STABILITY RELATIONS OF IRON-BEARING MINERALS IN THE $\text{H}_2\text{O}-\text{CO}_2$ MIXED-VOLATILE REGION AT LOWER TEMPERATURES

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Abstract Stability relations of iron-bearing minerals were thermodynamically discussed under the conditions of constant total $P_f (=P_{\text{H}_2\text{O}} + P_{\text{CO}_2} = 1 \text{ Kb})$ and lower temperatures. All the relations are considered to occur within the H_2O -rich region of a binary $\text{H}_2\text{O}-\text{CO}_2$ mixture. X_{CO_2} - T conditions for several low-grade metamorphic iron formations are estimated from the relations to be about 0.004 to 0.007 ($130 \pm 5^\circ\text{C}$) for the Sokoman I F, 0.0035 to 0.006 ($130 \pm 5^\circ\text{C}$) for the Biwabik I F, 0.0025 to 0.0045 ($102 \pm 3^\circ\text{C}$) for the Gunflint I F, and 0.0055 to 0.0178 ($128 \pm 10^\circ\text{C}$) for the Brockman I F (Dales Gorge Member). The X_{CO_2} at constant temperature is generally lower under a hematite-free condition probably equivalent to the Sokoman and Biwabik I Fs than under a hematite-bearing condition equivalent to the Gunflint and Brockman I Fs. It is therefore considered that the former condition indicates higher P_{CO_2} than the latter.

The P_{CO_2} during metamorphism, which is estimated independently of the total P_f from the assemblages of hematite-magnetite-siderite and magnetite-siderite, are about 5.5 to 9.8 bars for the Sokoman I F, 5.1 to 9.4 bars for the Biwabik I F, 2.5 to 4.2 bars for the Gunflint I F, and 5.2 to 17 bars for the Brockman I F. The P_{CO_2} values for the Gunflint and Brockman I Fs are in good agreement with those calculated from X_{CO_2} , respectively.

Introduction

The stability relations of iron-bearing minerals in low-grade metamorphic iron formations seem to be interpreted in the dominant $\text{H}_2\text{O}-\text{CO}_2$ region because the presence of hematite and absence of graphite suggest trivial proportions of other volatile species such as CH_4 , CO and H_2 (e. g. OHMOTO & KERRICK, 1977). Basic thermodynamic models for understanding of the mixed-volatile equilibria have been developed by GREENWOOD (1962, 1967) and KERRICK (1974, for a summary).

Qualitative discussion of the phase relations in the system $\text{Fe}-\text{Si}-\text{C}-\text{O}-\text{H}$ for the metamorphism of iron formations has been undertaken by BURT (1972) and MIYANO (1976b). But the system has not yet been well understood because of very poor experimental data. The iron-bearing phases in the system are hematite, magnetite, greenalite, minnesotaite, and

siderite. The last three phases are generally impure in the iron formations. Their compositions lie entirely on the joins of serpentine-greenalite, talc-minnesotaite, and magnetite-siderite (MIYANO, 1978 a, b). The ideal solution model may be applicable to these joins (MUELLER, 1973; MIYANO, 1976 b, 1978 b). Quartz is regarded as an excess phase in this paper.

The system $\text{Fe}-\text{Mg}-\text{Si}-\text{C}-\text{O}-\text{H}$ for the impure phases has not yet been quantitatively examined. The purpose of this paper is to define thermodynamically the stability relations of these phases in the system $\text{Fe}-\text{Mg}-\text{Si}-\text{O}-\text{C}-\text{H}$ under the $\text{H}_2\text{O}-\text{CO}_2$ mixed-volatile condition based on the phase equilibria data provided by MIYANO (1978 b).

Metamorphic reactions in the $\text{H}_2\text{O}-\text{CO}_2$ region

Most reactions in the system $\text{Fe}-\text{Mg}-\text{Si}-\text{C}-\text{O}-\text{H}$ have been predicted by FRENCH (1968, 1973), BURT (1972), KLEIN (1973), MIYANO (1976b) and others from mineral

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assemblages in the metamorphic iron formations. They are written in the presence of excess quartz as follows;

where abbreviations are Gn for greenalite, Hm for hematite, Mt for magnetite, Mi for minnesotaite, Gru for grunerite, Sd for siderite, and Qt for quartz, minerals in parentheses represent impure phases and other minerals are regarded as pure phases. According to FLORAN & PAPIKE (1975) and MIYANO (1976a, 1978a), Mg-rich minnesotaite (iron-talc) is associated with hematite and magnetite and then a reaction is proposed to account for this association:

Thermodynamic calculations in T-X_{CO₂} space

GREENWOOD (1962, 1967) developed the thermodynamic concept for determination of an equilibrium curve in the H₂O-CO₂ mixed-volatile region at constant P_{fluid} . This concept is based on the assumption of ideal mixing of H₂O and CO₂ volatile components and are generally consistent with the experimental determinations. GREENWOOD (1962, 1967) gave the following equation for the concept:

$$\left(\frac{\partial T}{\partial X_2} \right)_{P, \gamma=1} = \frac{RT^2}{\Delta H_r} \left(\frac{n_2}{X_2} - \frac{n_1}{X_1} \right) \dots (9)$$

The integrated expression is:

$$-\frac{1}{T} = A + \frac{R}{\Delta H_r} (n_2 \ln X_2 + n_1 \ln (1 - X_2)) \dots (10)$$

where subscripts P and γ in equation (9) denote constant pressure and activity coefficient of the volatile component, respectively, n is the number of moles of the volatile component, X is the mole fraction with a relation of $X_1 + X_2 = 1$, ΔH_r is the enthalpy change of a reaction and is not dependent upon the temperature, A is an integration constant, and R is gas constant. ΔH_r° (298) of reactions (1)

Table 1. The standard enthalpy changes of reactions.

Reaction No.	$\Delta H_{r, 298}^\circ$ (cal)	ΔV_s (cal/bar)
(1)	28,702	- 0.644
(2)	12,751	- 0.282
(3)	83,175	- 2.750
(4)	15,630	- 0.362
(5)	- 18,188	0.442
(6)	- 30,939	0.724
(7)	- 99,916	2.606
(8)	15,951	- 0.362

Data were taken from MIYANO (1976 a, 1978 b).

to (8) are listed in Table 1. If only a gas emanates in a reaction, equation (10) is rewritten as

$$\text{for CO}_2, \quad \ln X_{\text{CO}_2} = \frac{\Delta H_r}{R n_{\text{CO}_2}} \cdot \frac{T - T_r}{T \cdot T_r} \dots (11)$$

$$\text{for H}_2\text{O}, \quad \ln(1 - X_{\text{CO}_2}) = \frac{\Delta H_r}{R n_{\text{H}_2\text{O}}} \cdot \frac{T - T_r}{T \cdot T_r} \dots (12)$$

where T_r implies a reference temperature which is given from the T-P condition for the equilibrium reaction.

The determination of an univariant curve in T-X_{CO₂} space requires a knowledge of either a bracket (T,P) in the T-P space or (T, X_{CO₂}) in the T-X_{CO₂} space.

For reactions (1) to (4) and (8), the T-P conditions are estimated by the standard thermodynamic calculation using the data listed in MIYANO (1976b, 1978b) and fugacity data of CO₂ (RYZHENKO & VOLKOV, 1971) and those of H₂O (BURNHAM *et al.*, 1969) and are shown except reaction (8) in Fig. 1. The conditions of these reactions including impure phases are calculated by using their equilibrium constants.

In the case of reaction (2),

$$\log K_{(2)} = \log \frac{f_{\text{H}_2\text{O}} X_{\text{Mi}}}{X_{\text{Gn}}}$$

$$\log f_{\text{H}_2\text{O}} = \log K_{(2)} + \log X_{\text{Gn}} - \log X_{\text{Mi}} \quad (13)$$

where $K_{(2)}$ is the equilibrium constant of reaction (2), $f_{\text{H}_2\text{O}}$ is fugacity of pure water, and X_{Mi} and X_{Gn} are mole fractions Fe/(Fe+Mg) in minnesotaite and greenalite, respectively. The univariant curve of this reaction in the T-P space is expressed as a function of X_{Gn} and X_{Mi} . If X_{Mi} decreases at constant

Fig. 1. T-P diagram showing calculated univariant curves in the system Fe-Mg-Si-C-O-H. P_s is solid pressure and P_{fluid} is fluid pressure. For abbreviations see text. The numbered and dashed-numbered curves refer to the reactions in the text. They are drawn according to variations in X_{Sd} , X_{Gn} and X_{Mi} , (1) $X_{Gn}=1.0$, (1') $X_{Gn}=0.8$, (2) $X_{Gn}=X_{Mi}=0.8$ or 1.0, (2') $X_{Gn}=0.8$, $X_{Mi}=0.6$, (2'') $X_{Gn}=0.8$, $X_{Mi}=0.4$, (3) $X_{Mi}=1.0$, (4) $X_{Sd}=1.0$, (4') $X_{Sd}=0.8$, (4'') $X_{Sd}=0.6$.

X_{Gn} , the curve shifts toward lower temperatures (see Fig. 1). As X_{Gn} ranges from 0.8 to 0.95 in most iron formations, the largest deviation from an equilibrium curve of a reaction with pure greenalite is represented at $X_{Gn}=0.8$. Since the curve (2) in Fig. 1 is drawn at $X_{Gn}=0.8$ and $X_{Mi}=0.4$, 0.6 and 0.8, it has the same position at $X_{Mi}=0.8$ as at $X_{Gn}=X_{Mi}=1.0$ (pure phases), as understood from equation (13).

Similarly the curves of reactions (1) and (4) are drawn in Fig. 1 within the dominant ranges of the X_{Gn} (0.8 and 1.0) and X_{Sd} (mole fraction of siderite molecule, 0.6, 0.8 and 1.0, the siderite-magnesite solid solution is complete at temperatures as low as 300°C, ROSENBERG, 1963). In the case of reaction (8) where X_{Mi} is below 0.5, the T-P conditions are taken from the phase relations in the T- f_{O_2} diagram (MIYANO, 1978 b). They are 99°C ($X_{Mi}=0.5$), 105°C ($X_{Mi}=0.4$),

118°C ($X_{Mi}=0.3$) and 138°C ($X_{Mi}=0.2$) at $P_s=P_{H_2O}=1$ Kb.

Based on the (T, P) brackets estimated above, the univariant curves of reactions (1) to (4) and (8) are determined by using equations (11) or (12) for the T- X_{CO_2} space.

For reactions (5) to (7), the (T, X_{CO_2}) brackets are obtained diagrammatically from intersections of curves of reactions (1) and (4) for reaction (5), of reactions (2) and (5) for reaction (6), and of reactions (3) and (6) for reaction (7) in the T- X_{CO_2} space. In the field where reaction (8) occurs, the brackets are given from intersections of curves of reactions (4) and (8) for reaction (6), and of reactions (1) and (6) for reaction (5) in the space. On the basis of these (T, X_{CO_2}) brackets, the curves of reactions (5) to (7) are drawn by using equation (10) in the T- X_{CO_2} space.

Using the curves of reactions (1) to (8),

Fig. 2. T - X_{CO_2} diagram for the system Fe-Si-C-O-H. The numbered curves refer to the reactions in the text. All the curves are drawn for pure phases. Dashed line shows a boundary of one- and two-phase region in the H_2O - CO_2 system (data taken from TAKENOUCHI & KENNEDY (1964)). All of the reactions shown are considered to occur in the H_2O - CO_2 single-phase region.

the phase relations of iron-bearing minerals in the H_2O - CO_2 region are determined in the T - X_{CO_2} space (Figs. 2 to 5). Figs 2 and 3 are illustrated for pure phases, and Figs. 4 and 5 for impure phases. As shown in these figures, the relations are interpreted within the H_2O -rich region of the H_2O - CO_2 mixture. Parts of lower temperatures and X_{CO_2} in Fig. 2 are enlarged and demonstrated in Fig. 3, where the phase relations at $P_s = P_{\text{H}_2\text{O}} + P_{\text{CO}_2} = 2 \text{ Kb}$ are added by narrow solid lines.

Discussion

The phase equilibria without siderite have been examined in the system Fe-Mg-Si-O-H

Fig. 3. T - X_{CO_2} diagram for the system Fe-Si-C-O-H at $P_s = P_{\text{H}_2\text{O}} + P_{\text{CO}_2} = 1 \text{ Kb}$. The phase relations are same as in Fig. 2. Narrow solid curves are drawn at $P_s = P_{\text{H}_2\text{O}} + P_{\text{CO}_2} = 2 \text{ Kb}$.

by MIYANO (1978 b). Based on the results and the phase equilibria in the system Fe-Mg-Si-C-O-H presented here, the stability relations of iron-bearing phases and their significance in the low-grade metamorphism will be discussed within the H_2O - CO_2 single-phase region. In this system, two phases of CO_2 and siderite are added as already appeared.

Mineral assemblages in some low-grade metamorphic iron formation are briefly summarized below to make the present discussion clear. In the Biwabik I F (FRENCH, 1968) and Sokoman I F (KLEIN, 1974; KLEIN & FINK, 1976), the assemblage of greenalite-

minnesotaite-carbonates (mainly siderite and ankerite)-magnetite is common and hematite is rarely present in cherty taconite or silicate facies. The greenalite and minnesotaite are nearly close to pure phases ($X_{Gn}=0.8$ to 0.85 , $X_{Mi}=0.75$ to 0.85 for the Biwabik I F, $X_{Gn}=0.85$ to 0.95 , $X_{Mi}=0.85$ to 0.95 for the Sokoman I F, FLORAN & PAPIKE, 1975; KLEIN, 1974). $Fe/(Fe+Mg)(=X_{Sd})$ of siderite are 0.65 to 0.85 for the Biwabik I F, which were obtained from X-ray analyses by FRENCH (1968), and 0.75 to 0.95 for the Sokoman I F, which are taken from KLEIN (1974) and KLEIN & FINK (1976). In the Brockman I F, greenalite is generally absent, and the assemblages of minnesotaite-hematite-magnetite-carbonates and minnesotaite-magnetite-carbonates are usually observed. X_{Mi} of minnesotaite in the former assemblage ranges from about 0.2 to 0.3 and in the latter from about 0.3 to 0.4 . X_{Sd} of siderite is about 0.65 to 0.85 . Above compositional data are taken mainly from MIYANO (1978 a). For the Gunflint I F, the assemblages of greenalite-minnesotaite-hematite-carbonates, greenalite-minnesotaite-hematite-magnetite-carbonates, and greenalite-minnesotaite-magnetite-carbonates are probably common, but greenalite or minnesotaite is in places absent in each assemblage. From FLORAN & PAPIKE (1975), X_{Gn} , X_{Mi} and X_{Sd} are about 0.4 to 0.5 , 0.85 to 0.95 and 0.8 to 0.95 , respectively.

Since X_{Sd} varies up to 0.60 in the iron formations as described above, curves (4), (5) and (6) in Fig. 4 are drawn according to the variation in X_{Sd} , where both X_{Gn} and X_{Mi} are fixed conveniently at 0.80 which may be equivalent to lower values of the Sokoman and Biwabik I Fs. If the X_{Sd} becomes smaller, the stability regions of greenalite and minnesotaite shrink toward lower X_{CO_2} at constant temperature, and they shift up to higher temperatures at constant X_{CO_2} . If the X_{Mi} becomes smaller (dotted lines, $X_{Mi}=0.6$, in Fig. 4), the curve of reaction (2) shifts toward lower temperatures (this is also predicted from Fig. 1). Consequently, a greenalite-magnetite field shrinks considerably.

Fig. 4. T - X_{CO_2} diagram showing the phase relations with variation in X_{Sd} . X_{Sd} varies from 0.6 to 1.0 . Solid curves are drawn at $X_{Gn}=X_{Mi}=0.8$, dashed ones at $X_{Gn}=X_{Mi}=1.0$ (pure phases), and dotted ones at $X_{Gn}=0.8$ and $X_{Mi}=0.6$.

At $P_s = \text{total } P_f = 1 \text{ Kb}$, the T - X_{CO_2} conditions for low-grade metamorphisms of the Biwabik and Sokoman I Fs are determined by the similar way to the determination of the phase equilibria shown in Figs. 2 and 4. They are illustrated in Fig. 6 within the limits of the approximate range of X_{Sd} and temperature range¹⁾ estimated by MIYANO (1978 b). The minimum and maximum values of X_{CO_2} are about 0.004 (4 bars) and 0.007 (7 bars) for the Sokoman I F and about 0.0035 (3.5 bars) and 0.006 (6 bars) for the Biwabik I F, respectively. Numbers in parentheses refer to the approximate P_{CO_2} calculated from the X_{CO_2} values. In fact, the P_{CO_2} will be improved to a little higher values as mentioned later because X_{Sd} is dependent upon oxygen fugacity whose effect is not expressed in the T - X_{CO_2} space.

For the Dales Gorge Member of the Brockman I F, minnesotaite (X_{Mi} = about 0.2 to 0.3) is associated with hematite and magnetite but not with greenalite. Also no more substitution of Fe by Mg in greenalite than at X_{Gn} = 0.8 is generally expected in the iron formations (MIYANO, 1978 a, 1978 b). Accordingly, reaction (2) would not be at equilibrium during metamorphism and reaction (8) probably takes place to account for the minnesotaite-hematite-magnetite assemblage as already stated. In the Gunflint I F, reaction (2) is still possible at X_{Mi} = about 0.4 to 0.5, but reaction (8) can also take place since the iron-talc coexists with greenalite (X_{Gn} = 0.85 to 0.95). Above statements will be confirmed from the phase equilibria given below.

The phase relations including greenalite (X_{Gn} = 0.8), minnesotaite (X_{Mi} = 0.2, 0.3 and 0.4), and siderite (X_{Sd} = 0.8) are demonstrated in Fig. 5. According to the relations, the equilibrium curve of reaction (2) showing the association of greenalite-minnesotaite-magnetite (Figs. 2, 3 and 4) disappears and instead that of reaction (8) showing the association of minnesotaite(iron-talc)-hematite-magnetite appears. The field of the latter association extends toward higher X_{CO_2} with both of the decrease in X_{Mi} and increase in temperature. Although greenalite (X_{Gn} = 0.8) is not associated with iron-talc (X_{Mi} below 0.5), the greenalite can coexist with the iron-talc (X_{Mi} = 0.5) in the presence of hematite, magnetite and quartz at about 100°C and P_s = total P_f = 1 Kb, since curve (8) meets together with curve (1) (Fig. 5). Considering an intersection with curve (5), six phases; greenalite, iron-talc, hematite, magnetite, siderite and quartz, coexist together. This seems to be observed in the Gunflint I F.

At P_s = total P_f = 1 Kb, the T - X_{CO_2} conditions for low-grade metamorphism of the Gunflint and Brockman I Fs are determined within the limits of the approximate range of X_{Sd} and the temperature range²⁾ obtained by MIYANO (1978 b), and are shown in Fig. 6. The minimum and maximum values of X_{CO_2}

Fig. 5. T - X_{CO_2} diagram showing the phase relations with variation in X_{Mi} . Both X_{Sd} and X_{Gn} are fixed at 0.8. Solid curves are drawn at X_{Mi} = 0.3, narrow solid ones at X_{Mi} = 0.4, and dashed one at X_{Mi} = 0.2.

are about 0.0025 (2.5 bars) and 0.0045 (4.5 bars) for the Gunflint I F and about 0.0055 (5.5 bars) and 0.0178 (18 bars) for the Brockman I F, respectively. The P_{CO_2} values in parentheses is in good agreement with those calculated independently of the total P_f as described below.

1) and 2); The estimated temperature ranges are merely based on the variations in X_{Mi} and strictly also X_{Gn} . Using the ideal solution models applied to the variations, invariant points in the T - f_{O_2} diagram showing the stability relations of phases in the system Fe-Mg-Si-O-H can be used for estimate of temperatures and oxygen fugacities at constant P_s and $P_{\text{H}_2\text{O}}$ (see MIYANO, 1978 b for more explanation). Thus the estimated ranges indicate the possible metamorphic temperatures at $P_s = P_{\text{H}_2\text{O}} = 1$ Kbar and does not imply the uncertainties in the metamorphic temperatures. On the other hand, the temperatures are nearly unaltered with increasing X_{CO_2} at the part of lower X_{CO_2} than 0.02, that is, curves of reactions with H_2O only are almost parallel to the X_{CO_2} axis.

Fig. 6. T- X_{CO_2} conditions during low-grade metamorphism of some iron formations. The diagram is illustrated on the basis of the estimated temperatures (MIYANO, 1978 b) and the phase equilibria data reported in this paper. Solid univariant curves are drawn for pure phases.

The X_{Sd} varies depending on oxygen fugacity and P_{CO_2} at constant temperature. Then, the P_{CO_2} during metamorphism is estimated independently of the total fluid pressure by using reaction (4) and the following reaction at given temperatures and X_{Sd} .

In the cases of the Gunflint and Brockman I Fs where siderite coexists with hematite and magnetite, reaction (4) is used for the estimation. For the Biwabik and Sokoman I Fs where siderite is unlikely to coexist with hematite, reaction (14) is employed for it at the constant oxygen fugacity obtained by MIYANO (1978 b). The results are illustrated in terms of fugacity unit of carbon dioxide in common logarithm in Fig. 7. As MIYANO (1978 a) proposed, it is considered that the locational difference in four f_{CO_2} regions (dotted, in Fig. 7) is essentially related with that in oxygen fugacity rather than temperature. If we assume that a lower fugacity of CO_2 (below 50 bars) is nearly equal to P_{CO_2} because the fugacity coefficients are more than 0.94 below 50 bars at 150°C (data from MAJUMDAR & ROY, 1956), then the P_{CO_2} values are 2.5 to 4.5 bars for the Gunflint I F, 5.2 to 17 bars for the Brockman I F, 5.1 to 9.4 bars for the Biwabik I F and 5.5 to 9.8 bars for

the Sokoman I F. On the other hand, taking into account that the effect of P_{H_2O} on the equilibrium relations is almost negligible at lower temperatures (MIYANO, 1978 b) and the oxygen fugacity is buffered by an assemblage of hematite-magnetite, the P_{CO_2} values calculated from X_{CO_2} (Fig. 6, $f_{CO_2} = f_{CO_2}^* X_{CO_2}$, in which $f_{CO_2}^*$ is fugacity of pure carbon dioxide) may be also reasonable for the Gunflint and Brockman I Fs.

The metamorphic temperature in each iron formation is safely assumed to be constant because its stratigraphic thickness is below 200 m. The releasing degree of CO_2 from reactions with carbonates may be uniform at constant temperature in rocks as far as the carbonates are still stable. If the degree of the escape of CO_2 from the rocks is also uniform during low-grade metamorphism, the P_{CO_2} may be regarded to be constant in the system. It is possible under the conditions of constant temperature and P_{CO_2} that the variations in X_{Gn} , X_{Mt} and X_{Sd} in the iron formation may be caused by those in oxygen fugacity which are probably controlled by the reducing agent like carbonaceous matters. Such agent may be effective for frequently supplying a local high-reducing environment (MIYANO, 1976 a). This may bring about the local presence or absence of hematite in

Fig. 7. T- f_{CO_2} diagram showing the magnitude of P_{CO_2} during low-grade metamorphism.

A : Gunflint I F, B : Brockman I F (Dales Gorge M.), C : Biwabik I F, D : Sokoman I F. The diagram is illustrated on the basis of the temperatures and oxygen fugacities estimated by MIYANO (1978 b) and the variation in X_{Sd} .

the metamorphic iron formation.

Conclusion

The stability relations of iron-bearing minerals were discussed at constant total $P_f (= P_{\text{H}_2\text{O}} + P_{\text{CO}_2}) = 1 \text{ Kb}$ and lower temperatures on the basis of the GREENWOOD's thermodynamic model (1962, 1967). The relations are situated in the presence of excess quartz within the H_2O -rich region of the H_2O - CO_2 mixture.

The T- X_{CO_2} conditions for several low-grade metamorphic iron formations were determined according to the variations in X_{Gn} , X_{Mn} and X_{Sd} (on the assumption of ideal solutions) at the given temperatures. The conditions are largely dependent upon oxygen fugacity and then they are interpreted in the two T- X_{CO_2} spaces. The one is for a hematite-free condition probably equivalent to the Biwabik and Sokoman I Fs, and other is for a hematite-bearing condition equivalent to the Gunflint and Brockman I Fs. The former condition encounters generally the higher X_{CO_2} region than the latter.

P_{CO_2} during low-grade metamorphism of

several iron formations were estimated by two methods. For the hematite-bearing condition, the P_{CO_2} which is provided independently of the total fluid pressure is in good agreement with that by calculation from X_{CO_2} . But it is different to some extent for the hematite-free one, because the oxygen fugacity is not fixed. Thus, the P_{CO_2} for the Biwabik and Sokoman I Fs were calculated by using the given oxygen fugacity (MIYANO, 1978 b) from the equilibrium constant of reaction 3 siderite + $1/2\text{O}_2 = \text{Magnetite} + 3\text{CO}_2$.

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$\text{H}_2\text{O-CO}_2$ 混合気体領域の低温条件下における含鉄鉱物の安定関係

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(要 旨)

縞状鉄鉱層に産する含鉄鉱物の安定関係が、全流体圧 ($P_f = P_{\text{H}_2\text{O}} + P_{\text{CO}_2} = 1\text{Kb}$) 一定および低温条件下で、熱力学的に論ぜられた。

すべての安定関係は、 $\text{H}_2\text{O-CO}_2$ -相の H_2O に富んだ領域内で生ずるものと思われる。これらの安定関係から、いくつかの縞状鉄鉱層の変成時の $X_{\text{CO}_2}\text{-T}$ 条件は、Sokoman 含鉄累層で 0.004 から 0.007 ($130 \pm 5^\circ\text{C}$)、Biwabik 含鉄累層で 0.0035 から 0.006 ($130 \pm 5^\circ\text{C}$)、Gunflint 含鉄累層で 0.0025 から 0.0045 ($102 \pm 3^\circ\text{C}$)、Brockman 含鉄累層 (Dales Gorge 部層) で 0.0055 から 0.0178 ($128 \pm 10^\circ\text{C}$) と求められる。一般に、一定温度の場合、 X_{CO_2} は赤鉄鉱の存在しない条件下 (おそらく Sokoman および Biwabik 含鉄累層に相当) で

は、その存在する条件下 (Gunflint および Brockman 含鉄累層に相当) より低い。したがって、一定温度下では、前者は後者より低い P_{CO_2} を示すものと考えられる。

赤鉄鉱—磁鉄鉱—菱鉄鉱の共生と磁鉄鉱—菱鉄鉱の共生から、全流体圧 (P_f) とは独立に求められる変成時の P_{CO_2} は、Sokoman 含鉄累層で約 5.5 から 9.8 bars, Biwabik 含鉄累層で 5.1 から 9.4 bars, Gunflint 含鉄累層で 2.5 から 4.2 bars, Brockman 含鉄累層で 5.2 から 17 bars となる。

Gunflint および Brockman 両含鉄累層の P_{CO_2} 値は、それぞれ、上記の X_{CO_2} 値から求められる値とよく一致する。