

## Density of some titanium-bearing silicate liquids and the compositional dependence of the partial molar volume of TiO<sub>2</sub>

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**Abstract**—The densities of thirteen silicate liquids along the Na<sub>2</sub>SiO<sub>3</sub>-TiO<sub>2</sub> and CaSiO<sub>3</sub>-TiO<sub>2</sub> joins and six other titanium-bearing silicate liquids of the general formula  $X \frac{n}{2n} \text{TiSiO}_5$  (where  $X = \text{Li, Na, K, Rb, Cs, Ca, Sr, Ba}$ ) have been measured in equilibrium with air using the double Pt bob Archimedean method. The Na<sub>2</sub>SiO<sub>3</sub>-TiO<sub>2</sub> join was investigated from 10–50 mole% TiO<sub>2</sub> in the temperature range 1000–1150°C whereas the CaSiO<sub>3</sub>-TiO<sub>2</sub> join was investigated from 10–80 mole% TiO<sub>2</sub> in the temperature range of 1400–1625°C. Density increases with TiO<sub>2</sub> content along both joins.

Partial molar volumes of the binary endmembers, Na<sub>2</sub>SiO<sub>3</sub> and CaSiO<sub>3</sub>, and of TiO<sub>2</sub> have been computed. The partial molar volume of Na<sub>2</sub>SiO<sub>3</sub> agrees well with that determined by BOCKRIS et al. (1955). The partial molar volume of CaSiO<sub>3</sub> is in disagreement with that of TOMLINSON et al. (1958). The partial molar volume of TiO<sub>2</sub> derived from a linear fit to the Na<sub>2</sub>SiO<sub>3</sub>-TiO<sub>2</sub> join is 27.6(3) cm<sup>3</sup>/mole at 1150°C. The partial molar volume of TiO<sub>2</sub> derived from linear extrapolation of the CaSiO<sub>3</sub>-TiO<sub>2</sub> data to TiO<sub>2</sub> at 1600°C is 24.3(4) cm<sup>3</sup>/mole. Comparison of the partial molar volume data from these binary joins with TiO<sub>2</sub> liquid density data (DINGWELL, 1991) requires the existence of a large positive excess volume in the Na<sub>2</sub>SiO<sub>3</sub>-TiO<sub>2</sub> system at 1150°C.

### INTRODUCTION

TiO<sub>2</sub> IS A MINOR COMPONENT in the chemistry of most lavas. Concentrations up to 2–3 wt% are “averages” for Cenozoic alkali basalts and basanites (CHAYES, 1975) and intermediate members of the potassic series such as wyomingite (GUNTER et al., 1990). Values of up to 9 wt% are reported by FOLEY and WHELLER (1990) for the ultrapotassic lamproites of the West Kimberley area of western Australia. Recently, MITCHELL (1991) has demonstrated the presence of up to 11 wt% TiO<sub>2</sub> in glass inclusions in leucite from both Wyoming and West Kimberley, confirming that liquids of such unusual compositions exist in nature. In lunar glasses, up to 16 wt% TiO<sub>2</sub> is reported by DELANO (1986).

The structural role of Ti in silicate melts has been the goal of several spectroscopic investigations of silicate glasses (see MYSEN, 1988, for a summary). Evidence of both octahedral and tetrahedral coordination of Ti in “depolymerized” silicate glasses has been presented by HANADA and SOGA (1980). The comparison of liquid properties and phase equilibria with structural investigations based on spectroscopic observations of glass structure can be fraught with difficulties. This is because, at best, the structure of quenched glasses can be approximated to the frozen structure of a liquid at a single (fictive) temperature. Any temperature-dependent changes in structure must be investigated using quench rate as a variable in glass studies (DINGWELL and WEBB, 1990), and this is difficult for many compositions due to their moderate glass-forming ability. The second potential complication is, of course, incipient crystallization stable or metastable, which can produce ordered subdomains that may not necessarily be easily observed using X-ray diffraction. Determination of a range of relaxed liquid properties offers a chance to improve this situation by yielding more property comparisons wholly within the liquid state.

Preliminary work on TiO<sub>2</sub>-bearing melts (JOHNSON and CARMICHAEL, 1987; LANGE and CARMICHAEL, 1987) has indicated a composition-dependence of the partial molar volume of TiO<sub>2</sub> in silicate melts. Thus, in a more general sense, the investigation of physical properties of TiO<sub>2</sub>-bearing melts provides an indication of the type of effects that variable coordination number for any component may have on the behavior of silicate melts. The systems Na<sub>2</sub>SiO<sub>3</sub>-TiO<sub>2</sub> and CaSiO<sub>3</sub>-TiO<sub>2</sub> and the melts of the  $X \frac{n}{2n} \text{TiSiO}_5$  were chosen for this investigation to test for the contrasting roles of alkalis and alkaline earths in the coordination of TiO<sub>2</sub> in silicate melts.

### METHOD

The joins chosen for this investigation of density are (1) the the metasilicate-TiO<sub>2</sub> joins CaSiO<sub>3</sub>-TiO<sub>2</sub> and Na<sub>2</sub>SiO<sub>3</sub>-TiO<sub>2</sub>; and (2) a series of liquids of the general formula  $X \frac{n}{2n} \text{TiSiO}_5$ , where  $X$  represents Li, Na, K, Rb, Cs, Ca, Sr, and Ba. The starting materials for these density determinations were CaCO<sub>3</sub> (99.5%), Na<sub>2</sub>CO<sub>3</sub> (99.9%), Li<sub>2</sub>CO<sub>3</sub> (99%), K<sub>2</sub>CO<sub>3</sub> (99%), Rb<sub>2</sub>CO<sub>3</sub> (99%), Cs<sub>2</sub>CO<sub>3</sub> (99%), SrCO<sub>3</sub> (99%), TiO<sub>2</sub> (99.8%), and SiO<sub>2</sub> (99.95%). The starting oxides and carbonates were dried at 120°C for 24 h prior to weighing. Powder mixtures of the carbonates and oxides were weighed into plastic bottles in batches equivalent to 100 g of decarbonated material. The powders were mixed by agitation for approximately 5 min. The mixed powders were melted stepwise, in 75 cm<sup>3</sup> Pt crucibles in a MoSi<sub>2</sub> box furnace. The Na-bearing batches were melted at 1150°C to minimize Na volatilization in these fluid melts, and the other alkali-bearing batches were melted at 1050°C. The Ca-bearing and the Li-bearing batches were melted directly at 1600–1650°C. Each melt was poured from the Pt crucible onto a stainless steel plate for cooling. The Na-bearing liquids cooled to transparent colorless glasses, whereas the Ca-bearing liquids cooled to partly crystalline samples. Subsequent X-ray diffraction investigation of the Na-bearing “glasses” revealed a broad peak indicating poorly crystalline or fine-grained Na<sub>2</sub>TiSiO<sub>5</sub> crystals. Subsequent drop quenches of the Na<sub>2</sub>TiSiO<sub>5</sub> liquid into water yielded glasses with identical X-ray diffraction results. Due to this cryptocrystallinity, no investigations of supercooled liquid density

TABLE 1a. Glass analyses by electron microprobe\*

sample	XO/X <sub>2</sub> O	TiO <sub>2</sub>	SiO <sub>2</sub>	total
NTS1	46.06 ‡ (.14)	8.20 (.17)	45.74 (.55)	91.89 †
NTS2	42.54 (.10)	15.54 (.15)	41.93 (.37)	96.17 †
NTS3	39.37 (.20)	23.13 (.12)	37.50 (.16)	97.46 †
NTS4	33.98 (.16)	32.29 (.11)	33.73 (.12)	98.13
NTS5	29.33 (.10)	40.88 (.13)	29.78 (.14)	97.83
CTS1	45.36 (.21)	7.70 (.15)	46.94 (.22)	98.20
CTS2	40.98 (.15)	16.50 (.42)	42.52 (.35)	98.37
CTS3	37.60 (.30)	22.80 (.14)	39.61 (.26)	98.49
CTS4	33.82 (.17)	30.76 (.42)	35.38 (.35)	98.57
CTS5	28.98 (.13)	40.38 (.15)	30.66 (.20)	98.62
CTS6	24.24 (.09)	50.12 (.20)	25.65 (.12)	99.43
STS5	43.08 (.43)	32.64 (.20)	24.66 (.40)	100.38
BTS5	48.48 (.39)	27.46 (.45)	22.54 (.32)	98.48

\* Microprobe analyses obtained using wavelength dispersive analysis on a Cameca SX 50 instrument. Operating conditions: 15 kV accelerating voltage, 15 nA current on brass, 10 × 10 micron spot, and 20 sec counting times. Standards are albite (Na), wollastonite (Ca, Si), MnTiO<sub>3</sub> (Ti), and synthetic glasses BFS1 (Ba) and SFS1 (Sr).

† Low total due to H<sub>2</sub>O absorption. Analyses are averages of 10 spots, normalized to 100%.

‡ Numbers in brackets are 1σ of multiple analyses. Data are plotted in Fig. 1.

were attempted; and all the data presented here were obtained at superliquidus temperatures.

After the density experiments, the chemical compositions of glassy fragments of the quenched samples were determined using the electron microprobe. After density measurements, a number of the samples that were unanalyzable by microprobe (i.e., could not be quenched to glasses or were too hygroscopic) were analysed instead by solution-based ICP-AES methods. The results (Table 1) confirm the stoichiometric compositions of all the melts. The analysis conditions are listed in Tables 1a and b.

The densities of the experimental liquids were measured using the double Pt bob Archimedean method. The samples were loaded into a viscometry crucible in a vertical tube MoSi<sub>2</sub> furnace. The apparatus used for the measurement of density is that described by DINGWELL et al. (1988). This apparatus has been improved with the addition of a computer interface to the balance, and the data gathering and storage is performed by a computer. The computer interface allows time averaging of the buoyancy readings obtained from the balance resulting in an increased resolution in buoyancy. Differences in buoyancy near the noise level of individual readings can be better distinguished.

## RESULTS AND DISCUSSION

The density data are presented in Table 2a and b. The densities of liquids increase with increasing TiO<sub>2</sub> content in both the Na<sub>2</sub>SiO<sub>3</sub>-TiO<sub>2</sub> and CaSiO<sub>3</sub>-TiO<sub>2</sub> systems. The Na<sub>2</sub>SiO<sub>3</sub>-TiO<sub>2</sub> data can be extrapolated to Na<sub>2</sub>SiO<sub>3</sub> to yield good agreement with the data of BOCKRIS et al. (1955) extrapolated down from higher temperature. MORINAGA et al. (1974) have investigated the densities of Ca-Ti-Si-O liquids using the counterbalanced sphere method. Their data indicate a positive volume of mixing on the CaSiO<sub>3</sub>-TiO<sub>2</sub> join but are lower (1%) than those presented here. The discrepancy may be related to the assumption of a value for the surface force correction made by MORINAGA et al. (1974).

The density data of Table 2 have been converted into molar volumes based on the metasilicate and TiO<sub>2</sub> components. The variation of molar volume with composition along the Na<sub>2</sub>SiO<sub>3</sub>-TiO<sub>2</sub> and CaSiO<sub>3</sub>-TiO<sub>2</sub> joins is illustrated in Fig. 1. The fitted values of the partial molar volume of TiO<sub>2</sub> derived from linear fits to the volume composition data are included in Fig. 1. Note that, despite the much lower temperatures of measurement, the Na-bearing melts record a much larger partial molar volume of TiO<sub>2</sub>.

The expansivities of the Na<sub>2</sub>SiO<sub>3</sub>-TiO<sub>2</sub> liquids increase with TiO<sub>2</sub> content from 0.000280(9) g/cm<sup>3</sup> K for NTS1 to 0.00053(2) g/cm<sup>3</sup> K for NTS5 (see Table 3). In contrast, the expansivities on the CaSiO<sub>3</sub>-TiO<sub>2</sub> join remain roughly constant (0.00026–0.00034 g/cm<sup>3</sup> K) from CTS1 to CTS8 (see Table 3). The density of liquid TiO<sub>2</sub> has been determined at 1875–1925°C using a Ir-based double bob Archimedean

TABLE 1b. Glass analyses by ICP-AES\*

	XO/X <sub>2</sub> O	TiO <sub>2</sub>	SiO <sub>2</sub>	total
LTSS	17.1 †	47.0(1)	35.9(4)	100.0
NTSS	30.5(5)	39.6(1)	29.2(1)	99.3
KTSS	39.9(1)	34.9(2)	24.8(3)	99.6
RTSS	57(2)	24.7(4)	18.0(1)	99.7
CsTSS	67(4)	19.6(7)	14.4(2)	101.0

\* Analyses by inductively coupled atomic emission spectroscopy using an HBF<sub>4</sub>/HF dissolution of glasses and mixed "single element" standard solutions. Performed on a sequential JY 24 spectrometer from Instruments S.A. Numbers in brackets represent 1σ.

† By difference.

TABLE 2a. Liquid density data\*

Temp. (°C)	density (g/cm <sup>3</sup> )							
	CTS1	CTS2	CTS3	CTS4	CTS5	CTS6	CTS7	CTS8
1600	2.7012	2.7293	2.7577	2.7903	2.8491	2.9322	3.0269	3.1217
1575	-	-	-	-	-	-	3.0322	-
1550	2.7138	2.7454	2.7704	2.8041	2.8639	2.9514	3.0409	-
1525	-	-	-	-	-	-	3.0448	-
1500	2.7277	2.7586	2.7880	2.8274	2.8847	2.9583	-	-
1450	-	-	-	2.8382	2.8981	2.9767	-	-
1400	-	-	-	2.8549	2.9083	3.0011	-	-
		NTS1	NTS2	NTS3	NTS4	NTS5		
1150		2.2634	2.3017	2.3543	2.4025	2.4432		
1100		-	2.3198	2.3729	2.4211	2.4706		
1050		2.2940	2.3330	2.3956	2.4410	2.4934		
1000		2.3083	2.3472	-	2.4664	2.5243		

TABLE 2b. Liquid density data\*

Temp. (°C)	density (g/cm <sup>3</sup> )							
	CTS5	STSS	BTS5	LTS5	NTS5	KTS5	RTS5	CsTS5
1600	2.8491	3.3580	3.7302	2.3893	-	-	-	-
1550	2.8693	3.7343	3.7440	2.4057	-	-	-	-
1500	2.8847	3.3984	3.7598	2.4189	-	-	-	-
1100	-	-	-	-	2.4706	2.3517	-	-
1050	-	-	-	-	2.4934	2.3678	2.9994	3.4863
1000	-	-	-	-	2.5243	2.3853	3.0108	3.4974

\* Precision in density is  $\pm 0.2\%$  at  $1\sigma$ .

method (DINGWELL, 1991). The results of those measurements have been compared with the linear compositional extrapolation of molar volume to TiO<sub>2</sub> (at 1600°C) using the CaSiO<sub>3</sub>-TiO<sub>2</sub> data of Fig. 1. The expansivity resulting from a fit to the density values of DINGWELL (1991) and the

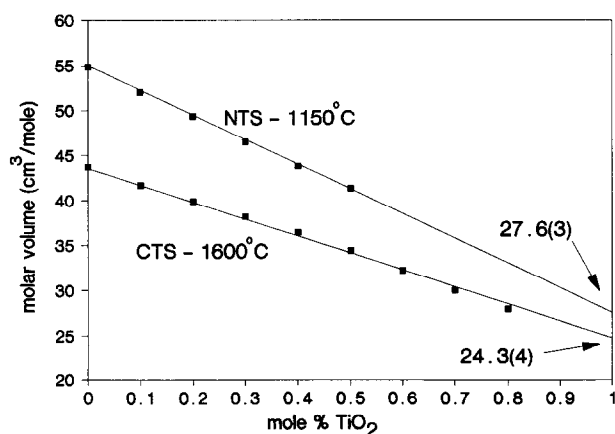


FIG. 1. Density-composition relationships in the Na<sub>2</sub>SiO<sub>3</sub>-TiO<sub>2</sub> and CaSiO<sub>3</sub>-TiO<sub>2</sub> systems.

extrapolation of this study is  $0.00028(1) \text{ g/cm}^3 \text{ K}$ . This value compares favorably with the expansivities of the CaSiO<sub>3</sub>-TiO<sub>2</sub> liquids of  $0.00026\text{--}0.00034 \text{ g/cm}^3 \text{ K}$ . LANGE and CARMICHAEL (1987) measured the density of two CaO-TiO<sub>2</sub>-SiO<sub>2</sub> and two Na<sub>2</sub>O-TiO<sub>2</sub>-SiO<sub>2</sub> melts. Table 5 in LANGE and CARMICHAEL (1987) can be used to estimate the densities of the compositions in this study. Those parameters predict a density ( $2.9014 \text{ g/cm}^3$ ) for CTS5 at 1500°C, which agrees well (0.6% high) with the measured value of this study. For NTS5, the comparison at 1500°C involves a 350°C extrapolation; and the agreement is less good with the predicted value several percent higher than measured in this study.

Do the higher expansivities of the NTS liquids reflect a temperature-dependent shift of the coordination number of Ti in these liquids? The probable temperature-dependence of liquid expansivity for these melts (WEBB et al., 1992; KNOCHÉ et al., 1992) precludes further speculation using the expansivity data available here. The densities, however, of an extensive range of Na<sub>2</sub>O-TiO<sub>2</sub>-SiO<sub>2</sub> glasses have been measured at room temperature by HAMILTON and CLEEK (1958). Thus, we can compare the partial molar volume of TiO<sub>2</sub> in liquids just above the glass transition temperature with our higher temperature liquids to estimate the temperature-dependence of the partial molar volume of TiO<sub>2</sub> over

TABLE 3. Density-temperature data\*

sample	intercept density	expansivity (g/cm <sup>3</sup> K)
NTS0 <sup>†</sup>		.00028(.000009)
NTS1	2.60887(.00534)	.00030(.000004)
NTS2	2.64728(.00166)	.00029(.000014)
NTS3	2.82856(.00167)	.00041(.000023)
NTS4	2.88769(.00249)	.00042(.000022)
NTS5	3.05499(.00235)	.00053(.000021)
CTS1	3.12498(.00053)	.00026(.000007)
CTS2	3.19858(.00118)	.00029(.000016)
CTS3	3.24173(.00200)	.00030(.000028)
CTS4	3.31220(.00160)	.00032(.000010)
CTS5	3.33862(.00516)	.00030(.000020)
CTS6	3.48720(.00144)	.00034(.000009)
CTS7	3.47490( - )	.00028( - )

\* Numbers in brackets are standard errors of the fit to density vs. temperature.

<sup>†</sup> Data from BOCKRIS et al. (1955).

a large temperature range. To do this, we need the glass densities available from HAMILTON and CLEEK (1958), the glassy thermal expansivities (available from HIRAYAMA and BERG, 1961), and the glass transition temperatures (available from TAKAHASHI et al., 1977). The glass transition temperatures are relatively constant from 10–40% TiO<sub>2</sub> for compositions similar to ours, lying between 500 and 525°C (TAKAHASHI et al., 1977). The glass densities of HAMILTON and CLEEK (1958), corrected to 525°C using the glass expansivity data of HIRAYAMA and BERG (1961), represent the densities of relaxed liquids at this temperature. They may be compared

with the density of TiO<sub>2</sub> liquid from the equation for its temperature-dependence given by DINGWELL (1991). That relationship (extrapolated from 1600°C) yields a density of 3.61 g/cm<sup>3</sup> at 525°C. The compositional extrapolation of density from the 525°C Na<sub>2</sub>O-TiO<sub>2</sub>-SiO<sub>2</sub> liquids yields 3.280 g/cm<sup>3</sup>. This indicates that a significant excess volume exists in the Na<sub>2</sub>SiO<sub>3</sub>-TiO<sub>2</sub> system at 525°C and is in agreement with the measurements of this study at 1000°C. A large positive volume of mixing is required to reconcile the Na<sub>2</sub>SiO<sub>3</sub>-TiO<sub>2</sub> density data with the CaSiO<sub>3</sub>-TiO<sub>2</sub> data of this study and the liquid TiO<sub>2</sub> data of DINGWELL (1991) at all temperatures.

Comparison of the liquid densities at 525 and 1000°C for Na<sub>2</sub>TiSiO<sub>5</sub> composition indicate a 15% volume change over 475°C. This corresponds to a mean expansivity of 0.00075 gm/cm<sup>3</sup> K. Comparison with the measured value of 0.00053(2) gm/cm<sup>3</sup> K at 1000°C indicates a negative temperature dependence of expansivity for this composition. A first derivative of expansivity large enough to account for such behavior has, for example, recently been measured for diopside liquid (KNOCHE et al., 1992). Less data are available for Ba and K titanium silicate glasses, but similar temperature-dependent expansivities appear to be required.

The densities of the "sphene" stoichiometry liquids are included in Table 2b. The apparent partial molar volume of TiO<sub>2</sub> in each of these liquids can be obtained from literature data on the corresponding TiO<sub>2</sub>-free metasilicate melt densities. These data, obtained from BOCKRIS et al. (1955) for Li<sub>2</sub>SiO<sub>3</sub>, Na<sub>2</sub>SiO<sub>3</sub>, and K<sub>2</sub>SiO<sub>3</sub>; obtained from TOMLINSON et al. (1958) for CaSiO<sub>3</sub>; and extrapolated from the results of SASEK and LISY (1972) for Rb<sub>2</sub>SiO<sub>3</sub> and Cs<sub>2</sub>SiO<sub>3</sub> were used to generate apparent partial molar volumes of TiO<sub>2</sub> for the sphene liquids. As a check on the extrapolation of the

TABLE 4. Partial molar volume of TiO<sub>2</sub>

X	(X <sup>n+</sup> <sub>2/n</sub> SiTiO <sub>5</sub> )		(X <sup>n+</sup> <sub>2/n</sub> SiO <sub>3</sub> )		V(TiO <sub>2</sub> )
	ρ	V <sub>m</sub>	ρ	V <sub>m</sub>	
1000°C					
Cs	3.4974 <sup>†</sup>	60.30	3.6078	94.77	25.8(5) <sup>‡</sup>
Rb	3.0108	54.29	3.0497	81.00	27.6(5)
K	2.3853	49.09	2.2154	69.64	31.3(5)
Na	2.5243	40.00	2.3042	52.97	29.1(5)
1600°C					
Li	2.3893	35.55	2.034	44.23	26.9(5)
Ba	3.7302	39.32	3.9200	54.45	24.2(5)
Sr	3.3580	36.28	3.3872	48.33	24.2(5)
Ca	2.8491	34.41	2.6392	44.02	24.8(5)

\* All densities in g/cm<sup>3</sup>. Data from BOCKRIS et al. (1955), SASEK and LISY (1972), TOMLINSON et al. (1958), and this study.

\*\* Molar volumes in cm<sup>3</sup>/mole.

Rb and Cs silicate densities, the density of Cs<sub>2</sub>SiO<sub>3</sub> was determined in this study to be 3.6078 g/cm<sup>3</sup> at 1000°C. This density yields a partial molar volume of Cs<sub>2</sub>O in excellent agreement with that derived by RIVERS and CARMICHAEL (1987) from the data of SASEK and LISY (1972). The apparent partial molar volumes of TiO<sub>2</sub> in the sphene liquids are presented in Table 4. The alkali titanium silicates indicate a partial molar volume of TiO<sub>2</sub> that depends strongly on the identity of the alkali. The partial molar volume in the Li silicate melt is similar to that observed for the alkaline earth silicate melts. With increasing alkali size, the partial molar volume rises to a value of 28.5(5) cm<sup>3</sup>/mole for the potassium silicate liquid. With further increase in the alkali size, the apparent partial molar volume of TiO<sub>2</sub> drops back to a lower value of 27.0(5) cm<sup>3</sup>/mole in the Cs silicate liquid.

### CONCLUSION

Titanium-bearing silicate melts exhibit volumes of mixing which vary strongly with composition and with temperature. The composition-dependence of the partial molar volume implies that K-bearing melts stabilize the greatest proportion of low coordination number Ti. Comparison with liquid TiO<sub>2</sub> density indicates that the highly coordinated component of TiO<sub>2</sub> exists in pure TiO<sub>2</sub> liquid, and the addition of other components is necessary to reduce this coordination number.

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### REFERENCES

- BOCKRIS J. O'M., TOMLINSON J. W., and WHITE J. L. (1955) The structure of the liquid silicates: Partial molar volumes and expansivities. *Trans. Faraday Soc.* **52**, 299–310.
- CHAYES F. (1975) Statistical Petrology. *Carnegie Inst. Wash. Yearb.* **74**, 542–550.
- DELANO J. W. (1986) Abundances of cobalt, nickel, and volatiles in the silicate portion of the Moon. In *Origin of the Moon* (ed. W. K. HARTMANN, R. J. PHILLIPS, and G. J. TAYLOR), pp. 231–247. Lunar and Planetary Institute.
- DINGWELL D. B. (1991) The density of liquid TiO<sub>2</sub>. *J. Amer. Ceram. Soc.* **74**, 2718–2719.
- DINGWELL D. B. and WEBB S. L. (1990) Relaxation in silicate melts. *Europ. J. Mineral.* **2**, 427–449.
- DINGWELL D. B., BREARLEY M., and DICKINSON J. E., JR. (1988) Melt densities in the Na<sub>2</sub>O-FeO-Fe<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> system and the partial molar volume of tetrahedrally coordinated ferric iron in silicate melts. *Geochim. Cosmochim. Acta* **52**, 2467–2475.
- FOLEY S. F. and WHELLER G. E. (1990) Parallels in the origin of the geochemical signatures of island arc volcanics and continental potassic igneous rocks: The role of residual titanates. *Chem. Geol.* **85**, 1–18.
- GUNTER W. D., HOINKES G., OGDEN P., and PAJARI P. E. (1990) Origin of leucite-rich and sanidine-rich flow layers in the Leucite Hills Volcanic Field, Wyoming. *J. Geophys. Res.* **95**, 15,911–15,928.
- HAMILTON E. H. and CLEEK G. W. (1958) Properties of sodium titanium silicate glasses. *J. Res. NBS* **61**, 89–94.
- HANADA T. and SOGA N. (1980) Coordination of titanium in sodium titanium silicate glasses. *J. Non-Cryst. Solids* **38/39**, 105–110.
- HIRAYAMA CH. and BERG D. (1961) *Phys. Chem. Glass* **2**, 145–151.
- JOHNSON T. M. and CARMICHAEL I. S. E. (1987) The partial molar volume of TiO<sub>2</sub> in molten silicates. *GSA Abstr. Prog.*, 719.
- KNOCHER R., DINGWELL D. B., and WEBB S. L. (1992) Temperature-dependent thermal expansivities of silicate melts: The system anorthite-diopside. *Geochim. Cosmochim. Acta* **56**, 689–698.
- LANGE R. A. and CARMICHAEL I. S. E. (1987) Densities of Na<sub>2</sub>O-K<sub>2</sub>O-CaO-MgO-FeO-Fe<sub>2</sub>O<sub>3</sub>-Al<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub>-SiO<sub>2</sub> liquids: New measurements and derived partial molar properties. *Geochim. Cosmochim. Acta* **51**, 2931–2946.
- LANGE R. A. and CARMICHAEL I. S. E. (1990) Thermodynamic properties of silicate liquids with emphasis on density, thermal expansion, and compressibility. In *Modern Methods of Igneous Petrology* (ed. J. NICHOLLS and J. K. RUSSELL), pp. 25–64. MSA.
- MITCHELL R. H. (1991) Coexisting glasses occurring as inclusions in leucite from lamproites: Examples of silicate liquid immiscibility in ultrapotassic magmas. *Mineral. Mag.* **55**, 197–202.
- MORINAGA K., ITO T., SUGINOHARA Y., and YANAGASE T. (1974) Density of the molten CaO-SiO<sub>2</sub>-TiO<sub>2</sub>. *J. Japanese Inst. Metall.* **38**, 1065–1070.
- MYSEN B. O. (1988) *Structure and Properties of Silicate Melts*. Elsevier.
- RIVERS M. L. and CARMICHAEL I. S. E. (1987) Ultrasonic studies of silicate melts. *J. Geophys. Res.* **92**, 9247–9270.
- SASEK L. and LISY A. (1972) The structure and properties of silicate melts II. The density of binary alkali-silicate glass melts. *Sb. Vys. Sk. Chem. Techn. Prazske Chem. Techn. Silik.* **L2**, 217–251.
- TAKAHASHI K., MOCHIDA N., and YOSHIDA Y. (1977) Properties and structure of silicate glasses containing tetravalent cations. *J. Ceramic Soc. Japan* **85**, 330–340.
- TOMLINSON J. W., HEYNES M. S. R., and BOCKRIS J. O'M. (1958) The structure of liquid silicates: Part 2—molar volumes and expansivities. *Trans. Faraday Soc.* **54**, 1822–1833.
- WEBB S. L., KNOCHER R., and DINGWELL D. B. (1992) Determination of silicate liquid thermal expansivity using dilatometry and calorimetry. *Europ. J. Mineral.* **4**, 95–104.