PHASE RELATIONS IN THE SYSTEM $\text{CaO-FeO}_x\text{-SiO}_2$ IN $\text{H}_2\text{O-CO}_2$ MIXTURES

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The phase relations among calcite, wollastonite, ferrobustamite, andradite, hedenbergite, magnetite and quartz in $\text{H}_2\text{O-CO}_2$ mixtures have been estimated on the basis of previous work in the systems $\text{CaO-SiO}_2\text{-CO}_2$ and $\text{CaO-FeO}_x\text{-SiO}_2\text{-O}_2$. The upper limit of CO_2 content of the condition favorable to the formation of skarn involving andradite and/or hedenbergite is restricted by the following reactions:

From the andradite and hedenbergite fields, the skarn consisting of these minerals is inferred to be formed in $\text{H}_2\text{O-CO}_2$ fluids containing less 30 mole % CO_2 at 500°C , and 0.5 mole % at 300°C , respectively. When ferrobustamite is stable, the phase relations are more complex. The above mentioned values, however, are independent on the stability of ferrobustamite.

INTRODUCTION

Grandite garnet and/or clinopyroxene of diopside-hedenbergite series are the most important minerals which characterize the skarn-type ore deposits. They frequently contain a considerable amount of iron. Besides them, the ore deposits of this type are usually composed of calcite, magnetite and quartz with sulfides and oxides as ore minerals. For this reason, the phase relations among calcite, andradite, hedenbergite, magnetite and quartz should indicate the favorable conditions of formation of ore-bearing skarn.

In this paper, the writer tries to estimate quantitatively the phase relations in the system $\text{CaO-FeO}_x\text{-SiO}_2$ under the fluids composed of water and carbon dioxide, on the basis of previous studies of the system $\text{CaO-SiO}_2\text{-CO}_2$ and $\text{CaO-FeO}_x\text{-SiO}_2\text{-O}_2$.

Compositions of phases considered in this paper are shown on a $\text{CaO-FeO}_x\text{-SiO}_2$

plot regardless CO_2 (Fig. 1), and listed in Table 1 with their abbreviations and molar volumes calculated from the data compiled by Strunz (1970) and Yamanaka *et al.* (1977).

Table 1. List of minerals.

Symbol	Mineral Name	Chemical Formula	Molar Volume* ($\text{cal.bar}^{-1}\text{.mole}^{-1}$)
ca	calcite	CaCO_3	0.8802
mt	magnetite	Fe_3O_4	1.0630
qz	quartz	SiO_2	0.5421
wo	wollastonite	CaSiO_3	0.9544
fb	ferrobustamite	$\text{Ca}_2\text{FeSi}_2\text{O}_{18}$	5.5478
ad	andradite	$\text{Ca}_3\text{Fe}_2\text{Si}_3\text{O}_{12}$	3.1403
hd	hedenbergite	$\text{CaFeSi}_2\text{O}_6$	1.6294

* Calculated from the data compiled by Strunz (1970), except ferrobustamite (Yamanaka *et al.*, 1977).

SOME STABLE REACTIONS IN THE SYSTEM Ca-Fe-Si-C-O AND RELATIONSHIP AMONG THEM

Fig. 2 shows the schematic, isobaric T - f_{CO_2} relations among calcite, andradite, hedenbergite and quartz under a controlled oxygen fugacity. In this diagram, there are apparently four invariant points and eleven univariant curves. These univariant

curves are equilibrium boundaries for the reactions listed in Table 2. These reactions are combined one another as follows:

$$\text{Reaction (2)} = \frac{1}{2} \{ 9 \cdot \text{Reaction (3)} - \text{Reaction (1)} \} \quad (1)$$

$$\text{Reaction (3)} = \frac{1}{9} \{ \text{Reaction (1)} + 2 \cdot \text{Reaction (2)} \} \quad (2)$$

$$\begin{aligned} \text{Reaction (4)} &= \frac{1}{3} \{ \text{Reaction (2)} - \text{Reaction (1)} \} \quad (3) \\ &= \frac{1}{2} \{ 3 \cdot \text{Reaction (3)} - \text{Reaction (1)} \} \end{aligned}$$

$$\text{Reaction (6)} = 9 \{ \text{Reaction (5)} - \text{Reaction (1)} \} \quad (4)$$

$$\text{Reaction (7)} = \text{Reaction (6)} - \text{Reaction (2)} \quad (5)$$

$$\text{Reaction (8)} = \frac{1}{3} \{ \text{Reaction (2)} - \text{Reaction (1)} + 9 \cdot \text{Reaction (5)} \} \quad (6)$$

$$= \frac{1}{3} \{ \text{Reaction (2)} + \text{Reaction (6)} \}$$

Fig. 1. Compositions of crystalline phases in the system Ca-Fe-Si-C-O projected on the CaO-FeO_x-SiO₂ plane.

Fig. 2. Schematic analysis of phase relations in the system CaO-FeO-Fe₂O₃-SiO₂-CO₂ as a function of CO₂ fugacity and temperature. Numerals correspond to the number of reaction (see Table 2). Capital letters in circles show isobaric, f_{O_2} -defined invariant points (see Table 4). Abbreviations are shown in Table 1 and Fig. 1.

Table 2. Volume changes, enthalpy changes and entropy changes of some stable reactions in the system CaO-FeO-Fe₃O₄-SiO₂-CO₂-O₂ (at atmospheric pressure).

Reaction	Volume Change ΔV_s° (cal.bar ⁻¹)	Enthalpy Change ΔH° (kcal)	Entropy Change ΔS° (cal.deg ⁻¹)	Remarks*
(1) $3\text{Ca}_3\text{Fe}_2\text{Si}_3\text{O}_{12} = 9\text{CaSiO}_3 + 2\text{Fe}_3\text{O}_4 + \frac{1}{2}\text{O}_2$	1.2947	119.7	80.6	Gu (see S2)
(2) $3\text{Ca}_3\text{Fe}_2\text{Si}_3\text{O}_{12} + \text{Fe}_3\text{O}_4 + 9\text{SiO}_2 = 9\text{CaFeSi}_2\text{O}_6 + 2\text{O}_2$	-0.6982	261.8	130.8	Gu, K (Fig. 3)
(3) $\text{Ca}_3\text{Fe}_2\text{Si}_3\text{O}_{12} + 2\text{SiO}_2 = \text{CaSiO}_3 + 2\text{CaFeSi}_2\text{O}_6 + \frac{1}{2}\text{O}_2$	-0.0113	71.5	38.0	Eq. (2)/Gu
(4) $3\text{CaSiO}_3 + \text{Fe}_3\text{O}_4 + 3\text{SiO}_2 = 3\text{CaFeSi}_2\text{O}_6 + \frac{1}{2}\text{O}_2$	-0.6643	47.4	16.7	Eq. (3)/Gu
(5) $\text{CaCO}_3 + \text{SiO}_2 = \text{CaSiO}_3 + \text{CO}_2$	-0.4679	23.1	38.2	H-T, Gw (see S1)
(6) $9\text{CaCO}_3 + 2\text{Fe}_3\text{O}_4 + 9\text{SiO}_2 + \frac{1}{2}\text{O}_2 = 3\text{Ca}_3\text{Fe}_2\text{Si}_3\text{O}_{12} + 9\text{CO}_2$	-5.5058	88.6	263.5	Gu, H-T, Gw (see S2)
		139.9	316.0	T-L
(7) $9\text{CaCO}_3 + 9\text{CaFeSi}_2\text{O}_6 + \text{Fe}_3\text{O}_4 + \frac{5}{2}\text{O}_2 = 5\text{Ca}_3\text{Fe}_2\text{Si}_3\text{O}_{12} + 9\text{CO}_2$	-4.8076	-173.2	132.8	Eq. (5)/Gu, H-T, Gw
		-121.9	185.2	" /Gu, T-L
(8) $3\text{CaCO}_3 + \text{Fe}_3\text{O}_4 + 6\text{SiO}_2 = 3\text{CaFeSi}_2\text{O}_6 + 3\text{CO}_2 + \frac{1}{2}\text{O}_2$	-2.0680	116.8	131.4	Eq. (6)/Gu, H-T, Gw
		133.9	148.9	" /Gu, T-L
(9) $\text{CaCO}_3 + 2\text{CaFeSi}_2\text{O}_6 + \frac{1}{2}\text{O}_2 = \text{Ca}_3\text{Fe}_2\text{Si}_3\text{O}_{12} + \text{SiO}_2 + \text{CO}_2$	-0.4566	-48.3	0.2	Eq. (7)/Gu, H-T, Gw
		-42.6	6.0	" /Gu, T-L
(10) $2\text{CaCO}_3 + 2\text{CaFeSi}_2\text{O}_6 + \frac{1}{2}\text{O}_2 = \text{CaSiO}_3 + \text{Ca}_3\text{Fe}_2\text{Si}_3\text{O}_{12} + 2\text{CO}_2$	-0.9245	-25.2	38.4	Eq. (8)/Gu, H-T, Gw
		-13.8	50.1	" /Gu, T-L
(11) $3\text{CaCO}_3 + 3\text{CaFeSi}_2\text{O}_6 + \frac{1}{2}\text{O}_2 = 6\text{CaSiO}_3 + \text{Fe}_3\text{O}_4 + 3\text{CO}_2$	-0.7394	22.1	98.0	Eq. (9)/Gu, H-T, Gw
		39.2	115.4	" /Gu, T-L

* Gu = Gustafson (1974), Gw = Greenwood (1967), H-T = Harker and Tuttle (1956), K = Kurshakova (1971a,b), L = Liou (1974), S1 = Shoji (1976b), S2 = Shoji (1977), T-L = Taylor and Liou (1978)

Reaction (9) = Reaction (3) - Reaction (5) (7)

$$= \frac{1}{9} \{ 2 \cdot \text{Reaction (2)} - \text{Reaction (6)} \}$$

Reaction (10)

$$= 2 \{ \text{Reaction (5)} - \text{Reaction (3)} \} \quad (8)$$

$$= \text{Reaction (3)} + 2 \cdot \text{Reaction (9)} \quad (9)$$

Reaction (11) = $\frac{1}{3} \{ 2 \cdot \text{Reaction (1)}$

$$+ \text{Reaction (7)} \} \quad (9)$$

Equations (1) to (9) mean that the number of independent reactions is three. Accordingly, if three equilibrium boundaries among them, for example Reactions (1), (2) and (5), have been already determined, the other reactions can be calculated by the thermodynamic procedure which is derived from the reaction isobar of van't Hoff (Shoji, 1976b),

$$\ln K_p = - \frac{\Delta H^\circ + \Delta V_s^\circ (p_t - 1)}{RT} + \frac{\Delta S^\circ}{R}.$$

On the estimation, Lewis' rule (ideal mixing of fluids) has been assumed, and fugacity data of carbon dioxide and oxygen, except that of the Pb-PbO buffer (see Appendix), have been taken from Melnikova (1971) and Huebner (1971), respectively.

REACTIONS (1) TO (4)

At first, let us consider the stability relations among wollastonite, andradite, hedenbergite, magnetite and quartz. Fig.

Fig. 3. Schematic analysis of phase relations at isobaric invariant point I, where the assemblage wollastonite-andradite-hedenbergite-magnetite-quartz is stable. Solid lines represent the isobaric univariant phase relations, and dotted lines buffer curves. Numerals correspond to the number of reaction (see Table 2). Abbreviations are shown in Table 1. NNO and FMQ represent the Ni-NiO buffer and the fayalite-magnetite-quartz one, respectively.

3 shows the schematic, isobaric f_{O_2} - T relations in the system Ca-Fe-Si-O. In this diagram, there are one invariant point and four univariant curves. The univariant curves are equilibrium boundaries for Reactions (1) to (4). Equations (1) to (4) mean that the number of independent reactions is two. Phase relations in the system have been investigated by Куршакова (1970, 1971a, b), Куршакова и Аветисян (1974), Gustafson (1974) and Liou (1974), using solid phase oxygen buffers. The equilibrium boundary for Reaction (1) was determined by Gustafson (1974). The experiments were carried out between 500 bars and 3000 bars. The enthalpy and entropy changes, and equilibrium constant of Reaction (1) were calculated by Shoji (1977) (Table 1).

The equilibrium boundary for Reaction (2) was determined by Куршакова (1971a, b), and by Gustafson (1974). Куршакова (1971b) stated that at 1000 bars P_{fluid} hedenbergite is stable below an oxygen fugacity of 10^{-14} bar at 750°C and 10^{-23} bar at 400°C. On the contrary, Gustafson (1974) concluded that at 2000 bars p_{fluid} hedenbergite is stable below an f_{O_2} of 10^{-13} bar at 800°C and 10^{-28} bar at 400°C. Both of the conclusions do not agree with each other at the low temperature. The data of their experiments, however, are approximately coincident with each other, as shown in Fig. 4, which represents a $\{2 \ln f_{O_2} + \Delta V_s(p_f - 1)/RT\}$ vs. $1000/T$ plot of their results. The low temperature experiments performed by Куршакова (1971a, b) seem to have not been demonstrated as equilibrium, because the assemblage andradite-hedenbergite-magnetite-quartz was synthesized at 400°C within a wide f_{O_2} range. The straight line in Fig. 4 has been drawn for the data of Gustafson (1974).

This line is not necessarily inconsistent with the results of Куршакова (1971a, b). From this line, the equilibrium constant of Reaction (2) is as follows:

$$\ln K_p = - \frac{261.8 \cdot 10^3 - 0.6982 (p_f - 1)}{RT} + \frac{130.8}{R}.$$

The equilibrium boundary for Reaction (3) was determined by Куршакова (1970, 1971a), and by Liou (1974). Куршакова (1971a) stated that at 1000 bars p_{fluid} the assemblage andradite-quartz is stable above an oxygen fugacity of 10^{-13} bar at 800°C, and 10^{-20} bar at 500°C. On the contrary, Liou (1974) concluded that at 2000 bars

Fig. 4. A $\{2 \ln f_{O_2} + \Delta V_s(p_f - 1)/RT\}$ vs. $1000/T$ plot of the experimental data on Reaction (2) reported by Куршакова (1971a, b) and Gustafson (1974). Open symbols indicate reaction to andradite-magnetite-quartz; closed symbols to hedenbergite.

p_{fluid} this assemblage is stable above an f_{O_2} of 10^{-13} bar at 800°C , and 10^{-26} bar at 500°C . Both of the conclusions do not agree with each other at the low temperature. Liou (1974) suggested that the experiments performed by Курмакова (1970, 1971a) had not been successfully demonstrated as equilibrium because of starting materials, run duration and experimental methods. Fig. 5 shows a $\left\{ \frac{1}{2} \ln f_{\text{O}_2} + \Delta V_s(p_f - 1)/RT \right\}$ vs. $1000/T$ plot of their experimental results. The solid line in Fig. 5 have been drawn for the data of Liou (1974). From the line, the enthalpy and entropy changes of Reaction (3) are calculated to be 86.1 kcal and $52.5 \text{ cal. deg}^{-1}$, respectively. On the other hand, the Gustafson's (1974) results suggest that the enthalpy and entropy changes of Reaction (3) are 71.5 kcal and $38.0 \text{ cal. deg}^{-1}$, respectively (Table 2). These values have been calculated using equation (2). The dashed line in Fig. 5 shows the calculated equilibrium boundary for Reaction (3). The dashed line is not necessarily inconsistent with the results of Курмакова (1970, 1971a), while it does not agree with the results of Liou (1974). Since Курмакова (1970, 1971a) and Liou (1974) carried out their experiments without any attention to the formation of ferrobustamite, $\text{Ca}_5\text{FeSi}_6\text{O}_{18}$ (see the section following the next), it is inferred that their experiments were not

Fig. 5. A $\left\{ \frac{1}{2} \ln f_{\text{O}_2} + \Delta V_s(p_f - 1)/RT \right\}$ vs. $1000/T$ plot of the experimental data on Reaction (3) reported by Курмакова (1970, 1971a) and Liou (1974). Open symbols indicate reaction to andradite-quartz; closed symbols to wollastonite (or ferrobustamite ?)-hedenbergite.

demonstrated as equilibrium. For this reason, the writer believes that the values obtained from the results of Gustafson (1974) are more accurate than those on the results of Курмакова (1970, 1971a) and Liou (1974)*.

The enthalpy and entropy changes of Reaction (4) can be calculated using equation (3) or (4). They are 47.4 kcal and $16.7 \text{ cal. deg}^{-1}$, respectively (Table 2).

The enthalpy and entropy changes of Reactions (1) to (4) are listed in Table 2, and the f_{O_2} - T relations of the reactions

* There are two other reasons that the writer considers thus. (i) On the basis of the results of Курмакова (1970, 1971a) and Liou (1974), the lowest temperature of hedenbergite field is calculated to be 625°C and 540°C at the oxygen fugacities defined by the NNO buffer and the FMQ buffer, respectively. These values seem to be too high for the formation of hedenbergite, because it is inferred that the oxygen fugacities favorable to the formation of ore-bearing skarn are between the MH buffer and the FMQ buffer (Shimazaki, 1974; Shoji 1978), and the temperatures are about 400°C or lower (Shoji, 1975, 1978). On the contrary, (ii) the thermochemical data of Reaction (1) determined from the Gustafson's (1974) results appear to have a high reliability, because the equilibrium boundary for Reaction (6) calculated from the data is nearly coincident with the one calculated only from the thermodynamic properties in spite of the independent procedure (Shoji, 1977).

are shown in Table 3.

REACTIONS (5) TO (11)

The equilibrium boundary for Reaction (5) was experimentally determined by Harker and Tuttle (1956) and Greenwood (1967). On the basis of the results, the enthalpy and entropy changes were calculated by Shoji (1976b).

The equilibrium boundary for Reaction (6) was thermodynamically calculated by Shoji (1977), and was experimentally determined by Taylor and Liou (1978). According to the former, when oxygen fugacity is represented by the MH buffer, the equilibrium boundary for Reaction (6) at 2000 bars approximately passes through the points: $T=550^{\circ}\text{C}$, $X_{\text{Co}_2}=44$ mole %; and $T=630^{\circ}\text{C}$, $X_{\text{Co}_2}=100$ mole %. Meanwhile, according to the latter, Reaction (6) occurs at $T=550\pm 10^{\circ}\text{C}$ at $X_{\text{Co}_2}=22$ mole %, $T=596\pm 8^{\circ}\text{C}$ at $X_{\text{Co}_2}=50$ mole %, and $650\pm 10^{\circ}\text{C}$ at 100 mole %. According to Taylor and Liou (1978), the enthalpy and entropy changes of Reaction (6) are 139.9 kcal and $316.0\text{ cal.deg}^{-1}$, respectively. These values differ from those estimated by Shoji (1977) over the limit of error. In the following statement, the case S means the discussion based on the values of Shoji (1977), and the case T means that on the results of Taylor and Liou (1978).

The enthalpy and entropy changes of Reactions (7) to (11) can be calculated using equations (6) to (10), respectively. The calculated values are listed in Table 2.

PHASE RELATIONS AMONG CALCITE, WOLLASTONITE, ANDRADITE, HEDENBERGITE, MAGNETITE AND QUARTZ

The $\log f_{\text{O}_2}$ - P - T relations of equilibrium boundaries for Reactions (1) to (4) are

listed in Table 3. The $\log f_{\text{Co}_2}$ - $\log f_{\text{O}_2}$ - P - T relations of the equilibrium boundaries for Reactions (5) to (11) are also listed in Table 3.

Fig. 6 shows the phase relations among calcite, wollastonite, andradite, hedenbergite, magnetite and quartz in H_2O - CO_2 fluids under the conditions where fluid pressures are 1000 bars and 2000 bars, and oxygen fugacities are defined by the NNO buffer and the FMQ buffer. The diagrams are drawn on the case S. The equilibrium boundary for Reaction (4) does not exist, because it is calculated to pass through the high temperature region.

Points A, B, C and D in Fig. 2 are invariant under a specified pressure and a defined oxygen fugacity. Among them, however, only points A and B are significant under high oxygen fugacities, such as the NNO buffer (Table 4, Figs. 6a and c). Meanwhile point C is significant under low oxygen fugacities, such as the FMQ buffer (Table 4, Figs. 6b and d), too. The mineral assemblages, temperatures and CO_2 contents at these isobaric, f_{O_2} -defined invariant points are given in Table 4. According to Table 4, the X_{Co_2} values of point A are smaller on the case T than the case S. The difference between both cases is about 0.4 in $\log X_{\text{Co}_2}$ (NNO buffer) or 1.0 (FMQ buffer). On the contrary, the X_{Co_2} values of point B are approximately equal to each other between the cases S and T. Consequently, on the case T, the point A sits on the CO_2 -poor position, and lines 7, 8 and 9 pass through the slightly CO_2 poor regions, compared with the diagrams shown in Fig. 6.

SYSTEM INVOLVING FERROBUSTAMITE (IRON-WOLLASTONITE)

Recently, ferrobustamite (iron-wo-

Fig. 6. Calculated X_{CO_2} - T relations of equilibrium boundaries for some stable reactions in the system $\text{CaO-FeO-Fe}_2\text{O}_3\text{-SiO}_2\text{-CO}_2\text{-H}_2\text{O}$. Numerals correspond to the number of reaction (see Tables 2 and 3). Capital letters in circles show the isobaric, f_{O_2} -defined invariant points (see Table 4). Abbreviations are shown in Table 1 and Fig. 1. Fluid pressures and oxygen fugacities are respectively as follows: (a) 1000 bars and Ni-NiO buffer, (b) 1000 bars and fayalite-magnetite-quartz buffer, (c) 2000 bars and Ni-NiO buffer, and (d) 2000 bars and fayalite-magnetite-quartz buffer.

Ilstonite) have been reported from many skarn-type ore deposits of Japan (e.g. Matsueda, 1973a; Shimazaki and Yamana, 1973). The composition of ferrobustamite is $\text{Ca}_5\text{FeSi}_6\text{O}_{18}$ on the join $\text{CaSiO}_3\text{-CaFeSi}_2\text{O}_6$. For this reason, if ferrobustamite is stable, the tie-line between andradite and quartz is cut by the reaction,

instead of Reaction (3). Accordingly, ferrobustamite may have been formed by the syntheses carried out by Курмакова (1970, 1971a) and by Liou (1974). The formation of ferrobustamite is one of the

Table 3. Equations of equilibrium boundaries for Reactions (1) to (11) and (A1) in CO₂-O₂ mixtures.

Case*	Equilibrium Boundary
Reaction (1)	$\log f_{O_2} = -52.32 \cdot 10^3/T + 35.20 - 0.566 \cdot (p_f - 1)/T$
Reaction (2)	$\log f_{O_2} = -28.60 \cdot 10^3/T + 14.29 + 0.076 \cdot (p_f - 1)/T$
Reaction (3)	$\log f_{O_2} = -31.24 \cdot 10^3/T + 16.61 + 0.005 \cdot (p_f - 1)/T$
Reaction (A1)	$\log f_{O_2} = -37.58 \cdot 10^3/T + 22.89 - 0.006 \cdot (p_f - 1)/T$
Reaction (4)	$\log f_{O_2} = -20.70 \cdot 10^3/T + 7.32 + 0.290 \cdot (p_f - 1)/T$
Reaction (5)	$\log f_{CO_2} = -5.06 \cdot 10^3/T + 8.35 + 0.102 \cdot (p_f - 1)/T$
Reaction (6)	S $\log f_{CO_2} = -2.15 \cdot 10^3/T + 6.40 + 0.134 \cdot (p_f - 1)/T + 1/18 \cdot \log f_{O_2}$
	T $\log f_{CO_2} = -3.40 \cdot 10^3/T + 7.67 + 0.134 \cdot (p_f - 1)/T + 1/18 \cdot \log f_{O_2}$
Reaction (7)	S $\log f_{CO_2} = 4.21 \cdot 10^3/T + 3.22 + 0.117 \cdot (p_f - 1)/T + 5/18 \cdot \log f_{O_2}$
	T $\log f_{CO_2} = 2.96 \cdot 10^3/T + 4.50 + 0.117 \cdot (p_f - 1)/T + 5/18 \cdot \log f_{O_2}$
Reaction (8)	S $\log f_{CO_2} = -8.51 \cdot 10^3/T + 9.57 + 0.151 \cdot (p_f - 1)/T - 1/6 \cdot \log f_{O_2}$
	T $\log f_{CO_2} = -9.75 \cdot 10^3/T + 10.85 + 0.151 \cdot (p_f - 1)/T - 1/6 \cdot \log f_{O_2}$
Reaction (9)	S $\log f_{CO_2} = 10.56 \cdot 10^3/T + 0.05 + 0.100 \cdot (p_f - 1)/T + 1/2 \cdot \log f_{O_2}$
	T $\log f_{CO_2} = 9.32 \cdot 10^3/T + 1.32 + 0.100 \cdot (p_f - 1)/T + 1/2 \cdot \log f_{O_2}$
Reaction (10)	S $\log f_{CO_2} = 2.75 \cdot 10^3/T + 4.20 + 0.101 \cdot (p_f - 1)/T + 1/4 \cdot \log f_{O_2}$
	T $\log f_{CO_2} = 1.51 \cdot 10^3/T + 5.48 + 0.101 \cdot (p_f - 1)/T + 1/4 \cdot \log f_{O_2}$
Reaction (11)	S $\log f_{CO_2} = -1.61 \cdot 10^3/T + 7.14 + 0.054 \cdot (p_f - 1)/T + 1/6 \cdot \log f_{O_2}$
	T $\log f_{CO_2} = -2.85 \cdot 10^3/T + 8.41 + 0.054 \cdot (p_f - 1)/T + 1/6 \cdot \log f_{O_2}$

* S = Shoji (1977), T = Taylor and Liou (1978).

Table 4. List of some isobaric, f_{O_2} -defined invariant points in the system CaO-FeO-Fe₂O₃-SiO₂-CO₂-O₂-H₂O.

Mineral Assemblage		HNO Buffer				FMQ Buffer			
		Temp.	$X_{CO_2}(\log X_{CO_2})$	$X_{CO_2}(\log X_{CO_2})$		Temp.	$X_{CO_2}(\log X_{CO_2})$	$X_{CO_2}(\log X_{CO_2})$	
			Case S*	Case T*			Case S*	Case T*	
Point A	calcite-andradite-hedenbergite-magnetite-quartz	1000 bars	467°C	17. (-0.8)	6.3 (-1.2)	272°C	0.37 (-2.4)	0.036 (-3.4)	
		2000	460	7.5 (-1.1)	2.8 (-1.5)	275	0.22 (-2.7)	0.022 (-3.7)	
Point B	calcite-wollastonite-andradite-hedenbergite-quartz	1000	603	37. (-0.4)	26. (-0.6)	461	3.1 (-1.5)	1.2 (-1.9)	
		2000	609	19 (-0.7)	13. (-0.9)	475	1.8 (-1.7)	0.71 (-2.1)	
Point C	calcite-wollastonite-andradite-hedenbergite-magnetite	1000	-	-	-	766	77. (-0.1)	92. (-0.0)	
		2000	-	-	-	791	45. (-0.3)	57. (-0.2)	

* S = Shoji (1977), T = Taylor and Liou (1978)

probable explanations for the incoincidence between the results of Liou (1974) and those Gustafson (1974), which is shown in Fig. 5. Let us consider the case that the experiments performed by Кypмакова (1970, 1971a) and by Liou (1974) indicate the equilibrium boundary for Reaction (A1). The calculated enthalpy and entropy changes of Reaction (A1) are 345.0 kcal and 209.5 cal.deg⁻¹, respectively. When ferrobustamite is stable, besides the previously mentioned reactions the following five reactions occur in the system Ca-Fe-Si-O:

These reactions are obtained by the linear combinations of Reactions (A1) and (2) or (3). In this case Reaction (4) is not stable.

Fig. 7a shows the $\log f_{O_2}$ -1000/T relations of equilibrium boundaries for Reactions (A1) to (A6), which are calculated on the assumption that the equilibrium boundary for Reaction (A1) was demonstrated by the experiments of Кypмакова (1970, 1971a) and Liou (1974).

Fig. 7a is not sufficient in the

Fig. 7. (a upper) Calculated $\log f_{\text{O}_2}$ - $1000/T$ relations of equilibrium boundaries for Reactions (A1) to (A6) to contain ferrobustamite. The $\log f_{\text{O}_2}$ - $1000/T$ relations of Reactions (1) to (3) are shown in Table 3. Dashed lines indicate the equilibrium boundaries to be excluded from Fig. 3 because of the appearance of ferrobustamite. Dotted lines represent $\log f_{\text{O}_2}$ - $1000/T$ relation of magnetite-hematite (MH) buffer, Ni-NiO (NNO) buffer, and fayalite-magnetite-quartz (FMQ) buffer (after Huebner, 1971). (b, lower) Schematic $\log f_{\text{O}_2}$ - $1000/T$ relations of equilibrium boundaries for Reaction (A1) to (A6), in the case that ferrobustamite breaks down to the assemblage wollastonite-hedenbergite with the increase of temperature.

quantitative sense. The experiments on Reaction (A1) used for the calculation were

carried out at temperatures from 550°C to 700°C (Fig. 5), while the result obtained by

the calculation indicates that Reaction (A1) takes place between 740°C and 790°C (Fig. 7a). That is, the calculated result does not satisfy the assumption which was taken to obtain it. This disagreement probably suggests that the experiments of Курманова (1970, 1971a) and Liou (1974) were not in equilibrium because of the existence of both of wollastonite and ferrobustamite. Fig. 7a does not also agree with the mode of occurrence of ferrobustamite. According to Fig. 7a, at any oxygen fugacity ferrobustamite is not stable below 740°C. Ferrobustamite, however, is presumed to be stable at the lower temperatures, because it is frequently found in skarn-type ore deposits, which are inferred to be formed below the melting temperatures of granitic rocks, and probably at temperatures of about 400°C or lower (Shoji, 1975, 1978).

On the other hand, Fig. 7a is not contradictory to the experimental results of Rutstein (1971) and the field evidence of ferrobustamite in the qualitative sense. According to Rutstein (1971), hedenbergite is replaced by andradite, wollastonite solid solution (may be ferrobustamite) and quartz at values of oxygen fugacity higher than the NNO buffer. This result agrees with the fact that the equilibrium boundary for Reaction (A1) passes between the MH buffer line and the NNO one in Fig. 7a. Any report does not describe ferrobustamite coexisting with magnetite from skarn (Matsueda, 1973a, b, 1974; Shimazaki and Yamanaka, 1973; Shimazaki and Bunno, 1976; Matsuoka, 1976; Sato, 1978; Matsueda and Arai, 1978). This seems to correspond to the fact that the assemblage ferrobustamite-magnetite is stable at higher temperatures than the assemblage andradite-hedenbergite (Fig. 7a).

If the enthalpy change of Reaction (A1) is smaller than the previously stated value in equilibrium state, the slopes of equilibrium boundaries for Reactions (A1) and (A3) are gentler than those shown in Fig. 7a, and then Reaction (A2) takes place at a lower temperature. It is expected, however, that the slope of line (A1) is surely steeper than that of line (3). If the slope is gentler, ferrobustamite breaks down to the assemblage wollastonite-hedenbergite with the increasing temperature, as shown in Fig. 7b. This does not agree with the considerations of Rutstein (1971), Shimazaki and Yamanaka (1973) and Matsueda (1974), according to which ferrobustamite exists stably between wollastonite and hedenbergite at high temperatures.

The schematic X_{CO_2} - T diagrams (Fig. 8) of some equilibrium boundaries in the system $\text{CaO-FeO-Fe}_2\text{O}_3\text{-SiO}_2\text{-CO}_2$ involving ferrobustamite were drawn on the basis of Fig. 6d. At low temperatures, ferrobustamite breaks down to the assemblage wollastonite-andradite-quartz or the assemblage wollastonite-hedenbergite by Reaction (A3) or (A2), respectively. Reactions (A3) and (A2) take place respectively at the higher and lower oxygen fugacities than that defined by the assemblage wollastonite-andradite-hedenbergite-quartz. Consequently, two diagrams corresponding to the high and low oxygen fugacities are illustrated in Fig. 8.

Compared with Fig. 7d, more six isobaric, f_{O_2} -defined invariant points appear in Fig. 8. The mineral assemblages at the points are as follows: calcite-ferrobustamite-andradite-hedenbergite-quartz at B', calcite-wollastonite-ferrobustamite-andradite-magnetite at C', calcite-wollastonite-ferrobustamite-andradite-quartz at P, calcite-ferrobustamite-andradite-hedenbergite-mag-

Fig. 8. Schematic analysis of phase relations in the system $\text{CaO-FeO-Fe}_2\text{O}_3\text{-SiO}_2\text{-CO}_2$ involving ferrobustamite as a functions of CO_2 fugacity and temperature. The upper (a) and lower (b) diagrams correspond respectively to the higher and lower oxygen fugacities than that represented by the assemblage wollastonite-andradite-hedenbergite-quartz. Capital letters in circles show the isobaric, f_{O_2} -defined invariant points. The mineral assemblages are as follows: calcite-ferrobustamite-andradite-hedenbergite-quartz at B', calcite-wollastonite-ferrobustamite-andradite-magnetite at C', calcite-wollastonite-ferrobustamite-andradite-quartz at P, calcite-ferrobustamite-andradite-hedenbergite-magnetite at Q, calcite-ferrobustamite-hedenbergite-magnetite-quartz at R, and calcite-wollastonite-ferrobustamite-hedenbergite-quartz at S. Abbreviations are shown in Table 1 and Fig. 1.

netite at Q, calcite-ferrobustamite-hedenbergite-magnetite-quartz at R, and

calcite-wollastonite-ferrobustamite-hedenbergite-quartz at S (unstable at low oxygen

fugacities, i.e. $f_{O_2} < \text{wo-ad-hd-qz}$ assemblage, Fig. 8b).

DISCUSSION

At oxygen fugacities lower than the value represented by the FMQ buffer, not only fayalite but also ferrotremolite is stable (Ernst, 1966). Since these minerals are scarcely found in skarn, they do not be discussed in this paper. Accordingly, Figs. 6b and d represent the phase relations at the value slightly higher than the oxygen fugacity defined by the FMQ buffer.

Figs. 6 and 8 are significant only on the condition where the oxygen fugacity in the system is controlled by the NNO or FMQ buffer. Such condition seems to simulate well the formation of skarn for the following reasons: (i) It is expected that the oxygen fugacity during the formation is buffered by any of reactions, or that it is controlled by the nature of $\text{H}_2\text{O}-\text{CO}_2$ fluid. (ii) The curves of solid oxygen buffers are approximately parallel to one another (e.g. Fig. 7). (iii) Many of univariant assemblage involving skarn minerals, such as Reactions (2), (3) and (A1), show the f_{O_2} - T relation which is slightly steeper than the buffer curves, but approximately parallel to them (Fig. 7). (iv) The f_{O_2} - T relation of $\text{H}_2\text{O}-\text{CO}_2$ fluid with excess carbon, by which the fluid drops in oxygen fugacity, is approximately parallel to the buffer curves (Shoji, 1978). Consequently, the following discussion is carried out for the system, whose oxygen fugacity changes parallel to any of the solid oxygen buffer curves.

The difference between Figs. 6 and 8, which is caused by the existence of ferrobustamite, appears most distinctly at the isobaric, f_{O_2} -defined invariant points. Though point A is not drawn in Fig. 8, it

remains in that condition. At low oxygen fugacities (Fig. 8b), point B remains, too. At high oxygen fugacities (Fig. 8a), however, it is replaced by point B', where calcite, andradite, hedenbergite and quartz associated with ferrobustamite instead of wollastonite. Point C is also replaced by point C', where calcite, wollastonite, andradite and magnetite coexist with ferrobustamite instead of hedenbergite. In Fig. 8, points P, Q, R and S (only at low f_{O_2}) appear.

In Fig. 6, only four equilibrium boundaries, that is Reactions (5), (7), (8) and (10), exist between the wollastonite-andradite field and the calcite-magnetite-quartz one. On the contrary, nine boundaries exist in Fig. 8, though a few of reactions are different between Figs. 8a and b.

The temperature of point B is about 610°C at the NNO buffer, and 470°C at the FMQ buffer. Fig. 7 suggests that the temperature of point B' is higher than that of point B. If ore-bearing skarns are formed below 400°C (Shoji, 1975, 1978), the temperature of formation is inferred to be below point B or B'. On the contrary, ferrobustamite occurring in mineralized skarn is frequently accompanied with Mg-poor hedenbergite. Consequently, ferrobustamite-bearing skarn is inferred to have been formed at the temperature above point B' or S. This disagreement depends mainly upon the fact that the slope of equilibrium boundary for Reaction (A1) is too steep as stated previously. Since the slope is inferred to be necessarily steeper than line (3) as mentioned previously, however, the temperature of point B' is always higher than that of point A, which is the lower limit of the hedenbergite field. If the slope of line (A1) is parallel to that of line (3), and the isobaric invariant point where line (2) intersects line (A1) in Fig. 6

scarcely move*, the temperature of point B' is calculated to be about 450°C at the FMQ buffer. If the limit of hedenbergite field is higher in f_{O_2} and low in temperature than the values determined by Gustafson (1974), it is expected that the assemblage ferrobustamite-hedenbergite is stable below this temperature.

The calcite-magnetite-quartz field contacts with the ferrobustamite one, the hedenbergite one, and the andradite one from high to low temperatures (Figs. 6 and 8). Accordingly, under the condition where hedenbergite is stable, the ferrobustamite field is always included in the hedenbergite one (Fig. 8). From Fig. 6, the upper limit of CO_2 content of the condition favorable to the formation of skarn involving andradite and/or hedenbergite is inferred to be as follows: $X_{\text{CO}_2}=30$ mole % at 500°C and $X_{\text{CO}_2}=0.8$ mole % at 300°C at $p_t=1000$ bars and the NNO buffer (Fig. 6a); $X_{\text{CO}_2}=50$ mole % at 500°C and $X_{\text{CO}_2}=0.7$ mole % at 300°C at $p_t=1000$ bars and the FMQ buffer (Fig. 6b); $X_{\text{CO}_2}=15$ mole % at 500°C and $X_{\text{CO}_2}=0.4$ mole % at 300°C at $p_t=2000$ bars and the NNO buffer (Fig. 6c); $X_{\text{CO}_2}=25$ mole % at 500°C and $X_{\text{CO}_2}=0.4$ mole % at 300°C at $p_t=2000$ bars and the FMQ buffer (Fig. 6d). Roughly speaking, the CO_2 content of $\text{H}_2\text{O-CO}_2$ fluid in which ore-bearing skarn involving andradite and/or hedenbergite was formed is less than about 30 mole % at 500°C and 0.5 mole % at 300°C.

On the other hand, the experiments of Taylor and Liou (1978) indicate that the CO_2 -richest limit of the andradite field is 100 mole % at 650°C and 22 mole % at 550°C. The stability limit of andradite

extrapolated to low temperatures from this result passes 0.07 mole % at 300°C. This is about one figure lower than the estimated value. The difference is larger than the considerable amount of estimation error. It is not clear what causes this incoincidence. The non-ideality of mixed fluid is one of the probable interpretations.

In some skarns, clinopyroxene occurs closer to limestone than garnet, and *vice versa* in other skarns. It is possible to explain the genesis of the normal zonal arrangement of garnet and clinopyroxene and the reverse one by the mixing of H_2O and CO_2 fluids having different oxygen fugacities (Shoji, 1976). According to Gustafson (1974), andradite coexists stably with hedenbergite between the oxygen fugacities approximately represented by the NNO and IM buffers. Consequently, under such condition, the formation of both minerals is independent on the oxygen fugacity. The mineral associating with calcite and quartz changes from andradite to hedenbergite by Reaction (9) with the increase of CO_2 fugacity. It is expected from this fact that hedenbergite occurs in the limestone side where carbon dioxide is generated by the decomposition of calcite. The typical example is found in the zoned skarn of the Yaguki mine, Fukushima Prefecture. According to Shimazaki (1969), the succession is as follows; slate, epidote skarn, andradite skarn, clinopyroxene skarn, quartz-scheelite rock and limestone. The andradite skarn consists chiefly of andradite with small amounts of calcite, quartz and others. If zoned skarn was formed at $T=300\text{--}400^\circ\text{C}$, $p_t=1000\text{--}2000$ bars, and $f_{\text{O}_2}=\text{FMQ buffer}$, the CO_2 content is inferred to

* Reaction (2) occurs only at the temperatures below the value represented by point J in Fig. 7a. Since Gustafson (1974) experimented on Reaction (2) up to 850°C, the temperature of point J is inferred not to change largely from point I.

have been 0.3–1 mole % at the place along the boundary between the andradite and hedenbergite skarns (Fig. 6). The similar zoned skarn is observed in the Doshinkubo deposit, the Chichibu mine, Saitama Prefecture, where the zones are characterized by garnet, magnetite and hedenbergite from quartz diorite to marble (Shoji, 1975). Each zone consists more or less garnet, clinopyroxene and calcite, but free from quartz. The mineral assemblage indicates that the zoned skarn was formed under the condition represented by the triangle restricted by lines 7, 9, 10 in Fig. 2. If this zoned skarn also was formed under the same condition assumed for the Yaguki mine, the CO₂ content is inferred to have been 0.3–1 mole % (Fig. 6). Both of the inferred values are equal to each other, because line 7 passes through the vicinities of lines 9 and 10. The zoned skarns of both mines are inferred to have been under the similar condition, but by the different mechanism. In the Chichibu mine, the formation of zoned skarn was due to the different rate of migrating ions. On the contrary, the causes forming the zonal arrangement in the Yaguki mine are not only the difference among migration rates, but also the CO₂ content of skarn-forming fluid.

CONCLUSION

The phase relations among calcite, wollastonite, ferrobustamite, andradite, hedenbergite, magnetite and quartz have been considered on the basis of previous work.

(1) Table 3 and Fig. 6 shows the equilibrium boundaries for Reactions (1) to (11) in H₂O–CO₂ mixtures under fluid pressures of 1000 bars and 2000 bars.

(2) Fig. 7 shows the schematic f_{O_2} – T

relations of some univariant assemblages in the system Ca–Fe–Si–O involving ferrobustamite.

(3) When ferrobustamite is stable, the phase diagrams shown in Fig. 6 must be modified as shown in Fig. 8.

(4) Fig. 6 indicates that the CO₂ content of H₂O–CO₂ fluid in which ore-bearing skarn containing andradite and/or hedenbergite was formed is less than about 30 mole % at 500°C and 0.5 mole % at 300°C, respectively.

(5) From this estimation, for example, the zoned skarns of the Yaguki mine and the Chichibu mine are inferred to have been formed in the fluids containing 0.3–1 mole % CO₂.

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APPENDIX

Using the thermochemical data compiled by Robie and Waldbaum (1968), the log f_{O_2} – T relation of the Pb–PbO buffer has been computed as follows:

$$\log f_{O_2} = 10.55 - \frac{22880}{T} + 0.0589 \cdot \frac{p - 1}{T},$$

where f_{O_2} is oxygen fugacity (bar), T is temperature (°K), and p is pressure (bar). The values calculated from the equation is nearly coincident with the values of Курманова (1971a).

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H₂O-CO₂ 混合流体中における CaO-FeO_x-SiO₂ 系の相関係

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H₂O-CO₂ 混合流体における方解石, 鉄バスタム石 (ferrobustamite), 灰バンザクロ石, ヘデン輝石, 磁鉄鉱, 石英の相関係を, 従来発表されている CaO-SiO₂-CO₂ 系および CaO-FeO_x-SiO₂-O₂ 系の研究結果をもとに考察した。灰バンザクロ石またはヘデン輝石を含むスカルの生成に適した条件の CO₂ 量の上限は, 次の2つの反応,

により決められる。灰バンザクロ石とヘデン輝石の安定領域から, これらの鉱物を含むスカルンを生成した H₂O-CO₂ 混合液体中の CO₂ 量は, 500°C で 30mole%, 300°C で 0.5mole% を越えないと推定される。もし鉄バスタム石が安定な場合には, この系の相関係はさらに複雑となる。しかし, 上述した値はその安定性に無関係である。