed from thermodynamic data compiled by Robie and Waldbaum/8/; data on pyrochroite were taken from Rossini et al. /9/ and high temperature and high pressure fugacities of CO_2 and H_2O fluids from Majumdar and Roy /10/ and Anderson /11/, respectively. The calculation covers a temperature range up to 1000 K and pressures up to 5 kb. It was assumed that reactant and product minerals are of stoichiometric composition and belong to the system MnO-SiO_2-CO_2-O_2-H_2O. The general formula used for equilibrium calculation is given by

$$\Delta G(T,P) = \Delta G^{o}(T,1) + \nu_j RT \ln f_j + \Delta V_i(P-1.01) \tag{1}$$

where $\Delta G^{o}(T,1)$ and $\Delta G(T,P)$ are the free energy change for a given reaction at a temperature T, at a pressure of 1.01 and P bars respectively; ν_j denotes a stoichiometric coefficient of volatile component j and f_j its fugacity; ΔV_i represents volume change of solid phases in the reaction.

Constructed phase diagrams agree qualitatively with the experimental results compiled by Burt /12/ and Momoi /13/ though the experimental data contain some discrepancies.

RESULTS

A *MnO and SiO_2 Potentials*

Fig. 3 shows molar free energies of the system MnO-SiO_2 at room temperature and atmospheric pressure. In the figure, a polygonal line connecting the neighboring points forms a convex trace. This means that manganosite, tephroite, rhodonite and quartz can all exist as stable phases under appropriate conditions. As the temperature rises, the molar free energies increase at different rates, but the stability relations of the system do not undergo substantial changes within the temperature-pressure range under consideration (Figs. 3 and 4). Pressure effect is very small, and rising pressure causes only slight increases in the molar free energies (Fig. 4).

It can be inferred from Fig. 4 that gradients of the chemical potential of MnO and SiO_2 across the ore bed existed when the zones were formed. The potentials may have varied with time and location but were always sloped gradually from the center of other ore stratum toward the neighboring chert strata. Adjacent ore zones were thermodynamically compatible with each other. although a section of ore stratum as a whole was never in equilibrium. This suggests that the zone formation must have taken place under conditions of local or partial equilibrium as discussed by Thompson /14/.

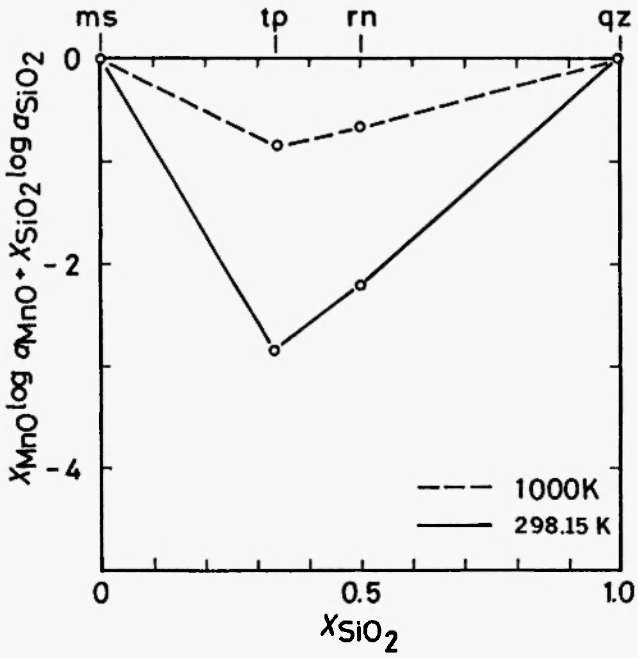

Fig. 3 Molar free energies of the solid phases in the system of MnO-SiO_2 at 298.15 and 1000 K and 1 atm.

B. *Oxygen Fugacity*

Whether oxygen potential was one of the deciding factors in the zoning or not can be judged by analyzing its influence upon the stability of MnO-SiO_2 minerals. Fig. 5 shows theoretical temperature-oxygen fugacity relations in the system MnO-SiO_2-O_2. Pressure effects are assumed to be negligible. Since equilibrium surfaces never cross each other within the temperature and pressure range under consideration, the phase relations of the system remain unaltered (Fig. 6a)

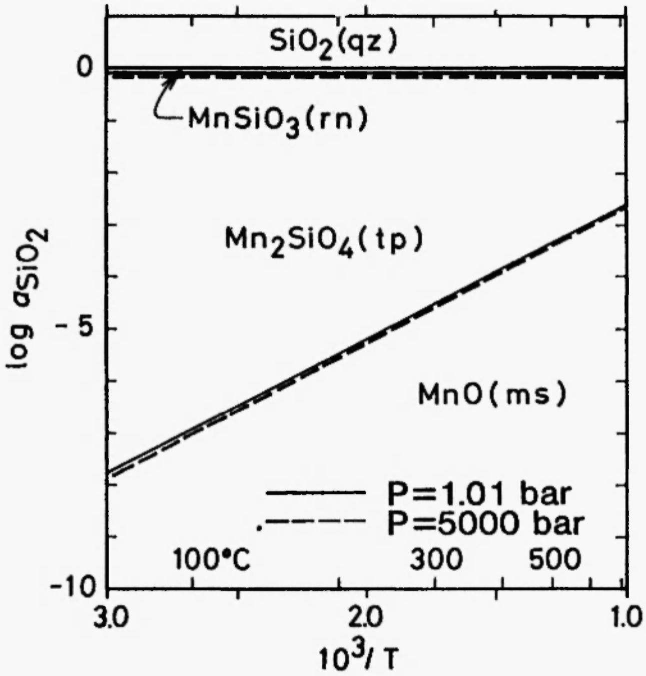

Fig. 4 SiO_2 activity-temperature diagram of the system of SiO_2-MnO at 1.01 and 5000 bar.

At a given pressure, five univariant curves in Fig. 5 divide the temperature-oxygen fugacity field into six regions, A-F. Each region is essentially a two-phase region. The equilibrium mineral pair in zone D, E. or F is fixed uniquely but that in zone A, B or C is variable and is determined by a ratio of MnO to SiO_2.

Although region A, as stated above, is a two-phase region probably all the four phases,

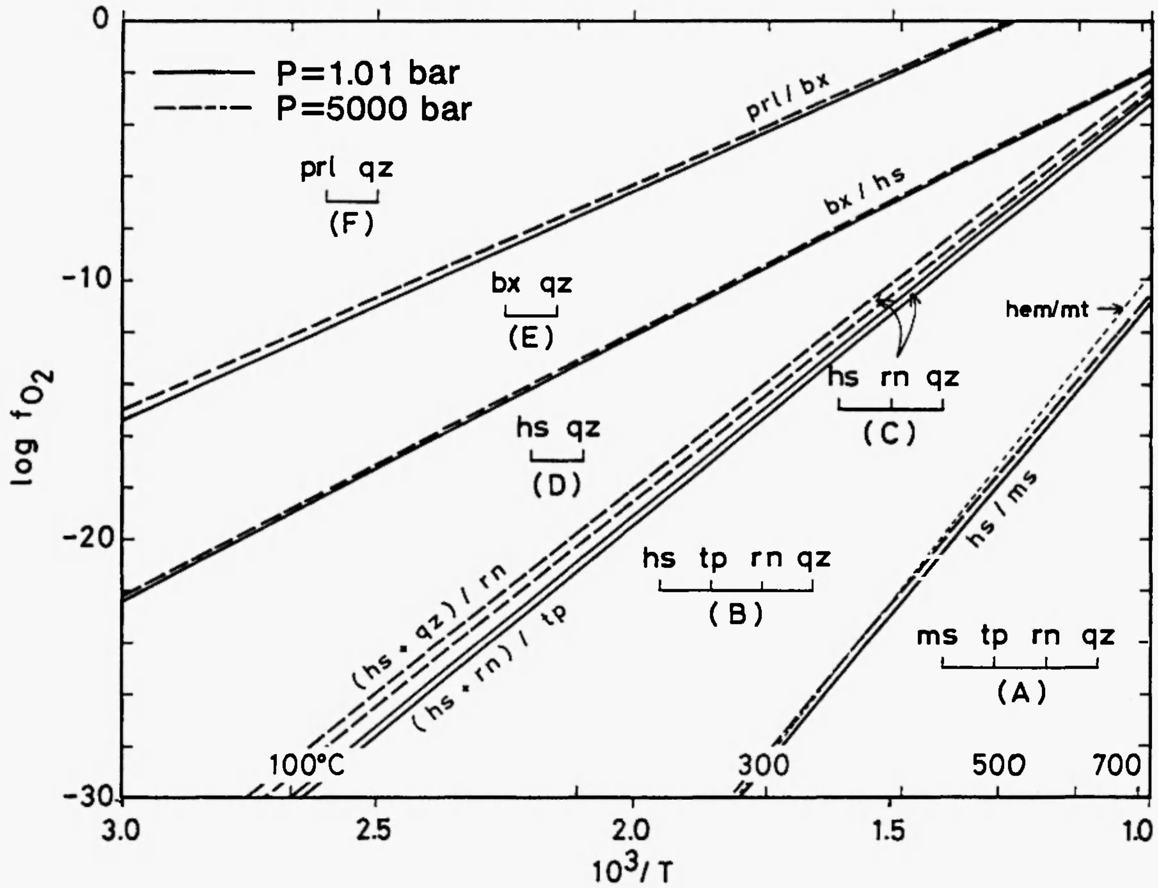

Fig. 5 The oxygen-fugacity-temperature diagram of the system of MnO-SiO_2-O_2 at 1.01 and 5000 bar. prl:pyrolusite, bx:bixbyite, ms:manganosite, qz:quartz, other symbols are identical to those in Fig. 1.

manganosite, tephroite, rhodonite and quartz, can exist simultaneously so long as they are arranged in this order. Incompatible phases are never in immediate contact with each other. The system under these conditions is thought to be in equilibrium with respect to oxygen and only in local equilibrium with respect to MnO and SiO_2. Similarly a partial equilibrium state in region B probably allows the three phases, hausmannite, tephroite and rhodonite, to exist in the same location in that order. Along the boundaries between regions A and B, an oxidation-reduction reaction occurs between manganosite and hausmannite while the other phases remain unchanged..

The above observations explain the actual zoning of the Noda-Tamagawa mine. Hausmannite and manganosite are limited to the central zone of ore strata together with rhodochrosite and do not coexist with rhodonite or chert. The actual zoning closely agrees with the mineral arrangement that can occur along the manganosite-hausmannite equilibrium curve in Fig. 5. These facts suggest that it is unnecessary to regard the oxygen potential as a deciding factor in zoning. Probably all zones of ore stratum were constructed under substantially the same oxygen potential.

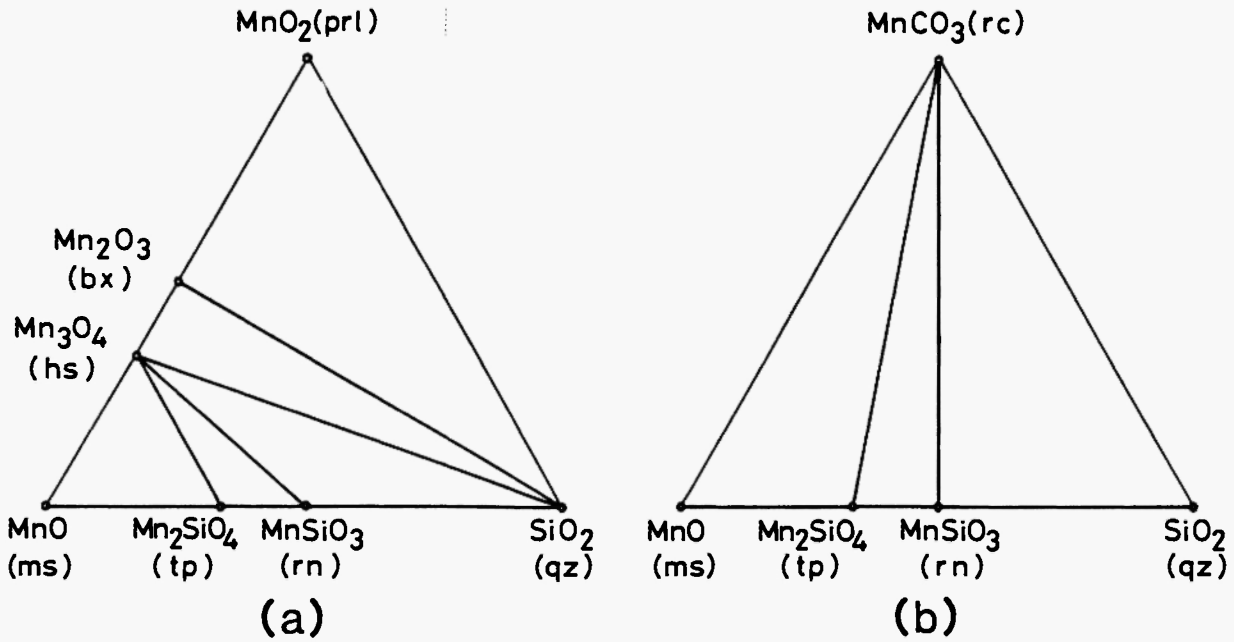

Fig. 6 Stable mineral assemblages of the MnO- MnO_2-SiO_2(a) and MnO-SiO_2-CO_2(b) systems at temperatures of 298 and 973 K and pressures between 1.01 and 5000 bar.

C. CO_2 *Fugacity*

Equilibrium CO_2 fugacity-temperature relations of the system MnO-SiO_2-CO_2 (Fig. 7) are similar to oxygen fugactiy-temperature relations of the system MnO-SiO_2-O_2 (Fig. 5), though pressure effects are much more significant in the former than in the latter. Within the temperature and pressure range under consideration, the univariant curves in Fig. 7 do not cross each other. Consequently, equilibrium tie-lines in a compositional triangle are not altered by a change in temperature or pressure (Fig. 6b).

If we ignore rhodochrosite of secondary origin, the zoning of the Noda-Tamagawa deposits can be described as a mineral arrangement in which MnO-SiO_2-CO_2 minerals are put in the order of rhodochrosite-manganosite, tephroite, rhodonite and quartz. This arrangement does not tell us anything about the CO_2 potential; it indicates MnO and SiO_2 potential gradients occurring across the ore stratum. The localization of rhodochrosite in the central zone, however, does not necessarily mean that CO_2 fugacity varies with distance. The arrangement is just the same as the one that can occur along the univariant curve representing equilibrium between manganosite and rhodochrosite in Fig. 6b. This allows us to propose that the assembly was probably formed under the same CO_2 fugacity at any given temperature and pressure.

The CO_2 fugacity of the deposits must have varied with temperature along the univariant curve, but one need not suppose that there must have been CO_2-fugacity differences among the ore zones. Probably CO_2 fugacity was substantially the same all over the ore strata, and, as a result, it

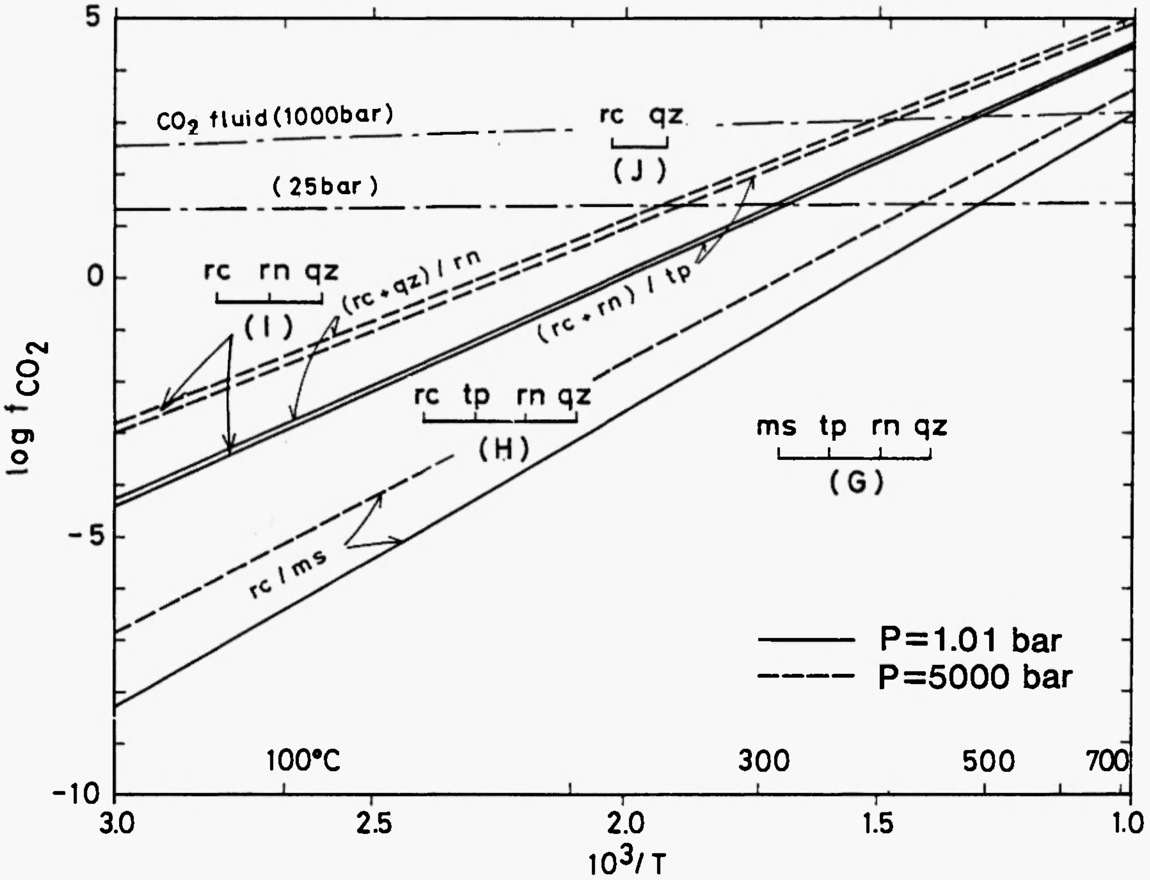

Fig. 7 CO_2 fugacity-temperature diagram of the system of MnO-SiO_2-CO_2 at 1.01 and 5000 bar.

may not have been a deciding factor in the zone formation.

D. Mechanism of Zoning

Most unmetamorphosed manganese deposits occurring near the Noda-Tamagawa district are rhodochrosite beds lying between chert strata /6, 15/. This suggests that the original ores of the Noda-Tamagawa deposits also had been in that form of rhodochrosite. They must have been in that form until the metamorphism took place, which means that as long as the deposits stayed in a diagenetic state, the CO_2 fugacity of the deposits must have been high enough to secure rhodochrosite against decarbonation reactions. It can be shown that a mineral arrangement identical to that of the Noda-Tamagawa deposits can be formed under uniform physicochemical conditions when a rhodochrosite bed intervening between chert strate is gradually heated. Consider the reactions that take place when a rhodochrosite bed is heated up gradually together with its underlying and overlying chert strate.

The beds are buried under approximately 6000 m of geosynclinal pelitic sediments whose specific gravity is 2.65 Mg/m^3. Pressure reaches about 1.4 kb at this depth /16/ and temperature

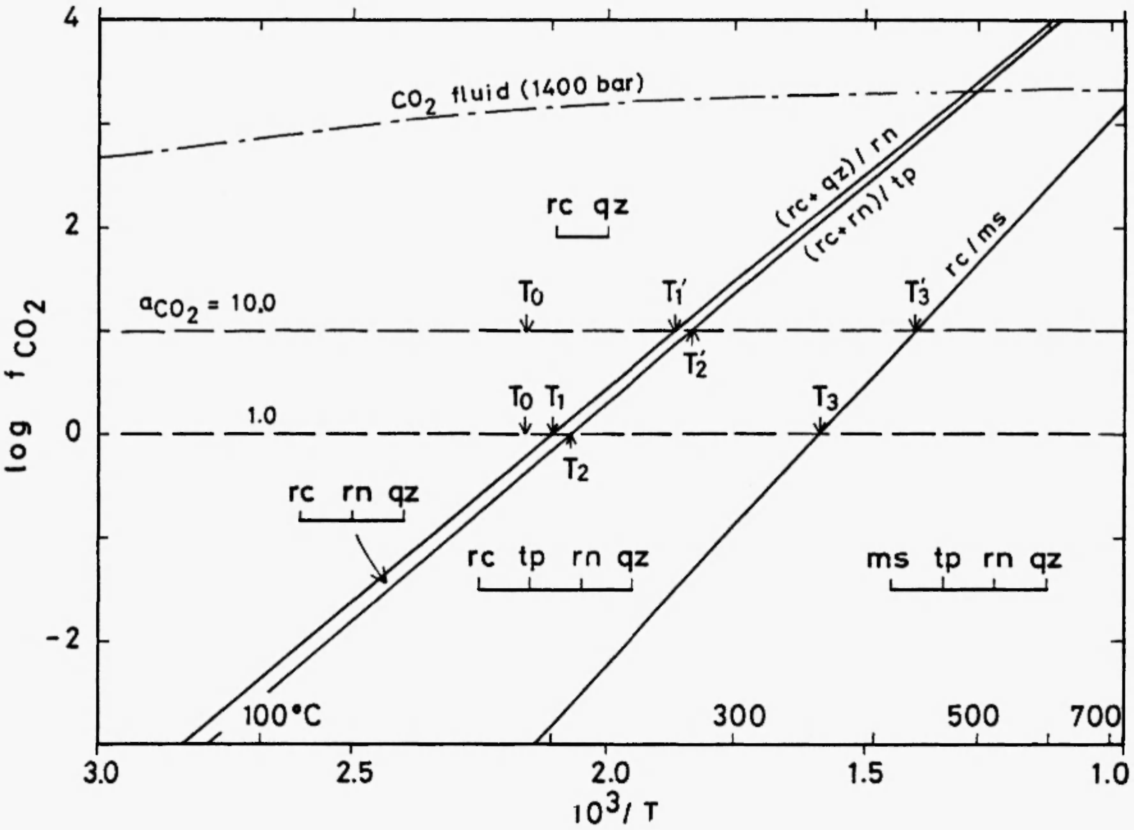

Fig. 8 CO_2 fugacity-temperature diagram of the system of MnO-SiO_2-CO_2 at 1.4 kb.

(T_O) about 463 K, assuming that the geothermal gradient is 2.89 degree per 100 m. If the rhodochrosite bed does not suffer any decarbonation reaction under these conditions (Fig. 8), the CO_2 fugacity of the deposit should be higher than about -0.2 on a logarithum scale (equal to 0.63 bar).

For the sake of simplicity, let us assume that the thermal metamorphism of the ore bed develops at a fixed CO_2 fugacity of one bar under a fixed total pressure of 1.4 kb (Fig. 8). The rhodochrosite and chert strate are compatible under these conditions and do not show any reactions unless temperature rises above about 472K (T_1 in Fig. 8). When temperature reaches 472 K, rhodochrosite and quartz begin to react to form rhodonite:

$$MnCO_3(rc) + SiO_2(qz) = MnSiO_3(rn) + CO_2 \qquad (2)$$

The reaction starts along the boundaries between the rhodochroosite and chert strata forming rhodonite layers there. As the reaction proceeds, the rhodonite layers become thicker and the rhodochrosite bed narrower. The reaction continues until the rhodochrosite is exhausted, providing the temperature remains below 478 K(T_2 in Fig. 8). The rhodochrosite bed is replaced by the rhodonite layers. This arrangement corresponds to a zoning of type I in Fig. 2.

If there is unreacted rhodochrosite adjacent to rhodonite layers when the temperature reaches 478 K(T_2), rhodochrosite and rhodonite react to each other to form tephroite;

$$MnCO_3(rc) + MnSiO_3(rn) = Mn_2SiO_4(tp) + CO_2 \quad (3)$$

Tephroite layers develop between the rhodochrosite and rhodonite layers. If the rhodochrosite is entirely consumed before the temperature reaches 629 K(T_3 in Fig. 8), the decarbonation reaction (3) comes to an end and a mineral arrangement of type II in Fig. 2 is obtained. However, if rhodochrosite is still present when the temperature has risen to 629 K(T_3), it begins to decarbonate by transforming into manganosite;

$$MnCO_3(rc) = MnO(ms) + CO_2 \quad (4)$$

If this occurs, a zoning of type III in Fig. 2 is obtained.

All the above gives a good explanation for the actual mineral arrangement in the Noda-Tamagawa deposits. Probably metamorphism of the Noda-Tamagawa district developed under conditions of rising temperature; the zoning must be the product of progressive thermal metamorphism which occurred in the rhodochrosite beds sandwiched between chert strata. Coexistence of manganosite with primary rhodochrosite indicates that the maximum temperature of metamorphism did not significantly exceed that corresponding to the equilibrium between these two minerals. If CO_2 fugacity was the equivalent of one atmospheric pressure at manganosite formation, the maximum temperature must have been around 629 K or a little higher.

If rhodochrosite had been exhausted, decarbonation reactions (2),(3) and (4) would not have occurred. However, a small amount of tephroite and/or rhodonite may have formed by the diffusion of MnO and SiO_2 components through tephroite and/or rhodonite layers.

$$MnO(ms) + MnSiO_3(rn) = 2Mn_2SiO_4(tp) \quad (5)$$

$$Mn_2SiO_4(tp) + SiO_2(qz) = 2MnSiO_3(rn) \quad (6)$$

The diffusional process is unlikely to proceed to completion.

Pyrochroite is thought to have been made from manganosite through a hydration process /4/. Equilibrium H_2O fugacity in manganosite-pyrochroite assemblage decreases more rapidly with a decrease in temperature than that in pure H_2O fluid (Fig. 9). This suggests that the pyrochoite in the Noda-Tamagawa mine is a product of retrogressive metamorphism.

DISCUSSION

The purpose of this paper is to present a logical and probable thermodynamic explanation for the zoning rather than to specify precise numerical values of temperature, pressure or chemical potentials at metamorphism. Nevertheless, internal consistency in

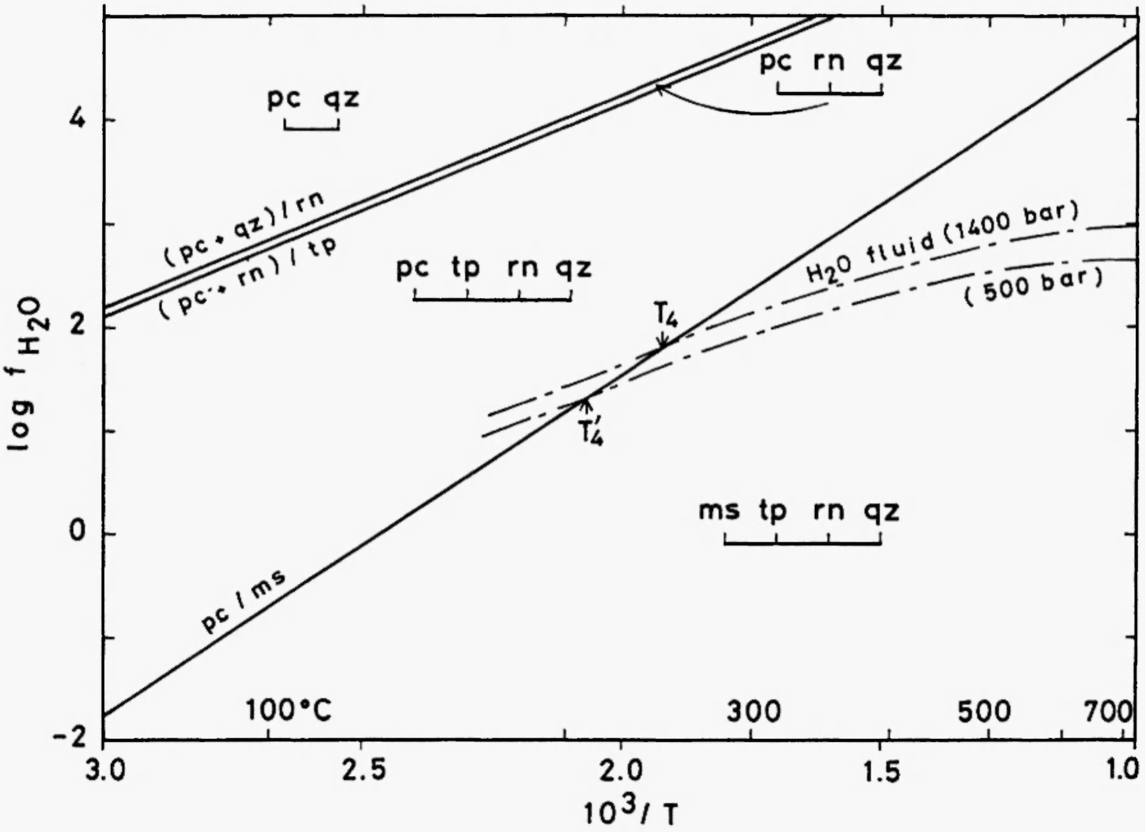

Fig. 9 H_2O fugacity-temperature diagram of the system of MnO-H_2O at 1.4 kb.

thermodynamic data is essential for the construction of correct diagrams which focuses in the interpretation of the actual geological events. Apparently, the data we used is reliable; the phase relations in the system Mno-SiO_2-CO_2 calculated from them are substantially with those constructed by Burt /12/ based on experimental acts.

The explanation presented here was developed on some hypothetical values of temperatures, pressures, and volatile component fugacity. They were taken only for illustration. The explanation does not lose its essence even if one or more of the physicochemical factors such as temperature, pressure and chemical potential take values different from those which are assumed. For example, even if a higher or a lower value for the pressure of metamorphism was assumed, it would have resulted in a rise or fall of the temperature for the beginning of decrabonation reactions (2), (3) and (4). The CO_2 fugacity may not always have been kept fixed during the metamorphism but may have changed with time or with temperature. However, such changes may have only had an effect on the beginning temperature of each decarbonation reaction. Thus, a guiding principle in our explanation, that rhodochrosite selects a different kind of MnO-SiO_2 mineral as its equilibrium partner according to a metamorphic temperature, does not need to be altered by altering the conditions of metamorphism.

If a thermal or a CO_2 fugacity gradient had occurred across the original rodochrosite strata, it might have been a key factor in deciding the arrangement of metamorphic manganese minerals /17/. It is rather improbable, however, that such steep gradients of temperature or CO_2 fugacity occurred within a distance of only one meter or so. It is more natural to suppose that the deposits were uniform in temperature and volatile component fugacities during the metamorphism. Therefore, the regular arrangement of $MnO-SiO_2$ minerals In the Noda-Tamagawa deposits must be a result of progressive metamorphism which occurred in rhodochrosite ore beds lying between chert strata.

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