

VAPORIZATION EXPERIMENTS IN THE SYSTEM PLAGIOCLASE-HYDROGEN

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Abstract: Vaporization experiments in the system plagioclase (An_{77})-hydrogen were carried out at temperatures between 1200 and 1475°C and in the pressure range from 10^{-9} to 10^{-4} bar. After partial vaporization, originally homogeneous plagioclase became zoned with increase of CaO and decrease of Na_2O from core to rim. The compositional change plotted on Si-Na-Ca, Al-Na-Ca, and Al-Na-Si diagrams revealed that plagioclase vaporized incongruently to form a gas with an atomic ratio close to Si:Al:Na=1:1:1 and non-stoichiometric residue over wide ranges of total pressure and oxygen fugacity. Increase of total pressure, which corresponds to increase of hydrogen pressure in the present experiments, enhanced vaporization; the Na_2O content at the surface of residue decreased and the depth of the Na_2O -depleted zone from the surface to the interior of the charges increased. Hydrogen may play the role of catalyst for the vaporization reaction. Another explanation for the role of hydrogen is that plagioclase reacts with carbon from the sample container and hydrogen to form a gas, carbon monoxide or dioxide, and methane. Non-stoichiometric composition of plagioclase in mare basalts may be due to vaporization in the high vacuum of the lunar surface.

1. Introduction

Vaporization and condensation are two of the most important chemical processes in cosmic environments including stars, comets, and super novae, and, in particular, the solar nebula in which we are most interested. In contrast to intensive thermodynamic calculations on condensation from gases of solar or non-solar compositions with or without consideration of kinetics of nucleation (LORD, 1965; BLANDER and KATZ, 1967; BLANDER, 1971; LEWIS, 1972; GROSSMAN, 1972; GROSSMAN and LARIMER, 1975; LATTIMER *et al.*, 1978; CAMERON and FEGLEY, 1982; SAXENA and ERIKSSON, 1983; PALME and FEGLEY, 1987; KOZASA and HASEGAWA, 1987, 1988; WOOD and HASHIMOTO, 1988), a limited number of vaporization and condensation experiments were conducted.

LIPSCHUTZ and coworkers did systematic heating experiments in order to investigate compositional changes in chondrites accompanying thermal metamorphism (*i.e.*, MATZ and LIPSCHUTZ, 1978). However, as the starting materials were natural chondrites, complex solid-solid reactions occurred during the experiments, and details of the vaporization are not well known. NOTSU *et al.* (1978) heated the Allende meteorite up to 2000°C and showed that the residue became enriched in Fe, Mg, and Si and subsequently in Al and Ca with increasing temperature, and suggested that

chondrules and Ca-Al-rich inclusions in the Allende were residues of high temperature heating. HASHIMOTO *et al.* (1979) heated the matrix of the Murchison (CM) chondrite and investigated compositional changes of released gas and residue with increasing temperature. TSUCHIYAMA *et al.* (1981) measured the vaporization rate of sodium from a glass of chondrule composition at 1 atm, which enabled them to estimate sodium loss during chondrule formation. The experiments were, however, conducted at 1 atm, and the results are not directly applicable to the natural chondrules. Furthermore, the rates of vaporization of other elements were not measured. HASHIMOTO (1982) carried out experiments in synthetic FeO-MgO-SiO₂-CaO-Al₂O₃ systems at pressures down to 10⁻¹¹ bar and at high temperatures (1700 to 2000°C). He investigated the compositional changes of the residual melts with change of temperature, and discussed fractionation of primitive materials in the solar nebula. Though the compositional changes of melts at high temperatures were well studied, those of solids were not known.

Recently, MYSEN *et al.* (1985) constructed a furnace in a vacuum chamber which enabled them to control vaporization temperature and total pressure and to estimate condensation temperature. They determined the phase relations for diopside composition at low hydrogen pressures based on vapor pressure measurements. They further determined the phase relations in the system Mg-Si-O-H and showed that liquid is stable at pressures higher than about 10⁻² bar total pressure for the averaged solar nebula composition (MYSEN and KUSHIRO, 1988). They also showed that condensation occurred at high temperatures (1150°–800°); the condensates were large enough to be investigated with EPMA (KUSHIRO and MYSEN, 1989). NAGAHARA *et al.* (1988) vaporized olivine and demonstrated that the iron-rich gas formed from olivine condensed forsterite, enstatite, silica mineral, iron-bearing pyroxene, ferrous olivine, and metallic iron with decrease in condensation temperature. They showed that olivine vaporized stoichiometrically to form magnesian olivine and iron-rich gas, which is essentially the same as the relationship between solid and liquid in the olivine solid solution system.

In order to investigate gas-solid-liquid relationships and kinetic effects in vaporization and condensation processes in various complex systems, especially in the system with the solar composition, we have constructed a new vacuum furnace in our laboratory at the Geological Institute of the University of Tokyo. In this paper, we will show preliminary results of vaporization experiments on the plagioclase solid solution system at low pressures.

2. Experimental Methods

The design of the vacuum chamber and the furnace is essentially the same as that described in MYSEN *et al.* (1985). The furnace 10 mm in inside diameter and 100 mm long is placed in the center of the vacuum chamber 150 mm in diameter and 360 mm long, which is connected with a turbomolecular pump (Fig. 1). The furnace is a tungsten-wound aluminum tube, and temperature is controlled by changing electric current and measured with a W₀₅Re₅-W₇₄Re₂₆ thermocouple. There was no temperature gradient within the sample container.

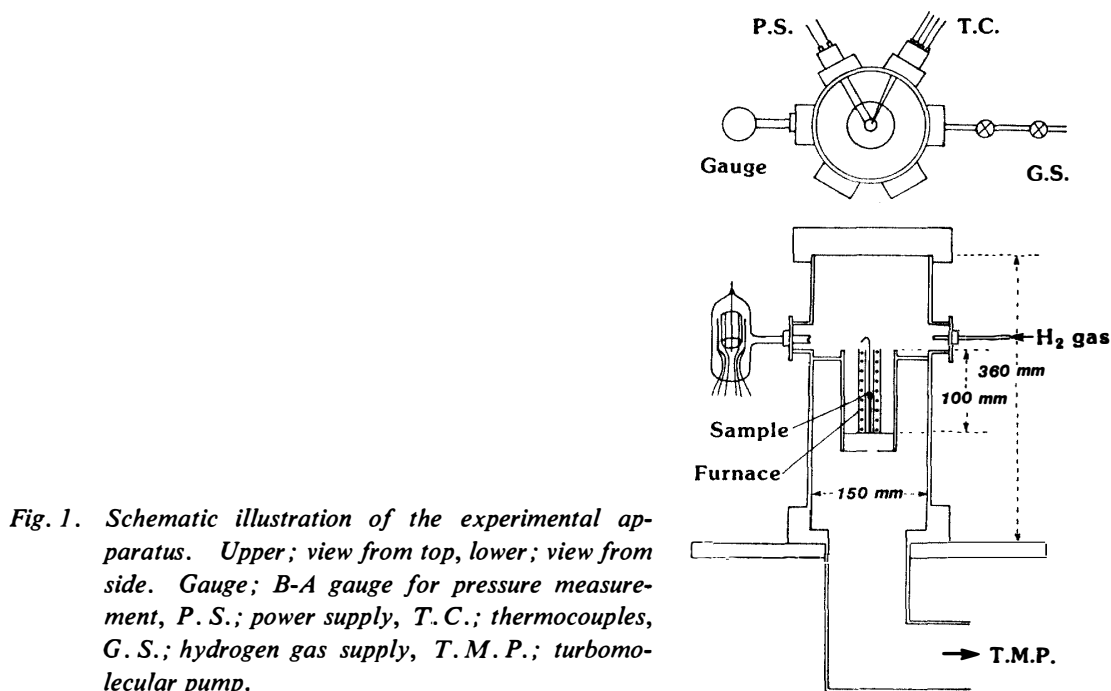


Fig. 1. Schematic illustration of the experimental apparatus. Upper; view from top, lower; view from side. Gauge; B-A gauge for pressure measurement, P. S.; power supply, T. C.; thermocouples, G. S.; hydrogen gas supply, T. M. P.; turbomolecular pump.

The total pressure was measured with an ion gauge connected to one of the ports of the chamber, and hydrogen gas was introduced into the chamber through a valve to control total pressure (exactly speaking, flow rate). The total pressure shown in the present study may be about 1.8 times larger than the actual value because of ionization of hydrogen during measurement with the gauge, but no correction was carried out in this paper. The top and bottom of the furnace are open, and the total pressure would be constant in the furnace. The sample is contained in a graphite capsule with 2 mm inside diameter and 4.5 mm long. The capsule with a tight-fitting cap has two holes on the sides, from which vaporized gas flows out. Redox condition inside the sample container where vaporization takes place is not well known, but is supposed to be fairly reducing because graphite is used as a capsule, which can not be a buffer in the presence of gas species such as SiC, CO, CO₂, SiO, SiO₂, and H₂O. The total pressure is the sum of vapor pressure of plagioclase and pressure of hydrogen with a minor amount of air contamination. At a low total pressure with a small amount of hydrogen gas, the oxygen fugacity depends on both vaporized gas and hydrogen. The vapor pressure of plagioclase ranges from 10⁻⁸ to 10⁻⁶ bar at temperatures between 1100 and 1500°C (MYSEN and KUSHIRO, unpublished data), so that the vaporized gas could affect oxygen fugacity significantly at total pressures below 10⁻⁶ bar but would have little effect at higher total pressures.

The starting material is plagioclase in anorthosite from Duluth, Minnesota, which is An₇₇ with several minor elements (Table 1). Approximate liquidus and solidus temperatures of An₇₇ at 1 atm are 1420 and 1240°C, respectively. Coarsely crushed plagioclase (about 100 to 500 μm in size) was used for experiments. Plagioclase in a sample container was pre-heated at 500°C for several hours to eliminate hydrocarbon contamination and then heated up to experimental temperatures at a rate of 20°C per minute. The samples were kept at the experimental temperatures for 6 to 96 h as

Table 1. Composition of the starting material.

SiO ₂	48.96	Si	2.249
Al ₂ O ₃	32.09	Al	1.737
FeO	0.36	Fe	0.014
CaO	15.61	Ca	0.768
Na ₂ O	2.53	Na	0.225
K ₂ O	0.05	K	0.003
Total	99.60	Sum	4.996
		An	77.1
		Ab	22.6
		Or	0.3

Table 2. List of run conditions.

Run #	Starting material	T (°C)	P* (bar)	t (h)	Remarks
9	P1	1300	3.9E-5 H ₂	16.3	
10	P1	1350	1.4E-4 H ₂	27	melting
11	P1	1300	1.2E-4 H ₂	15.2	
12	P1	1300	5.3E-9	15.2	
13	P1	1300	4.3E-7 H ₂	15.2	
18	P1	1300	3.9E-5 H ₂	10	
19	P1	1200	2.6E-9	48	
20	P1	1300	5.9E-5 H ₂	15.2	
28	P1	1200	1.3E-9	45	
29	P1	1200	1.4E-4 H ₂	45	
35	P1	1300	7.9E-10	72	
36	P1	1250	1.2E-9	96	
37	P1	1300	2.0E-7 H ₂	72	
38	P1	1300	6.8E-10	120	
39	P1	1350	2.0E-10	24	
40	P1	1200	1.6E-9	120	
41	P1	1200	1.3E-7 H ₂	120	
42	P1	1400	3.9E-9	6	
43	P1	1450	3.3E-9	22	melting
44	P1	1475	6.6E-9	20	melting
45	P1	1400	2.6E-9	48	melting
53	P1	1400	2.1E-7 H ₂	48	melting

* Runs without notation of H₂ were carried out without hydrogen gas, and pressure in those runs are due to the gas evaporated from plagioclase. No correction was carried out.

listed in Table 2, and quenched to room temperature by cutting the power supply off. They cooled within several minutes from the experimental temperatures to about 500°C which is low enough to stop vaporization. After runs, the charges were removed from the chamber, mounted in epoxy resin, and made into polished thin sections. A JEOL JSM840 scanning electron microscope equipped with LINK-SYSTEM AN10000 EDS and a JEOL JCXA 733 Mk-II electron microprobe were used for observation and analysis. Standard ZAF correction was applied to EPMA and EDS analyses. Accelerating voltage of 15 kV, sample current of 1 and 12 nA, and counting time of 100 and 10 s were chosen for EDS and EPMA analyses, respectively.

3. Results

After runs, most residues changed their compositions. Composition of residues depends on starting material composition, temperature, pressure, and run duration. Although some charges melted, which are noted in Table 2, most residues are crystalline after partial vaporization. Because of compositional change with time, the present experiments are not in equilibrium.

Plagioclase in the experiment above 1450°C for 22 h without hydrogen gas (Run #43) melted to decompose into two phases. Figure 2a is a photograph of the charge where the light portion is anorthite and the dark irregular portion is Si-rich and Ca-poor non-stoichiometric material; the irregular shape and non-stoichiometric composition suggest that the dark portion is a melt. All sodium was lost from the charge and it comprises Si, Al, and Ca. Representative chemical compositions of the two phases are listed in Table 3.

Plagioclase in the runs heated below 1450°C did not necessarily melt but changed its composition depending on temperature, pressure, and duration of experiments, and the shape of the crystal has not changed (Fig. 2b). At a pressure of 1.4×10^{-4} bar with hydrogen for 27 h, plagioclase melted at 1350°C, which is about 100°C lower than the melting temperature without hydrogen.

Originally homogeneous plagioclase of the starting material became zoned after partial vaporization regardless of experimental conditions. An example of the zonal pattern in the charge of Run #20 made at 1300°C for 15.2 h at total pressure of 5.9×10^{-5} bar is shown in Fig. 3. CaO increases, SiO₂ and Al₂O₃ are almost constant, and Na₂O and K₂O decrease from the center to the rim of the grain. Representative chemical compositions along the traverse are shown in Table 3. Figure 4 shows the

Table 3. Representative chemical composition of residues.

	1	2	3	4	5	6	7	8
SiO ₂	43.2	56.8	49.7	49.8	49.3	49.2	49.3	49.3
Al ₂ O ₃	33.0	26.4	31.9	31.8	31.8	31.7	31.7	32.0
FeO	0.18	0.93	—	—	—	—	—	—
CaO	18.4	9.17	15.7	15.9	16.3	16.5	17.1	17.2
Na ₂ O	0.0	0.0	2.33	1.85	1.47	1.14	0.78	0.32
K ₂ O	0.0	0.0	0.08	0.06	0.08	0.08	0.06	0.04
Total	94.8	93.3	99.6	99.4	98.8	98.6	98.9	98.9
Cation at O=8								
Si	2.099	2.658	2.273	2.280	2.270	2.270	2.271	2.266
Al	1.891	1.457	1.717	1.717	1.726	1.726	1.719	1.735
Fe	0.007	0.036	—	—	—	—	—	—
Ca	0.958	0.460	0.772	0.781	0.804	0.817	0.843	0.849
Na	0.000	0.000	0.206	0.164	0.131	0.102	0.069	0.029
K	0.000	0.000	0.004	0.004	0.005	0.005	0.004	0.002
Total	4.955	4.614	4.973	4.946	4.936	4.920	4.906	4.881

1-2: Run #43 light and dark portions, respectively. EDS analysis, 3-8: Compositional change from core to rim of the charge of Run #20. EPMA analysis. 1 is non-stoichiometric crystal and 2 is interstitial glass.

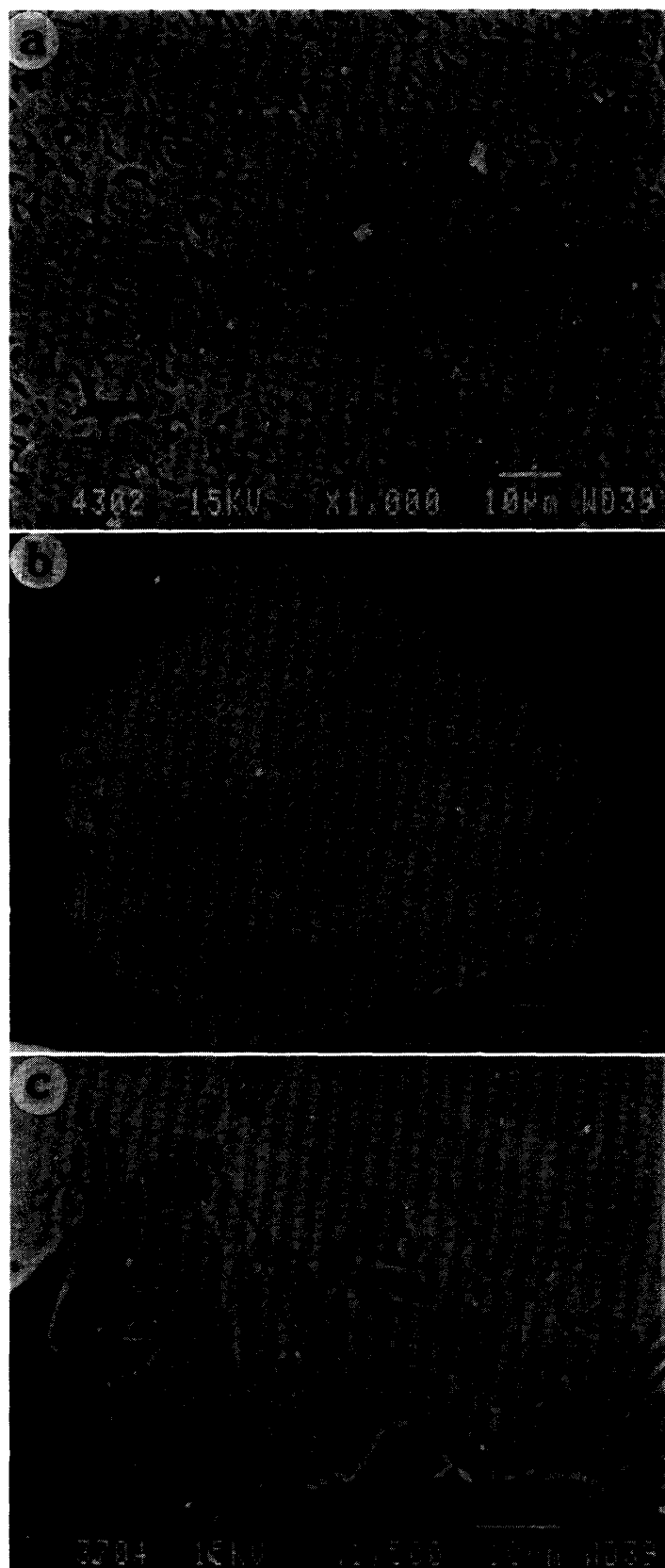


Fig. 2.

change of the Al/Ca ratio along the same traverse of the charge. The fact that the Al/Ca ratio decreases from core to rim suggests that Al was more intensively lost from plagioclase than Ca was, in spite of the lower volatility for pure Al_2O_3 than for CaO. This indicates that vaporization did not take place in a form of pure oxide but in the complex form. Distribution of each oxide in a charge is shown in compositional

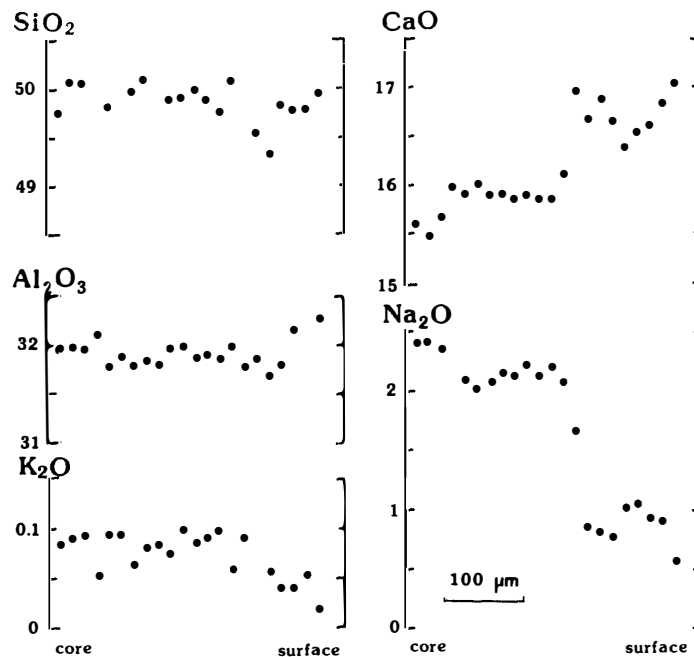


Fig. 3. Compositional changes from core to surface of a residue. Run #20 made at 1300°C and 5.9×10^{-5} bar with hydrogen for 15.2 h.

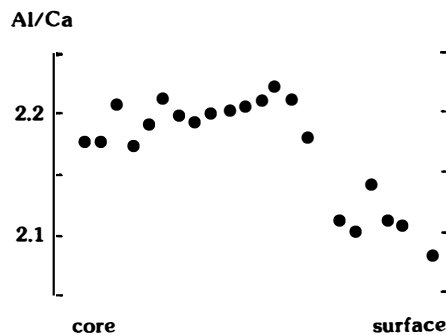


Fig. 4. Change of Al/Ca ratio in the same traverse of the residue in Fig. 3. Run #20. The surface mullite layer is eliminated.

Fig. 2. SEM photographs of experimental charges.

(a) Two phases in a melted charge. Run #43 made at 1450°C and 3.3×10^{-9} bar without hydrogen for 22 h. Light; anorthite, dark; Si-rich liquid. (b) Representative view of the charge. Run #12 made at 1300°C and 5.3×10^{-9} bar without hydrogen for 15.2 h. The outline of the charge shows little change after vaporization. (c) Mullite crystals on the surface of the charge and interstitial glass. Run #37 made at 1300°C and 2.0×10^{-7} bar with hydrogen for 72 h. Interstices of mullite crystals are K- and Na-bearing Si-rich glass.

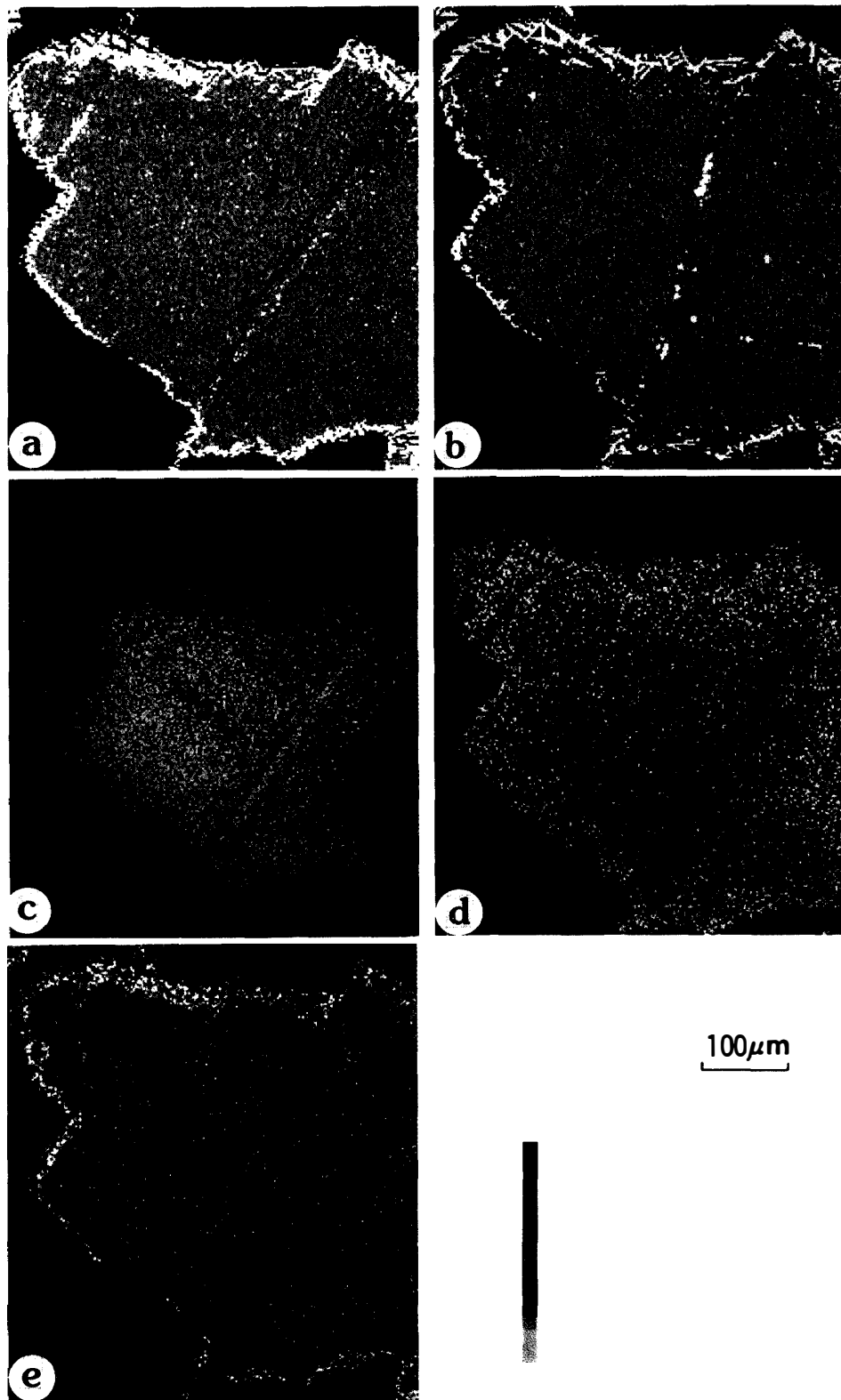


Fig. 5. Color-mapped elemental distributions in the residue of Run #20 for which compositional changes in a charge are shown in Figs. 3 and 4. (a) Si, (b) Al, (c) Na, (d) Ca, (e) K.

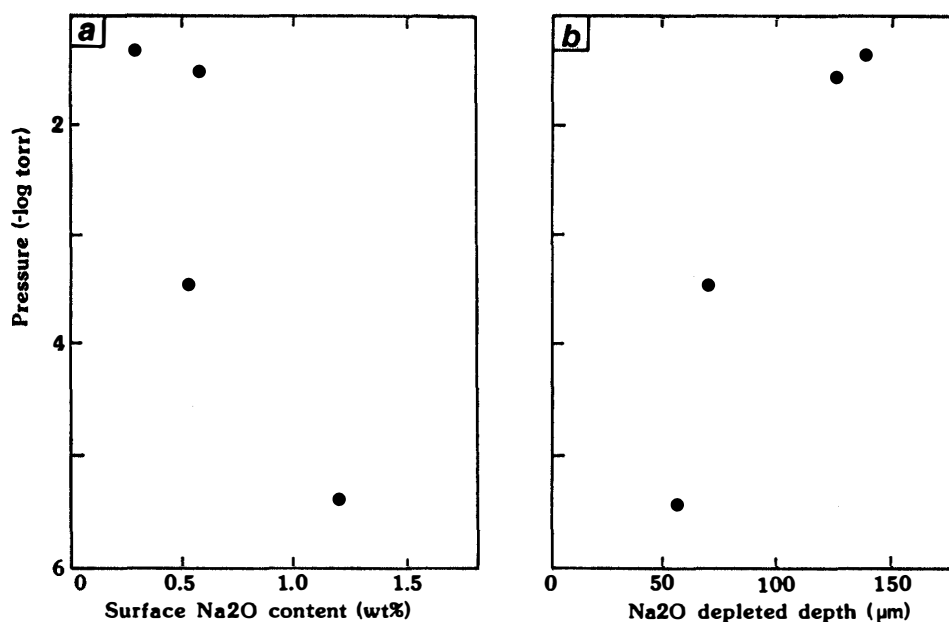


Fig. 6. Relationships between hydrogen gas and degree of vaporization. Runs made at 1300°C for 10 to 16 h. (a) Relationship between the Na₂O content in the surface of the residue and the total pressure. (b) Relationship between the depth of Na₂O-depleted zone and the total pressure.

maps in Fig. 5 which were made with the JCXA 733 Mk-II map analysis program. CaO increases and Na₂O decreases gradually from center to surface of the charge. SiO₂ and Al₂O₃ are almost homogeneously distributed in the charge, but are highly enriched on the very surface of the charge. As shown in the figure, Al₂O₃ is distributed in acicular crystals on the surface which are identified as mullite. The interstitial portion is a SiO₂-rich and CaO-poor glass with considerable amounts of K₂O and some Na₂O (Fig. 2c). This reaction occurs only very near the surface, but is observed in almost every charge except for very short runs. In Figs. 3 and 4 such a surface zone is excluded. It is interesting that K₂O is enriched near the surface of the grain, and is contained in the glass interstitial to mullite crystals. This indicates that K₂O was not completely lost from the melt.

Degree of vaporization depends on the total pressure and the duration of experiments. Figure 6 shows the relationship between the Na₂O content on the surface of the charge and the total pressure, and that between the depth of Na₂O-depleted zone and the total pressure. The total pressure corresponds to the sum of hydrogen pressure and gas pressure from the sample, and the former is much larger than the latter above about 10⁻⁷ bar total pressure. The depth of the Na₂O-depleted zone increases and the Na₂O content on the surface decreases with increasing total pressure.

4. Discussion

4.1. Mode of vaporization

In liquid-solid relationships, both olivine and plagioclase form complete solid

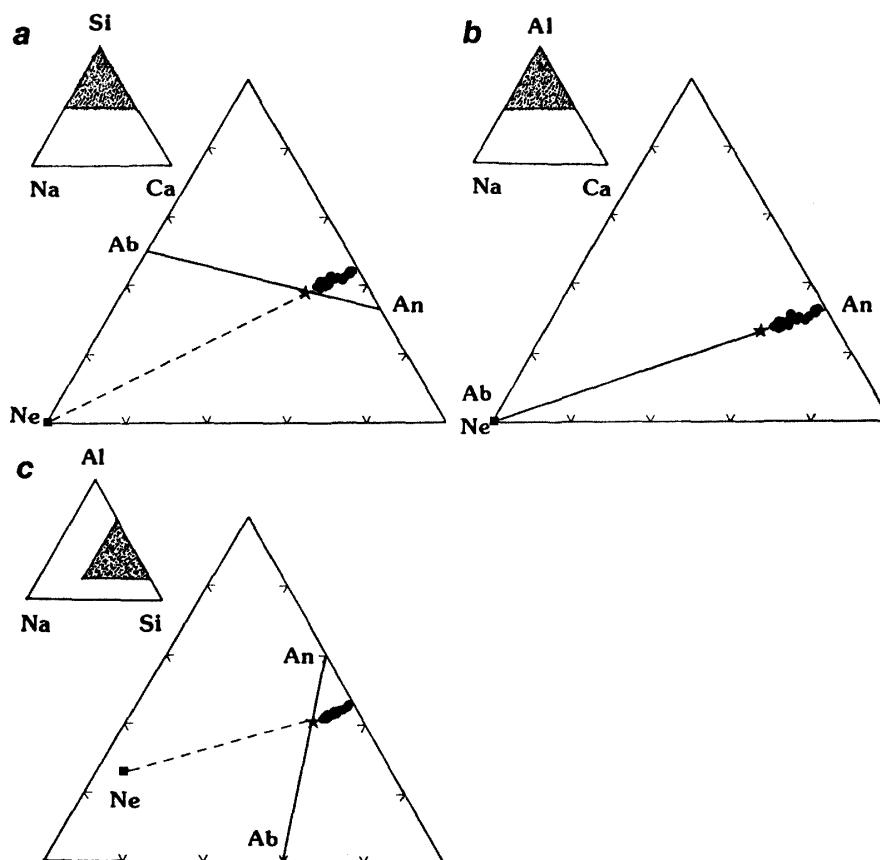
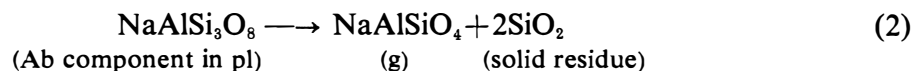


Fig. 7. Si-Na-Ca, Al-Na-Ca, and Al-Na-Si diagrams for compositional variation of the residue of Run #20 for which compositional changes in a charge are shown in Figs. 3, 4, and 5. Solid circles; compositional change in a residual grain, star; composition of the starting material, solid square; composition of the gas with a ratio of Si: Al: Na=1: 1: 1, solid line; composition of plagioclase solid solution.

This equation is written on the basis of two principles: one is that the cation ratio of the gas is approximately unity (Si: Al: Na=1: 1: 1), and the other is that oxygen number in the residue is assumed to be enough to maintain charge balance. Although the apparent reaction is shown above, the actual reaction occurred would be shown by a more simple equation as indicated below:



NaAlSiO_4 would not be an actual gas species, which would be decomposed into several gas species such as Na, Al, SiO, SiO_2 , or O_2 which reacts with hydrogen to form H_2O . Gas species of the above cations which are stable at high temperatures in the solar nebula are Na, Al, and SiO (GROSSMAN, 1972), but the species in the present experimental conditions are not known. HASHIMOTO (1989) showed that SiO_2 is formed from solid SiO_2 and forsterite instead of SiO under the kinetic (evacuating) condition regardless of redox conditions of the gas, which suggests the possibility of formation of gaseous SiO_2 also in the present experiments. Accordingly, the gas species is tentatively shown as NaAlSiO_4 in eq. (2).

It is concluded from the above observations that the plagioclase vaporizes incongruently to form a gas with a ratio close to Si:Al:Na=1:1:1 and non-stoichiometric residue. The difference of vaporization mode of plagioclase from olivine which vaporizes without losing olivine stoichiometry may be due to mineral structure. Olivine is a nesosilicate where SiO_4 tetrahedra exist as discrete units, whereas plagioclase is a tectosilicate where $(\text{SiAl})\text{O}_4$ tetrahedra form three-dimensional network structures without discrete units. When olivine is heated at low pressure, the unit of $(\text{Mg, Fe})_2\text{SiO}_4$ is hardly destroyed and stoichiometric olivine remains during and after partial vaporization, though the $\text{Mg}/(\text{Mg}+\text{Fe})$ ratio varies from that before heating. On the other hand, plagioclase can contain large non-stoichiometry within its structure in the form of Si_4O_8 . The composition of the residue shown in eq. (1) can be shown as a solution of 0.77 mol anorthite and 0.46 mol SiO_2 . A question is whether the residue is highly non-stoichiometric plagioclase or is a mixture of anorthite and silica mineral which will be mentioned below.

4.3. Effect of hydrogen pressure and run duration

Figure 8 compares the effects of hydrogen gas in the experiments at the same temperature and duration. The core composition of the residue of the run made at 1300°C without hydrogen (Run #35) lies a little off the plagioclase join and the surface composition is between the plagioclase join and the Si-Ca join (Fig. 8a). In other words, the core of the residue has still a composition very close to plagioclase stoichiometry and the surface has a considerably non-stoichiometric composition. In the run made at the same temperature and for the same duration but at a pressure of 2.0×10^{-7} bar with hydrogen (Run #37), the core composition lies away from the plagioclase join and the surface composition reaches the Si-Ca join (Fig. 8b). This shows that almost all the Na_2O was lost and the residue is highly non-stoichiometric. In the experiment at 1200°C , almost the same results are obtained. Evaporation is enhanced when hydrogen pressure is high.

Enhancement of evaporation in the presence of hydrogen is explicable by the

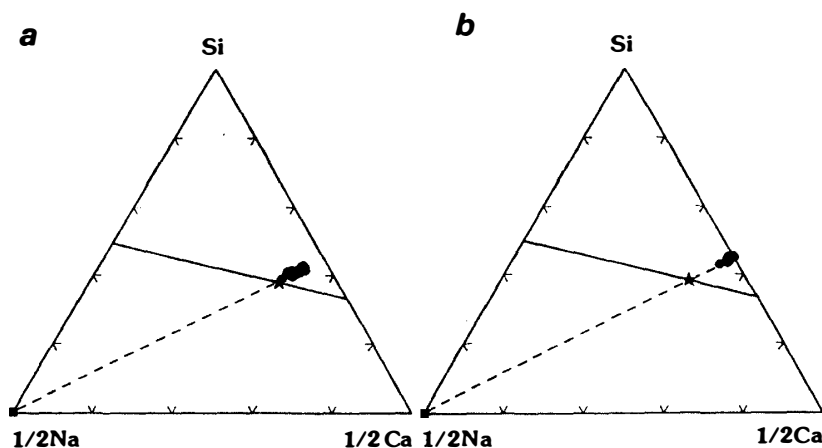
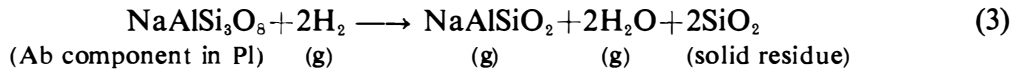
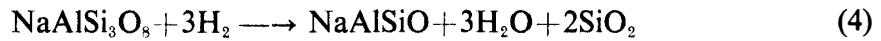


Fig. 8. Si-Na-Ca diagrams showing the effect of hydrogen on vaporization of the gas from plagioclase. (a) Run #35 made at 1300°C for 72 h without hydrogen, (b) Run #37 made at the same temperature for the same duration as (a) but with hydrogen.

following two cases; incorporation of hydrogen in the vaporization reaction, or the role of hydrogen as a catalyst for the reaction. The former case is shown by the following equations:



or



Equation (3) is applicable when the gas species are Na, Al, and SiO_2 , and (4) is when Na, Al, and SiO are the gas species. These equations well explain the hydrogen pressure dependence of vaporization. Incorporation of hydrogen in the vaporization equation is, as a result, plausible.

The latter possibility, hydrogen plays the role of catalysis, may also be plausible. In this case, hydrogen itself does not participate in the reaction but it facilitates the vaporization reaction as a catalyst. Hydrogen may break the network of (SiAl)-O in the plagioclase structure. Monovalent cations often break the network in silicate melts (KUSHIRO, 1974), suggesting that it also plays the same role in solids. However, in this case, hydrogen pressure dependence of the reaction is not well understood. The reaction is not necessarily depending on the amount of catalysis. In summary, the formation of a gas with oxygen-deficient stoichiometry or the role of hydrogen as a catalyst may be plausible, but is problematical.

4.4. Residual material

Compositional change of residues with time is well observed in experiments at constant temperature and pressure but for different durations. Figure 9 shows compositions of residues of runs made at 1300°C and at nearly the same total pressure for 15.2 h and 72 h. The core composition of the run made for 15.2 h still lies on the plagioclase join and the surface composition is close to the Si-Ca join (Fig. 9a).

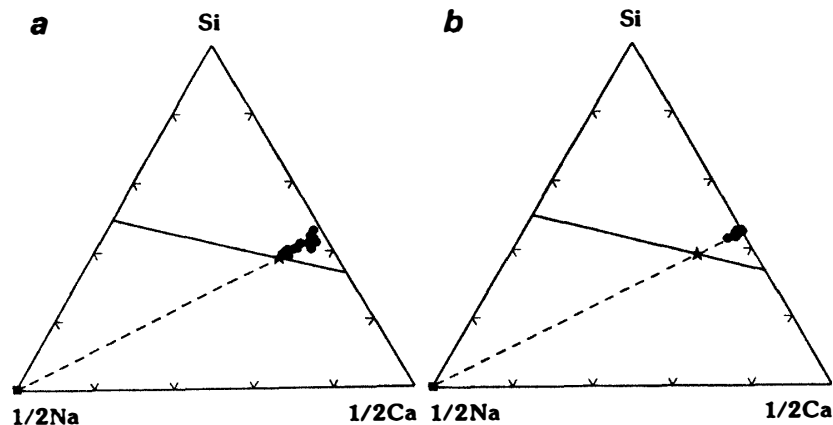


Fig. 9. Si-Na-Ca diagrams showing the effect of experimental duration on vaporization of the gas from plagioclases heated at 1300°C and a pressure on the order of 10^{-7} bar with hydrogen. (a) Run #13 for 15.2 h, (b) Run #37 for 72 h. Symbols are the same as those in Fig. 7.

By contrast, the composition of residue of the run made for 72 h is close to the Si-Ca join showing that almost all Na_2O has been lost (Fig. 9b). The diffusion of vaporizing component in plagioclase is thus shown to be fast enough to be lost during experiments. Diffusion coefficient for oxygen in anorthite at 1300°C is about 10^{-12} cm^2/s and that for CaAl-NaSi interdiffusion in An_{80} plagioclase is about 10^{-17} cm^2/s in order (GROVE *et al.*, 1984). These values give a diffusion distance of oxygen and CaAl-NaSi after 120 h (maximum duration of the present experiments at 1300°C) as about 700 nm and 20 nm, respectively. Such small diffusion distances will form residue with sodium-depletion only in a very thin layer near the surface and most of the sodium should be left in the interior. Diffusion of vaporizing component in plagioclase during vaporization, therefore, should proceed by different mechanisms, such as partial breaking of (SiAl)-O bonding or destruction or deformation of (SiAl) O_4 tetrahedra.

Next problem which arises is whether the highly non-stoichiometric residue is of one phase or a mixture of two phase. Preliminary X-ray study presents a diffraction pattern of pure anorthite (NAGAHARA and TOMEOKA, in prep.). Accordingly, the residue would be either anorthite with abundant vacancies (Si_4O_8) or anorthite with amorphous silica. Solubility of silica in anorthite is up to 10 mol% at the maximum at 1350°C and 1 atm (BEATY and ALBEE, 1980), which is too small to explain the largest non-stoichiometry in the residues of the present work. It is not known whether the large non-stoichiometry in the residues is due to the presence of vacancies or not. More detailed X-ray and TEM work is now planned.

4.5. Lunar plagioclase

BEATY and ALBEE (1980) showed that plagioclase in mare basalts had a vacancy component, Si_4O_8 up to 7 mol%, resulting in the apparent presence of excess silica. Calcic plagioclase in anorthosites, norites, and troctolites from the highlands, however, does not have non-stoichiometry. It was noted that plagioclase with abundant vacancies still possesses the structure of feldspar. They considered that the vacancy was due to solubility of SiO_2 into plagioclase and to relatively high crystallization temperatures compared to terrestrial plagioclase. However, solution of SiO_2 in plagioclase can always occur in magmas, and the crystallization temperature of plagioclase in terrestrial basalts is not so largely different from that in mare basalts. Non-stoichiometry of lunar plagioclase due to solubility of SiO_2 as a function of temperature is, therefore, questionable.

In order to investigate the composition of plagioclase in mare basalts, their compositions are plotted on Si-Na-Ca and Al-Na-Si diagrams (Fig. 10). The variation of compositions on these diagrams, which is due to difference of grains from different parental rocks, is essentially different from variations in Figs. 6, 7, and 8 which are continuous compositional changes in an originally homogeneous single grain. Though primary compositions of lunar plagioclases are not known, compositions shown in Fig. 10 are systematically shifted away from the plagioclase join. Therefore, non-stoichiometry of mare basalt plagioclase may be the result of partial vaporization during or after crystallization of mare basalts under high vacuum at the lunar surface or silica solubility as a function of pressure. This well explains the fact that the amount of the vacancy increases outward in a single grain accompanied with Ab

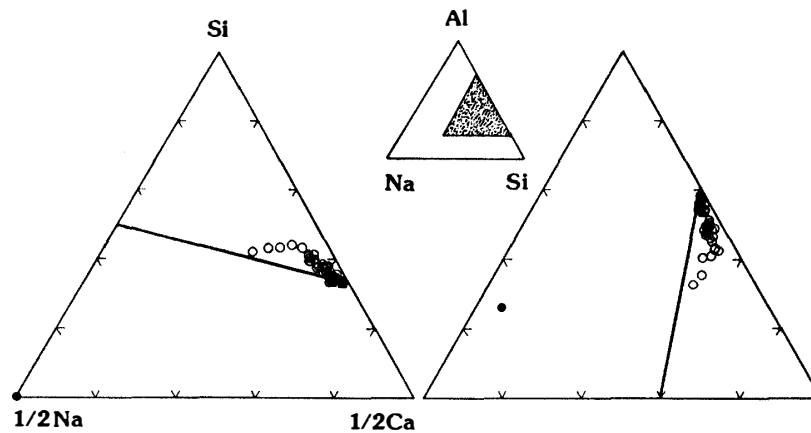


Fig. 10. Si-Na-Ca (a) and Al-Na-Si (b) diagrams showing the compositions of lunar plagioclases. Open circle; plagioclase from mare basalts, solid square; plagioclase from ANT rocks in lunar highlands, solid circle; composition with a ratio of Si: Al: Na = 1: 1: 1, solid line; composition of plagioclase solid solution. Data source; BALDRIDGE *et al.* (1979), BEATY and ALBEE (1978), BEATY *et al.* (1979), DUNGAN and BROWN (1977), GAMBLE *et al.* (1978), KURAT and KRACHER (1981), MCGEE *et al.* (1978), NEHRU *et al.* (1978), VANIMAN and PAPIKE (1977), and WARNER *et al.* (1978a, b).

component enrichment (BEATY and ALBEE, 1980).

It is worth noting that meteoritic plagioclases do not show non-stoichiometry. Meteorites, especially chondrules, are thought to have been formed in the solar nebula, which is thought to be at low pressure (about 10^{-5} to 10^{-3} bar at meteorite forming orbit). However, plagioclase in chondrules does not show Si-enrichment. The reason would be the calcic composition of plagioclase in chondrules in highly primitive chondrites, as well as that from lunar highlands and that in the Ca-Al-rich inclusions in carbonaceous chondrites. Though plagioclase in type 6 ordinary chondrites is mostly sodium-rich (oligoclase), plagioclase in highly primitive chondrites is exclusively calcic which occurs only in Ca and/or Al-rich chondrules (BISHOFF and KEIL, 1984). As is well shown in the Si-Na-Ca diagram (Fig. 10), calcic plagioclase hardly changes its composition by vaporization because of lack of a vaporizing component. So even if calcic plagioclase in chondrules and also anorthite in CAIs crystallized in the solar nebula which should have been high in hydrogen pressure compared to that on the atmospheres of small bodies such as the Moon, the composition of such plagioclase is stoichiometric. Sodic plagioclase in type 6 ordinary chondrites crystallized inside the parental body (or bodies) and was not directly exposed to a high vacuum, so that vaporization did not take place. DELANEY *et al.* (1984) showed that plagioclases in the unequilibrated mafic clasts in most polymict eucrites also have non-stoichiometry. On the contrary, some analytical results on eucrite plagioclases (*i.e.*, TAKEDA *et al.*, 1979) showed that they are stoichiometric. Further studies will be needed on eucrite plagioclases.

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