

Densities of melts in the system $\text{CaMgSi}_2\text{O}_6 - \text{CaAl}_2\text{Si}_2\text{O}_8$ at low and high pressures, and their structural significance

H. Taniguchi

Science Education Institute of Osaka Prefecture, Karita 4-13-23, Sumiyoshiku, Osaka 558, Japan

Abstract. Density measurements have been carried out on the melt system diopside-anorthite from room temperature to 1600° C at 1 atm, and from 1400° C to 1800° C at pressures up to 20 Kb. The densities were determined based on the dilatometric curve and density at 22° C for low-temperatures, the double-bob Archimedean method for high-temperatures at 1 atm, and on the sinking and floating spheres method for high-pressure conditions.

The results at 1 atm indicate that the thermal expansion coefficient of the glassy state is almost constant, while that of the liquid state decreases with increasing temperature. Density decreased with increasing anorthite content for both glassy and liquid states. Melts in the liquid-state mix ideally with respect to volume, while the glassy state exhibits a maximum excess volume at *Di30An70*. Density-pressure relations clearly show a density reversion between diopside-rich and anorthite-rich melts; the anorthite-rich melt becomes denser than diopside-rich melt at pressures above 8 kb.

The free volumes of both the liquid and glassy states decreased with increasing anorthite content.

Isothermal compressibilities and the hard-sphere diameter have been calculated based on the hard-sphere liquid model using thermal expansion coefficients and surface tension data. Calculated compressibilities for diopside-rich melt (*Di*:>*Di60*) agreed well with the experimental data, while calculated and observed compressibilities for anorthite-rich melt did not. This evidence indicates that diopside melt may be regarded as a discrete-melt composed of small constituent units (about 10 Å in average diameter) and much interstitial space, while anorthite melt is a three-dimensional network melt with little interstitial space. The critical composition *Di60An40* is similar to that of the eutectic and corresponds to breaks between composition and other physical properties. It is proposed that the composition may reflect a kind of "critical state" in the substitution of the "continuous structure" of anorthite melt for the "discrete structure" of diopside melt. The critical state may be interpreted based on the site-percolation theory.

melt and mineral is the determining factor for differentiation of magma. For example, this contrast is believed to govern the upward segregation of ultrabasic magma and to be the major factor in the differentiation of the mantle in the early history of the earth (Stolper et al. 1981; Ohtani 1984).

Recent density measurements at 1 atm for magmatic silicate melts were made by Murase and McBirney (1973), Shiraishi et al. (1978), Nelson and Carmichael (1979), Ličko and Daněk (1982), Mo et al. (1982), Stein et al. (1986) and by Lange and Carmichael (1987). Densities at high pressures were reported by Fujii and Kushiro (1977), Scarfe et al. (1979), Kushiro (1982) and Rigden et al. (1984, 1988).

In the present study, systematic measurements of melt density have been made on the join diopside – anorthite under various conditions; room temperature to 1600° C at 1 atm, and liquidus temperature to 1800° C at pressures up to 20 Kb.

The reasons for the choice of the present melt system are that firstly, this system is petrologically important, and secondly, other important properties such as viscosity (Scarfe et al. 1983; Taniguchi and Murase 1986, 1987b), low-temperature thermal expansion and infrared spectra (Taniguchi and Murase 1987b), oxygen-diffusion (Dunn 1982), thermochemical properties (Weill et al. 1980) and surface tension (Taniguchi 1988) have been already measured. The physical and thermochemical properties of the end-member melts (diopside and anorthite) have been also reported by many researchers (Cukierman and Uhlmann 1973; Kirkpatrick 1974; Cranmer and Uhlmann 1981; Ličko and Daněk 1982; Urbain et al. 1982; Richet 1984; Richet and Bottinga 1984; Shimizu and Kushiro 1984; Hummel and Arndt 1985; Brearley et al. 1986; Tauber and Arndt 1986). In addition, the structure of the end-member melts have been investigated by X-ray diffraction, spectroscopy and molecular dynamics (Taylor and Brown 1979; Okuno et al. 1982; Binsted et al. 1985; Mysen et al. 1980, 1983; Seifert et al. 1982; Sharma et al. 1983; McMillan 1984; Matson et al. 1986; Murdoch et al. 1985; Kirkpatrick et al. 1986; Matsui and Kawamura 1984).

This paper is one in a series concerned with the investigation of various physical properties such as thermal-expansion at low temperatures, infrared spectra (Taniguchi and Murase 1987b), viscosity (Taniguchi and Murase 1986, 1987b) and surface tension (Taniguchi 1988). The purpose of the present paper is to present new systematic data on densities including at high pressures, and to discuss their relationship to the melt structure.

Introduction

Density is one of the most important physical properties for igneous petrology, because the density contrast between

Sample preparation

The sample melts studied are those used in the previous investigations on thermal expansion (Taniguchi and Murase 1987b) and surface tension (Taniguchi 1988).

The melts were made up from reagent-grade chemicals: SiO_2 , Al_2O_3 , MgO and CaCO_3 , and were prepared by melting thoroughly ground mixtures of suitable amounts in a platinum crucible, at temperatures above the liquidus for 3 h. They were stirred with a platinum stick to eliminate bubbles and sample inhomogeneity. After remelting for about 3 h, direct measurements of the physical properties, including density, were performed at temperatures above the liquidus.

After the high temperature measurements, the melts were poured into a graphite mold to cool, and cut into columnar-shaped pieces approximately 1.5 cm in length. These glass pieces were then annealed at $T_g + 15^\circ\text{C}$, where T_g is the glass transition temperature roughly estimated using the relation T_g/T_l (liquidus temperature) $\approx 2/3$ (Sakka and Mackenzie 1971). They were then annealed to $T_g - 200^\circ\text{C}$ at the rate of $0.33^\circ\text{C}/\text{min}$. I could find no thermal strain in the sample glasses by examining them with polarized films. These annealed glasses were used to determine the density at room temperature and an expansion curve.

The glass powders used in the high-pressure density measurements were made from the quenched glasses.

The analysed chemical compositions of the sample glasses were given in previous papers (Taniguchi and Murase 1987b; Taniguchi 1988). Compositions were found to deviate from the ideal (the deviation for SiO_2 component: $-1.47 \sim 1.12\%$, Al_2O_3 : $-0.39 \sim 2.92\%$, CaO : $-1.42 \sim -2.90\%$, MgO : $-0.54 \sim 3.30\%$), but the differences were small enough for the accuracy required for the present purpose.

Measurements

The densities of the glassy state ($< T_g$) and the super-cooled liquid state ($T_g \leq T < T_l$; liquidus temperature) near the glass transition temperatures at 1 atm were determined using the thermal-expansion curves and densities, at room temperature, of the sample glasses. Density at room temperature was measured by the pycnometer method at about 22°C . The error was estimated to be less than $\pm 0.005 \text{ g/cm}^3$. The thermal-expansion curves were measured using a vertical high-sensitive dilatometer (Sinku Riko DLYT-1500H) calibrated using standard samples of corundum and quartz-glass. The heating rate was $3^\circ\text{C}/\text{min}$. The linear thermal expansion coefficient of SRM (a standard sample prepared by the Government Industrial Research Institute, Osaka) determined in the present measurement ($89.4 \times 10^{-7}/\text{K}$) is in good agreement with the nominal value ($89.8 \times 10^{-7}/\text{K}$). The total error for the density determination was estimated to be about $\pm 0.007 \text{ g/cm}^3$.

The density of the liquid state ($\geq T_l$) at 1 atm was determined with the double-bob Archimedean method (Sugai and Somiya 1982; Stein et al. 1986). The apparatus used for the measurement is identical to that used for surface tension measurements (Taniguchi 1988), except for the bob. As already shown in the previous paper, it consists of five main parts; chemical balance with a precision of $\pm 0.0001 \text{ g}$, electrical furnace, differential transformer, platinum-bob and platinum-crucible with melt. The diameter of the larger bob and smaller bob are 10 mm and 8 mm, respectively. Table 1 shows the density of NBS-710 (a standard glass prepared by the US National Bureau of Standards) melt compared with the literatures. The values by Daněk and Ličko (1981) were estimated from Fig. 8 in their paper. Although the methods differ, the present values agree well within an error of about $\pm 0.01 \text{ g/cm}^3$.

The density at high pressure was determined with the sinking and floating spheres method of Fujii and Kushiro (1977) in a solid-media, piston-cylinder apparatus at the Institute for Study of the Earth's Interior, Okayama University. Pressures have an uncertainty of $\pm 0.5 \text{ kb}$, and temperatures, measured with W Re5/W Re26 thermocouples, have an uncertainty of $\pm 20^\circ\text{C}$. Figure 1 shows an example of a temperature-time record for a given mea-

Table 1. Comparison of melt densities of NBS-710 glass

Method	T ($^\circ\text{C}$)	D (g/cm^3)	Reference
Archimedean method (double-bob)	1100	2.361	Present study
	1200	2.354	Present study
	1300	2.346	Present study
	1400	2.341	Present study
	1500	2.339	Present study
Falling-body method	1150	2.350	Daněk and Ličko (1981)
	1200	2.346	Daněk and Ličko (1981)
	1300	2.338	Daněk and Ličko (1981)
	1400	2.329	Daněk and Ličko (1981)
	1500	2.322	Daněk and Ličko (1981)
Archimedean method (single-bob)	1000	2.37	Murase and McBirney (1973)
	1100	2.35	Murase and McBirney (1973)
	1200	2.34	Murase and McBirney (1973)
	1300	2.34	Murase and McBirney (1973)
	1400	2.33	Murase and McBirney (1973)
	1500	2.33	Murase and McBirney (1973)

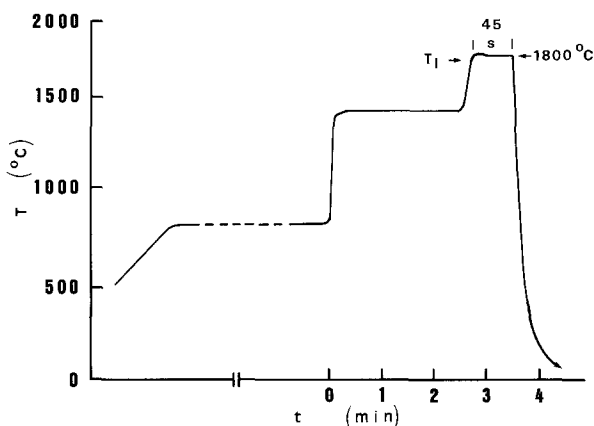


Fig. 1. An example temperature-time record for density measurements under high pressures (anorthite, $1800^\circ\text{C}/20 \text{ Kb}$, 45 s). T_l liquidus temperature

surement (anorthite, 1800°C , 20 kb, 45 s). As shown in this record, two step annealings (at 750 and 1400°C in this case) were made, and a slight overshoot of temperature was observed at the beginning of the measurement. The uncertainty in the temperature measurements are mainly due to this overshoot. The average quench rate was about $100^\circ\text{C}/\text{s}$. The furnace assembly is identical to that used by Kushiro (1976). The sinking sphere is made of SiC (nominal values: density at room temperature; 3.15 g/cm^3 , thermal expansion; $13.7 \times 10^{-6}/\text{K}$, compressibility; $4.6 \times 10^{-13} \text{ cm}^2/\text{dyne}$). Sometimes two sinking spheres made of SiC and Al_2O_3 were used simultaneously for comparison, but only the data of SiC were used for density calculation because of a slight melting of Al_2O_3 at higher temperatures. At the low temperature, the calculated density using Al_2O_3 sphere almost coincided with that using SiC sphere within the experimental error. Floating sphere is made of BN (nominal values: 2.34 g/cm^3 , $38.6 \times 10^{-6}/\text{K}$, compressibility data depended on the personal communication with Prof. Yagi, T.). The diameter of SiC spheres were $0.35\text{--}0.5 \text{ mm}$, and those of BN spheres were $0.3\text{--}0.5 \text{ mm}$. Under each set of temperature-pressure conditions, more than two runs were attempted. Run durations ranged from about 20 s (for diopside melt) to 180 s (for anorthite melt). Figure 2 shows an example of the relation between $|l|/r^2$ and run duration (l : distance of moving sphere, r : radius of sphere) for anorthite melt. This figure indicates that the spheres begin to move as soon as the temperature is raised to the run temperature. Unfortunately,

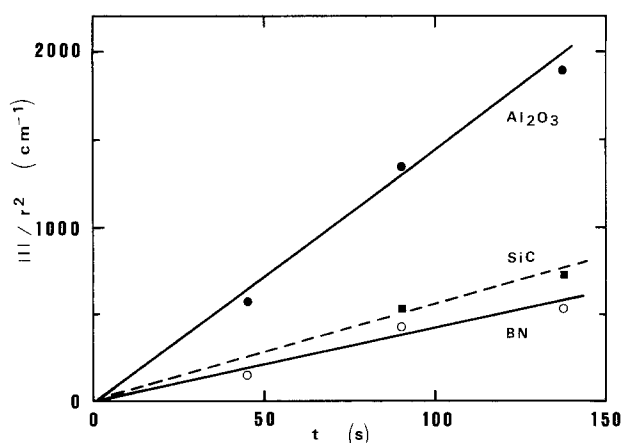


Fig. 2. Figure showing the relation between $|l|/r^2$ and time for anorthite melt. l distance of moving spheres, r radius of spheres

it was impossible to make runs with different duration for diopside melt because of its low viscosity. The runs for diopside melt were repeated under almost the same duration. In the present measurements it was assumed that the time lag of the beginning of sphere movement was zero in all measurements. The mean deviations of the experimental results were about $\pm 0.02 \text{ g/cm}^3$ ($0.01 - 0.04 \text{ g/cm}^3$). The error for the density measurements at high pressures was estimated to be less than $\pm 0.07 \text{ g/cm}^3$.

Results

Glass densities of fourteen compositions below the glass transition temperature at 1 atm are given in Table 2. The data were fitted to an empirical polynomial-equation with an average reproducibility of $\pm 0.004 \text{ g/cm}^3$ ($\Sigma |D_c - D_m|/N$, where D_c and D_m are calculated and measured density, respectively, N is the number of measurements). Compared to the literature, for diopside glass (2.846 g/cm^3 : Berman et al. 1942) and anorthite glass (2.700 g/cm^3 : Berman et al. 1942; 2.64: Cukierman and Uhlmann 1973; 2.701: Arndt and Häberle 1973; 2.66: Seifert et al. 1982), the present data

at room temperature are found to be the largest (D_i : 2.870 g/cm^3 , A_n : 2.704). It is generally accepted that the density of a glass is dependent on the thermal history of the glass sample. Therefore, if the annealing time is of insufficient duration, a smaller density compared with the "real one" may be measured. The fact that the present values are the largest may suggest that the present measurements are more reliable.

Densities of fourteen melt compositions just above the glass transition temperature (super-cooled liquid state), and those of six compositions in the stable-liquid state were measured at 1 atm. Table 3 shows the results and an experimental polynomial equation with an average reproducibility of $\pm 0.006 \text{ g/cm}^3$. Although the data for the super-cooled liquid state near the glass transition temperature are important for the better understanding of the nature of silicate melt, we have no data available for comparison. For the stable-liquid state, the density of diopside melt has been determined by Ličko and Daněk (1982, the falling body method) and by Lange and Carmichael (1987, the double-bob Archimedean method), and the density of anorthite melt at 1720°C has been determined by Ogino and Nishiwaki (1976, the multi-bob Archimedean method, number of bobs ≥ 3). Ličko and Daněk's values are somewhat lower than the present data by an average of 0.8%, whereas the values by Lange and Carmichael (1987) agree well with the present values within 0.4% error. The calculated density of anorthite melt at 1720°C (2.52 g/cm^3) using the present density at 1580°C and the thermal expansion coefficient estimated from the data by Lange and Carmichael (1987) agrees well with Ogino and Nishiwaki's value of 2.53 g/cm^3 .

High-pressure melt densities of three compositions along the join were measured at temperatures above the liquidus and pressures up to 20 Kbar. Table 4 shows the results and experimental equations. For the calculation of the equation, the effect of temperature was assumed to be negligible because the variation ($0.01 - 0.05 \text{ g/cm}^3$) in the temperature range measured at 1 atm is well within the experimental error ($\pm 0.07 \text{ g/cm}^3$) due to pressure. There are two sets of published data available for comparison (D_i : Scarfe

Table 2. Glass densities

D_i (mole%)	$D(\text{g/cm}^3)$							
	22° C	200	300	400	500	600	650	700
100	2.870	2.858	2.851	2.843	2.835	2.827	2.822	—
90	2.849	2.838	2.831	2.824	2.817	2.809	2.804	—
80	2.817	2.807	2.801	2.794	2.787	2.779	2.776	—
75	2.817	2.807	2.801	2.794	2.787	2.779	2.775	—
70	2.811	2.801	2.795	2.788	2.781	2.774	2.771	—
66	2.796	2.786	2.781	2.774	2.768	2.761	2.757	—
64	2.791	2.781	2.775	2.768	2.761	2.754	2.751	—
60	2.788	2.779	2.773	2.767	2.761	2.754	2.751	—
55	2.771	2.762	2.757	2.751	2.745	2.739	2.735	—
46.1	2.763	2.754	2.749	2.743	2.737	2.731	2.728	—
40	2.748	2.740	2.735	2.729	2.723	2.717	2.714	—
24.3	2.723	2.715	2.710	2.705	2.699	2.694	—	2.688
20	2.715	2.707	2.703	2.698	2.692	2.687	2.685	2.682
0	2.704	2.697	2.693	2.689	2.684	2.679	—	2.674

$$D = 2.700 - 3.651 \cdot 10^{-5} X - 1.241 \cdot 10^{-8} X^2 + 9.432 \cdot 10^{-4} Y - 5.412 \cdot 10^{-8} XY - 2.389 \cdot 10^{-10} X^2 Y + 7.916 \cdot 10^{-6} Y^2 - 2.069 \cdot 10^{-9} XY^2 + 1.806 \cdot 10^{-12} X^2 Y^2$$

X: temperature ($^\circ \text{C}$), Y: diopside content (mole%), average reproducibility: $\pm 0.004 \text{ g/cm}^3$

Table 3. Liquid densities including the super-cooled liquid state

<i>Di</i> mole %	<i>T</i> (° C)			<i>D</i> (g/cm ³)								
	T _g	T ₁	T ₂	T _g	T ₁	T ₂	1350	1400	1450	1500	1550	1580
100	720	728	738	2.814	2.810	2.804	—	2.630	2.623	2.619	2.611	—
90	723	730	740	2.796	2.794	2.788	—	—	—	—	—	—
80	720	730	740	2.768	2.765	2.760	2.631	2.624	2.619	2.617	2.610	—
75	726	734	747	2.767	2.765	2.759	—	—	—	—	—	—
70	727	736	747	2.763	2.761	2.755	—	—	—	—	—	—
66	733	742	756	2.749	2.747	2.741	—	—	—	—	—	—
64	734	742	753	2.743	2.741	2.736	2.618	2.616	2.605	2.591	2.585	—
60	736	746	757	2.742	2.740	2.735	—	—	—	—	—	—
55	738	748	760	2.728	2.725	2.721	—	—	—	—	—	—
46.1	747	760	771	2.720	2.717	2.714	—	—	—	—	—	—
40	748	761	776	2.707	2.704	2.700	—	—	2.568	2.557	2.552	—
24.3	780	791	806	2.682	2.680	2.676	—	—	—	—	—	—
20	798	810	824	2.675	2.673	2.669	—	—	—	—	2.554	—
0	842	856	870	2.666	2.664	2.661	—	—	—	—	—	2.538

$$D = 2.964 - 4.650 \cdot 10^{-4} X + 1.226 \cdot 10^{-7} X^2 - 3.088 \cdot 10^{-3} Y + 6.365 \cdot 10^{-6} XY - 2.560 \cdot 10^{-9} X^2 Y + 4.910 \cdot 10^{-5} Y^2 - 7.317 \cdot 10^{-8} XY^2 + 2.743 \cdot 10^{-11} X^2 Y^2$$

X: temperature (° C), *Y*: diopside content (mole%), average reproducibility: ±0.006 g/cm³

* The calculation of experimental equation includes the data by Ogino and Nishiwaki (1976) for anorthite melt (1720° C: 2.53)

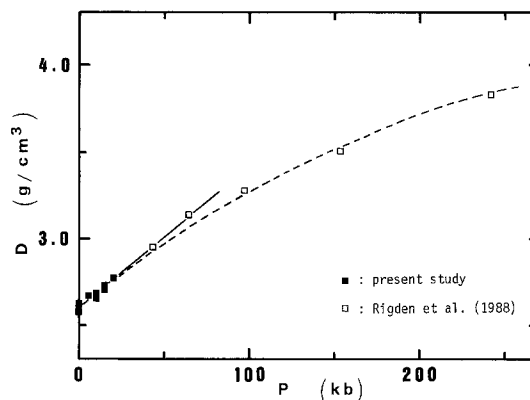
Table 4. Densities at high pressures. Values in parenthesis are calculated based on the polynomial equation in Table 3

<i>T</i> (° C)	<i>D</i> (g/cm ³)					
	10 ⁻³ Kb	5	7.5	10	15	20
Diopside						
1550	2.611	2.63	—	—	—	—
1650	(2.60)	2.60	—	2.63	2.70	—
1800	(2.59)	2.63	—	2.60	—	2.64
Di₆₄An₃₆						
1400	2.616	2.67	—	2.68	—	—
1500	2.591	—	—	2.67	2.70	—
1650	(2.57)	—	—	2.65	2.73	2.77
Anorthite						
1650	(2.53)	2.64	2.65	2.66	—	—
1800	(2.52)	2.62	—	2.74	2.73	2.82

$$D = A \cdot 10^{-3} P + B, \text{ P: pressure (Kb)}$$

	A	B	Average reproducibility
Diopside	3.13	2.60	±0.02 g/cm ³
Di ₆₄ An ₃₆	8.18	2.60	±0.02 g/cm ³
Anorthite	14.16	2.54	±0.02 g/cm ³

et al. 1979; Di₆₄An₃₆: Rigden et al. 1984, 1988). According to Fig. 58 of Scarfe et al. (1979), the density of diopside melt at 1640° C/12.5 Kb is about 2.96 ± 0.03 g/cm³, and that at 1640° C/15 Kb is about 3.00 ± 0.03 g/cm³. Although they used the same technique as the present measurement, there is discrepancy between their values and the present values (1650° C/10 Kb: 2.63 ± 0.07 g/cm³, 1650° C/15 Kb: 2.70 ± 0.07 g/cm³). The reason for this discrepancy is not clarified yet. The present values for diopside melt at 1650° C/10, 15 Kb do not contradict the calculated values

**Fig. 3.** Density-pressure relation for Di₆₄An₃₆ melt. For the lines and temperature conditions, see the text

(1640° C/12.5 Kb: 2.72 g/cm³, 15 Kb: 2.75 g/cm³) of Lange and Carmichael (1987) based on ultrasonic sound velocity data (Rivers and Carmichael 1987). Although there are critical comments (Lange and Carmichael 1987) on the applicability of the sinking and floating spheres method to diopside melt, the present results indicate that the method is applicable.

Rigden et al. (1984, 1988) measured the densities of Di₆₄An₃₆ melt at pressures up to 339 Kb using the shock wave technique. Figure 3 shows the pressure-density relation for Di₆₄An₃₆ melt including the data up to 250 Kb by Rigden et al. (1988). Using these data we can evaluate the constants *K* (bulk modulus at 1 atm) and *K'* (the pressure derivative of the bulk modulus) for a third-order Birch-Murnaghan equation of state:

$$P = \frac{3}{2} K \left\{ \left(\frac{D}{D_0} \right)^{\frac{7}{3}} - \left(\frac{D}{D_0} \right)^{\frac{5}{3}} \right\} \left\{ 1 - \frac{3}{4} (4 - K') \left[\left(\frac{D}{D_0} \right)^{\frac{2}{3}} - 1 \right] \right\} \quad (1)$$

where *D*₀ is the 1 atm density of the melt. If we neglect the difference between the isothermal and adiabatic moduli

(less than 3.4% for *Di-An* melt system: data by Rivers and Carmichael 1987) and use the average density between 1400 and 1650° C at 1 atm (D_0 : 2.593 g/cm³), the calculated constants are: $K=257$ Kb, $K'=4.37$ (cf. $K=242$ Kb, $K'=4.85$, Rigden et al. 1988). It seems that all data give one compression curve, although the measurements by Rigden et al. (1988) were done under very high temperature conditions (e.g., 2400° C at 250 Kb). Figure 3 also shows the calculated lines based on the linear equation in Table 4 and on the third-order Birch-Murnaghan equation ($P < 250$ Kb). The linear line pass through two data points of Rigden et al. (1988). According to Fig. 10 of Rigden et al. (1988), the calculated shock temperatures (about 1500 and 1600° C) for the two data are within the range of present temperature condition, while those for other high pressure data exceed about 1750° C. The calculated line by Birch-Murnaghan deviates downward from the linear line. The main factor affecting the downward deviation could be the effect of pressure on K , K' , but in this case, the effect of temperature might not be negligible.

Discussion

Temperature, pressure and composition effects on density

Figure 4 shows the density-temperature relationship at 1 atm. Solid lines are based on the polynomial equations listed in Tables 2–3, and broken lines indicate the glass transition temperatures and liquidus temperatures (Yoder 1976).

Two characteristic features about the thermal dependence of density can be seen from the figure. The first is the break in the expansion line at the glass transition temperature. The second is that the density of the liquid state generally changes along a curved line, while that of the glassy state changes linearly with temperature. For anorthite melt, however, it seems that a linear extrapolation of the supercooled liquid density fits well the high-temperature datum. For the liquid state, it is also obvious that the slope of the expansion curve near the glass transition temperature is steeper than that at higher temperatures. Figure 5 shows the relation between the thermal expansion coefficient and temperature for diopside and anorthite melts. The thermal expansion coefficient is defined in several ways. The figure contains the mean coefficient (Eq. 2) based on the raw density data, and the instantaneous coefficient (Eq. 3) based on the polynomial equations listed in Tables 2–3.

$$\alpha_m \equiv \frac{1}{V} \frac{V - V_0}{T - T_0} \quad (2)$$

$$\alpha_i \equiv \frac{1}{V} \frac{\partial V}{\partial T} \quad (3)$$

where V_0 is the volume at a reference temperature, T_0 (the lowest temperature in the temperature range calculated). The thermal expansion coefficient of the glassy state is almost constant, while that at liquid state decreases with increasing temperature. The jump in coefficients at the glass transition temperature is very prominent. The jump is due to a change in the mechanism for thermal expansion between the glassy and liquid states.

As already shown in Fig. 4, it is clear that density decreases with increasing anorthite content at any state of

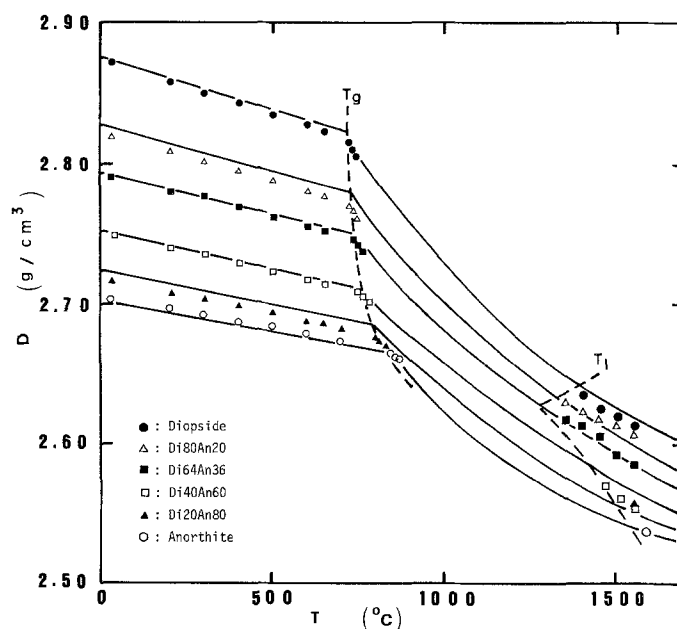


Fig. 4. Density-temperature relation at 1 atm. Solid lines calculated using the polynomial equations listed in Tables 2–3. The broken lines indicates the glass-transition (T_g) and liquidus (T_l) temperatures

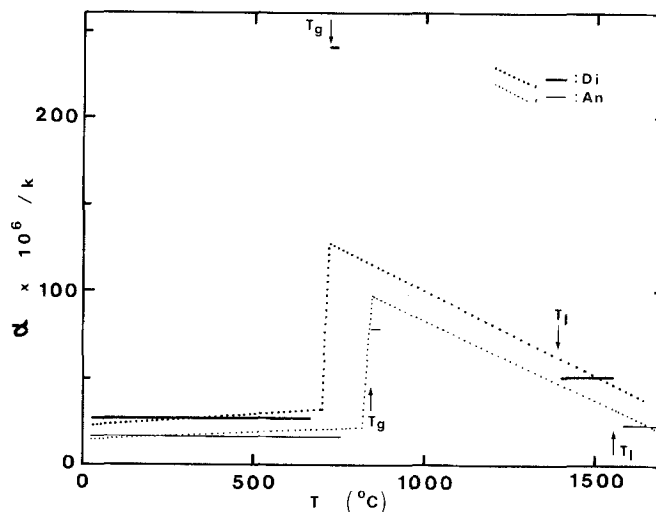


Fig. 5. Figure showing the relations between thermal expansion coefficients and temperature for diopside and anorthite melts. Solid lines indicate the mean coefficient, and dotted lines indicate the instantaneous coefficient

melt. Generally speaking, the volume of solution of real binary-system is not a simple addition of its components. To estimate the real volume of mixture melt with the additive law, we need the partial molar volume and excess volume (V^{ex}). In addition, we can know about the non-ideality of the mixing process through the excess volume. Figure 6 shows the calculated results of excess volumes of the glassy state (600° C) and liquid state (1600° C) in accordance with the following equation.

$$V^{ex} = V^{Di-An} - (N_{Di} V^{Di} + N_{An} V^{An}) \quad (4)$$

where V^{Di} , V^{An} , V^{Di-An} are the melt volumes of diopside, anorthite and mixtures respectively, and N_{Di} and N_{An} are the mole fractions of diopside and anorthite respectively.

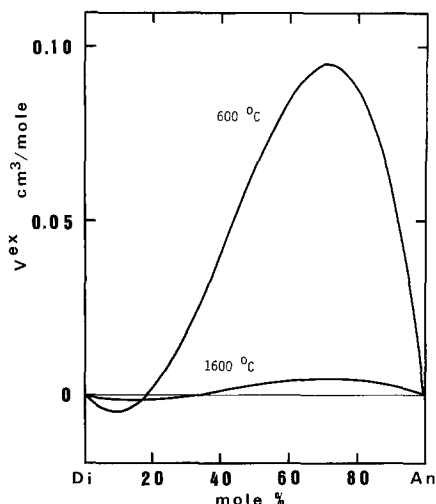


Fig. 6. Figure showing the excess volumes of the glassy and liquid states

These two lines exhibit a minimum at the diopside-rich side and a maximum at the anorthite-rich side. The estimated error for the liquid state is about $\pm 0.1 \text{ cm}^3/\text{mole}$, whereas for the glassy state it is about $\pm 0.07 \text{ cm}^3/\text{mole}$. The calculated excess volumes in the liquid state can be regarded negligible when compared to the estimated error, i.e., the liquid state mixes ideally with respect to volume. Contrary to this, the maximum in the glassy state around *Di*₃₀*An*₇₀ seems to exist because the excess value exceeds the error. Present glass samples have different fictive temperature (\approx glass transition temperature), because they were annealed at the temperature $T_g + 15^\circ \text{C}$. The glass transition temperature deviates from linear relation and shows a minimum at about *Di*₄₀*An*₆₀. This deviation must bring the glass volume to minimum. Then the maximum in the glass volume around *Di*₃₀*An*₇₀ is unusual. The different mixing behaviors between glassy and liquid states may reflect a structural change with temperature, and is another indication of the incomplete description of liquids given by glasses.

Figure 7 shows the pressure dependence of density for diopside, *Di*₆₄*An*₃₆ and anorthite melts, and calculated lines based on the experimental equations listed in Table 4. The slope of the lines clearly increase with increasing anorthite content, i.e., the "isothermal" compressibility increases from $1.2 \pm 0.7 \times 10^{-12} \text{ cm}^2/\text{dyne}$ (*Di*) to $5.6 \pm 0.8 \times 10^{-12} \text{ cm}^2/\text{dyne}$ (*An*) with increasing anorthite content. The compressibilities are somewhat larger than that of the corresponding crystals (*Di*: $0.88 \times 10^{-12} \text{ cm}^2/\text{dyne}$, Levien and Prewitt 1981, *An*: $4.3 \times 10^{-12} \text{ cm}^2/\text{dyne}$, calculated based on the data by Birch 1961). If we assume that the compressibility relates linearly to composition (compressibility = $5.66 \times 10^{-12} - 4.30 \times 10^{-14} Y \text{ cm}^2/\text{dyne}$, Y : diopside mol%), we can estimate the density at high temperatures and pressures using the polynomial equation listed in Table 3. Figure 8 shows an example at 1650°C . The increase of compressibility with anorthite induces the density reversion at pressures above about 8 kb.

On the concept of structure through density and other related physical properties

Previous papers on the "structure" of magmatic silicate melts emphasized the combinations of constituent silicate

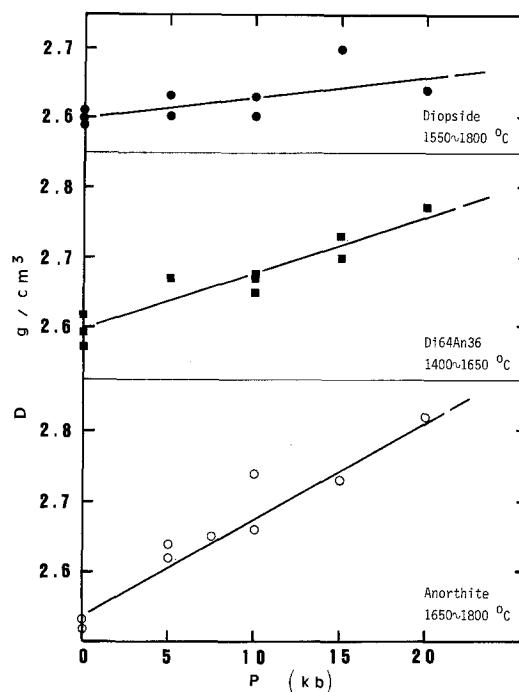


Fig. 7. Density-pressure relations. Lines are based on the linear equations given in Table 4

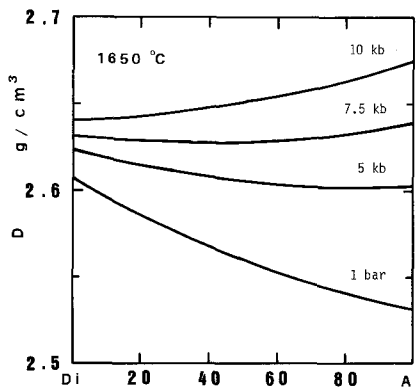


Fig. 8. Effect of pressure on the density-composition relations at 1650°C . Curves were calculated using the linear equation of compressibility-composition relation and polynomial equation listed in Table 3

(or aluminosilicate) units in melts (e.g., Taylor and Brown 1979; Mysen et al. 1980; Taniguchi and Murase 1987b). Knowledge about the type of silicate units in a melt is useful for understanding the relationship between melt structure and physical properties. In order to treat this relationship quantitatively, however, our concept of melt "structure" at the present level seems to be not sufficient. Contrary to this, the hard (rigid) sphere liquid approaches (e.g., Reiss et al. 1960; Mayer 1963), where liquid is composed of hard spheres (constituent units) and interstitial space (free volume), seems to offer more useful and fruitful discussions on the problem. So, melt structure will be discussed through physical properties based on this simple liquid model.

Free volume at 1 atm

Free volume has been defined in different ways (Bondi 1954; Taniguchi and Murase 1987a, b). But the main definitions

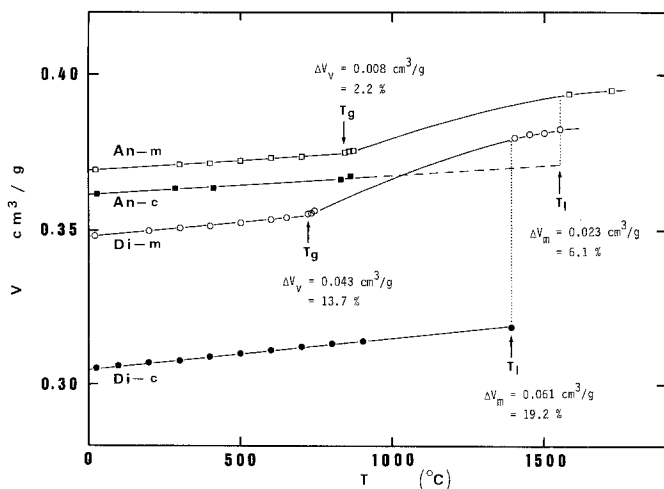


Fig. 9. Specific volume-temperature relations of diopside and anorthite for melt and crystal. Numerical values in the figure are volume changes accompanied by the transformations from crystal to melt (*v* subscript vitrification, *m* melting)

are divided into two types. One is the volume difference between a liquid and corresponding crystal (free volume as excess volume), and the other is the difference between the volumes of liquid at T and at 0 K (free volume as expansion volume).

Figure 9 shows the relation between specific volume and temperature for diopside and anorthite. The density data for crystals were taken from Berman et al. (1942), Dane (1942), Foit and Peacor (1973), Finger and Ohashi (1976) and Okuno et al. (1982). The volume difference between melt in the glassy state and corresponding crystal is almost constant. This is due to the fact that the thermal expansion coefficients of melt at glassy state and crystal are almost identical. Contrary to this, the difference increases with increasing temperature in the liquid state, i.e., the free volume as excess volume in the glassy state is almost constant, but that of the liquid state increases with increasing temperature. It is evident that the volume difference between melt and crystal for diopside is always larger than that for anorthite. Generally speaking, the corresponding crystalline material for magma is neither a single-crystal nor a monomineral rock but a poly-crystalline material composed of several kinds of minerals. For this kind of crystalline material, it is difficult to measure the precise density-change with temperature. Therefore the application of free volume as excess volume is not suitable to igneous petrology.

Contrary to this, the free volume as expansion volume does not need the data of crystalline material, and is given by the following equation (Taniguchi and Murase 1987a, b)

$$V_f = 1 - \frac{D_T(1 + \alpha_g T)}{D_{T_g}(1 + \alpha_l T_g)} \quad (5)$$

where V_f is free volume in volume fraction, D_T and D_{T_g} are densities at T and T_g respectively, α_g and α_l are thermal expansion coefficients in the glassy and super-cooled liquid states near T_g respectively. Free volumes as expansion volume for the melts in the glassy and liquid states decrease similarly with increasing anorthite content. It ranges from 0.21 (*Di*) to 0.10 (*An*) in liquid state (1600°C), and from 0.17 (*Di*) to 0.06 (*An*) in glassy state (600°C). Taniguchi and Murase (1987a) showed that the free volumes at the

glass transition temperature of some silicate melts, including igneous rock compositions, decrease with an increase of NBO/T (number of nonbridging oxygen per tetrahedrally coordinated cation). NBO/T values for the present melt system decrease from 2 to 0 with the increase of anorthite content. Consequently, we may deduce that the interstitial space in a silicate melt in not only glassy state but also in liquid states decreases with an increase of polymerization.

Constituent unit

The hard (rigid)-sphere liquid theory (Reiss et al. 1960; Reiss and Mayer 1961; Mayer 1963) can be summarized briefly as follows: an equation of state for the hard-sphere liquid has been obtained by essentially computing the reversible work of creating a spherical cavity in the liquid. The equation of state is presented in the form

$$\frac{PV}{RT} = \frac{1 + y + y^2}{(1 - y)^3} \quad (6)$$

where P is the pressure, V is the molar volume, R is the gas constant, y is $\pi a^3 N/6V$, N is Avogadro's number, and a is the hard-sphere diameter of the molecules comprising the pure liquid. From the equation of state, we can easily obtain the expansion coefficient, α ,

$$\begin{aligned} \alpha &\equiv \frac{1}{V} \frac{\partial V}{\partial T} \\ &= \frac{1 - y^3}{T(1 + 2y)^2} \end{aligned} \quad (7)$$

and isothermal compressibility, β ,

$$\begin{aligned} \beta &\equiv -\frac{1}{V} \frac{\partial V}{\partial P} \\ &= \frac{V(1 - y)^4}{RT(1 + 2y)^2} \end{aligned} \quad (8)$$

The theory has been extended to the surface tension of a real liquid, γ .

$$\gamma = \frac{kT}{4\pi a^2} \left[\frac{12y}{1 - y} + \frac{18y^2}{(1 - y)^2} \right] - \frac{Pa}{2} \quad (9)$$

where k is the Boltzmann constant. Usually the term $Pa/2$ is of negligible magnitude and can be ignored (Reiss and Mayer 1961). It is clear from the relationships mentioned above that we can correlate one parameter with the others, e.g., we are able to use the thermal expansion coefficient (Eq. 7) and the surface tension (Eq. 9) to estimate the isothermal compressibility using Eq. 8. It is also clear that we can estimate not only the parameter but also the hard-sphere diameter and the molar volume. This has been done successfully for a whole range of liquids, e.g., simple liquids composed of nonmetallic elements, hydrocarbon liquids, liquids composed polar organic molecules, liquid metals and molten salts (Reiss and Mayer 1961; Mayer 1963). Boyer et al. (1967) and Fray (1970) applied the theory to phosphate and alkali silicate melts, and deduced some meaningful results for the understanding of melt structures. Fray (1970) compared the isothermal compressibility of alkali silicate melts calculated from the surface tension and thermal expansion coefficient with an experimental adiabatic compressibility, and found that both values agreed well

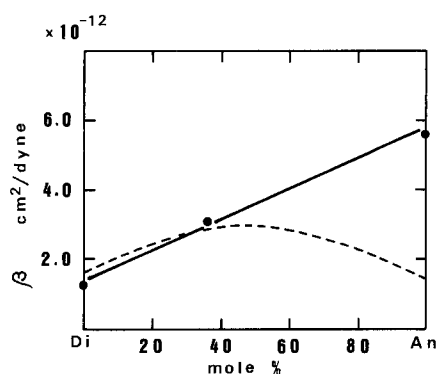


Fig. 10. Relation between isothermal compressibility and composition. The solid line and circles are based on experiment; the broken line is the calculated result (1650° C) using thermal expansion coefficients and surface tension data at 1 atm based on the hard-sphere liquid theory

with each other. This may prove the validity of the theory to silicate melts. Figure 10 shows the comparison between experimental and calculated compressibilities at 1650° C. For the calculation, the surface tension was estimated from the polynomial equation given by Taniguchi (1988), and the mean coefficient of expansion around 1650° C estimated from the polynomial equation was used. The measured compressibilities are linear functions of composition, while calculated values show a maximum at about *Di60An40*. The disagreement between experimental and calculated compressibilities is clear at the *An*-rich side above *Di60An40*. This result indicates that the theory is applicable to the diopside-rich melt, but not to the anorthite-rich melt above *Di60An40*. Then, what is the reason for this disagreement from a structural point of view? The fact that the theory is applicable to the diopside-rich melt indicates that the diopside-rich melt can be regarded as a mixture of hard-sphere and interstitial space. Contrary to this, the non-applicability of the theory to anorthite melt may be essentially explained by the difference of structures between the real and the model, i.e., the structure of anorthite melt is a three-dimensional network of interconnected four-membered rings (Taylor and Brown 1979).

The characteristic composition *Di60An40* is almost identical to the eutectic composition (*Di64An36*). I have already pointed out the possibility of a basic "structural change" around the eutectic composition (Taniguchi and Murase 1987b; Taniguchi 1988) based on the relation between composition and other physical properties. I could not observe a remarkable change on infrared spectra at the eutectic composition (Taniguchi and Murase 1987b). This may suggest that the "structural change" is not explained by the change of the types of constituent silicate units. It seems that the percolation theory is the only theory to interpret the problem. According to the site-percolation theory (Shante and Kirkpatrick 1971), the volume fraction of spheres in the lattice at the critical state (at which the percolation occur or not) depends only on the dimension of the lattice. For the 3-dimensional cases, the critical volume is about 15 vol.%. It is already known that the changes of some physical properties occur at the critical state in some amorphous materials (Murayama 1987). From a structural point of view, the present melt system changes from 3-dimensional network structure with little free volume (*An*) to discrete structure with much free volume (*Di*).

This change may be approximated by the change from 3-dimensional network to discrete structure with the introduction of interstitial space. If this idea is reasonable, we can expect the break of property-composition relation at the composition at which the percolation occur. The free volume of the eutectic composition at liquid state is about 15 vol.% (14.7%/1300° C–15.6%/1600° C). This value coincide with the critical volume. Thus, the "structural change", around the eutectic composition, may reflect a "critical state" in the substitution of "continuous structure" of anorthite melt for "discrete structure" of diopside melt. In this case, the critical state is the formation of percolation cluster of free volume.

According to the calculation based on the hard-sphere liquid theory, the hard-sphere diameters is about 10 Å for diopside-rich melt (*Di* > *Di60*). In the previous paper the diameter was taken as the gas equilibrium distance for molten salt (Reiss and Mayer 1961), and as the interionic distance in phosphate melts (Boyer et al. 1967). If we assume that the hard-sphere diameter represents the average diameter of the constituent units in the melt, and if we use the simplification that the unit is composed of oxygen ions, the number of oxygen ions in one unit for diopside-rich melt is about 45 (radius of oxygen ion: 1.4 Å). This number of oxygens may correspond to the silicate anion $\text{Si}_{20}\text{O}_{45}^{10-}$ (Fray 1970).

Acknowledgements. The author wishes to thank T. Murase, I. Kushiro and E. Takahashi for their help in the measurements and stimulating discussions. The author also thanks N. Fujii and D. Sykes for their constructive comments and critical reading of an early draft of the manuscript. The author is indebted to Y. Matsui, S. Akimoto, E. Ito, T. Fujii and T. Yagi for their useful comments. High-pressure measurements were done while the author was a visiting scientist at the Institute for Study of the Earth's Interior, Okayama University. This study was supported by the Grant-in-Aid for Special Project Research from the Ministry of Education, Science and Culture of Japan (Nos. 60121015, 61113014 to H. Taniguchi and No. 62103007 to I. Kushiro).

References

- Arndt J, Häberle F (1973) Thermal expansion and glass transition temperatures of synthetic glasses of plagioclase-like compositions. *Contrib Mineral Petrol* 39:175–183
- Berman H, Daly RA, Spicer HC (1942) Density at room temperature and 1 atmosphere. In: Birch F, Schairer JF, Spicer HC (eds) *Handbook of physical constants*, No. 36. *Geol Soc Am Spec Pap*, pp 7–26
- Binsted N, Greaves GN, Henderson CMB (1985) An EXAFS study of glassy and crystalline phases of compositions $\text{CaAl}_2\text{Si}_2\text{O}_8$ (anorthite) and $\text{CaMgSi}_2\text{O}_6$ (diopside). *Contrib Mineral Petrol* 89:103–109
- Birch F (1961) The velocity of compressional waves in rocks to 10 kilobars. *J Geophys Res* 66:2199–2224
- Bondi A (1954) Free volumes and free rotation in simple liquids and liquid saturated hydrocarbons. *J Phys Chem* 58:929–939
- Boyer AJG, Fray DJ, Meadowcroft TR (1967) Application of the rigid sphere model to the pure molten phosphates of calcium, sodium, and zinc. *Phys Chem Glasses* 8:96–100
- Brearley M, Dickinson JE Jr, Scarfe CM (1986) Pressure dependence of melt viscosities on the join diopside-albite. *Geochim Cosmochim Acta* 50:2563–2570
- Cranmer D, Uhlmann DR (1981) Viscosities in the system albite-anorthite. *J Geophys Res* 86:7951–7956
- Cukierman M, Uhlmann DR (1973) Viscosity of liquid anorthite. *J Geophys Res* 78:4920–4923

- Dane EB Jr (1942) Density at high temperature; Thermal expansion In: Birch F, Schairer JF, Spicer HC (ed) Handbook of physical constants, No. 36. Geol Soc Am Spec Pap, pp 30–37
- Daněk V, Ličko T (1981) Apparatus for the measurement of physico-chemical properties of oxide melts. *Silikaty* 25:153–164 (in Czechoslovak)
- Dunn T (1982) Oxygen diffusion in three silicate melts along the join diopside-anorthite. *Geochim Cosmochim Acta* 46:2293–2299
- Finger LW, Ohashi Y (1976) The thermal expansion of diopside to 800° C and a refinement of the crystal structure at 700° C. *Am Mineral* 61:303–310
- Foit FF Jr, Peacor DR (1973) The anorthite crystal structure at 410 and 830° C. *Am Mineral* 58:665–675
- Fray DJ (1970) The structure of alkali silicate melts. *Phys Chem Glasses* 11:219–222
- Fujii T, Kushiro I (1977) Density, viscosity, and compressibility of basaltic liquid at high pressures. *Carnegie Inst Washington Yearb* 76:419–424
- Hummel W, Arndt J (1985) Variation of viscosity with temperature and composition in the plagioclase system. *Contrib Mineral Petrol* 90:83–92
- Kirkpatrick RJ (1974) Kinetics of crystal growth in the system $\text{CaMgSi}_2\text{O}_6\text{-CaAl}_2\text{SiO}_6$. *Am J Sci* 274:215–242
- Kirkpatrick RJ, Oestrike R, Weiss CA Jr, Smith KA, Oldfield E (1986) High-resolution ^{27}Al and ^{29}Si NMR spectroscopy of glasses and crystals along the join $\text{CaMgSi}_2\text{O}_6\text{-CaAl}_2\text{SiO}_6$. *Am Mineral* 71:705–711
- Kushiro I (1976) Changes in viscosity and structure of melt of $\text{NaAlSi}_2\text{O}_6$ composition at high pressures. *J Geophys Res* 81:6347–6350
- Kushiro I (1982) Density of tholeiite and alkali basalt magmas at high pressures. *Carnegie Inst Washington Yearb* 81:305–309
- Lange RA, Carmichael ISE (1987) Densities of $\text{Na}_2\text{O-K}_2\text{O-CaO-MgO-FeO-Fe}_2\text{O}_3\text{-Al}_2\text{O}_3\text{-TiO}_2\text{-SiO}_2$ liquids: New measurements and derived partial molar properties. *Geochim Cosmochim Acta* 51:2931–2946
- Levien L, Prewitt CT (1981) High-pressure structural study of diopside. *Am Mineral* 66:315–323
- Ličko T, Daněk V (1982) Densities of melts in the system $\text{CaSiO}_3\text{-CaMgSi}_2\text{O}_6\text{-Ca}_2\text{MgSi}_2\text{O}_7$. *Physics Chem Glasses* 23:67–71
- Matson DW, Sharma SV, Philpotts JA (1986) Raman spectra of some tectosilicates and of glasses along the orthoclase-anorthite and nepheline-anorthite joins. *Am Mineral* 71:694–704
- Matsui Y, Kawamura K (1984) Computer simulation of structures of silicate melts and glasses. In: Sunagawa I (ed) *Materials science of the earth's interior*, Terra Scientific Publications, Tokyo, pp 3–23
- Mayer SW (1963) A molecular parameter relationship between surface tension and liquid compressibility. *J Phys Chem* 67:2160–2164
- McMillan P (1984) A raman spectroscopic study of glasses in the system CaO-MgO-SiO_2 . *Am Mineral* 69:645–659
- Mo X, Carmichael ISE, Rivers ML, Stebbins JF (1982) The partial molar volume of Fe_2O_3 in multicomponent silicate liquids and the pressure dependence of oxygen fugacity in magmas. *Mineral Mag* 45:237–245
- Murase T, McBirney AR (1973) Properties of some common igneous rocks and their melts at high temperature. *Geol Soc Am Bull* 84:3563–3592
- Murayama K (1987) Amorphous and fractal. In *Fractal science*, Asakura, Tokyo, pp 170–207 (in Japanese)
- Murdoch JB, Stebbins JF, Carmichael ISE (1985) High-resolution ^{29}Si NMR study of silicate and aluminosilicate glasses: the effect of network-modifying cations. *Am Mineral* 70:332–343
- Mysen BO, Virgo D, Scarfe CM (1980) Relations between the anionic structure and viscosity of silicate melts – a Raman spectroscopic study. *Am Mineral* 65:690–710
- Mysen BO, Virgo D, Danckwerth P, Seifert FA, Kushiro I (1983) Influence of pressure on the structure of melts on the joins $\text{NaAlO}_2\text{-SiO}_2$, $\text{CaAl}_2\text{O}_4\text{-SiO}_2$, and $\text{MgAl}_2\text{O}_4\text{-SiO}_2$. *Neues Jahrb Mineral Abh* 147:281–303
- Nelson SA, Carmichael ISE (1979) Partial molar volumes of oxide components in silicate liquids. *Contrib Mineral Petrol* 71:117–124
- Ogino K, Nishiwaki J (1976) Density and electrical conductivity of slags in the system $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3$. Molten Salt Committee Meeting, Abstract:31–32 (in Japanese)
- Ohtani E (1984) Generation of komatiite magma and gravitational differentiation in the deep upper mantle. *Earth Planet Sci Lett* 67:261–272
- Okuno M, Marumo F, Ossaka J, Ishizawa N, Minato I (1982) The crystal and melt structures of anorthite at high temperature. *J Jpn Assoc Mineral Petrol Econ Geol, Spec Vol* 3:19–26 (in Japanese)
- Reiss H, Mayer SW (1961) Theory of the surface tension of molten salts. *J Chem Phys* 34:2001–2003
- Reiss H, Frisch HL, Helfand E, Lebowitz JL (1960) Aspects of the statistical thermodynamics of real fluids. *J Chem Phys* 32:119–124
- Richet P (1984) Viscosity and configurational entropy of silicate melts. *Geochim Cosmochim Acta* 48:471–483
- Richet P, Bottinga Y (1984) Anorthite, andesine, wollastonite, cordierite and pyrope: thermodynamics of melting, glass transitions, and properties of the amorphous phases. *Earth Planet Sci Lett* 67:415–432
- Rigden SM, Ahrens TJ, Stolper EM (1984) Densities of liquid silicates at high pressures. *Science* 226:1071–1074
- Ridgen SM, Ahrens TJ, Stolper EM (1988) Shock compression of molten silicate: results for a model basaltic composition. *J Geophys Res* 93:367–382
- Rivers ML, Carmichael ISE (1987) Ultrasonic studies of silicate melts. *J Geophys Res* 92:9247–9270
- Sakka S, Mackenzie JD (1971) Relation between apparent glass transition temperature and liquids temperature for inorganic glass. *J Non-Cryst Solids* 6:145–162
- Scarfe CM, Mysen BO, Virgo D (1979) Changes in viscosity and density of melts of sodium disilicate, sodium metasilicate, and diopside composition with pressure. *Carnegie Inst Washington Yearb* 78:547–551
- Scarfe CM, Cronin DJ, Wenzel JT, Kauffman SA (1983) Viscosity-temperature relationships at 1 atm in the system diopside-anorthite. *Am Mineral* 68:1083–1088
- Seifert F, Mysen BO, Virgo D (1982) Three-dimensional network structure of quenched melts (glass) in the system $\text{SiO}_2\text{-NaAlO}_2$, $\text{SiO}_2\text{-CaAl}_2\text{O}_4$ and $\text{SiO}_2\text{-MgAl}_2\text{O}_4$. *Am Mineral* 67:696–717
- Shante VKS, Kirkpatrick S (1971) An introduction to percolation theory. *Adv Phys* 20:325–357
- Sharma SK, Simons B, Yoder HS Jr (1983) Raman study of anorthite, calcium Tschermak's pyroxene, and gehlenite in crystalline and glassy states. *Am Mineral* 68:1113–1125
- Shimizu N, Kushiro I (1984) Diffusivity of oxygen in jadeite and diopside melts at high pressures. *Geochim Cosmochim Acta* 48:1295–1303
- Shiraishi Y, Ikeda K, Tamura A, Sairo T (1978) On the viscosity and density of the molten FeO-SiO_2 system. *Trans Jpn Inst Met* 19:264–274
- Stein DJ, Stebbins JF, Carmichael ISE (1986) Density of molten aluminosilicates. *J Am Ceram Soc* 69:396–399
- Stolper E, Walker D, Hager DH, Hays JF (1981) Melt segregation from partially molten source regions: The importance of melt density and source region size. *J Geophys Res* 86:6261–6271
- Sugai M, Somiya S (1982) Measurement of density, viscosity and surface tension of the melt of the system $\text{SiO}_2\text{-TiO}_2\text{-Al}_2\text{O}_3$ at 1600° C. *Yogyo Kyokai Shi* 90:262–269 (in Japanese)
- Taniguchi H (1988) Surface tension of melts in the system $\text{CaMgSi}_2\text{O}_6\text{-CaAl}_2\text{Si}_2\text{O}_8$ and its structural significance. *Contrib Mineral Petrol* 100:484–489
- Taniguchi H, Murase T (1986) Physical properties and structures in the melt system diopside-anorthite. Preliminary Rep Spec Res Project 1986:31–34 (in Japanese)

- Taniguchi H, Murase T (1987a) Role of free volume in the viscous behavior of magma. *J Jpn Assoc Mineral Petrol Econ Geol* 82:189–202
- Taniguchi H, Murase T (1987b) Some physical properties and melt structures in the system diopside-anorthite. *J Volcanol Geotherm Res* 34:51–64
- Tauber P, Arndt J (1986) Viscosity-temperature relationship of liquid diopside. *Phys Earth Planet Int* 43:97–103
- Taylor M, Brown GE Jr (1979) Structure of mineral glasses-I. The feldspar glasses $\text{NaAlSi}_3\text{O}_8$, KAlSi_3O_8 , $\text{CaAl}_2\text{Si}_2\text{O}_8$. *Geochim Cosmochim Acta* 43:61–75
- Urbain G, Bottinga Y, Richet P (1982) Viscosity of liquid silica, silicates and alumino-silicates. *Geochim Cosmochim Acta* 46:1061–1072
- Weill DF, Hon R, Navrotsky A (1980) The igneous system $\text{CaMgSi}_2\text{O}_6$ - $\text{CaAl}_2\text{Si}_2\text{O}_8$ - $\text{NaAlSi}_3\text{O}_8$: variation on a classic theme by Bowen. In: Hargraves RB (ed) *Physics of magmatic processes*. Princeton University Press, Princeton New Jersey, pp 49–92
- Yoder HS Jr (1976) Generation of basaltic magma. *National Academy of Sciences, Washington*, pp 91

Received September 22, 1988; Accepted June 26, 1989
Editorial responsibility: J. Carmichael