Structural change of albite ($\text{NaAlSi}_3\text{O}_8$) melt quenched at high pressure: density and Al K_α X-ray emission

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Density and Al K_α X-ray emission band of the albite melts quenched at high pressure up to 8 GPa were measured. The density of the glass increases continuously from 2.473 g/cm³ at 2 GPa to 2.743 g/cm³ at 8 GPa. The rate of density increase however is not constant but relatively large in the pressure range of 2-6 GPa, suggesting that some structural change of the albite glass takes place in this pressure range. Measurement of Al K_α emission bands of the albite glass revealed that the emission band shifts towards the higher energy side with increasing pressure. Present measurements of density and Al K_α emission band of the albite glass are consistent with the results of the ²⁷Al NMR spectrometry of the glass (Ohtani *et al.*, 1985), suggesting a coordination change of Al³⁺ ions in the melt from 4-fold to 6-fold with increasing pressure.

Introduction

Density of magma is one of the most important properties affecting genesis of various magmas and chemical structure of the mantle, since the density of magma controls the modes of fractionation and transportation of the melt from the source. Examples are seen in the lunar and terrestrial cases. Floatation of plagioclase in the dry basaltic magma has been used to explain the lunar anorthositic crust. A possibility of floatation of olivine in the basic and ultrabasic magma at high pressures above 5 GPa has been suggested by various authors (*e.g.*, Stolper *et al.*, 1981; Nisbet and Walker, 1982; Ohtani, 1983; Rigden *et al.*, 1984). The density crossover and floatation of olivine in the deep upper mantle have important implications to the chemical structure of the earth as have been discussed by various authors (*e.g.*, Ohtani, 1986; Agee and Walker, 1988).

A possibility of the coordination change in

Al³⁺ and Si⁴⁺ ions from 4-fold to 6-fold has been suggested to explain increase in magma density at high pressure (Waff, 1975). Various works have been made to clarify the structure of the aluminosilicate melts and glasses. Kushiro (1976, 1978) reported the viscosity of the albite and jadeite melts and density of the glasses quenched at pressures to 2.5 GPa. He reported a drastic decrease in viscosity and an increase in the density at around 1 GPa.

Recent development of the multi-anvil (MA8) apparatus made it possible to conduct melting experiments at pressures exceeding 10 GPa. Using this technique, Ohtani *et al.* (1985) synthesized albite glass up to 8 GPa. Above this pressure, the glass cannot be obtained even by quenching from the melt. The results of ²⁷Al NMR spectrometry of the glass strongly suggest a structural change of the albite melt at pressures above 6 GPa; the coordination change of Al³⁺ in the glass from 4-fold to 6-fold occurs with increasing pressure. This coordi-

nation change is similar to that observed in the crystalline phases; albite→jadeite+quartz.

The other example of the coordination change in Al is also suggested in the pyrope melt by Fujino *et al.* (1983) and Irifune and Ohtani (1986). According to these authors, the melting curve of pyrope shows a significant bending at pressure around 6 GPa. Since the coordination change of Al^{3+} ions in the pyrope melt from 4-fold to 6-fold causes a volume decrease in the melt, bending of the melting curve of pyrope may be explained by such a structural change of the melt. The change of the quench crystal from aluminous pyroxene to garnet may be also explained by such change in coordination in the pyrope melt (*e.g.*, Irifune and Ohtani, 1986).

In this paper, we present an additional evidence of the coordination change of Al^{3+} from 4-fold to 6-fold in the albite melt by measuring the density and Al K_{α} X-ray emission band of the melt quenched at various pressures.

Experimental procedure

A piston cylinder apparatus of the Australian National University was used to synthesize albite glasses at 2 and 3 GPa, whereas the multi-anvil (MA8) high pressure systems of Nagoya University and the Australian National University were used to synthesize the glass at higher pressures.

The platinum capsule was used for the runs made by the piston cylinder apparatus. Various materials such as carbon, boron nitride, and platinum were used as the capsule material for the runs made by the multi-anvil apparatus. Carbon was used as the heating material both for the piston cylinder and multi-anvil systems. Temperature was measured by a Pt-Pt10%Rh thermocouple with a diameter of 0.2 mm for the piston cylinder apparatus, and a W25%Re-W3%Re thermocouple with a diameter of 0.2

mm for the multi-anvil apparatus. The albite crystallized at an atmospheric pressure was used as starting material. It was confirmed as a single phase material of albite using X-ray powder diffraction technique. Details of the description of the high pressure cell of the multi-anvil apparatus are given elsewhere (*e.g.*, Ohtani *et al.*, 1982). The quenching method was adopted to make the albite glass. The temperature was elevated to the desired value above the liquidus temperature of the albite composition at high pressure, and was held at constant for 1 to 2 minutes. The charge was quenched at high pressure by shutting off the electric power supply of the charge. After that the charge was recovered by releasing pressure.

Densities of the albite glasses synthesized at various pressures were measured at room temperature by a floatation method using Clerici solutions as immersion liquids. The densities of the solutions were calibrated by means of standard glass cubes with known densities.

Al K_{α} emission bands of two albite glasses made at 2 and 8 GPa, crystalline albite, and corundum were measured by using a wave-dispersive electron microprobe (JEOL JXA-5A) with a TAP diffraction crystal. The operating conditions were accelerating voltage of 15 kV and a beam current of 0.1×10^{-9} A. Special care was made on precise control and stabilization of beam current. The electron beam was defocused to about 50 microns to prevent contamination and loss of sodium in the glass. Intensities of 60 points across the Al K_{α} emission band were measured by a step scanning method for 80 seconds in each points.

Results and discussion

The experimental conditions and results for synthesis of the albite glass were shown in Table 1 and Fig. 1. The glass with albite composition was obtained up to the pressure of 8 GPa. No albite glass was obtained by quen-

Table 1. Experimental conditions and the results for synthesizing the albite glasses at high pressures

Run no.	Pressure GPa	Temperature °C	time (min.)	capsule	products
P1*	2	1500	5	Pt	gl
P2*	3	1600	5	Pt	gl
N17	6	1650	1	BN	gl
N20	6	1850	1	BN	gl
N21	6	1740	2	carbon	gl#
N23	6	1740	2	carbon	gl#
A10	6	1740	2	carbon	gl
A11	6	1740	2	carbon	gl
N15	6	1500	2	Pt	jad+coe
N19	6	1500	2	BN	jad+coe
N0	8	2000	2	carbon	gl#
N26	8	1970	3	carbon	gl#
A12	8	2000	2	carbon	gl#
A0	10	2000	2	carbon	jad+st

gl, glass; jad, jadeite; coe, coesite; st, stishovite.

*, piston cylinder apparatus was used in the experimnt.

#, crystals are observed at the top and bottom parts of the charge due to the temperature gradient of the furnace.

Fig. 1. Experimental conditions for synthesis of the albite glass at high pressures.

ching from 10 GPa and 2000°C but the run product was composed of fine grained quench crystals of jadeite and stishovite.

The results of density measurement of the

albite glass were summarized in Table 2, and illustrated in Fig. 2. The densities determined by Kushiro (1978) in the lower pressure range up to 2.5 GPa are also illustrated in the same

Table 2. Results of density measurement of the albite glass at high pressures

Pressure GPa	Run no.	Density of the glass g/cc
2	P1	2.480 > d > 2.467
3	P2	2.555 > d > 2.523
6	N21, N23	2.678 > d > 2.667
8	N26	2.769 > d
	N0	2.769 > d > 2.717

* , contamination of carbon is observed in the glass.

Fig. 2. Density of the albite glass to 8 GPa. Previous result by Kushiro (1978) up to 2.5 GPa is also shown in this figure.

figure. The measured density of the albite glass is 2.473 ± 0.003 g/cm³ at 2 GPa, 2.539 ± 0.013 g/cm³ at 3 GPa, 2.673 ± 0.006 g/cm³ at 6 GPa, and 2.743 ± 0.026 g/cm³ at 8 GPa. Kushiro (1978) reported that the density of the albite glass increases with increasing pressure of quenching from 2.38 g/cm³ at 1 atm to 2.525 g/cm³ at 2.5 GPa. Our results indicate continuous increase of the glass density at least up to 8 GPa. The rate of density increase, however, is not constant but relatively large between 2 and 6 GPa, which suggests that some structural change of the albite glass takes place in this pressure range. This result is consistent with

the result of ²⁷Al NMR spectrometry of the albite glass made by Ohtani *et al.* (1985). They observed clear evidence of existence of six coordination of Al³⁺ ions in the albite glass quenched at 6 and 8 GPa. The densities of the crystalline phases, such as albite below 3 GPa and jadeite and quartz (and coesite) above this pressure are also shown in Fig. 2. The density of the glass is lower than that of the crystalline phases in all pressure ranges, although the density of the glass increases continuously with increasing pressure, and it approaches to the density of crystalline albite at *ca.* 3 GPa.

Since the K_β emission band corresponds to an electronic transition from valence state to the ground state for the third-period elements such as Al, the energy shift due to a coordination change should be maximum in this emission band. We measured the Al K_β shift of the albite glasses synthesized at 2 and 8 GPa together with the crystalline albite and corundum. The Al K_β emission spectra of crystalline corundum and albite represent two extremes for rock-forming minerals, *i.e.* all Al³⁺ cations occupy 6-fold coordination in corundum, whereas 4-fold in albite. Fig. 3 shows the shift of Al K_β emission bands of the albite glasses and crystalline corundum from that of albite. The spectral peak of corundum shifts about 8×10^{-3} Å towards the high-energy side from the peak position of albite. Such displacement of the Al K_β emission band appears to reflect the nature of chemical bond, and coordination change of the Al³⁺ ions. We observed clear shift of Al K_β emission band of the glass quenched from 2 GPa and 1500°C towards high-energy side from the peak position of crystalline albite. Velde and Kushiro (1978) measured the Al K_β shift of albite glasses synthesized at pressures up to 3 GPa, which is consistent with present result of the glass quenched from 2 GPa. Further shift of the emission band was observed in the glass quenched from

Fig. 3. The Al K_{α} peak shift of albite glasses synthesized at 2 and 8 GPa. The shift of crystalline albite and corundum is also shown in this figure.

8 GPa and 2000°C; *i.e.* the amount of shift of the Al K_{α} emission band of the albite glass increases with increasing pressure. This observation is consistent with the gradual change of coordination state of Al^{3+} ions in the albite glass, which has been suggested by the NMR measurement by Ohtani *et al.* (1985) and the present results of density measurement of the glass.

Kushiro (1976, 1978) determined viscosities of the jadeite and albite melts to 2.5 GPa, and showed that the viscosities decrease with pressure. They suggested that such decrease in viscosity of the melts is related to the structural change in these melts; *i.e.* coordination change of Al^{3+} ions in these melts. Present observation of gradual change of the coordination of Al^{3+} from 4-fold to 6-fold in the quenched albite melt suggests that viscosity of the melt continues to decrease at least up to 8 GPa. Most of the alminosilicate melt, such as natural magmas, may have similar changes in the structure and physical properties under the conditions of the deep upper mantle.

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高圧下で急冷凍結したアルバイトメルト (NaAlSi₃O₈) の 構造変化: 密度及び Al K_α 線の測定

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8GPa までの圧力で急冷凍結したアルバイト組成のガラスの密度と Al K_α 線の波長のずれを測定した。ガラスの密度は 2GPa の 2.473 g/cm³ から 8GPa の 2.743 g/cm³ まで連続的に増加するが 2GPa から 6GPa までの密度の増加率は大きい。これはこの圧力においてアルバイトメルト中で何らかの構造変化が起こり始める為かも知れない。アルバイトガラスの Al K_α 線の波長は急冷凍結の圧力が高いほど高エネルギー側にずれ、8GPa ではコランダムのものに近くなる。この様な密度と Al K_α 線の波長測定の結果は、6GPa 以上の圧力において 6 配位の Al の存在を示唆する急冷凍結したアルバイトガラスの ²⁷Al-NMR スペクトルの測定結果と矛盾しない。