

Proc. NIPR Symp. Antarct. Meteorites, 7, 164–177, 1994

VOLATILIZATION OF ALKALI METALS FROM THE HEATED MURCHISON (CM2) METEORITE

Taro K. SHIMAOKA^{1*}, Nobuo MIYANO^{2**}, Toshiyuki BABA^{2***},
Koshi YAMAMOTO² and Noboru NAKAMURA^{1,2}

¹*Department of Science of Material Differentiation, Graduate School of Science and Technology, Kobe University, 1-1, Rokkodai-cho, Nada-ku, Kobe 657*

²*Department of Earth Sciences, Faculty of Science, Kobe University, 1-1, Rokkodai-cho, Nada-ku, Kobe 657*

Abstract: In order to examine volatilization processes of alkali metals at high temperature, heating experiments were carried out using a starting material prepared from Murchison (CM2) (grain-size: $\sim 10\ \mu\text{m}$) at temperatures of 1200–1400°C under a constant pressure of 8×10^{-6} Torr, and heating duration up to 80 min. Analyses of alkalis (Na, K, Rb), major and minor elements and petrographic examinations were performed for run products. Results show that fractional volatilization of alkali metals occurred during heating. It is suggested that the volatilization rates of alkali metals are influenced by the chemical composition of partial melt.

1. Introduction

Alkali metals are moderately volatile lithophile elements which may be fractionated in high temperature processes, and thus can be useful indicators of formation conditions of planetary materials. SHIMAOKA and NAKAMURA (1989) examined vaporization of sodium from partially molten chondritic material and showed that there are no differences in the vaporization mechanism between vaporization from partial melts and vaporization from total melts. They also performed vaporization experiments on sodium, potassium and rubidium on partially molten chondritic material at a constant temperature (1300°C) and at a constant heating duration (40 min), but under various total pressures ($\sim 10^{-5}$ – $\sim 10^{-1}$ Torr) controlled with pure helium. The results suggested that the vaporization rates of Na, K and Rb decreased in the order $\text{Na} > \text{K} > \text{Rb}$ with increasing total pressure (SHIMAOKA and NAKAMURA, 1991).

Preliminary results of volatilization experiments by NAKAMURA and SHIMAOKA (1988) indicated unusual trends in ratios of alkali metals depending on temperature of the melt. In particular, the Rb/K ratio appeared to depend on the

* Present address: Department of Chemistry, Faculty of Science, Tokyo Metropolitan University, 1-1, Minami-osawa, Hachioji-shi, Tokyo 192-03.

** Present address: Osaka Gas Industry System Research Institute, Toyonaka 565.

*** Present address: Mineralogical Institute, Faculty of Science, University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113.

composition of the melts (for example, sulfur contents). Similar trends are found in some Allende chondrules (MATSUDA *et al.*, 1990).

To further study the vaporization of alkali metals during formation of chondritic and/or planetary material, we have carried out additional vaporization experiments using the carbonaceous chondrite Murchison (CM2) as starting material. Experiments were done in the temperature range of 1200–1400°C under a constant total pressure (8×10^{-6} Torr) and duration of up to 80 min. In this article we report the results of chemical and petrographic examinations of the run products and discuss the vaporization behavior of Na, K and Rb.

2. Experimental

2.1. Starting material

Starting material was prepared from the Murchison (CM2) by using the following procedure. A fragment of the Murchison meteorite was washed with 1M-HCl, distilled water and distilled acetone. It was then broken into small chunks using an agate mortar. Chondrules and fusion crust were picked out and the remaining material was crushed into fine powder and then sieved using a teflon 50 μm sieve. The coarser grains were repeatedly pulverized into fine powder. Since the matrix material of C2 chondrites is closest in composition to the sun (MCSWEEN and RICHARDSON, 1977), this sample was used as a starting material, which has been utilized as a substitute for primitive dust materials (HASHIMOTO *et al.*, 1979). Grain-sizes of this sample were in most cases below 20 μm , occasionally grains were encountered up to 50 μm .

2.2. Apparatus and heating procedures

The vaporization apparatus is very similar to that reported in SHIMAOKA and NAKAMURA (1989). In this work, a new sample holder and new crucibles made of Mo instead of Ta were used.

The heating procedure is also similar to previous work (SHIMAOKA and NAKAMURA, 1989) except for minor differences (Table 1). An increased heating rate (51°C/min) was employed in this work compared to that in previous work ($\sim 30^\circ\text{C}/\text{min}$). This change does not seem to have a significant effect on the vaporization behavior of alkalis.

2.3. Analyses

Run products were broken into fragments in an agate mortar. A few fragments were used for preparation of thin sections, and the rest (main part) fraction was finely crushed to prepare it for chemical analysis. A part of the powdered sample (15–40 mg) was subjected to acid (HF-HClO₄) decomposition, dissolution in HCl and analysis of Na by atomic absorption spectroscopy (SHIMAOKA and NAKAMURA, 1989). The rest of the powdered sample (about 1 mg) was decomposed with a similar procedure as mentioned above, and analyzed for K and Rb by isotope dilution mass spectrometry using a direct loading technique (NAKAMURA *et al.*,

Table 1. Bulk concentrations of alkalis in run products and experimental conditions.

Run No.	Temp. (°C)	Duration (min)	Weight loss (%)	Na (ppm)	K (ppm)	Rb (ppm)
MR6	1200	0	15.4	2950	541	1.93
MR7	1200	20	17.1	802	335	1.02
MR8	1200	40	16.5	631	217	0.297
MR9	1200	60	16.8	410		
MR10	1200	80	17.7	386		
MR11	1250	0	16.0	2720	557	1.65
MR12	1250	20	17.5	668	231	0.613
MR13	1250	40	17.8	167	93.5	0.209
MR14	1250	60	16.5	65		
MR1	1300	0	17.0	3170	550	1.93
MR2	1300	20	16.8	474	105	0.287
MR3	1300	40	17.5	75	7.0	0.015
MR4	1300	60	18.8	6		
MR15	1330	0	18.5	2170	403	1.35
MR16	1330	20	18.4	33	37.9	0.120
MR17	1330	40	18.6	21	25.8	0.094
MR18	1400	0	17.9	1090	221	1.10
MR19	1400	20	19.7	10	20.8	0.097
MR20	1400	40	21.5	2	2.5	0.010

1989).

The procedural blanks of Na, K and Rb are 68, 3.2 and 0.0034 ng, respectively. Contributions of the blank to samples were less than a few % for analyses of Na but are ~30% for samples with Na contents below about 10 ppm. For K analyses, contributions of the blank to samples were less than 2% without only one exception (20%) and for Rb, they were less than 3%.

Chemical composition of minerals and interstitial glassy materials were determined with a scanning electron microscope (SEM) equipped with an energy dispersive spectrometer (EDS) (focused beam) (JEOL-840 A with KEVEX DELTA-2000). Operating voltage was 15 kV and the beam current was 2 nA. A ZAF correction procedure was used. Petrographic examinations were also performed using SEM-EDS.

3. Results and Discussion

3.1. Melting textures of heated samples

Examples of SEM back-scattered electron images (BEI) of run products are shown in Fig. 1. The textures include mainly olivine phenocrysts (light dark), glassy materials (irregularly shaped light portion), troilite and/or metal (rounded light portion) and holes (black parts). The following four features are worth noting here.

(1) Run products heated to temperatures below 1330°C contain abundant holes which are about 10 μm in radius. These holes decrease clearly with the increasing temperature and holes are absent in samples heated to 1400°C (Fig. 1c),

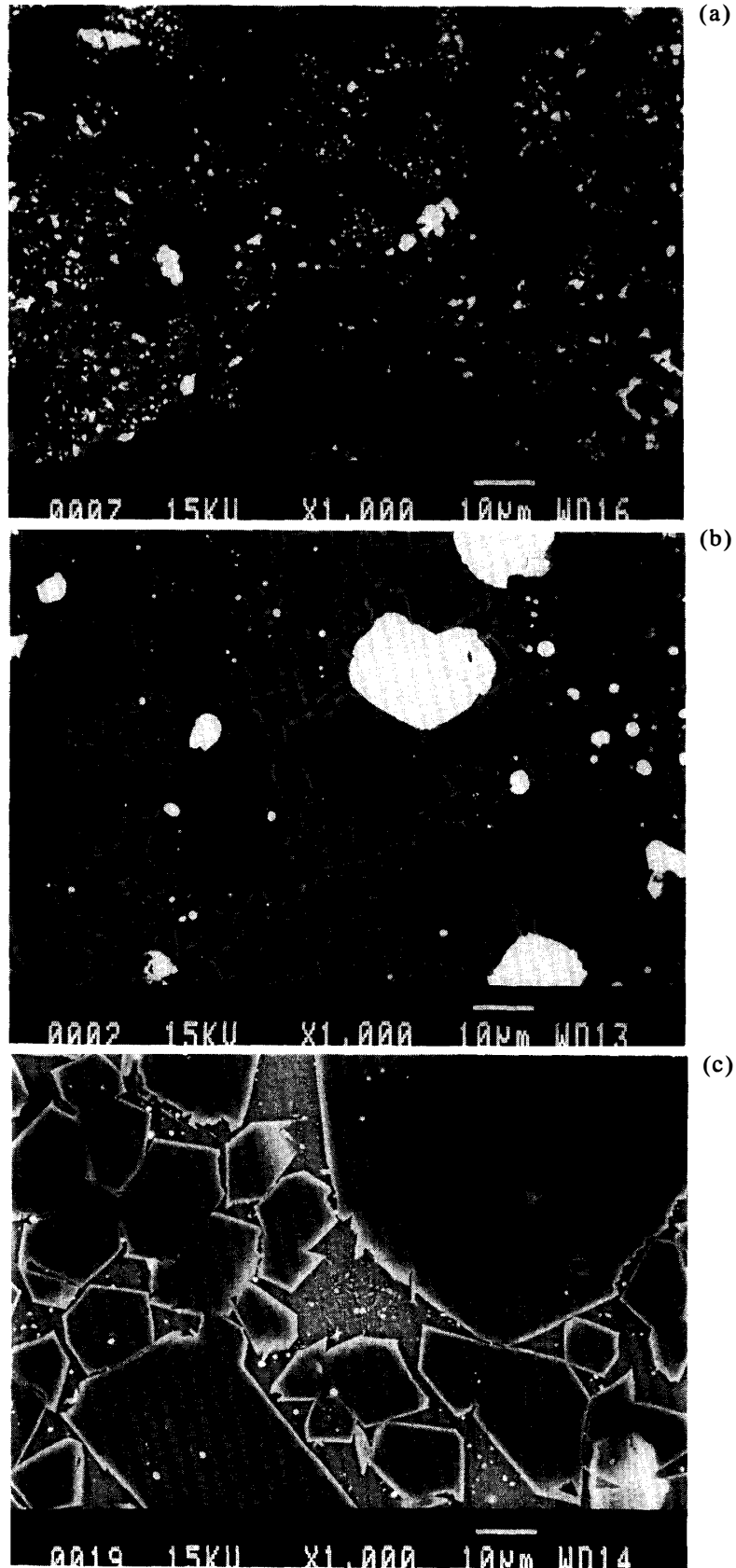


Fig. 1. SEM back-scattered electron images (SEM-BEI) of the heated samples.

- (a) Run product at 1200°C for 20 min. The texture consists of mostly unmelted materials and irregularly shaped holes (black) and indicates a very low degree of melting.
- (b) Run product at 1300°C for 20 min. One hole (black), glass materials representing partial melt (light), Fe-rich olivine (light dark) zoned with forsterite (dark) and rounded troilite grains (white) are noted.
- (c) Run product at 1400°C for 20 min. No troilite grains or zoned olivine grains are noted.

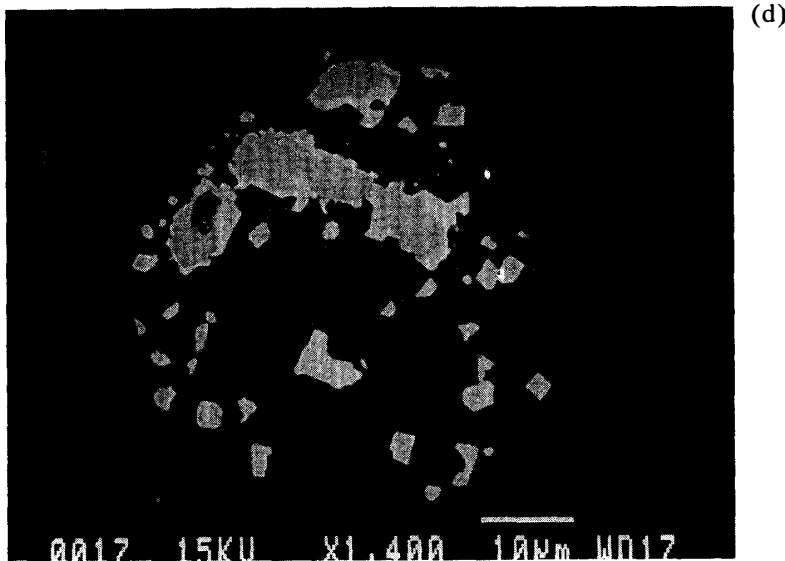


Fig. 1. (Continued)
 (d) Rounded troilite grains (dark area) containing some euhedral metal particles and non euhedral metal portions in run products of 1330°C.

suggesting that most holes were not formed by vesiculation of heated samples but represent open spaces unfilled with partial melts. This is supported by the presence of more abundant holes in run products from the starting material with coarser grain sizes at the same heating temperature, as discussed by SHIMAOKA and NAKAMURA (1989). In samples heated to 1400°C, spaces are filled entirely with partial melts.

(2) Significant amounts of interstitial glassy materials are present in all run products heated to temperatures above 1250°C. The fraction of glassy material is significantly higher in run products of the 1400°C experiments (Fig. 1c). In run products heated at 1200°C, very little partial melt is present (Fig. 1a). The Fe-rich rims were formed on olivine crystals by overgrowth during quenching, suggesting that the cooling rate ($\sim 500^\circ\text{C}/\text{min}$) in the experiment has not been fast enough to quench all the partial melts (SHIMAOKA and NAKAMURA, 1989).

(3) Some olivine phenocrysts are remarkably zoned (Table 2, Fig. 1b, c). Table 2 shows that the central part (so called "core" in Table 2; dark gray portion in Fig. 1b, c) is poor in iron; the outer part (so called "rim" in Table 2) rich in iron was formed by overgrowth during quenching as mentioned above. It is also shown in Table 2 that the degree of zoning (the difference in Fa content between core and rim) is lower for samples heated at higher temperature and for longer duration. FUCHS *et al.* (1973) reported that the Fa content of most olivines in the Murchison matrix was lower than 1%, perhaps suggesting that Fe-rich olivine around Fe-poor olivine crystallized from partial melts. The diffusion coefficients of Fe and Mg in olivine are about $10^{-10}\text{cm}^2\cdot\text{s}^{-1}$ at 1400°C (BUENING and BUSECK, 1973). The calculated diffusing distances of Fe and Mg in olivine at 1400°C for 20 min are a few μm . This suggests that Fe in the rim cannot diffuse into olivine cores during heating, resulting in strong zonation. Diffusion can also explain the lower degree of zoning and higher Fa content in the core for samples heated to higher temperatures and for longer durations.

Table 2. Chemical compositions of olivine rims and cores in run products (value in wt%).

Run No.	MR2		MR16		MR17		MR19		MR20	
Temp. (°C)	1300		1330		1330		1400		1400	
Duration (min)	20		20		40		20		40	
	core	rim	core	rim	core	rim	core	rim	core	rim
SiO ₂	41.8	35.7	42.4	36.3	41.7	36.5	40.6	37.1	41.3	36.7
TiO ₂	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Al ₂ O ₃	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Cr ₂ O ₃	0.4	0.3	0.2	0.4	0.5	0.3	0.3	0.4	0.3	0.5
CaO	0.3	0.4	0.6	0.2	0.2	0.2	0.4	0.2	0.4	0.2
FeO	1.4	32.5	1.0	33.0	3.6	25.0	7.7	23.7	4.7	26.7
MgO	54.7	29.3	54.9	29.3	53.2	35.1	49.5	36.3	52.5	34.0
MnO	0.2	0.4	0.1	0.3	0.3	0.5	0.3	0.4	0.2	0.4
NiO	0.3	0.3	0.2	0.4	0.3	0.4	0.3	0.3	0.3	0.3
Na ₂ O	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
K ₂ O	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Total	99.2	99.0	99.5	99.9	99.9	98.0	99.1	98.6	99.8	99.0
Fa (%)	1.5	46	1.4	47	5.0	36	10	34	6.0	38

(4) The troilite and metal grains in this work are more abundant than in the previous experiment (SHIMAOKA and NAKAMURA, 1989). This is caused by residual particles in the starting material due to the failure to remove metal with a magnet as mentioned by SHIMAOKA and NAKAMURA (1989). In heated samples at 1400°C, troilite grains are very scarce (Fig. 1c). SHIMAOKA and NAKAMURA (1989) noted that in the experiments at high temperatures the melting and the filling of open spaces with partial melts may have resulted in trapping of most troilite melts within the silicate melts and then decomposition of troilite was suppressed, but the part of the troilite which avoided trapping was decomposed and dissolved in melts. In this experiment, heating at a higher temperature (1400°C) causes decomposition and dissolution of most troilite in melts; no troilite grains were observed in samples heated to 1400°C. The variations of iron and sulfur contents in partial melts are discussed in the following section.

Figure 1d shows euhedral metal grains in a spherical troilite grain. Some anhedral metal grains are suggested to have formed by decomposition of troilite under imperfect equilibrium conditions, as discussed in SHIMAOKA and NAKAMURA (1989).

3.2. Chemical compositions of glasses

Chemical compositions of glasses are presented in Table 3 together with the bulk chemical composition of Murchison matrix material from MCSWEEN and RICHARDSON (1977). Figures 2 and 3 show the variations of major and minor element concentrations at various heating temperatures. In these figures, the bars indicate ranges of concentrations due to samples having been obtained at different heating durations (20 min and 40 min) at temperatures of 1330°C and 1400°C. The

Table 3. Chemical compositions of partial melts in run products and of Murchison (CM2) matrix (value in wt%).

Run No.	MR12	MR2	MR16	MR17	MR19	MR20	Murchison matrix*
Temp. (°C)	1250	1300	1330	1330	1400	1400	
Duration (min)	20	20	20	40	20	40	
SiO ₂	47.4	47.0	46.8	47.0	45.8	46.4	22.3
TiO ₂	0.6	0.6	0.7	0.6	0.6	0.6	0.04
Al ₂ O ₃	13.7	13.2	13.2	13.2	12.7	12.9	3.33
Cr ₂ O ₃	0.4	0.6	0.5	0.6	0.4	0.6	0.31
CaO	11.3	10.2	10.4	10.7	10.1	10.3	0.85
FeO	19.2	19.9	20.8	20.5	23.5	23.4	33.4
MgO	2.5	2.3	2.3	2.4	1.3	1.9	14.0
MnO	0.3	0.3	0.3	0.3	0.4	0.4	0.18
NiO	0.3	0.3	0.3	0.3	0.2	0.3	2.05
Na ₂ O	0.0	0.0	0.0	0.0	0.0	0.0	0.31
K ₂ O	0.0	0.0	0.0	0.0	0.0	0.0	0.13
S	0.2	0.3	0.3	0.4	0.6	0.3	3.41
Total	96.1	95.0	95.9	96.4	96.2	97.4	80.31

* Bulk composition reported for the Murchison (CM2) matrix (McSWEEN and RICHARDSON, 1977).

variations may be caused partly by heterogeneous distribution of elements in the glasses owing to imperfect equilibrium for 20–40 min heating.

In Fig. 2, except for FeO and SiO₂, the differences of major element compositions for different duration and for different heating temperatures are not clearly recognized. The SiO₂ content decreases with increasing temperature. The FeO content complementarily increases with increasing temperature. In the same way, the sulfur content increases with increasing temperature (Fig. 3). In Fig. 4, a clear positive correlation is noted between FeO and S contents. This correlation suggests

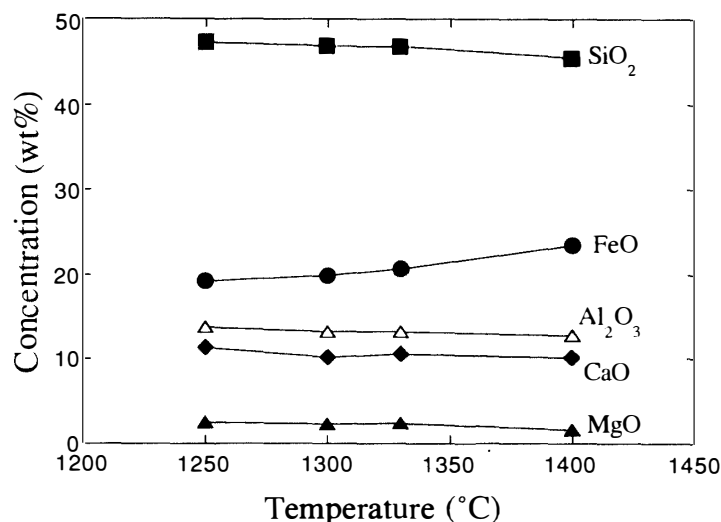


Fig. 2. Plot of major oxide concentration (wt%) against heating temperature (°C) for partial melts in run products.

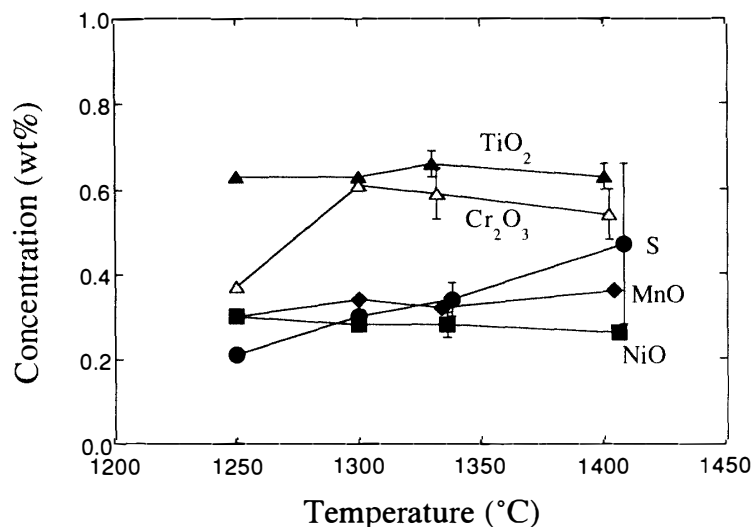


Fig. 3. Plot of minor oxide, sulfur concentration (wt%) in partial melts in run products against heating temperature (°C). Bars show the variations of concentration for different heating duration.

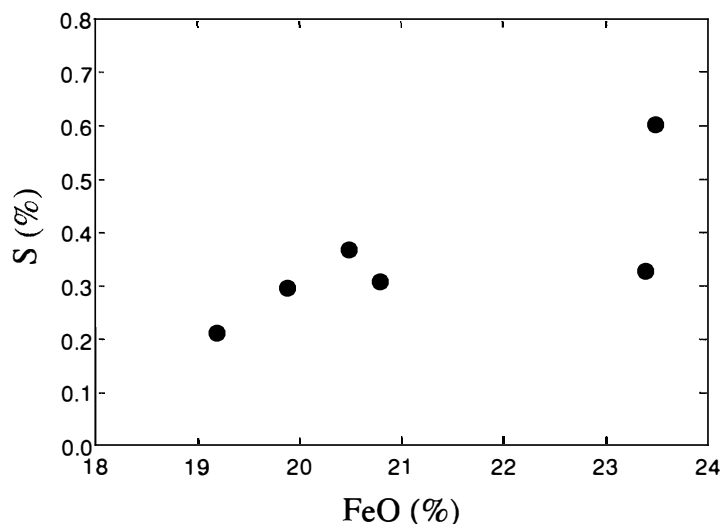


Fig. 4. Plot of iron oxide concentration (wt%) against sulfur concentration (wt%) for partial melts in run products.

that decomposition and dissolution of troilite melts occurred at the higher temperature. The constant concentrations of Al and Ca (Fig. 2) suggest that at temperatures above 1250°C, plagioclase, which is host phase of Al and Ca, was completely exhausted.

Except for sulfur, minor elements show no correlation with temperature. Sulfur content shows a positive correlation with temperature, thus with FeO content (Fig. 4). The change (0.2–0.6%) of sulfur content with temperature, by a factor of about two, is much larger than that of FeO content (~19–~23%), by a factor of about 0.2. This may be understood because Fe was used in crystallization of olivine rims but sulfur remained in partial melts.

3.3. Concentrations of alkalis in the heated samples

The results of analyses of alkali metals in the bulk run products are presented in Table 1, Figs. 5, 6 and 7. All concentrations are corrected for analytical blanks. In these figures, horizontal lines show duration time (t) and vertical lines show logarithmic value of concentration of alkali metal in run product relative to starting material (C/C_0). Assuming that alkali vaporization from "total" molten silicate material is controlled by the loss of the element from surface of charge, $\ln(C/C_0) - t$ plots such as Figs. 5, 6 and 7 show straight lines for each set of temperatures (TSUCHIYAMA *et al.*, 1981). These figures show the negative correlations between relative concentrations of alkalis and heating durations and do not show straight lines. The comparatively small depletions of K and Rb of 1330°C, 40 min (MR17)

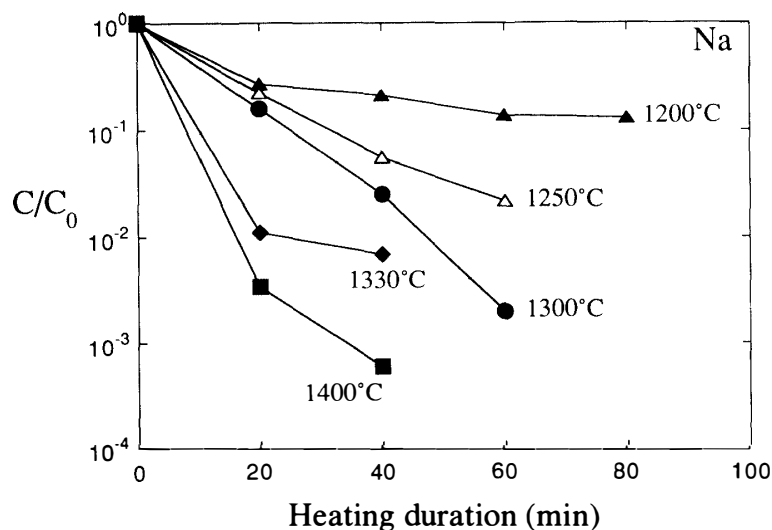


Fig. 5. Plot of concentration of Na in the heated samples relative to starting materials as a function of heating duration.

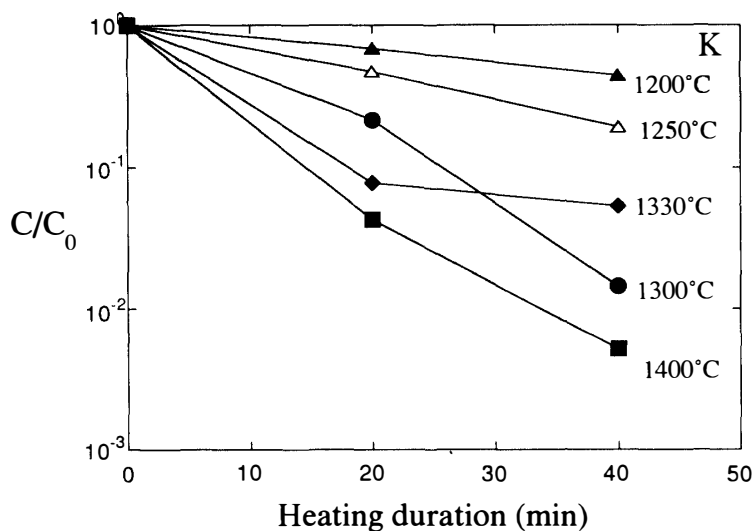


Fig. 6. Plot of concentration of K in the heated samples relative to starting materials as a function of heating duration.

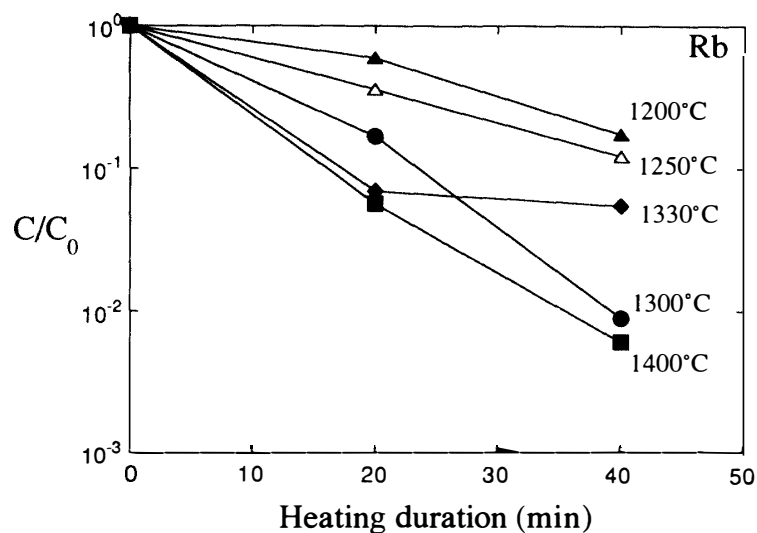


Fig. 7. Plot of concentration of Rb in the heated samples relative to starting materials as a function of heating duration.

compared with data points of 1300°C and 40 min appear unusual. SHIMAOKA and NAKAMURA (1989) noted that these unusual phenomena occurred due to irregular variations of surface areas and depended on the fraction of “partial” melt present in the samples. In this work, however, surface areas and degrees of partial melting were not estimated because of technical difficulties in estimation of them from the complex SEM images using an on-line computer image reader. MR17 is considered to contain relatively small amounts of holes, resulting in the low surface area of the partial melts useful for vaporization of alkalis.

3.4. Fractionations of alkali metals

Figures 8 and 9 show the fractionation trends of Na/K and Rb/K respectively. In these figures, vertical lines show the fractionation factor (F) among alkalis, which indicate the relative vaporization loss of alkalis to K.

In Fig. 8, the relative vaporization loss of Na to K increases with increasing temperature except for samples heated at 1330°C; the Na/K fractionation factors relative to starting material ($F_{\text{Na/K}}$) are always smaller than unity. STOREY (1973) reported Na/K fractionations for a terrestrial basalt which are very similar to those observed here (Fig. 8). This type of fractionation is, however, opposite to that observed in heated lunar samples (DE MARIA *et al.*, 1971; GIBSON and HUBBARD, 1972) and to that expected from thermochemical data (BREWER, 1953). This behavior may be explained by large differences in activity coefficients of alkalis between silicate melts with and without higher volatiles (STOREY, 1973) and/or more aluminosilicate components (FEGLEY and CAMERON, 1987). This trend is similar to that obtained by NAKAMURA and SHIMAOKA (1989) for the Etter ordinary chondrite.

As shown in Fig. 9, large temperature-dependent Rb/K fractionations are observed, which indicate a gradual increase of fractionation factor ($F_{\text{Rb/K}}$) from < 1 to > 1 at temperatures above 1330°C. This systematic Rb/K fractionation is similar

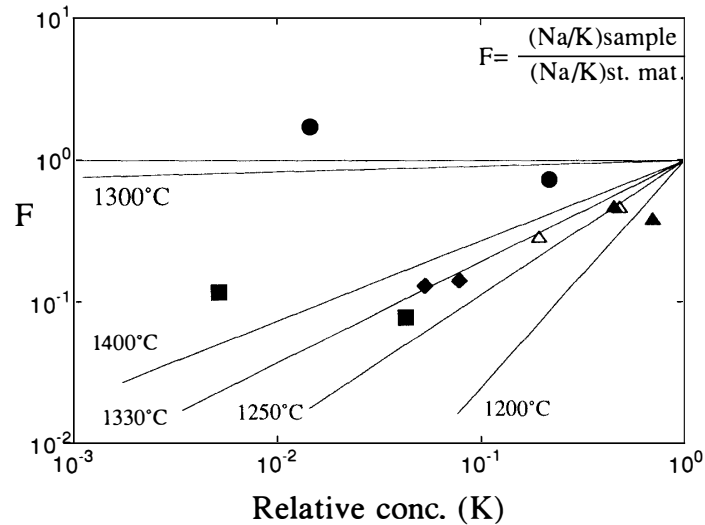


Fig. 8. Plot of fractionation factor (relative to starting material) of Na relative to K vs. residual fraction of K.

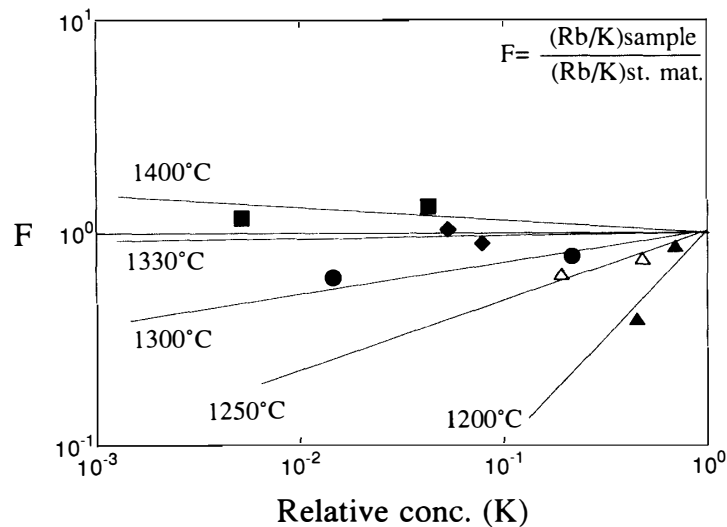


Fig. 9. Plot of fractionation factor (relative to starting material) of Rb relative to K vs. residual fraction of K.

to that found by NAKAMURA and SHIMAOKA (1989), in which $F_{\text{Rb/K}}$ is larger than unity at temperatures above 1280°C. Fractionation factors of Rb/K larger than unity are opposite to those of heated lunar samples (DE MARIA *et al.*, 1971; GIBSON and HUBBARD, 1972) and to those estimated from thermochemical data (BREWER, 1953), but similar fractionations are observed in some Allende chondrules (MATSUMURA *et al.*, 1990).

The temperature-dependent Rb/K fractionation may be caused by differences in the oxygen fugacities and/or in starting materials. The most important reactions considered to control the oxygen partial pressure within the heating chamber in this work may be those of the partially molten charges themselves and/or Ta-Ta₂O₅ and Mo-MoO₃ buffer (SHIMAOKA and NAKAMURA, 1989). If this is the case, the oxygen

fugacities may have been different from those of our previous experiments, because the atmosphere of the experiments using Ta for a sample holder and crucibles is more reduced than that using Mo. Calculated vapor pressures of Rb_2O under equilibrium condition from thermochemical data are always larger than those of K_2O at various oxygen partial pressures and temperatures.

We also performed the vaporization experiment using Mo for a sample holder and crucibles instead of Ta, and obtained similar results. Therefore, the temperature-dependent Rb/K fractionations observed in this work appear to not be caused by differences in the oxygen fugacities between Mo- and Ta-crucibles. Further experimental work, however, may be needed in order to evaluate clearly the most relevant factors.

The chemical compositions of glassy materials (Table 3) are considered to be dependent on the degree of partial melting at different temperatures. Thus, the dependence of alkali fractionation on the extent of partial melting suggests that the fractionation factors ($F_{\text{Rb/K}}$) can be influenced by the chemical compositions of partial melts. As mentioned in Section 3.2., both iron and sulfur contents of glassy materials indicate a positive correlation with temperature. The trends of Na/K fractionation are not systematic (Fig. 8), but most $F_{\text{Rb/K}}$ values are smaller than unity (Fig. 9). On the other hand, the $F_{\text{Rb/K}}$ are systematically changing with temperature (the higher temperature, the larger $F_{\text{Rb/K}}$). According to the preliminary results of the vaporization experiment on ordinary chondrite (Etter (L5)) (NAKAMURA and SHIMAOKA, 1988), this is one of the typical Rb/K fractionations found for Etter.

The present data indicate that the fractional vaporization of Rb/K is dependent on temperature. Rb/K fractionation factors larger than unity were found in some chondrules (MATSUDA *et al.*, 1990) and/or in some lithic fragments in chondrites (WLOTZKA *et al.*, 1983). Thus, the observation may be very important in considering the thermal histories of the early solar nebula and of protoplanets. This could perhaps be understood as a result of fractional vaporization caused by chemical compositions of melts as noted in this work. In order to clarify the detailed mechanism, more detailed searches of our data presented here as well as further experiments may be required.

Acknowledgments

We are indebted to Dr. E. J. OLSEN, Field Museum, for providing us with the Murchison specimen, and to Prof. N. FUJII and Dr. H. MAEKAWA, Kobe University, for allowing us to use the SEM-EDS.

This work was supported in part by a Grant-in-Aid for Scientific Research on Priority Areas (Origin of the Solar System) of the Ministry of Education, Science and Culture, Japan, to N. NAKAMURA (No. 6311003).

References

- BREWER, L. (1953): The thermochemical properties of the oxides and their vaporization processes. *Chem. Rev.*, **52**, 1–75.
- BUENING, D. K. and BUSECK, P. R. (1973): Fe-Mg lattice diffusion in olivine. *J. Geophys. Res.*, **78**, 6852–6862.
- DE MARIA, G., BALDUCCI, G. and PIACENTE, V. (1971): Mass spectrometric investigation of the vaporization process of Apollo 12 lunar samples. *Proc. Lunar Planet. Sci. Conf.*, 2nd, 1367–1380.
- FEGLEY, B., Jr. and CAMERON, A. G. W. (1987): A vaporization model for iron/silicate fractionation in the Mercury protoplanet. *Earth Planet. Sci. Lett.*, **82**, 207–222.
- FUCHS, L. H., OLSEN, E. and JENSEN, K. J. (1973): Mineralogy, mineral-chemistry, and composition of the Murchison (C2) Meteorite. *Smithson. Contrib. Earth Sci.*, **10**, 1–39.
- GIBSON, E. K., Jr. and HUBBARD, N. J. (1972): Thermal volatilization studies on lunar samples. *Proc. Lunar Sci. Conf.*, 3rd, 2003–2014.
- GOODING, J. L. (1982): Survey of chondrule average properties in H-, L-, and LL-group chondrites; Are chondrules the same in all unequilibrated ordinary chondrites? *Chondrules and Their Origins*, ed. by E. A. KING. Houston, Lunar Planet. Inst., 61–87.
- GOODING, J. L. and MUENOW, D. W. (1977): Experimental vaporization of the Holbrook chondrite. *Meteoritics*, **12**, 401–408.
- GROSSMAN, J. N. and WASSON, J. T. (1982): Evidence for primitive nebular components in chondrules from the Chainpur chondrite. *Geochim. Cosmochim. Acta*, **49**, 1081–1099.
- GROSSMAN, J. N. and WASSON, J. T. (1983): Refractory precursor components of Semarkona chondrules and the fractionation of refractory elements among chondrites. *Geochim. Cosmochim. Acta*, **47**, 759–771.
- HASHIMOTO, A., KUMAZAWA, M. and ONUMA, N. (1979): Evaporation metamorphism of primitive dust material in the early solar nebula. *Earth Planet. Sci. Lett.*, **43**, 13–21.
- KREUTZBERGER, M. E., DRAKE, M. J. and JONES, J. H. (1986): Origin of the Earth's Moon; Constraints from alkali volatile trace elements. *Geochim. Cosmochim. Acta*, **50**, 91–98.
- KURAT, G., PERNICKA, E. and HERRWERTH, I. (1984): Chondrules from Chainpur (LL-3): Reduced parent rocks and vapor fractionation. *Earth Planet. Sci. Lett.*, **68**, 43–56.
- MCSWEEN, H. Y., Jr. and RICHARDSON, S. M. (1977): The composition of carbonaceous chondrite matrix. *Geochim. Cosmochim. Acta*, **41**, 1145–1161.
- MASUDA, A. and TANAKA, T. (1979): Experimental studies on behaviors of major and minor lithophile elements in vaporization under evacuated condition. *Meteoritics*, **14**, 13–28.
- MATSUDA, H., NAKAMURA, N. and NODA, S. (1990): Alkali (Rb/K) abundances in Allende chondrules: Implication for the melting conditions of chondrules. *Meteoritics*, **25**, 137–143.
- MISAWA, K. and NAKAMURA, N. (1988a): Demonstration of REE fractionations among individual chondrules from the Allende (CV3) chondrite. *Geochim. Cosmochim. Acta*, **52**, 1699–1710.
- MISAWA, K. and NAKAMURA, N. (1988b): Rare earth elements in chondrules from the Felix (CO3) chondrite; Comparison with Allende (CV) chondrules. *Proc. NIPR Symp. Antarct. Meteorites*, **1**, 215–223.
- NAKAMURA, N. and SHIMAOKA, T. (1989): Experimental investigation of vaporization and fractionation of alkali metals during melting of a chondritic material and their bearing on chondrule formation. *Lunar Planet. Sci. Conf. (abstract)*, 20th, 756–757.
- NAKAMURA, N., YAMAMOTO, K., NODA, S., NISHIKAWA, Y., KOMI, H., NAGAMOTO, H., NAKAYAMA, T. and MISAWA, K. (1989): Determination of picogram quantities of rare-earth elements in meteoritic materials by direct-loading thermal ionization mass spectrometry. *Anal. Chem.*, **61**, 755–762.
- OSBORN, T. W., WARREN, R. G., SMITH, R. H., WAKITA, H., ZELLMER, D. L. and SCHMITT, R. A.

- (1974): Elemental composition of individual chondrules from carbonaceous chondrites, including Allende. *Geochim. Cosmochim. Acta*, **38**, 1359–1378.
- SHIMAOKA, T. and NAKAMURA, N. (1989): Vaporization of sodium from a partially molten chondritic material. *Proc. NIPR Symp. Antarct. Meteorites*, **2**, 252–267.
- SHIMAOKA, T. and NAKAMURA, N. (1991): The effect of total pressure on vaporization of alkalis from partially molten chondritic material. *Proc. IAU Colloq. No. 126 Origin and Evolution of Interplanetary Dust*, ed. by A. C. LEVASSEUR REGOIND and H. HASEGAWA, 79–82.
- STOREY, W. C. (1973): Volatilization studies on a terrestrial basalt and their applicability to volatilization from the lunar surface. *Science*, **241**, 154–157.
- TSUCHIYAMA, A., NAGAHARA, H. and KUSHIRO, I. (1981): Volatilization of sodium from silicate melt spheres and its application to the formation of chondrules. *Geochim. Cosmochim. Acta*, **45**, 1357–1367.
- WLOTZKA, F., PALME, H., SPETTEL, B., WÄNKE, H., FREDRIKSSON, K. and NOOMAN, A. F. (1983): Alkali differentiation in LL-chondrites. *Geochim. Cosmochim. Acta*, **47**, 743–757.

(Received June, 1993; Revised manuscript received January 4, 1994)