Evaporation metamorphism in the early solar nebula — evaporation experiments on the melt $\text{FeO-MgO-SiO}_2\text{-CaO-Al}_2\text{O}_3$ and chemical fractionations of primitive materials

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Evaporation experiments were performed in vacuo on the multicomponent melt, $\text{FeO-MgO-SiO}_2\text{-CaO-Al}_2\text{O}_3$ with the solar elemental abundances. The analysis of experimental results shows that the rate-determining step of evaporation is the vaporization reactions occurring on the melt surface, amongst other possible rate processes. The reaction modes are determined for the components, FeO , MgO and SiO_2 . FeO , unlike other components, vaporizes through the disproportionation reaction into metallic and ferric irons in the melt phase.

'Volatility' is defined as a physical quantity so as to describe the evaporational fractionations of elements. On the basis of this concept, the experimental results of the present and previous works together with thermodynamic data are organized to characterize the evaporation sequence of primitive condensed materials. Its gross feature is the sequential evaporation of the components in the order of Fe , Mg , Si , Ca and Al . The details of the evaporation sequence depend on temperature and initial valences of Fe .

The evaporation sequence is comparatively discussed with the condensation sequence of the nebular gas, which has been well examined by previous workers. Both sequences, combined together, provide a basic framework to clarify the chemical fractionation processes which have differentiated primitive materials into the planetary and meteoritic materials. The chemical diversity of chondrules and inclusions in meteorites is interpreted as mainly due to the evaporational or condensational fractionation, but it also invokes other processes such as metal/silicate separation and non-equilibrium reaction with a surrounding gas.

INTRODUCTION

Evaporation and condensation, accompanied by the subsequent gas/dust separation, are supposedly the most important fractionation mechanisms to have caused chemical differentiations of primitive nebular materials. The thermodynamic theory of gas-solid equilibrium (LARIMER, 1967; GROSSMAN, 1972) has provided an important knowledge about the elemental partitioning between gas and dust. Coupled with the condensation model of the high-temperature nebular gas, it has been applied to a number of problems on the origin of meteorites and planets (e.g., GROSSMAN and LARIMER, 1974). Generally speaking, however, the chem-

ical aspect of the nebular evolution has been rather concerned with consideration of condensation processes. Because of the complementary natures of evaporation and condensation, we need to examine the possible role of evaporation. Chemical fractionations in planetary materials should have been controlled by evaporation and condensation.

Kinetics is indispensable for comprehensive understanding of the early fractionation phenomena, because equilibrium might not have been reached in evaporation and condensation. The study on nucleation and growth processes of dust grains from the cooling nebular gas (e.g., BLANDER and KATZ, 1967; YAMAMOTO and HASEGAWA, 1977) has brought about a kinetic

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aspect to the condensational fractionation. The evaporational fractionation should be also investigated as a kinetic process.

The purpose of our study is to characterize the kinetic processes of evaporational fractionation or 'evaporation metamorphism' (HASHIMOTO *et al.*, 1979), and to gain an insight into the chemical differentiations of meteoritic materials and protoplanets (MIZUTANI, 1973).

The important role of evaporation metamorphism has been demonstrated by some preliminary works. NOTSU *et al.* (1978) and HASHIMOTO *et al.* (1979) have carried out the evaporation experiments using Allende (CV3) and Murchison (CM2) meteorites as analogues of primitive materials in air and in vacuo, respectively. They showed an agreement in chemical composition and mineral constitution of some meteoritic materials including CAI, with the experimental solid residues subjected to various degrees of evaporation. MASUDA and TANAKA (1979) and NAGASAWA and ONUMA (1979) have shown the enrichment in REE and other refractory trace elements in the evaporation residues, similar to that in CAI.

In the first part of this paper, we describe the result and interpretation of the evaporation experiments done in vacuo, for the material with the initial composition of the solar elemental abundances, as a function of time and temperature. The solar abundances may be appropriate to represent the chemical composition of primitive materials. To deduce the gross trend of the evaporation metamorphism, we have limited the components to FeO, MgO, SiO₂, CaO and Al₂O₃ which comprise about 95 mol% of the volatile-free solar material. The experiment in vacuo makes it possible to eliminate the complicated interaction between the gas and condensed phases. So that the result would benefit to clarify the intrinsic nature of the vaporization process of the compound materials. It is likely that the gas-solid or gas-liquid interaction associated with evaporation may have actually happened in the solar nebula.

In the second part of this paper, we clarify the evaporation sequence of primitive materials

on the basis of the experimental results and thermodynamic consideration. A comparative examination is made on the evaporation and condensation sequences, and its results are preliminarily applied to the interpretation of the chemistries of chondrules and inclusions in chondritic meteorites.

EXPERIMENTS

Sample preparation Chemical reagents of 5N purity were prepared; periclase (MgO), dehydrated amorphous silica (SiO₂), lime (CaO), corundum (Al₂O₃) and hematite (Fe₂O₃). Mixing and sintering (1,100°C at P_{CO₂}/P_{H₂} = 1; the stability field of ferrous iron) were repeated to avoid local chemical heterogeneity in the starting material. Olivine (Fa ≈ 45%) and periclase were identified with X-ray diffraction as crystalline phases in the starting material produced. The initial mineralogy, except the valence of Fe (ferrous, initially), has no effect on the experimental results because the material is totally molten at the experimental temperatures. Several test pieces randomly sampled from a mass of the starting material, were analyzed with EPMA (analytical conditions are described in the following sub-section) in order to check the prescribed composition on mixing and chemical homogeneity. The result is satisfactory as shown in Table 1.

The material in a powder state was pressed and shaped into tubes of 4 mm height and 4 mm diameter with a straight hole of 1.2 mm diameter. They were semi-sintered in vacuum for one minute to remove pores and absorbed water, and finally their weights were adjusted to 100.0 mg with a knife.

Experimental device Figure 1 shows the furnace assembly set in a vacuum chamber (400 mm height, 300 mm diameter). The heating element is a tungsten resistant heater of cylinder type (inner diameter 32 mm, height 120 mm, thickness 0.3 mm). The thermal shields made of tungsten-molybdenum alloy cover the heater four-foldly. The crucible (inner diameter 11.5-

Table 1. Chemical composition of the starting material (wt %, 100% normalized)

Sample	SiO ₂	Al ₂ O ₃	FeO	MgO	CaO	N.A. #
1	35.19	3.26	34.94	24.08	2.54	10
2	35.56	3.03	34.84	24.03	2.54	10
3	35.52	3.00	35.03	24.05	2.40	10
4	35.52	3.18	34.89	23.92	2.50	10
5	35.37	3.06	35.18	23.89	2.49	10
6	35.48	3.25	35.19	23.48	2.60	20
7	35.34	3.34	35.24	23.46	2.62	20
(1) Ave.	35.43	3.16	35.04	23.84	2.53	
(2) σ	0.12	0.12	0.15	0.25	0.07	
(3) P.C.	35.50	3.00	35.00	24.00	2.50	
(4) S.C.	35.17	2.53	34.91	25.03	2.36	
(5) S.C.	39.15	2.46	33.14	23.41	1.83	

Notes

Number of points analyzed.

(1) The composition shown here is regarded as the starting composition in the experiments.

(2) Standard deviation.

(3) Prescribed composition on mixing.

(4) Solar elemental composition on the five component basis (after CAMERON, 1973).

(5) *ibid.* (after ROSS and ALLER, 1976).

Fig. 1. Schematic illustration of the heating system in the vacuum chamber. 1. Sample; before thrown into the crucible 2. Stopper 3. Leading wire 4. Graphite crucible 5. Tungsten electric lead 6. Tungsten heater 7. Supporting rod 8. Thermal shields.

16.0mm, height 75 mm) is made of a high purity graphite block commonly used in atomic piles. The tungsten wire (0.2mm in diameter) hung downward, is a leading guide of a tubulous sample into the crucible.

The use of graphite as a container, was successful in keeping a silicate melt from reaction with the container. In all the experimental runs, the silicate sample showed a single spherule after quenching. This indicates that the silicate melt made a point contact with the graphite crucible as a result of the surface tension of silicate melt. The contact reaction is considered to have been minimized in this situation. The reaction with sublimated carbon is negligible because the vapor pressure of graphite is orders of magnitude smaller than that of the present silicate melt.

Temperature measurement was made on the crucible surface with an optical pyrometer, of which reading was corrected for a thermal emissivity of 0.95 (graphite rough surface). Thermocouples (Pt/Pt-13%Rh, W/W-26%Re) inserted in the wall of the crucible were used only for monitoring the temperature because thermal emf changed with time by carbon diffusion into the thermocouple metals. In a short time experiment, however, the measure-

ment by thermocouples agreed with the pyrometry within 10°C . Because of the good thermal shielding, temperature was fairly uniform along the crucible. A check was made on a temperature difference between the outside and inside of the crucible, with one thermocouple attached on the surface and the other inserted into the inside of the crucible. Both temperatures agreed within 3°C after thermal equilibrium was reached, in the temperature range $1,700\text{--}2,000^{\circ}\text{C}$.

Vacuum was kept by operation of a diffusion pump (evacuation rate $100\ell/\text{sec.}$, maximum vacuum reached 7×10^{-8} Torr.). As the vacuum gauge was set close to the pump, the pressure level in the chamber might have been a little higher than reading.

Experimental conditions and procedures Temperatures and durations of heating are shown in Table 2. A notation such as 19B8 indicates the experimental condition, $1,900^{\circ}\text{C}$ -5.99 minutes, or the sample itself processed under the above condition. Two or more runs were carried out at $1,700$ and $1,800^{\circ}\text{C}$.

A silicate sample is thrown into the crucible by removing the stopper after the furnace temperature becomes stable at the prescribed temperature. By controlling a power supply, temperature is maintained with an accuracy of $\pm 5^{\circ}\text{C}$. The pressure reading is about 10^{-5} Torr. before throwing a sample into the crucible. On throwing, pressure abruptly increases more than one order of magnitude ($\sim 1.5 \times 10^{-4}$, $\sim 3 \times 10^{-4}$, $\sim 7 \times 10^{-4}$ and $\sim 2 \times 10^{-3}$ Torr. at $1,700$, $1,800$, $1,900$ and $2,000^{\circ}\text{C}$, respectively), and then it becomes lower with time. Quenching is made by cutting off the power supply.

The procedure of 'sample throwing' has an advantage in avoiding a solid state reaction between the graphite crucible and a silicate sample, otherwise the sample is reduced by the graphite during temperature rise from the room temperature to the melting range. A test was done to check a solid state reaction on the same starting material set in the crucible beforehand. The samples recovered after heating up to $1,900$ or $2,000^{\circ}\text{C}$ for various durations, all contained metallic iron of sub-millimeter size. In addition, the bottom of the crucible was hollowed just at the contact position with the samples. These results indicated a reduction reaction of iron oxide with graphite. On the other hand, metal did not appear following the procedure adopted in the present experiment, as shown in the next section. Owing to no or little reaction, one crucible sufficed dozens of experimental runs.

Splashing of melt droplets sometimes occurred right after throwing a sample. This may have been caused by a sudden release of gas which was trapped or absorbed in a starting sample. The chemical composition of the sample was not so much affected by splashing, because the resultant mass loss was in most cases several percent of the bulk mass. Some samples of $1,800^{\circ}\text{C}$ experiments, which splashed little, were used in order to examine the valence state of iron.

Analytical procedures All the recovered samples were single spherules. They were weighed by a microbalance with an accuracy of $\pm 0.1\text{mg}$ in order to determine the vaporized mass, and then they were processed in the following two ways. The sample with $<30\%$ vaporization was finely ground, pressed, sintered

Table 2. Heating conditions and run notations

$T(^{\circ}\text{C}) \backslash \text{Time (min.)}$	1.29	2.15	3.59	5.99	10.0	16.7	27.8	46.4	77.4	129
1,700					C1	C3	C5	C7	C9	D2
1,800			B6	B8	C1	C3	C5			
1,900	B2	B4	B6	B8	C1					
2,000	B2	B4	B6							

Symbols B, C and D denote time ranges; 1-10, 10-100 and 100-1,000 minutes, respectively.

(1,300-1,350°C for 30 min.; $P_{\text{CO}_2}/P_{\text{H}_2} = 1$) and thin-sectioned. This procedure was to homogenize the sample because its coarse texture was not suitable for EPMA analyses. The sample with >30% vaporization, which has a fine texture, was thin-sectioned across the midplane. Some samples with <30% vaporization were also processed by the same procedure, in the cases where duplicate or more runs were performed under the same experimental condition.

Bulk compositions were examined on the thin sections by electron microprobe analyzer (JEOL, Model JXA-5A) operated at acceleration voltage 15 keV and absorbed current 0.015 μA . A defocused beam (beam diameter $\sim 50 \mu\text{m}$) was used and counting was integrated for 80 seconds. Raw data were corrected for drift, dead time and background, and for differential matrix effects (absorption, fluorescence and atomic number) after BENCE and ALBEE (1968). Because of the fine textures compared with the beam diameter, corrections for the broad beam effect were not necessary, and fourteen to thirty point analyses on one sample were sufficient to represent its bulk composition. For the samples, 17C1 and 18B6(1), the constituent minerals were analyzed using 3 μm beam under the same analytical conditions described above.

Mineral constitutions and textures were examined by microscopic observation on the thin sections, and with X-ray diffraction using residual pieces after making the thin sections. Another set of the samples of 1,800°C runs was served to examine the Fe valence in the evaporation residues. They were heated at 1,100°C in the stability field of ferrous iron ($P_{\text{CO}_2}/P_{\text{H}_2} = 1$). The weight differences before and after this procedure correspond to the released oxygen by the valence change from ferric to ferrous, and are used to obtain the $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio for these samples.

EXPERIMENTAL RESULTS

Experimental results are summarized in Table 3. As an index of vaporization degree, we

use vaporized fraction (VF) which is an integrated mass of vaporization normalized to the initial mass. VF is identical with the mass of vaporization in unit of mg when it is expressed by percentage, as the weight of starting sample is 100.0 mg.

Texture, mineralogy and chemical homogeneity

Figure 2 shows some examples of the recovered samples, arranged in the order of increasing VF from the left to the right. Dark color becomes faint with decreasing size, reflecting a selective vaporization of Fe component.

Two types of textures are observed as shown in Fig. 3. The sample with $\text{VF} < 35\%$ has a lamellar texture which is the alternation of olivine and glass platelets (Fig. 3(a)-(c)). The sample with larger VF exhibits a fibrous or blarred appearance (Fig. 3(d)-(f)). The coexistence of both types is found in a few samples with $\text{VF} = 30\text{--}40\%$ (Fig. 3(g) and (h)).

These two textures are known as 'barred-olivine' texture and 'cryptocrystalline' texture, respectively, in the petrographic description of chondrules in meteorites (KIMURA and YAGI, 1980; NAGAHARA, 1981). TSUCHIYAMA *et al.* (1980) have reproduced several texture types of chondrules by changing chemical composition and cooling rate from the melting temperature. In our experiments, the change in composition is the determinant factor to cause the textural

Fig. 2. Run products of 1,800°C heating. From left to right, 18B8(1), C1(1), C3(1) and C5(1). All the recovered evaporation residues are single spherules. Scale - 1 mm.

Table 3. Summary of experimental results

Sample	VF ¹	Composition (wt %, 100% normalized)					n.a.	Texture ²	Minerals ³
		SiO ₂	Al ₂ O ₃	FeO	MgO	CaO			
17C1	8.2			n.d.				B	MP+OL+G
C3 (1)	(17.0)			n.d.				B	MD+OL+G
C3 (2)	10.8	39.09	3.57	27.92	26.32	3.09	14	—	—
C5 (1)	18.6	41.74	4.11	22.74	27.88	3.52	30	B	MD+OL+G
C5 (2)	18.4			n.d.				B	MD+OL+G
C5 (3)	19.7	41.74	3.83	21.81	29.09	3.53	16	—	—
C7	27.2	45.24	4.49	15.53	30.97	3.78	30	B	OL+G
C9 (2)	35.5	48.04	4.92	8.56	34.34	4.14	20	C	OL+G
D2	43.3	49.03	5.48	2.88	37.81	4.80	20	C&B	OL+G
18B6 (1)	11.2			n.d.				B	MP+OL+G
B6 (2)	12.3	38.73	3.55	28.40	26.26	3.07	14	—	—
B8 (1)	17.2	40.41	3.80	23.82	28.56	3.40	30	B	MP+OL+G
B8 (2)	15.8	39.55	3.88	25.78	27.26	3.53	24	—	—
B8 (3)	(20.2)			v				—	—
C1 (1)	(31.3)	44.22	4.87	14.39	32.49	4.05	30	B&C	OL+G
C1 (2)	25.0	42.84	4.05	19.10	30.41	3.59	16	—	—
C1 (3)	—			v				—	—
C3 (1)	(41.1)	45.60	4.61	11.84	33.89	4.06	20	B	OL+G
C3 (2)	33.1	45.30	4.33	12.87	33.57	3.93	16	—	—
C3 (3)	(42.3)	46.12	4.99	9.95	34.38	4.55	20	B&C	OL+G
C3 (4)	(41.8)			v				—	—
C5 (1)	45.0	47.35	5.33	4.18	38.43	4.70	20	C	OL+(G)
C5 (2)	(49.4)	47.05	5.14	3.85	39.14	4.82	20	C	OL+(G)
19B2	12.2	37.94	3.55	29.14	26.09	3.29	20	—	—
B4	17.2	39.64	3.74	25.60	27.76	3.27	14	—	—
B6	26.3	41.09	4.02	20.59	30.74	3.56	30	B	MD+OL+G
B8	38.7	44.23	5.03	11.49	34.77	4.48	20	B&C	OL+G
C1	49.3	45.56	5.88	4.55	38.94	5.07	20	C	OL+(G)
20B2	27.0	40.87	4.14	20.46	30.81	3.72	16	—	—
B4	40.5	43.00	5.40	12.27	34.56	4.76	20	B	OL+G
B6	52.5	43.74	6.24	3.15	41.10	5.77	20	C	OL+(G)

1. Vaporized fraction, wt %. Parentheses denote samples with some splashing.

2. B: Barred-olivine texture. C: Cryptocrystalline texture.

3. MP: Polygonal-shaped magnetite. MD: Dendritic magnetite. OL: Olivine. G: Glass.

n.a. Number of analyses.

n.d. Not determined.

v Sample was used for determination of the valence of iron.

variation, as the cooling rate is similar in every run at the same prescribed temperature.

The barred-olivine samples with VF=0-25%, have a mineral assemblage of olivine+glass+magnetite. Two distinct morphologies are observed for magnetite as in Fig. 4. In Table 4 the result of EPMA analyses on these coexisting phases are shown. Magnetite and glass are uniform in composition, while olivine has a zonation normal to the elongating direction. Olivine and glass are the minerals observed in the barred-olivine samples with VF=25-35%, and in the cryptocrystalline samples. Because of their finer textures, EPMA analyses on individual mineral grains were not made.

The defocused beam analyses (50 μ m beam) by EPMA on the barred-olivine samples show rather heterogeneous chemical compositions from spot to spot. Statistically, however, there is no significant difference in composition between outer and inner parts of the spherical samples (e.g., Fig. 5(a)). This indicates that the microscopic chemical heterogeneity resulted from the local-scale differentiation during crystallization, and that the concentration gradient of significant level did not exist in molten state. The chemical homogeneity in molten state is more evident in the cryptocrystalline samples. They show fairly uniform chemical compositions and reveal no concentration gradient from

the center to the surface (e.g., Fig. 5(b)). These observations are important to assess the efficiency of mass transfer in the melt phase as will be inquired in the later discussion.

Valence state of iron The presence of magnetite was confirmed by X-ray powder diffraction, microscopic observation and EPMA analysis on the samples with $VF < 25\%$. Because the starting material has no ferric iron, ferrous iron must have been converted to ferric iron during heating.

Figure 6 shows the change in Fe^{3+}/Fe^{2+} atomic ratio in the recovered solid after heating at $1,800^{\circ}C$. The proportion of ferric iron increases with progressive vaporization, and it reaches about 40% of the total iron at $FeO + FeO_{3/2} < 10\%$.

Two processes are possible for the production of ferric iron: one is the oxidation of samples by the atmosphere, and the other is the selective vaporization of iron relative to oxygen. The first process is quite unlikely for the following reasons.

Fig. 3(a), (b), (c)

Fig. 3(d), (e), (f)

Fig. 3(g), (h)

Fig. 3. Photomicrographs of thin sections of spherules with various textures. (a): 17C1(VF=8.2), (b): 17C5 (2) (18.4) and (c): 18B6(1) (11.2), showing barred-olivine textures. (d): 18C5(1) (45.0), (e): 19C1 (49.3) and (f): 20B6 (52.5), showing fibrous or cryptocrystalline textures. (g): 18C1(1) (31.3) and (h): 19B8 (38.7), exhibiting both textures. Transmitted light. Scale bar - 0.5mm.

Fig. 4. Photomicrographs showing the presence of magnetite in evaporation residues. Magnetite(M) occurs only in a glass phase in the glass/olivine lamellar texture (G: glass, OL: olivine). (a): 19B6(VF=26.3), showing dendritic crystals of magnetite (black). Transmitted light. Scale bar - 30 μ m. (b) 17C1(VF=8.2), showing polygonal crystals of magnetite (white). Reflected light. Scale bar - 100 μ m.

The vacuum level in the chamber was about 10^{-4} Torr. during the experiments. The pressure of this magnitude, even if the atmosphere is composed only of oxygen, is close to the f_{O_2}

level at the wüstite-metal boundary extrapolated to the liquid field in the f_{O_2} -temperature diagram (DARKEN and GURRY, 1945; 1946). In the graphite crucible, moreover, a high f_{O_2} to keep

Table 4. Chemical compositions of magnetite, olivine and glass (wt %, average)

Sample 18B6(1)	SiO ₂	Al ₂ O ₃	FeO	Fe ₂ O ₃	MgO	CaO	Total	Number of analyses
Magnetite	1.00	5.23	29.55	59.94	1.85	0.15	97.72	5
Olivine	37.71	0.16	23.68	—	37.58	0.24	99.37	26
Glass	48.84	11.79	24.01	—	1.58	12.20	98.42	5
Sample 17C1	SiO ₂	Al ₂ O ₃	FeO	Fe ₂ O ₃	MgO	CaO	Total	Number of analyses
Magnetite	0.93	5.07	29.19	60.15	1.93	0.17	97.44	7
Olivine	38.91	0.14	18.89	—	41.24	0.23	99.41	7
Glass	48.45	12.38	23.47	—	1.31	12.78	98.39	7

Fig. 5(a)

Fig. 6. Redox state of iron in the recovered solids after heating at 1,800°C for various heating durations. Molar concentration of Fe (abscissa) decreases with progressive evaporation. S: the valence of the starting material, i.e., ferrous. Open circles: data obtained by P_{O_2} control experiments. Error bar originates in the precision of the microbalance. Triangles: results by the modal analysis combined with the EPMA analysis on the constituent minerals in the evaporation residue. All Fe^{3+} was assumed to be accommodated in the magnetite phase (M), or in both the glass and magnetite (GM).

Fig. 5(b)

Fig. 5. Examples of defocused-beam analysis by EPMA (50 μ m beam). The chemical compositions at the ~ 500 μ m mesh points over the entire sectional area were rearranged in order to show the uniformity of composition along radial direction. Apparent clustering of points on a horizontal axis results from the square-mesh distribution of analyzed spots on the section. (a) 18B6(1) (50 spots analyzed). The sample with coarse barred-olivine texture (see Fig. 3(c)), shows considerable variation of chemical compositions from spot to spot because of its coarse texture relative to the beam diameter of EPMA. Statistically, however, there is no significant difference in composition, between outer and inner parts of the entire sectional area. (b) 18C5(1) (20 spots analyzed). The sample with fine cryptocrystalline texture (see Fig. 3(d)) shows a fairly uniform composition.

iron in ferric state cannot be sustained. Thus the second process is suggested to be the case from elimination of the first process, and its detail is presented in the later section.

Mass of vaporization as a function of time and temperature

Figure 7 shows residual masses of the five components which remained unvaporized. At all the temperatures studied, FeO shows the largest vaporization, indicating that

the vapor pressure of FeO overwhelms those of other components. SiO_2 is the second volatile component, whose flux of vaporization is about three times larger than that of MgO. CaO and Al_2O_3 are the least volatile components and show no detectable loss of mass. With increasing temperature the proportion of FeO component in the total vaporization diminishes, while those of SiO_2 and MgO increase.

Figures 8 (a) - (c) show mass of vaporization as a function of time (i.e., vaporization curve) for FeO, SiO_2 and MgO, respectively. At the initial stage, vaporization rates are kept constant as shown by the linear portions of the vaporization curves. At the later stage (e.g., $M_t/M_o > 0.5$ in Fig. 8(a)), the rates become smaller with time as indicated by the decreasing slopes of the vaporization curves. The data points at $1,700^\circ\text{C}$ for MgO, appear to suggest a slight curvature even at the low vaporization stage.

The vaporization curves of the total mass in

Fig. 7. Residual mass of each component in evaporation residues. The vaporized fraction in wt % is identical with the total mass in mg of vaporization because the initial weight is set for 100mg.

Fig. 8(d), reflect the whole effect of individual vaporizations. The initial stage of their curves is controlled mainly by that of FeO curves, because the vaporization rate of FeO is much larger than those of the other components. However, the curves run parallel with those of SiO_2 and MgO at $VF \geq 40\%$ where Fe in the melt is diminished below 10% of its initial mass.

DISCUSSION ON EXPERIMENTAL RESULTS

1. Elementary rate processes involved in vaporization

Vaporization is a combinational phenomenon of the three kinetic processes; chemical reactions occurring on a surface of a condensed phase (solid or liquid), vapor transfer from the surface to outer space, and migration of vaporiz-

Fig. 8(a)

Fig. 8(b)

Fig. 8(c)

Fig. 8(d)

Fig. 8. Mass of vaporization by the time t , M_t , normalized to the initial mass, M_o . (a): FeO. (b): SiO₂. (c): MgO. (d): total mass. Ferric iron is included as FeO in (a).

ing elements in the condensed phase.

Here, these rate processes are examined one by one with regard to the present experimental results. The key point to interpret the experimental vaporization rates (Fig. 8), is that the most sluggish process determines the rate of vaporization as these processes are series-coupled.

Vapor transfer The vaporization rate should be equal to the vapor flux transferred through a vacuum path and also to the evacuation rate by a vacuum pump, if the generated vapor does not condense on a wall of the chamber. These relations are expressed as,

$$F = U \cdot \Delta P \quad (1)$$

and

$$F = S \cdot P_o \quad (2)$$

where F denotes the vaporization rate, U the conductance of the vacuum path, ΔP the pressure difference along the path, S the capacity of the vacuum pump ($10^5 \text{ cm}^3/\text{s}$) and P_o the pressure near its high vacuum gate.

The conductance U is approximated by that of the sample crucible because the latter is the smallest in the entire path of the present vacuum

system. ΔP almost equals the pressure difference between the bottom and top of the crucible, and the pressure at the top of the crucible is approximated by P_o . Then eqn. (1) is rewritten as,

$$F = U (P_b - P_o) \quad (1')$$

where P_b is the pressure at the bottom of the crucible. The effective conductance $U (\text{cm}^3/\text{s})$ is given by the sum of the following two factors,

$$U_k = \frac{4r^3}{3h} \sqrt{\frac{2\pi RT}{M}} \quad (\text{Knudsen flow}) \quad (3)$$

$$U_v = \frac{\pi r^4}{8h} \frac{\bar{P}}{\eta} \quad (\text{viscous flow}) \quad (4)$$

where r and h are the inner radius and the length of the crucible, M molecular weight of vapor species, η viscosity, $\bar{P} = (P_b + P_o)/2$, R the gas constant and T temperature.

P_b and P_o are obtained from eqns. (1)' and (2) with F (the experimental vaporization rate at the initial stage of vaporization, i.e., the maximum vaporization rate), and M and η (the values of oxygen diatomic molecule). In Table 5, P_b , P_o , $\bar{P}$, U_k and U_v determined are shown together with F used in the calculation.

Table 5. Pressures and conductances in the present experimental system

T °C	F mol/s	P _b Torr.	P _o Torr.	$\bar{P}^*$ Torr.	U _k cm ³ /s	U _v cm ³ /s	U _k + U _v cm ³ /s
1,700	3.9×10^{-7}	6.6×10^{-3}	7.5×10^{-5}	3.3×10^{-3}	7.38×10^3	0.041×10^3	7.42×10^3
1,800	1.6×10^{-6}	2.6×10^{-2}	3.0×10^{-4}	1.3×10^{-2}	7.57×10^3	0.162×10^3	7.73×10^3
1,900	4.6×10^{-6}	7.7×10^{-2}	8.6×10^{-4}	3.9×10^{-2}	7.75×10^3	0.459×10^3	8.21×10^3
2,000	1.0×10^{-5}	1.6×10^{-1}	1.9×10^{-3}	8.2×10^{-2}	7.93×10^3	0.948×10^3	8.88×10^3

$$*\bar{P} = (P_b + P_o)/2.$$

The effect of viscous flow becomes important with increasing temperature, as indicated by comparison between U_k and U_v. Within the experimental range, however, Knudsen flow is the predominant flow mechanism.

The P_o calculated is similar to the value measured experimentally by the vacuum gauge. It is noted that P_o is two orders of magnitude smaller than P_b (the pressure around the sample). This result indicates that the capacity of the vacuum pump is not a controlling factor in the present experiments.

The conductance is insensitive to temperature and pressure because it varies by only 20 percent from 1,700 to 2,000°C and from 10⁻³ to 10⁻¹ ($\bar{P}$, Torr.), as indicated in the table. Accordingly the process of vapor transfer has no effect on the time- and temperature-dependent variations of the vaporization rates.

Mass transfer in a melt Diffusion and hydrodynamic flows are considered to be main mechanisms of mass transport in the present melt phase. The occurrence of hydrodynamic flows is suggested from the observation of the bulk motion of the melt spherule, which vibrated and sometimes bumped onto the side wall of the crucible. A convective overturn may have occurred as a result of temperature gradient in the melt, though the heating system was designed to obtain a uniform temperature. In addition, non-uniform emission of vapor (the lower hemisphere of the melt was being faced to the bottom of the crucible) may have activated hydrodynamic flows and/or the bulk motions.

The mass transfer by hydrodynamic flows contributes to an effective increase in diffusion coefficient, and the overall effect of mass trans-

port is described by diffusion equation.

Diffusion equation in a sphere is written by,

$$\frac{\partial C}{\partial t} = D \left(\frac{\partial^2 C}{\partial r^2} + \frac{2}{r} \frac{\partial C}{\partial r} \right) \quad (5)$$

where C is the concentration of a particular component in the sphere (here the molten spherule) as a function of time, t, and radius, r, and D is the effective diffusion constant.

The mass flux to the surface of the sphere is equal to the surface reaction rate, and the boundary condition is written by assuming a first order reaction for the surface reaction as follows.

$$-D \frac{\partial C}{\partial r} = \epsilon C \quad (r = a) \quad (6)$$

where a is the radius of the sphere and ϵ is the effective surface emissivity ($\epsilon = ka/3$; k is the reaction rate constant). The initial condition is,

$$C = C_o \quad (r \leq a) \quad (7)$$

where C_o is the concentration in the sphere at t = 0.

CRANK (1956) has solved eqn. (5) under conditions (6) and (7), and has given the amount of vaporizing substance by the following equation.

$$\frac{M_t}{M_o} = 1 - \sum_{n=1}^{\infty} \frac{6L^2 \exp(-\beta_n^2 Dt/a^2)}{\beta_n^2 \{ \beta_n^2 + L(L-1) \}} \quad (8)$$

where M_t is the vaporized mass of the concerned component by the time t and M_o its initial mass in the sphere. β_n 's are the positive roots of

$$\beta_n \cot \beta_n + L - 1 = 0 \quad (9)$$

where $L = a\epsilon/D$ is a non-dimensional parameter denoting the relative importance of surface reaction and diffusion; $L = 0$ corresponds to a reaction control and $L = \infty$ a diffusion control.

The application of eqn. (8) to the experimental data of the FeO component leads to $\log L = -2.5 \pm 0.5$ at all the temperatures studied. One data point, 18C3(2), is omitted in the calculation because of its considerable deviation from a general trend. The small L values ($\ll 1$) obtained indicate that the vaporization was not controlled by the mass transfer process in the melt phase, but controlled mostly by surface reactions. This result is consistent with the fact that no concentration gradient was observed in a radial direction in all the recovered samples (e.g., Fig. 5).

Surface reactions It has become clear from the foregoing discussion, that surface reactions are essentially rate-controlling in the process of vaporization. So that reaction orders and activation energies of surface reactions are derived from the experimental data on the basis of time-dependent and temperature-dependent variations of their vaporization rates, respectively. We present both estimates for FeO component. Activation energies are determined for SiO_2 and MgO , but their data are not suitable for reaction order analyses owing to their small spans of concentration change in the melt. No analysis was made on CaO and Al_2O_3 .

Let us consider a surface reaction to evaporate a particular component, i . Then, the vaporization rate of i normalized to a surface area of the molten spherule is expressed as (MOELWYN-HUGHES, 1961),

$$J_i = k_i(T) \cdot C_i^{\nu_i} \quad (10)$$

where C_i is the molar concentration of i in the melt, J_i is the mass in moles of i , evaporated per unit time from unit area of the melt surface, and ν_i is the reaction order of the surface reaction. $k_i(T)$ is the reaction rate constant written by,

$$k_i(T) = k_{i0} \exp\left(-\frac{E_i}{RT}\right) \quad (11)$$

where k_{i0} is a constant and E_i the activation energy of the reaction.

The reaction order ν_i is obtained as a slope of linear regression curve on $\ln J_i - \ln C_i$ plot, as shown in Fig. 9 for the vaporization of FeO component. It is noted that the reaction order becomes smaller with increasing temperature; from 1.204 at 1,700°C to 0.798 at 2,000°C.

The activation energy E_i is obtained as a slope of linear regression curve on $\ln J_i - 1/T$ plot given at the same concentration C_i . The results are shown in Fig. 10. The activation energy of FeO vaporization lies in the range 93.7–107.9 kcal/mol, and shows a trend to increase with lowering molar concentration of FeO. For SiO_2 and MgO , the values 131.6 and 123.6 kcal/mol are derived, respectively.

According to the absolute reaction theory (e.g., GLASSSTONE *et al.*, 1941), activation energy of vaporization is equal to $\Delta H^*/z$, where ΔH^* is activation enthalpy of vaporization and z is moles of 'activated' molecules produced from one mole of reactants in a condensed phase. In

Fig. 9. Graphical determination of reaction order, ν , for the vaporization reaction of FeO component. Open circles: calculated from successive two points of the experimental data in the vaporization curves (Fig. 8(a)). Solid circles: calculated from intermittent two points.

Table 6. Vaporization reactions and enthalpies of vaporization

No.	Vaporization reaction *			ΔH°	$\Delta H^\circ/z$
1	Fe	$\rightarrow$	Fe	89.243	89.243
2	FeO	$\rightarrow$	Fe + 1/2O ₂	150.637	100.425
3	FeO	$\rightarrow$	Fe + O	211.657	105.829
4	FeO	$\rightarrow$	FeO	109.476	109.476
5	Fe ₂ O ₃	$\rightarrow$	2Fe + 3/2O ₂	352.832	100.809
6	Fe ₂ O ₃	$\rightarrow$	2Fe + 3O	535.892	107.178
7	Fe ₃ O ₄	$\rightarrow$	3Fe + 2O ₂	506.610	101.322
8	Fe ₃ O ₄	$\rightarrow$	3Fe + 4O	750.690	107.241
9	Fe ₂ O ₃	$\rightarrow$	2FeO + 1/2O ₂	270.510	108.204
10	Fe ₂ O ₃	$\rightarrow$	2FeO + O	331.530	110.510
11	Fe ₃ O ₄	$\rightarrow$	3FeO + 1/2O ₂	383.127	109.465
12	Fe ₃ O ₄	$\rightarrow$	3FeO + O	444.147	111.037
13	SiO ₂	$\rightarrow$	SiO + 1/2O ₂	184.198	122.799
14	SiO ₂	$\rightarrow$	SiO + O	245.218	122.609
15	SiO ₂	$\rightarrow$	SiO ₂	137.071	137.071
16	SiO ₂	$\rightarrow$	Si + O ₂	317.250	158.625
17	SiO ₂	$\rightarrow$	Si + 2O	439.290	146.430
18	MgO	$\rightarrow$	Mg + 1/2O ₂	156.353	104.235
19	MgO	$\rightarrow$	Mg + O	217.373	108.687
20	MgO	$\rightarrow$	MgO	121.392	121.392

* All reactants are in liquid states and all products in gas states.

ΔH° : enthalpy of vaporization (kcal/mol) at 2,000°K (JANAF, 1971).

z : moles of gas.

Table 6 enthalpies of vaporization, $\Delta H^\circ/z$, are shown for various reactions, and they are compared with the observed values of activation energies in the followings.

Reactions (13)-(17) for SiO₂ and (18)-(20) for MgO cover the possible reactions pertinent to their vaporizations. It is pointed out by comparison that reactions (15) and (20) give the values (i.e., 137.071 and 121.392 kcal/mol) closest to the activation energies determined (131.6 and 123.6 kcal/mol) for SiO₂ and MgO, respectively. This implies the possibility that the vapor molecules of SiO₂ and MgO are the 'activated' molecules in their vaporization reactions.

As for the FeO vaporization, two sorts of reactions must be concurrent in view of the temperature-dependency of the reaction orders and the concentration-dependency of the activation energies. One of them should have a high reaction order and a low activation energy, and the other is of a low reaction order and a high activation energy. The observed ranges of reaction orders and activation energies are interpreted to lie between those of the two reactions.

Among reactions (1)-(12) in Table 6, only

Fig. 10. Arrhenius plots for FeO, SiO₂ and MgO components. C denotes the molar concentration in the melt and E the activation energy derived from a slope of regression line.

reaction (1) (vaporization of metallic iron) gives a value lower than the lowest one (93.7 kcal/mol) of the observed activation energies. This suggests reaction (1) as the reaction of lower activation energy.

Similarly, reactions (4), (9)-(12) have a possibility to be the reaction of higher activation energy, as indicated by comparison of their $\Delta H^\circ/z$ with the highest activation energy (107.9 kcal/mol) obtained.

The observed variation in the $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio (Fig. 6) restricts possible reactions of the higher activation energy. It requires such a vaporization reaction which includes ferric iron in reactants. Otherwise, ferric iron would accumulate in the melt by more than twice as large in quantity as observed, as a result of the advance of reaction (1). Accordingly, we presume reactions (9)-(12) rather than (4), as a complement of reaction (1).

On the basis of the above assignment of vaporization reactions, the reaction order of reaction (1) is expected to be higher than 1.204. The vaporization reaction of ferric oxide complementary to reaction (1) is considered to have a reaction order lower than 0.798.

2. Vaporization mode of FeO component

The equilibrium vapor pressure of pure FeO calculated from thermodynamic data (JANAF, 1971), is almost on the same level as those of pure SiO_2 and MgO . However, the experimental result shows that the vaporization flux of FeO is several to ten times larger than those of SiO_2 and MgO when they are compared at the same concentration in the melt.

The results similar to ours have been reported by DEMARIA *et al.* (1971) and PIACENTE *et al.* (1975) in the Knudsen cell mass spectrometric analyses on the vapors over the heated lunar samples and olivine ($F_a = 10\%$). They observed the iron vapor pressure equivalent to that of pure iron irrespective of Fe concentration in the condensed phases, and suggested the following reactions as a possible explanation.

Their observation is of considerable importance, but their interpretation (reaction (a)) is somewhat doubtful. The calculation from thermodynamic data (JANAF, 1971) indicates that the equilibrium P_{O_2} in reaction (a) is 6×10^{-13} atm. at 1,500°K. As the number of Fe atoms produced in reaction (a) is twice that of O_2 , P_{Fe} never exceeds twice the P_{O_2} . Therefore, P_{Fe} should be less than 1.2×10^{-12} atm. according to reaction (a), while P_{Fe} over pure Fe-metal is 1.4×10^{-7} atm. at the same temperature. Thus, reaction (a) is contradictory to their experimental results.

We note that any equilibrium reaction, including (a), which is accompanied by gaseous oxygen does not explain the high vaporization flux of iron.

Based on the present result that ferric iron increased with progressive vaporization, we examine the possibility of some disproportionation reactions occurring in a solid or liquid phase. In a solid state, three reactions are possible:

In a liquid state, two reactions are possible:

where parenthesized notation s denotes a solid, s.s a solid solution with MgO-complement, and soln a liquid solution.

Disproportionation reactions in a solid state

In the system Fe-O, the mineral assemblage of Fe metal and magnetite is stable below 560°C at 1 atm. total pressure (DARKEN and GURRY, 1946). MUELLER (1965) predicted that even at higher temperatures magnetite might form a stable boundary curve with metallic Fe in the quaternary system Fe-MgO-SiO₂-O₂.

Recently, however, NITSAN (1974) has presented the stability fields of olivine of various fayalite contents with respect to oxidation and reduction at 1 atm. total pressure on the basis of thermodynamic calculations. His result shows that there is no equilibrium oxygen fugacity-temperature condition which allows the coexistence of Fe metal and magnetite. Therefore, we assume that the chemical equilibria of (b) and (c) do not directly proceed to the right side without some non-equilibrium process intervening in it.

Reactions (d) and (d)' are the homogeneous auto-redox reactions which we suggest to occur in olivine by heating under a vacuum condition. In the following context, we present the evidences of homogeneous oxidation and homogeneous reduction of olivine, and then examine the possibility of the auto-redox reactions.

The homogeneous oxidation of olivine is accompanied by the formation of a vacancy in cation site corresponding to the conversion of two ferrous irons into ferric ones. This results in the formation of non-stoichiometric olivine as shown on the right sides of reactions (d) and (d)'.

Natural olivines in some instances contain Fe³⁺ up to several percent (DEER *et al.*, 1964), although most of Fe³⁺ may constitute independent oxide phases of small dimension. The content and site-preferency of Fe³⁺ in olivine lattice structures have been determined for some natural and synthetic olivines by means of Mössbauer spectroscopy or electron spin resonance technique (DUBA *et al.*, 1973; CHATELAIN and WEEKS, 1973; NIEBUHR, 1975; SHINNO

1981). Their results, some samples showing Fe³⁺ accommodation in M1 site and others in M2 or tetrahedral site, seem to reflect different conditions of olivine formation or oxidation. CHATELAIN and WEEKS and SHINNO have also verified the formation of Fe³⁺ in the olivine lattice by heat treatments under oxidizing conditions.

The indirect evidences of Fe³⁺ formation have been presented from the studies of optical absorption and electrical conductivity on olivines heat-treated under various redox conditions (e.g., PITT and TOZER, 1970; DUBA and NICHOLLS, 1973). They interpreted the variation in absorption spectra or electrical conductivity in terms of variation of Fe³⁺ content in olivine.

The reported Fe³⁺ content of olivine is usually low. However, we note as a polymorph of Fe³⁺-containing olivine, laihunite Fe²⁺Fe³⁺₂(SiO₄)₂, of which structure is essentially like that of olivine with Fe³⁺ in M1 and Fe²⁺ in (000) and (0½0) of M2 but leaving (00½) and (½½½) sites vacant (FLEISCHER *et al.*, 1978). Recently, KONDO *et al.* (1982) have succeeded in reproducing the same phase experimentally from pure fayalite at 400 and 600°C in air. We suggest that this mineral might be an alternative for olivine on the right sides of reactions (d) and (d)', or possibly substitutes olivine with increasing Fe³⁺/Fe²⁺ ratio.

Fe⁰ on the right side of reaction (d) designates the metallic iron which might exist interstitially making a Frenkel type defect with a cation vacancy in the olivine structure. Its existence, although not decisive, has been implied by BOLAND and DUBA (1981) as the matrix strain field contrast effect in electron microscopy on the experimentally reduced olivine (San Carlos olivine, initially Fo92). They also noted in the further annealed specimen the fine-grained metal blebs of 0.2-1.5 μm distributed homogeneously over the entire sample but microscopically located in dislocation sub-boundaries. The free metal shown on the right side of reaction (d)' represents such a metal. The formation of metallic iron by decomposition of olivine phase has been also reported by

other workers (GORES *et al.*, 1972; HAGGERTY, 1977).

Contrary to our suggestion of reactions (d) and (d)', there has been no definite observation which depicts the equilibrium coexistence of ferric and metallic irons in the olivine structure, or of ferric iron in the olivine structure and metallic iron as an independent phase. However, we assume that such an association is possible at least metastably in view of the phase relation in the system Fe-O. Stoichiometric FeO is not stable, but decomposes into Fe_{1-t}O ($0 < t \leq 1$) wüstite and metallic iron at 560-1,370°C. The valence state of wüstite may correspond to that of non-stoichiometric olivine shown in reactions (d) and (d)'. Metal and magnetite assemblage, stable below 560°C in the Fe-O system, is suggestive of the metastable coexistence of metal and laihunite. Therefore, as one of the possibilities to explain the high vaporization flux of FeO from olivine, we propose that these metastable states take place by heating in unbuffered condition with respect to P_{O_2} (e.g., vacuum condition).

Disproportionation reactions in a liquid state

Reactions (e) and (f) are the auto-redox reactions which we suggest to take place at high temperatures in a silicate liquid containing ferrous iron. These reactions indicate the coexistence of metallic and ferric irons in a melt phase of the present silicate system. Actually, the viewpoint to support their coexistence is required by the results of the analyses on activation energy and reaction order, as described in the former section. However, any metallic phase was not observed in the recovered evaporation residues by the present experiment. This poses a question about the state of existence of metallic iron in the melt.

One possibility is that a metallic phase is present at high temperatures, whereas it disappears on cooling by reverse reactions of (e) and (f). The metallic phase should be sufficiently small in size to react with the surrounding silicate. Moreover, the time scales of exsolution growth and coalescence growth of metal should

be large relative to a life time of metal particles before evaporation. Such a condition might be possible because of the high volatility of metallic iron.

An alternative possibility is that metallic iron is in solution with the silicate melt. High metal solubility is commonly observed in salt melts such as halides and chalcogenides (CORBETT, 1964). In their Knudsen vaporization experiment on olivine, PIACENTE *et al.* (1975) found that the vapor pressure of iron steeply decreased at $1,920 \pm 15^\circ\text{K}$ when increasing temperature. This singular temperature is most likely the melting point of olivine. Therefore, it is plausible that a metal phase disappeared by dissolving into the olivine melt, as they also commented. This suggests that the state of iron atoms in the melt is metallic rather than covalent under this condition.

In the above context, we presumed the proposed disproportionation reactions to occur in the bulk phase of solid and liquid. However, they may take place only at the surface, because the mode and rate of vaporization should reflect physical and chemical properties of the surface layers rather than the bulk phase. In a somewhat different sense, moreover, it seems possible that the surface atomistic states of olivine and the present melt are virtually equivalent to the product assemblies in reactions (d)-(f).

3. Chemical fractionations by evaporation

Here, we describe the concept of volatility, and thereby interpret the chemical fractionation of the melt caused by evaporation.

Volatility - definition 'Volatility' has been used commonly for describing the relative easiness of vaporization of a particular component among others. However, it is a vague concept that has not been defined strictly. It means the relative vaporization rate in one case, while it does just a vapor pressure in the other case, either of a pure material or of a solute in a multicomponent phase.

For the convenience of unambiguous discussion, we define 'volatility' in the following way.

$$\zeta_i = J_i/C_i \quad (12)$$

where J_i and C_i are the vaporization rate (mol/cm² sec) and the molar concentration (mol/cm³), respectively, of the i -th component in a condensed phase. It represents a combinational property which includes the reaction kinetics on a surface and the kinetics of mass transfers both in the condensed and vapor phases. When the vaporization is rate-controlled by surface reactions as in the present study, ζ is proportional to the reaction rate constant (see eqns. (10) and (11)).

Volatility is a measure to describe the escaping tendency of a component, and is particularly useful for characterizing a chemical fractionation of the condensed material caused by evaporation. For example, the time-dependent variation of the abundance ratio of components, i and j in the condensed phase, is written simply by their difference in volatility.

$$\frac{d}{dt} \ln (C_i/C_j)/(C_i^0/C_j^0) = -\frac{S}{V}(\zeta_i - \zeta_j) \quad (13)$$

where C_i/C_j is the abundance ratio of the i -th and j -th components and C_i^0/C_j^0 its initial value. S and V are the surface area and the volume of the condensed medium. When $\zeta_i = \zeta_j$, there occurs no change in their abundance ratio by evaporation. If $\zeta_i > \zeta_j$, the i -th component depletes relative to the j -th. In a special case where $\zeta_i \gg \zeta_j$, the abundance ratio is determined only by ζ_i and the logarithmic term on the left of eqn. (13) is referred to as a depletion factor of the i -th component.

Under the vacuum condition the vaporization rate, J_i , is written as (KENNARD, 1938),

$$J_i = \frac{\alpha_i P_i}{\sqrt{2\pi M_i RT}} \quad (14)$$

where P_i , M_i and $\alpha_i (\leq 1)$ are the equilibrium partial vapor pressure, the molecular weight and the vaporization coefficient (LEE and SATA, 1977) of the i -th component. Substitution of eqn. (14) for J_i in eqn. (12) gives,

$$\zeta_i = \frac{\alpha_i P_i}{\sqrt{2\pi M_i RT}} \cdot \frac{1}{C_i} \quad (15)$$

which we call 'vacuum volatility' as a special case of volatility in vacuum evaporation.

Equation (15) is useful to evaluate a trend of evaporational fractionation of condensed materials in terms of thermochemical data if α_i is known. For example, the relative escaping tendency between the components, i and j , may be given by,

$$\frac{\zeta_i}{\zeta_j} = \frac{\alpha_i \gamma_i}{\alpha_j \gamma_j} \frac{P_i^0 \sqrt{M_j}}{P_j^0 \sqrt{M_i}} \quad (16)$$

where P^0 is the equilibrium vapor pressure of the pure substance and γ the activity coefficient of the component in the melt.

Volatilities and the change in chemical composition

Fig. 11. Volatilities of FeO, SiO₂ and MgO components at the molar concentration, 0.009, 0.020 and 0.023 mol/cm³, respectively. Slope of each line is equal to $-E/2.303R$, where E is the activation energy of vaporization reaction of the concerned component. The volatilities are almost constant at constant temperature despite the concentration changes of the components (0.015-0.001, 0.019-0.022 and 0.019-0.027 mol/cm³ for FeO, SiO₂ and MgO, respectively, in the present experiments).

tion of the melt Figure 11 shows experimentally determined volatilities of the components, MgO, SiO₂ and FeO (practically Fe+Fe₃O₄ or Fe+Fe₂O₃, as suggested in the previous discussion). Slopes of the lines are equal to $-E/2.303R$ (E : activation energy of the surface reaction). The differences in volatility between FeO and other two components, become smaller with increasing temperature. Especially, it is noteworthy that the volatility of SiO₂ exceeds that of FeO above $2,900 \pm 100^\circ\text{K}$, by the extrapolation of their lines.

SiO₂ is slightly volatile than MgO. The difference between their volatilities is insensitive to temperature variation, because of the small difference ($\sim 8\text{kcal/mol}$) in activation energy between their vaporization reactions.

Volatility differences among the components, are reflected in various plots of the chemical compositions of evaporation residues. Figure 12 shows the variation in Fe/(Fe+Mg) atomic ratio. Because of the higher volatility of FeO than MgO, the ratio decreases with progressive evaporation. However, the higher the temperature, its decreasing rate becomes the smaller. Evidently, this temperature effect originates in the activation energy difference ($\sim 20\text{kcal/mol}$) between their vaporization reactions.

Fig. 12. Variation in the atomic ratio, Fe/(Fe+Mg), in evaporation residues. VF: vaporized fraction.

Figure 13 shows the variation in (Fe+Mg)/Si atomic ratio. The solar atomic ratio is close to two (i.e., the olivine stoichiometry). The ratio becomes smaller with progressive evaporation in the present temperature range. Based on Fig. 11, we predict that the composition of evaporation residue approaches the pyroxene stoichiometry by evaporation at $\sim 1,500^\circ\text{C}$, whereas it remains in the olivine stoichiometry at $\sim 2,300^\circ\text{C}$.

Figure 14 shows the variation in Mg/Si atomic ratio (note that the abscissa is different from those in Figs. 12 and 13). The positive slope indicates the higher volatility of SiO₂ than MgO. The trend observed here is applicable to a wider temperature range, because it depends on temperature only weakly as shown in the figure.

DISCUSSION ON EARLY CHEMICAL FRACTIONATIONS

LARIMER (1967) and GROSSMAN (1972) have revealed the equilibrium condensation sequence of elements as a function of temperature, from the cooling nebular gas with the solar elemental abundances. One of the purposes of our study is

Fig. 13. Variation in the atomic ratio, (Fe+Mg)/Si, in evaporation residues. Dashed lines: calculations based on the temperature dependence of the volatilities (Fig. 11). Ol: olivine stoichiometry. Px: pyroxene stoichiometry. VF: vaporized fraction. Symbols are the same as in Fig. 12.

to characterize the chemical fractionation of primitive materials as a sequence from the beginning of evaporation to its completion. The evaporation sequence is complementary to the condensation sequence and may be another important clue to elucidating the chemical differentiations of the planetary and meteoritic materials.

1. Evaporation sequence

In this section, we clarify the evaporation sequence of the five component melt in vacuo. It may give a gross picture for the evaporation sequence of primitive materials with many other components. The important point is that the sequence described here is characteristic of the evaporation metamorphism controlled by surface vaporization reactions on the evaporating

Fig. 14. Variation in the atomic ratio, Mg/Si , in evaporation residues. VF^* denotes the vaporized fraction with respect to the two component system, $MgO-SiO_2$. Solid line shows a general trend defined by all the data points. Symbols are the same as in Fig. 12.

Fig. 15. Sequential change in chemical composition of evaporation residues. RF (residual fraction) = $100 - VF$ (vaporized fraction). Triangles: the present experimental data at $1,800^\circ C$. Circles: the data of HASHIMOTO *et al.* (1979) at $1,800^\circ C$ except *e* ($1,700^\circ C$) and *i* ($1,900^\circ C$). Data between $RF = 40$ and 20 are lacking, so that the lines of MgO and SiO_2 are interpolated by taking account of their relative volatilities in this compositional range (see text). Roman numerals, I-IV, at the top denote the evaporation stages (see text).

medium.

Figure 15 shows the change in chemical composition of the melt with the initial composition, the solar composition, caused by progressive evaporation at $1,800 \pm 200^\circ\text{C}$. Based on this diagram, the evaporation sequence is divided into four stages. Stage I is defined as, from the initial state to the extinction of FeO in the melt. This stage, almost covered by the experiment described in this report, corresponds to RF (residual fraction) = 100-50% at $1,800 \pm 200^\circ\text{C}$. Stage II is defined as, from the extinction of FeO to the point where the reversal of volatilities takes place between SiO_2 and MgO (viz., RF = 50-30%). At Stages I and II, SiO_2 is more volatile than MgO, and hence the Mg/Si ratio increases with progressive evaporation. Stage III is defined as, from the volatility reversal to the extinction of MgO (viz., RF = 30-6%). MgO is more volatile than SiO_2 at this stage and the Mg/Si ratio decreases, down to zero at the end of this stage. Finally, Stage IV is defined as, from the extinction of MgO to the SiO_2 extinction (viz., RF = 6-3.5%).

Each stage is examined in detail in the following subsections. The description of Stage I is based on the present experimental results. Stage II is examined by thermodynamic considerations. Stages III and IV are described on the basis of both thermodynamic considerations and the experimental results by HASHIMOTO *et al.* (1979).

Stage I Evaporation stage I is characterized by the intense evaporation of Fe component. It originates in the highly volatile nature of ferrous iron, possibly as a result of the disproportionation reactions proposed in the previous section.

CaO and Al_2O_3 , most refractory among others, are being enriched in the melt monotonously with decreasing RF. Concentrations of MgO and SiO_2 also tend to increase, but they show a slight vaporization.

The bulk composition, initially near the olivine stoichiometry, becomes pyroxenic by the selective evaporation of FeO. On further evaporation (RF > 60%), it tends to approach the for-

sterite stoichiometry owing to the higher volatility of SiO_2 than MgO.

Stage II The system is reduced to quaternary $\text{MgO-SiO}_2\text{-CaO-Al}_2\text{O}_3$ at Stage II, but the $\text{CaO+Al}_2\text{O}_3$ content is relatively low, typically 8-16 mol%. So that the evaporational trend is approximated by that of the MgO-SiO_2 system.

Figure 16 shows the activity coefficients (γ) of SiO_2 and MgO at $1,600^\circ\text{C}$ in the MgO-SiO_2 melt. Though the system is below the liquidus at the Mg/Si ratio > 1.1 at $1,600^\circ\text{C}$, we treat the system as a liquid state in order to see the evaporational trend of the melt.

At Mg/Si = 1.0 (the solar ratio), γ_{SiO_2} is 25 times larger than γ_{MgO} . The ratio of vacuum volatility of SiO_2 to that of MgO is given approximately by the product of the ratio of their activity coefficients and the vapor pressure ratio of their pure phases (see eqn. (16); $\alpha_i/\alpha_j = 1$ is assumed in this case). As the latter factor is ~ 0.7 at $1,600^\circ\text{C}$, the vacuum volatility of SiO_2 is about twenty times as large as that of MgO. Accordingly, the Mg/Si ratio increases by the selective evaporation of SiO_2 .

At Mg/Si $\simeq 1.3$ (i.e., the beginning of Stage II), the vacuum volatility of SiO_2 is about seven times as large as that of MgO. Therefore, the Mg/Si ratio continues to increase.

At Mg/Si = 1.7, MgO and SiO_2 should show the same vacuum volatility. Eventually, the Mg/Si ratio does not change by further evaporation (i.e., congruent vaporization).

The trend described above for $1,600^\circ\text{C}$ holds at higher temperatures, e.g., at $1,800 \pm 200^\circ\text{C}$, because the ratio of vacuum volatility of MgO to that of SiO_2 is insensitive to temperature. The latter view is based on their similar vaporization enthalpies (i.e., the slopes of their vapor pressure curves; compare $\Delta H^\circ/z$ between (13) and (18) or between (14) and (19) in Table 6), and on the weak temperature dependences of activity coefficients in most binary silicate melts (RICHARDSON, 1974). An additional support of this view is obtained from the experimental result that the volatility ratio of MgO to SiO_2 varies only little with temperature as indicated

in Fig. 11.

Stage III At Stage III, SiO_2 and MgO are still main vaporizing components as at Stage II. However, the volatility of MgO is higher than that of SiO_2 , resulting in the relative depletion of MgO in the melt. As shown in Fig. 15, the extinction of MgO occurs prior to SiO_2 (at $\text{RF} = 6\%$) whereas SiO_2 remains in the melt as much as 15 mol%. Concentrations of CaO and Al_2O_3 increase monotonously in the melt owing to the selective evaporation of MgO and SiO_2 .

The enrichment of CaO and Al_2O_3 in the melt is evidently responsible for reversing the volatilities of MgO and SiO_2 . In the melt structure, CaO is a stronger network modifier than MgO (YOKOKAWA and NIWA, 1969). Therefore, it is supposed that the strong interaction of CaO with silica makes the silica activity decrease and releases MgO from the interaction with silica. On the other hand, Al_2O_3 is an amphoteric component in a silicate melt and does not show a strong interaction with both SiO_2 and MgO (WOOD and HESS, 1980). These natures of CaO and Al_2O_3 are seen in the ternary activity diagrams, CaO-MgO-SiO_2 and $\text{Al}_2\text{O}_3\text{-MgO-SiO}_2$ (REIN and CHIPMAN, 1965). The addition of CaO by 20 mol% into the MgO-SiO_2 binary melt decreases γ_{SiO_2} by an order of magnitude and increases γ_{MgO} by the same order, while these activity coefficients are insensitive to the addition of Al_2O_3 . As a result, CaO is considered to play a major role in changing relative volatilities of MgO and SiO_2 .

Such an effect of CaO becomes larger with the advance of evaporation stages, because CaO is enriched in the melt owing to its refractoriness. In the followings, we describe how it affects the evaporational behaviors of MgO and SiO_2 through the evaporation stages, I to III.

Figure 17 is a portion of the MgO-SiO_2 phase diagram wherein three pieces of information are shown. Symbols a, b, c and denote the Mg/Si ratio of the melt at the $\text{CaO+Al}_2\text{O}_3$ ($\text{CaO/Al}_2\text{O}_3 \approx 1$ molar ratio) concentrations of 5, 10, 20 and 50 wt%, respectively. Symbols o', a', b', c' and d' denote the Mg/Si ratio where MgO and

SiO_2 should vaporize congruently at $\text{CaO+Al}_2\text{O}_3 = 0, 5, 10, 20$ and 50 wt%, respectively. They are determined using eqn. (16) ($\alpha_i/\alpha_j = 1$ is assumed) and the activity data of MgO and SiO_2 in the CaO-MgO-SiO_2 system (REIN and CHIPMAN, 1965). Lines a'', b'' and c'' are projections onto the MgO-SiO_2 system of the liquidus in the $\text{CaAl}_2\text{O}_4\text{-MgO-SiO}_2$ system at $\text{CaO+Al}_2\text{O}_3 = 5, 10$ and 20 wt%, respectively.

The selective evaporation of SiO_2 relative to MgO causes the composition of the melt to shift leftwards (e.g., $a \rightarrow b \rightarrow c$ at $1,800^\circ\text{C}$). Meanwhile, the concentration of $\text{CaO+Al}_2\text{O}_3$ increases in the melt. By this effect the liquidus surface is successively depressed ($a'' \rightarrow b'' \rightarrow c''$) (IRVINE, 1975). At the same time, the volatility difference between MgO and SiO_2 reduces, resulting in the rightward shift of the chemical composition ($a' \rightarrow b' \rightarrow c'$) at which MgO and SiO_2 should exhibit the same vacuum volatility.

Fig. 16. Activity coefficients of MgO and SiO_2 in the binary MgO-SiO_2 at $1,600^\circ\text{C}$. Standard states are pure liquids. Solid lines: RICHARDSON (1953). Dashed lines: extrapolations of the solid lines to the points a. a: activity coefficients at $1,600^\circ\text{C}$ derived from the activity coefficients at the eutectic point ($1,850^\circ\text{C}$) by assuming regular solution (excess entropy is put at zero). b: ibid. (excess entropy of configuration only is put at zero; the empirical relation is used between excess thermal entropy and excess thermal enthalpy, $\Delta S^E \approx \Delta H^E/3,000$ (RICHARDSON, 1974)). Arguments in the text are based on a, but do not differ qualitatively on b. Roman numerals, I and II, denote the evaporation stages.

So that the congruent vaporization is realized at a SiO_2 concentration (i.e., at $c = c'$) higher than in the pure MgO-SiO_2 system (at o') described in the previous section. The point $c (= c')$ corresponds to the end of Stage II at $1,800^\circ\text{C}$.

With the successive enrichment of $\text{CaO} + \text{Al}_2\text{O}_3$ due to further evaporation of MgO and SiO_2 , the composition of the congruent vaporization continues to shift rightwards ($c' \rightarrow d' \rightarrow$).

So that the composition of the melt begins to shift backwards ($c \rightarrow d \rightarrow$) until MgO vaporizes out. This stage belongs to Stage III by the criterion, viz., the higher volatility of MgO than SiO_2 .

The circumstances explained above take place at temperatures $\geq 1,600^\circ\text{C}$, where the melt composition does not intersect the liquidus surface because of the successive depression of liquidus temperatures by the successive enrichment in CaO and Al_2O_3 .

Below $1,550^\circ\text{C}$ and from Stage II on, evaporation occurs from the crystalline phase composed mainly of enstatite (MgSiO_3) and forsterite (Mg_2SiO_4). In their vacuum vaporization experiments at $1,350$ – $1,580^\circ\text{C}$, SATA *et al.* (1978) have found the selective vaporization of SiO_2 from these crystals. So that the solid state evaporation also changes the composition of the system into the MgO -rich side. If the system were of MgO-SiO_2 , the final solid after significant evaporation would be pure MgO , because no stable phase exists between periclase (MgO) and forsterite. In the present quaternary system, however, the enrichment in CaO and Al_2O_3 changes the mineral constitution and also reduces liquidus temperatures, by which a partial or bulk melting does occur as a result of selective evaporation from solids. The detailed analysis of such a low-temperature evaporation is left for future systematic studies.

Fig. 17. Change in chemical composition of the melt by progressive evaporation, represented on the MgO-SiO_2 phase diagram. Heavy solid lines are phase boundaries in the MgO-SiO_2 system. Symbols with or without primes indicate a: the initial state before evaporation ($\text{RF} = 100$; $\text{CaO} + \text{Al}_2\text{O}_3 = 5\text{wt}\%$), b: the point of transition from Stage I to II at $1,800^\circ\text{C}$ ($\text{RF} = 50$; $\text{CaO} + \text{Al}_2\text{O}_3 = 10\text{wt}\%$), c: the point of transition from Stage II to III ($\text{RF} = 30$; $\text{CaO} + \text{Al}_2\text{O}_3 = 20\text{wt}\%$) and d: the point where the initial Mg/Si ratio recurs ($\text{RF} = 10$; $\text{CaO} + \text{Al}_2\text{O}_3 = 50\text{wt}\%$). Symbols a-d without prime indicate the chemical composition of the melt with respect to the MgO-SiO_2 binary, a'-d' indicate the chemical composition of congruent vaporization (C.V.) which includes the effect of CaO (cf., o' is that of the pure MgO-SiO_2 binary), a''-c'' are projections of the liquidus surface in the pseudo-ternary, $\text{CaAl}_2\text{O}_4\text{-MgO-SiO}_2$ (IRVINE, 1975). Arrows show successive movements of these points or lines with progress of evaporation.

Stage IV and further stages The evaporation of CaO starts at the very point of the extinction of MgO as seen in Fig. 15. The experimentally determined volatility of CaO is about $1/3$ of that of SiO_2 at this stage.

The ratio of CaO to SiO_2 in vacuum volatility is calculated from thermochemical data (JANAF, 1971) and the activity data in the $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$ system (REIN and CHIPMAN, 1965). If α_i/α_j is assumed to be unity in eqn. (16), the ratio is 0.36 (at $1,600^\circ\text{C}$) at the chemical composition of the melt in the beginning of Stage IV. This agrees well with the value experimentally determined, suggesting that the above

assumption for the vaporization coefficients is valid.

After the complete vaporization of SiO_2 , the system is reduced to $\text{CaO-Al}_2\text{O}_3$. By further evaporation, CaO is expected to vaporize out prior to Al_2O_3 as predicted from Fig. 15.

In the actual meteoritic and planetary materials, refractory components other than CaO and Al_2O_3 might be concentrated to a detectable degree at Stage IV and the later evaporation stages. TiO_2 , only 0.1 mol% in the bulk of Murchison meteorite, has been concentrated to 2-3 mol% at Stage IV (HASHIMOTO *et al.*, 1979). Other refractory elements such as Sc, REE, Th, etc. should be also enriched in the evaporation residues at smaller RF and actually was so in the experiments by NOTSU *et al.* (1978), MASUDA and TANAKA (1979) and

Fig. 18. Change in chemical composition of evaporation residues at various temperatures. Solid lines: experiments. Dashed lines: calculations based on the temperature dependences of the volatilities (Fig. 11).

Fig. 19. Temperature dependence of evaporation sequence. Symbols, I-IV, denote the evaporation stages described in the text. Ia and Ib are variations of Stage I which appear above $\sim 2,200^\circ\text{C}$.

NAGASAWA and ONUMA (1979). The study on the evaporational behaviors of these refractory elements is an important subject for the clarification of later evaporation stages.

Temperature dependence of evaporation sequence If we know temperature dependences of the volatilities, evaporational trends can be predicted in a wide temperature range. This is made for the RF range 100-50% on the basis of Fig. 11, and is shown in Fig. 18 as the compositional change in residual melts. A notable feature is that at higher temperatures FeO and SiO_2 show a simultaneous vaporization rather than a selective vaporization of FeO. The trend of MgO enrichment does not change significantly with temperature, because of the large volatility difference between MgO and FeO or SiO_2 .

Though we do not have satisfactory data on the volatilities of the present five components in the entire RF range, the gross picture of temperature dependence of the evaporation sequence is tentatively shown in Fig. 19. An important character of low-temperature vaporization is the strong selectiveness of vaporizing components. It stems from the growing difference in volatility among the components with decreasing temperature. As a result of this

nature, the chemical components disappear one after another from the condensed phase with the progress of evaporation. On the other hand, the non-selectiveness of components is indicated for high-temperature vaporizations for the same reason. Accordingly, the transition between each evaporation stage shifts to a smaller RF with increasing temperature (a, c and d in Fig. 19), and the range of Stage I is broadened.

The II-III transition precedes the I-II transition supposedly above $\sim 2,200^{\circ}\text{C}$. Eventually, a different evaporation sequence appears, which we temporarily designate as Stages Ia and Ib. The earlier appearance of II-III transition at higher temperatures (b in Fig. 19) originates in the relative enhancement of SiO_2 vaporization among the components, by which the congruent vaporization with respect to MgO-SiO_2 occurs at larger RF.

Effect of redox state on evaporation In the present experiments Fe was originally included in ferrous state. However, the Fe valences in primitive materials might have been various. Some redox agents (solids such as graphitic carbon and gases such as H_2 , CO ; H_2O , CO_2) may affect the valence during the course of evaporation metamorphism. Here, we consider the relative efficiencies of evaporation for different valences of iron, i.e., ferrous, ferric or metallic iron in the silicate melt.

Ferrous iron is not a vaporizing species in itself, but vaporizes through the disproportionation reactions as suggested in the former discussion. The real vaporizing species are considered to be metallic and ferric irons. Accordingly, the volatility of ferrous iron appears to be relatively high, almost at the same level as that of pure iron.

Ferric iron has an escaping tendency lower than metallic one as indicated by the Fe^{3+} enrichment in the experimental solid residues. This is consistent with the fact that the equilibrium vapor pressure of pure Fe_2O_3 is 1/4 of that of metallic iron at $2,000^{\circ}\text{K}$. Therefore, the silicate material initially with ferric iron is expected to show a smaller rate of Fe vaporiza-

tion than with ferrous iron.

Metallic iron has the largest vapor pressure among the three Fe components of different valence states when they are compared as pure phases. However, when it forms globular particles in a silicate melt as is often observed, Fe vaporizes only from the metal surface exposed to a free space. This makes a contrast with the case where Fe is dissolved in the silicate and thus utilizes a whole surface area of the evaporating medium. Because of such a geometric factor, the existence of metal in place of ferrous and ferric irons does not necessarily result in a high rate of Fe vaporization.

2. Comparison of evaporation and condensation sequences

In this section, we make a comparative examination of the evaporation and condensation sequences on the basis of the discussion in the former section and the equilibrium condensation theory by GROSSMAN (1972).

Figure 20 shows diagrammatically the evaporation and condensation sequences with respect to the major elements. The trajectories of evaporation and condensation indicate the sequential changes in chemistry of evaporation residue and condensate, respectively. The ternary Si-Mg-Fe represents a major chemistry of the condensed material in the early sequence of evaporation and in the later sequence of condensation, while the ternary Si-Mg-(Ca+Al) does in the later evaporation sequence and in the early condensation sequence.

Temperature (T) and the nebular total pressure (P_T) are important physical parameters for the evaporation and condensation sequences, respectively. Temperature variation affects a volatility (ζ) of each component according to the relation;

$$\ln \zeta = -E/RT + \text{const.} \quad (17)$$

where E is the activation energy of vaporization. On the other hand, variation in the nebular total pressure changes the condensation temperature (T_C) of each component according

to the relation;

$$1/T_C = -R \ln P_T / \Delta H^\circ + \text{const.} \quad (18)$$

where ΔH° is the enthalpy of vaporization reaction. In derivation of eqn. (18) the constitution of nebular molecular species is assumed unchanged by P_T change at constant temperature (SHIMAZU, 1967; GROSSMAN, 1972). Due to different E 's and ΔH° 's among the components, different sequences of evaporation and condensation appear as a result of temperature and pressure variations, respectively.

Evaporation and condensation sequences in the Si-Mg-(Ca+Al) system are rather insensitive to wide range variations of these parameters. It

stems from the small difference in vaporization energies (both E and ΔH°) between MgO and SiO₂, and from the far large volatilities of MgO and SiO₂ relative to CaO and Al₂O₃ in wide ranges of physical conditions (temperature and the nebular pressure). Eventually, the trend of evaporation trajectory shown in the diagram holds from the melting temperature ($\sim 1,873^\circ\text{K}$) to at least $3,000^\circ\text{K}$. The condensation sequence does not change appreciably from the one at $P_T = 10^{-3}$ atm. with the variation of P_T to a few orders of magnitude.

In the Si-Mg-(Ca+Al) system, the evaporation and condensation sequences are generally similar in trajectory. The deflection of the

Fig. 20. Evaporation and condensation paths. Evaporation paths: the present work. Condensation paths ($P_T = 10^{-3}$ atm.): the theoretical calculation by GROSSMAN (1972), and the later reports on the chemical compositions of condensates (GROSSMAN and CLARK, 1973; GROSSMAN, 1975). The condensation trajectories at $P_T = 10^{-4}$ and 10^{-5} atm. in the Si-Mg-Fe system, are reconstructed from that at 10^{-3} atm. on the basis of the pressure-dependences of condensation temperatures for metal and silicates (GROSSMAN, 1972). E: the original composition used for the experiments. C and R: the solar elemental compositions by CAMERON (1968) and by ROSS and ALLER (1976), respectively. The latter authors have estimated the ambiguity of elemental abundances, as shown in the figure. M/S: the metal/silicate separation from E. The encroaching figures in the lower right show the details of both paths in the Si-Mg-(Ca+Al) system; condensation at $P_T = 10^{-3}$ atm. and evaporation at $2,100 \pm 200^\circ\text{K}$. Mol%.

evaporation trajectory at *a* in the diagram indicates the reversal of the relative magnitudes in volatility between MgO and SiO₂ as explained in the previous discussion. A similar deflection appears at *a'* in the condensation trajectory where forsterite begins to react with the remaining SiO gas and is partially substituted by enstatite. This and other deflections seen in the condensation trajectory correspond to the changes in mineral constitution owing to the condensation of particular elements. In the evaporation sequence, however, the trajectory does not show distinct deflections other than at *a* and at the intersection with the Si-(Ca+Al) tie line.

In the Si-Mg-Fe system, on the other hand, the trajectories of evaporation and condensation show strong dependences on temperature and pressure, respectively. This is a result of the differences in vaporization energies (i.e., the differences in the proportionality constants in eqns. (17) and (18)) between Fe component and other two components (MgO and SiO₂). The difference in activation energy between them is 20-30 kcal/mol as indicated by the present experimental results (Fig. 10). The difference between their vaporization enthalpies is also 20-30 kcal/mol (compare (1) with (14) and (19) in Table 6).

The trajectories of evaporation are shown for four different temperatures in the Si-Mg-Fe diagram (1-4). The dotted region (denoted by A) is the composition area covered by various trajectories for temperatures from 1,873 to 3,000°K. In correspondence to the change of evaporation sequences (Stages I and II Δ Ia and Ib in Fig. 19), the trajectory changes its trend: it deflects halfway to the SiO₂ apex at >2,500°K. As a result, the trajectories at different temperatures cross at the same composition with respect to the Si-Mg-Fe ternary. For example, trajectory 4 intersects trajectories 1, 2 and 3 at some points in region A.

The condensation trajectories are shown in the same diagram for $P_T = 10^{-3}$, 10^{-4} and 10^{-5} atm. The drastic change of trajectories with P_T originates in the crossover of condensation tem-

peratures of Fe metal and silicates (forsterite and enstatite) in the vicinity of $P_T = 10^{-4}$ atm. (Fig. 5 in GROSSMAN, 1972). Chemical compositions in region A are covered by the trajectories from $P_T = 10^{-4}$ to 10^{-5} atm., and are also covered by the trajectories at $P_T < 10^{-5}$ atm. Thus, condensations at different pressures generate the same chemical composition of condensates with respect to the Si-Mg-Fe ternary.

We summarize the character of the chemical differentiation of primitive materials which results from the evaporational and condensational fractionations, as follows. The major chemical compositions of later evaporation residues and early condensates are constrained to a relatively narrow range regardless of wide range variations of temperature and the nebular pressure. In the early evaporation and in the later condensation, on the other hand, various compositions are attained depending on these physical conditions. Two or more paths are possible to reach a particular chemical composition in region A in both evaporational and condensational fractionations.

3. Chondrules and inclusions in chondrites as products of early chemical fractionations

In this section we apply the evaporation and condensation sequences to the interpretation of the chemistry of chondrules and inclusions in chondrites. These meteoritic components show wide ranges of chemical compositions, which may reflect (1) different fractionation processes in the early solar nebula, (2) different physical conditions in those processes and (3) chemical diversity of their source materials.

Ca, Al-rich inclusions (CAI) in carbonaceous chondrites have been interpreted as condensates from a hot nebular gas with the solar elemental abundances (CHRISTOPHE MICHEL-LÉVY, 1968; LARIMER and ANDERS, 1970; GROSSMAN and CLARK, 1973; BLANDER and FUCHS, 1975), or evaporation residues from a primitive Cl-like material (KURAT, 1970; CHOU *et al.*, 1976; NOTSU *et al.*, 1978; HASHIMOTO *et al.*, 1979). Some modifications have been suggested about their origin (for a critical discussion, see WOOD,

1981) in relation to the constraints imposed by the isotopic anomalies found in these inclusions (WASSERBURG *et al.*, 1980). In any proposal of their origin, however, there seems to be an agreement in that their chemical compositions were essentially established in the process of chemical fractionations governed by the volatility differences among elements.

Chondrules in carbonaceous chondrites have been discussed separately from CAI by most of the workers. However, they may have a genetically close relation with CAI, because there is a continuity in chemical composition between these two groups of materials and because the chondrules also possess the oxygen-isotopic anomalies similar to those in CAI, though of a lesser degree. In the two-component model of carbonaceous chondrites (ANDERS *et al.*, 1976), the chondrules have been interpreted as volatile-poor complements to the matrix materials. Such an interpretation lends support to the origin of the chondrules as condensation or evaporation products as well as CAI.

Chondrules in ordinary chondrites have been also regarded as volatile-poor complements by the two-component model (KEYS *et al.*, 1971; LAUL *et al.*, 1973). In the chemical analyses of individual chondrules, however, depletion of volatiles has not been observed relative to the solar elemental abundances for moderately volatile elements such as Mn, Cr, Na and K (e.g.,

WALTER, 1969; EVENSEN *et al.*, 1979), and relative to the whole rocks for much more volatile elements (GROSSMAN *et al.*, 1978; 1979). On the other hand, siderophile elements are depleted in the chondrules relative to lithophile elements (e.g., OSBORN *et al.*, 1973; GOODING *et al.*, 1980). These observations suggest that chondrules in ordinary chondrites are deficient in siderophiles but not in volatiles.

In the followings, we compare the chemical compositions of chondrules and inclusions with the evaporation and condensation sequences clarified in the previous section. The chemical data of chondrules and inclusions are those from MCSWEEN (1977a; b; c), KIMURA and YAGI (1980) and NAGAHARA (1981). The petrologic classification used here follows MCSWEEN (1977c, Table 1), and is shown in Table 7.

The chemical compositions on the major component basis, are shown in Fig. 21 (a)-(c) for different types of chondrules and inclusions, together with the trajectories of evaporation and condensation. If a particular grain is formed exclusively by evaporation or condensation process under the constraints (initial composition, T , P_T , etc.) described in the previous section, its composition should lie somewhere on their trajectories in the Si-Mg-(Ca+Al) diagram. In the Si-Mg-Fe diagram it should lie somewhere in region A or on the tie line Mg-Si ($Mg/Si < 1.7$), depending on the physical

Table 7. Petrologic classification of chondrules and inclusions (after MCSWEEN, 1977c)

Petrographic type	Distinguishing characteristics
<u>Chondrules</u>	
Type I	Granular olivine ($\sim Fo_{90-100}$) $\pm$ pyroxene $\pm$ spinel in clear glassy mesostasis.
Type I; opaque-mineral-bearing	Similar to type I with addition of disseminated opaque grains; usually larger and more irregular in shape than type I chondrules.
Type II	Porphyritic or barred olivine ($\sim Fo_{50-85}$) + Cr-rich hercynite in brown glassy mesostasis.
Type III	Excentroradial pyroxene ($\sim En_{90-100}$) + glass; generally smaller than other chondrule types.
Type IV	Usually anorthite, spinel, diopside, melilite $\pm$ glass molded into well-rounded chondrules.
<u>Inclusions</u>	
Amoeboid Olivine	Irregular micron-sized aggregates of olivine (Fo_{80-100}), sometimes containing pyroxene, feldspathoid minerals, spinel in small amounts.
Coarse-grained CAI	Melilite, spinel, diopside, perovskite, hibonite, anorthite, fassaite.
Fine-grained CAI	Aphanitic pyroxene, spinel, grossular, and feldspathoid minerals in irregular aggregates.

Fig. 21(a)

Fig. 21(c)

Fig. 21. Chemical compositions of chondrules and inclusions as compared with the sequences of evaporation and condensation. (a) Inclusions and Ca, Al-rich chondrules in carbonaceous chondrites (CV3: Allende, Arch, Bali, Coolidge, Efremovka, Grosnaja, Kaba, Mokoia, Renazzo and Vigarano. CO3: Felix, Isna, Kainsaz, Lancé, Ornans and Warrenton. Anomalous chondrites: Kakangari and Karoonda. Data from MCSWEEN (1977a; b; c)). (b) Ca, Al-poor chondrules in carbonaceous chondrites (ibid. Data from MCSWEEN (1977a; b; c)). (c) Chondrules in ordinary chondrites (Chainpur-LL3, Tieschitz-H3 and Bishunpur-L3; MCSWEEN (1977c). ALH77015-L3; NAGAHARA (1981). Yamato74191-L3; KIMURA and YAGI (1980)). Notations other than noted follow those in Fig. 20. Mol%.

condition (T or P_T) and the degree of evaporation or condensation.

Figure 21(a) shows the chemical compositions of inclusions (CAI and amoeboid-olivine inclusions) and Ca, Al-rich chondrules in carbonaceous chondrites. Most of the amoeboid-olivine inclusions are located in region A, suggesting that they are either of evaporation or of condensation origin. On the other hand, the compositions of CAI and Ca, Al-rich chondrules show wider distributions: in the Si-Mg-(Ca+Al) diagram they appear to be spread toward the Si apex from positions of the trajectories, and in the Si-Mg-Fe diagram toward the Si apex from region A or toward the Fe apex from the Mg-Si tie line. The material enriched in both Ca+Al

and Fe could be produced in the condensation process at $P_T > 10^{-3}$ atm., but this does not explain the Si excess. Some additional process other than the normal evaporation and condensation must have existed and caused enrichments in Si and Fe simultaneously or independently.

The origin of the rim structure observed commonly in CAI may be one possible clue to such compositional deviations of Ca, Al-rich inclusions and chondrules as noted above. These rims are peculiar in that they concentrate volatile elements such as Na and Cl (WARK and LOVERING, 1977) which by no means condense at high temperatures nor remain unvaporized at high VF. They are also rich in Fe and are sili-

ceous as compared with the inner portions of the inclusions. MACPHERSON *et al.* (1981) have interpreted the rims as the layers produced in a diffusion-controlled process by the reaction of pre-existing CAI grains with a surrounding, (Si, Fe, Na, etc.)-containing gas. CHOU *et al.* (1976) have observed the concentration gradients, high to low from the surface to the center, of Mn, Fe, Co, Ni, alkalis, and other volatile elements in some CAI. Their observation implies that the reaction with the ambient gas have affected even the deep interiors of the CAI. We suggest that the Ca, Al-rich chondrules which do not have noticeable rim structures might have been also influenced by the reaction with a gas rich in Si, Fe, etc.

Figure 21(b) shows the chemical compositions of Ca, Al-poor chondrules in carbonaceous chondrites. Most of type I and II chondrules (McSWEEN, 1977c) are located in region A or A', implying that these chondrules have formed simply by evaporational fractionation or by condensational fractionation. Type II chondrules might be interpreted as early (*viz.*, least vaporized) evaporation residues or later condensates. Some type II chondrules located outside region A or A', have relatively high Ca+Al concentrations. They may reflect merely a dispersion of chemical compositions in their source materials, or involve a certain additional process.

Some type I chondrules which have Mg-rich compositions extending outside region A, might invoke an additional factor that has not been discussed explicitly, but they can be interpreted within the framework of evaporational or condensational fractionation. The key is such a trend that the Mg-rich chondrules are depleted in Ca+Al. As explained in the previous discussion, Ca has the effect to decrease the volatility difference between Si and Mg, thereby a congruent vaporization is realized at the higher Si concentration with the higher Ca concentration. If the original material has a Ca concentration lower than the present experimental composition E, the congruent vaporization occurs at a Mg concentration higher than

the Mg-sided border of region A. A similar situation might be possible in a condensational fractionation, if the original nebular gas has a low abundance of Ca relative to the solar one. The chemical compositions of some amoeboid-olivine inclusions (Fig. 21(a)), which are deviated from region A to the Mg-rich side, are interpreted in the same way. The consideration made here requires the existence of Ca-poor materials prior to the last chemical fractionations, suggesting the necessity of multiple-stage fractionation processes in the early solar nebula.

Figure 21(c) shows the chemical compositions of chondrules in ordinary chondrites. The general characteristics are (1) depletion of Fe relative to the solar composition as observed in the Si-Mg-Fe diagram, and (2) dispersion of chemical compositions around the solar composition as observed in the Si-Mg-(Ca+Al) diagram. These could be interpreted as a result of low temperature evaporation imposed on the chemical heterogeneity of their source materials. However, the chondrules are depleted neither in Mn and Cr which have similar volatilities to Fe nor in much more volatile elements such as Na and K. The depletion of Fe is rather regarded as a result of metal/silicate separation, which might have been accompanied by the removal of other siderophile elements.

The dispersion of lithophile elemental compositions around the solar composition can be explained neither by evaporational and condensational fractionations nor by metal/silicate separation. Therefore, it might be intrinsic in precursor materials (DODD, 1978; McMAHON and HAGGERTY, 1980), or might have originated in different source materials and their mixing on chondrule formation (OSBORN *et al.*, 1974; GOODING *et al.*, 1980; LUX *et al.*, 1981).

CONCLUSION

The experimental study of evaporation metamorphism comprises two parts; the analysis of elementary processes of evaporation, and the analysis of chemical effects as a result of evaporation. In the first analysis, it is the most im-

portant to determine and to characterize the rate-controlling process among all the possible processes. The result of the present experiments indicates that the rate-controlling process is the surface reactions on the melt surface. In the second analysis the escaping tendency is examined for each element by using the 'volatility' introduced as a quantitative indicator. The description of volatilities as a function of temperature and composition of the melt provides a basis to characterize the chemical fractionations caused by evaporation. The chemical fractionations revealed here directly reflect the kinetics of surface reactions and the thermochemical properties of the melt.

The study of the early chemical fractionations is more reinforced by the addition of the systematic study of evaporation metamorphism. The chemical sequences of evaporation and condensation are definitive keys to the fates of primitive materials to have evolved in the early solar nebula. Although the sequences described here do not cover all the possible, chemical and physical conditions in the early solar nebula, they would be a milestone for further investigations.

Comparison of the sequences with the chemical compositions of meteoritic and planetary materials discriminates the mechanisms of early chemical processing operated on their source materials. The investigation on the chemical compositions of chondrules and inclusions attests the critical role of evaporation and condensation in their formation processes. At the same time, the systematic deviations of compositions from the sequences observed for some groups of chondrules and inclusions suggest some additional processes involved in their formation histories.

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