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Compressibility of titanosilicate melts

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Abstract The effect of composition on the relaxed adiabatic bulk modulus (K_0) of a range of alkali- and alkaline earth-titanosilicate [$X^{n+}_{2/n}TiSiO_5$ (X = Li, Na, K, Rb, Cs, Ca, Sr, Ba)] melts has been investigated. The relaxed bulk moduli of these melts have been measured using ultrasonic interferometric methods at frequencies of 3, 5 and 7 MHz in the temperature range of 950 to 1600° C ($0.02 \text{ Pa s} < \eta_s < 5 \text{ Pa s}$). The bulk moduli of these melts decrease with increasing cation size from Li to Cs and Ca to Ba, and with increasing temperature. The bulk moduli of the Li-, Na-, Ca- and Ba-bearing metasilicate melts decrease with the addition of both TiO_2 and SiO_2 whereas those of the K-, Rb- and Cs-bearing melts increase. Linear fits to the bulk modulus versus volume fraction of TiO_2 do not converge to a common compressibility of the TiO_2 component, indicating that the structural role of TiO_2 in these melts is dependent on the identity of the cation. This proposition is supported by a number of other property data for these and related melt compositions including heat capacity and density, as well as structural inferences from X-ray absorption spectroscopy (XANES). The compositional dependence of the compressibility of the TiO_2 component in these melts explains the difficulty incurred in previous attempts to incorporate TiO_2 in calculation schemes for melt compressibility. The empirical relationship $K \propto V^{-4/3}$ for isostructural materials has been used to evaluate the compressibility-related structural changes occurring in these melts. The alkali metasilicate and disilicate melts are isostructural, independent of the cation. The addition of Ti to the metasilicate composition (i.e. X_2TiSiO_5), however, results in a series of melts which are not isostructural. The alkaline-earth metasilicate and disilicate compositions are not isostructural, but the addition of Ti to the metasilicate compositions (i.e. $XTiSiO_5$) would appear, on the basis of modulus-volume systematics, to result in the melts becoming isostructural with respect to compressibility.

Introduction

Titanium oxide appears as a component of minor to major element concentration in the chemistry of the vast majority of terrestrial and extraterrestrial magmatic rocks. Of all the major elements occurring in terrestrial lavas, titanium has the distinction of being widely accepted to have a strongly compositionally dependent structural role in silicate melts of synthetic and natural composition; its structural specificity (see review by Mysen 1988; Paris et al. 1993; Dingwell et al. 1994) has measurable consequences for melt properties (Richet and Bottinga 1985; Johnson and Carmichael 1987; Lange and Carmichael 1987; Dingwell 1992a,b; Lange and Navrotsky 1993).

The compressibility of silicate melts is a subject of great importance to the understanding of magma ascent and eruption within the Earth and terrestrial planets. Accordingly several experimental studies of the elastic properties of silicate melts have been carried out over the past decade. The relaxed bulk modulus of silicate melts has been studied for a wide variety of silicate melt compositions, and calculational models have been derived for the estimation of multicomponent melt compressibilities (Rivers and Carmichael 1987; Kress and Carmichael 1991). The TiO_2 component has, however, not yet been integrated into such calculation schemes (see discussion in Kress and Carmichael 1991).

Two aspects of the role of Ti in alkali- and alkaline earth-bearing silicate melts have led to the present study of the compressibility of such melts. A series of melt compositions including those investigated in this

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Table 1 Molar volume at 1000 °C and 1600 °C (after Dingwell, 1992a)

X	X_2TiSiO_5 cm^3 mol^{-1}	X_2SiO_3 cm^3 mol^{-1}	TiO_2 cm^3 mol^{-1}
1000 °C			
Li	66.16	41.89	24.27
Na	80.00	52.97	27.03
K	98.18	69.64	28.54
Rb	108.58	81.69	26.89
Cs	120.61	94.77	25.84
X	$XTiSiO_5$ cm^3 mol^{-1}	$XSiO_3$ cm^3 mol^{-1}	TiO_2 cm^3 mol^{-1}
1600 °C			
Ca	34.41	44.02	24.08
Sr	36.28	48.33	24.23
Ba	39.32	54.45	24.19

study illustrate a strong variation in the partial molar volume of TiO_2 in high temperature melts (Dingwell 1992a). For the alkali-titanosilicate melts, the partial molar volume of TiO_2 derived from a linear fit varies by 15% as a function of the alkali identity. At 1000 °C, with increasing alkali size, the partial molar volume increases from 24.3 cm^3 mol^{-1} (Li) to 27.0 cm^3 mol^{-1} (Na), reaches a maximum of 28.5 cm^3 mol^{-1} for the K-bearing titanosilicate composition, and then decreases to 26.9 cm^3 mol^{-1} (Rb) and 25.8 cm^3 mol^{-1} (Cs) (see Table 1; Dingwell 1992a). This has been interpreted to imply that the K-bearing melt stabilises the greatest proportion of low co-ordination number Ti (possibly tetrahedrally co-ordinated titanium), with there being a larger amount of octahedrally co-ordinated titanium in the Li- and Cs-compositions. Liquid TiO_2 density (extrapolated molar volume of TiO_2 is 23.0 cm^3 mol^{-1} at 1000 °C and 24.1 cm^3 mol^{-1} at 1600 °C; Dingwell 1991) indicates that it is in a high co-ordination state, with the addition of other components reducing the co-ordination. The partial molar volume of TiO_2 calculated from the alkaline earth-silicate and -titanosilicate melts is 24.2 cm^3 mol^{-1} at 1600 °C, independent of cation for Ca-, Sr- and Ba-titanosilicate melts (see Table 1). The low partial molar volume of TiO_2 in these melts has been taken to imply that the Ti is mainly in octahedral co-ordination.

Recent investigations of the structural role of Ti in the presently investigated melt compositions using X-ray absorption spectroscopy indicates a variation in specific features of the Ti-Kα absorption edge that are consistent with a varying average co-ordination number of Ti in these melts (Paris et al. 1993; Dingwell et al. 1994). Such a co-ordination shift for Ti would explain the difficulty encountered in incorporating this component into multicomponent models for melt compressibility (Kress and Carmichael 1991).

We have determined the relaxed bulk modulus K_0 of a range of alkali- and alkaline earth-titanosilicate $X^{n+}_{2/n}TiSiO_5$ (X = Li, Na, K, Rb, Cs, Ca, Sr and Ba) melts as well as a range of alkali- and alkaline earth -metasilicate and -disilicate melts [$X^{n+}_{2/n}SiO_3$ (X = Rb, Cs, Ba; with Li, Na, K and Ca data from the literature) and $X^{n+}_{2/n}Si_2O_5$ (X = Ba; with Li, Na, K, Rb, Cs, Ca, Sr and Ba data from the literature)]. These melts have very low viscosities (e.g. 0.02–5 Pa s; see Dingwell 1992b) in the temperature range 900–1600 °C, such that the relaxed bulk moduli of the melts can be determined using ultrasonic techniques in the 3–7 MHz range. For these frequencies and viscosities, the period of the sinusoidal acoustic wave is always at least 2 orders of magnitude more than the structural relaxation time of the melt and therefore the relaxed velocity of a compressional wave propagating through the melt is measured (Webb and Dingwell 1990; Webb 1991). As we are in the relaxed regime for each melt composition, the shear modulus (G) is zero and hence the shear wave contribution to the measured compressional wave velocity is also zero and the relaxed longitudinal modulus (M) is equal to the relaxed bulk modulus of the melt as:

$$M = K + 4/3\,G. \tag{1}$$

The presence of Ti in alkali-titanosilicates results in anomalous negative temperature dependence of heat capacity in the 400 °C above the glass transition temperature (Richet and Bottinga 1985) and a doubling of the Δc_p at the glass transition (Lange and Navrotsky 1993). The large step in heat capacity at T_g reflects the significant configurational rearrangements in the melt which do not occur in Ti-free melts. The decrease in heat capacity with temperature indicates that these configurational changes cease at higher temperatures. In view of the anomalous heat capacity and composition dependent partial molar volume of TiO_2 observed in titanosilicate melts, it is expected that the co-ordination state of titanium will affect the physical properties (e.g. density, thermal expansion, heat capacity, compressibility) of titanium-bearing melts in a non-linear manner as a function of both temperature and composition.

Experimental technique

The starting materials for these glasses were powders of Na_2CO_3 (99.9%), Li_2CO_3 (99%), K_2CO_3 (99%), Rb_2CO_3 (99%), Cs_2CO_3 (99%), $BaCO_3$ (99%), $SrCO_3$ (99%), $CaCO_3$ (99%), TiO_2 (99.8%) and SiO_2 (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 decarbonated material. The powders were mixed by agitation for approximately 5 min. The mixed powders were melted stepwise, in 75 cm^3 Pt crucibles in a $MoSi_2$ box furnace. The Na-, K-, Rb- and Cs-bearing batches were melted at or below 1150 °C to minimise alkali volatilisation in these fluid melts. The Li-, Ca-, Sr- and Ba-bearing batches were melted at 1600 °C. Each melt was poured

Table 2 Composition of melts (mol%) determined by ICP-AES .

	$X^{n+}_{2/n}O$	SiO_2	TiO_2
Li_2TiSiO_5	29.94	36.46	33.60
Na_2TiSiO_5	30.17	36.19	33.63
K_2TiSiO_5	26.78	35.87	37.36
Rb_2TiSiO_5	31.78	34.12	34.10
Cs_2TiSiO_5	31.24	33.95	34.81
NTS1	42.78	50.31	6.91
$CaTiSiO_5$	32.66	34.16	33.18
$SrTiSiO_5$	34.94	31.84	33.22
$BaTiSiO_5$	33.30	33.20	33.50
Rb_2SiO_3	49.43	50.57	
Cs_2SiO_3	50.43	49.57	
$BaSi_2O_5$	32.90	67.06	
$SrSiO_3$	50.60	49.40	
$BaSiO_3$	49.79	50.21	

from the Pt crucible into a cylindrical stainless-steel form, such that the resulting 50 g glass patty fitted into the Mo crucible used for the ultrasonic measurements. The Li-, Ca-, Sr- and Ba-bearing titanosilicate melts crystallised to a glass-crystal ceramic upon quenching. The other liquids cooled to transparent glasses. The composition of the samples was determined using ICP-AES (inductively coupled plasma – atomic emission spectroscopy) methods (see Table 2).

The velocity of longitudinal waves propagating through these melts was determined at ultrasonic frequencies using a furnace and twin buffer-rod apparatus similar to that of Macedo and Litovitz (1965) (see Webb 1991). The furnace is a molybdenum wound tube furnace. The buffer-rods are polycrystalline molybdenum, 310 mm long and 12 mm in diameter. There is a constant flow of forming gas ($95\%N_2$–$5\%H_2$) across the furnace elements and the molybdenum crucible and buffer-rods. Chrome-gold coaxially-plated ZMHZ quartz X-cut compressional wave transducers were used at frequencies of ~ 3, ~ 5 and ~ 7 MHz. The cylindrical surfaces of both buffer-rods and crucible, have 0.5 mm deep grooves in order to reduce the side-wall reflections of the ultrasonic waves. The transducers are glued to both buffer-rods using Crystal Bond®. This apparatus can be used in both the reflection and transmission mode (see Webb 1991). The present measurements are performed in the reflection mode; with the transducer on the lower buffer rod acting as both sender and receiver. The interferometric technique of Katahara et al. (1981) was used. The buffer-rods were aligned at room-temperature at 3, 5 and 7 MHz in acetone using the compressional wave signal. Pulsed sinusoidal signals of 80 μs duration were propagated through the melt and the change in amplitude of the returned signal (the sum of a semi-infinite number of echoes within the melt) was monitored as the upper buffer-rod was moved. The amplitude of the reflected signal is;

$$|A_r|^2 = \frac{R^2[\exp(4\alpha L) - 2\exp(2\alpha L)\cos(4\pi Lf/c) + 1]}{\exp(4\alpha L) - 2R^2\exp(2\alpha L)\cos(4\pi Lfc) + R^4} \qquad (2)$$

(Rivers 1985) where α is the attenuation coefficient, L the melt thickness, c the wave velocity and R is the reflection coefficient at the buffer rod-melt interface; where

$$R = \frac{\rho_{melt}c_{melt} - \rho_{Mo}c_{Mo}}{\rho_{melt}c_{melt} + \rho_{Mo}c_{Mo}} \qquad (3)$$

for ρ and c the density and wave velocity for the melt and molybdenum. The density of the molybdenum buffer-rods was taken to be $10.213\ g\ cm^{-3}$ (Bujard 1982) and the high temperature velocities of compressional waves travelling through polycrystalline molybdenum were taken from Bujard (1982).

The alkali-titanosilicate melts were investigated at temperatures such that the viscosity was greater than 0.1 Pa s (and less than 5 Pa s, see Table 3); except for the Li-bearing melt which was investigated over a viscosity range of 0.05 to 0.02 Pa s. The alkaline earth-titanosilicate melts were investigated at high temperatures (up to 1600 °C) at viscosities 0.05–0.3 Pa s (see Table 4). The lower temperature limit was the crystallisation of the melt. For the Cs_2TiSiO_5 composition, the melt did not crystallise until the viscosity increased to 6 Pa s. Therefore it was possible to measure the longitudinal velocity in the unrelaxed range (see Table 3). Figure 1 illustrates the increase in velocity due to the contribution of the unrelaxed shear and longitudinal waves when the period of the applied sinusoid is within 2 orders of magnitude of the structural relaxation time of the melt.

In view of the discrepancy in the densities of Rb- and Cs-silicate melts observed by Šašek and Lisý (1972a,b), Rivers and Carmichael (1987) and Dingwell (1992a), the densities of Rb_2SiO_3 and Cs_2SiO_3 were measured by the double-bob Archimedes method (Dingwell and Brearley 1988) (see Table 3). The densities agree with that of Dingwell (1992a) for Cs_2SiO_3 and are in agreement with that calculated from Fig. 8 of Rivers and Carmichael (1987). The present densities for the Rb- and Cs-metasilicates and the densities for the disilicates of Rivers and Carmichael were used in the calculation of the bulk moduli of the respective melts.

Results and Discussion

The relaxed bulk moduli of the alkali-titanosilicate melts are presented in Fig. 2 and Table 3, together with the Rb- and Cs-metasilicate melts. The relaxed bulk moduli of the alkaline earth-titanosilicate melts are presented in Fig. 3 and Table 4, together with the Ba-metasilicate and disilicate melts. The magnitude of the bulk modulus decreases with increasing cation size and with temperature. Within the temperature range of the measurements a straight line can be fitted to the bulk moduli as a function of temperature. The temperature dependence of the bulk moduli ranges from $-1\ MPa\ °C^{-1}$ for the Na-titanosilicate to $-8\ MPa\ °C^{-1}$ for the Sr-titanosilicate melt (see Tables 5 and 6). This is within the previously observed range of the temperature dependences of the relaxed bulk moduli of silicate melts (Baidov and Kunin 1968; Manghnani et al. 1981; Rivers and Carmichael 1987). There appears to be no anomalous behavior of the bulk moduli of these titanosilicate melts as a function of temperature. Thus we have no indication of large changes in structure occurring at these high temperatures and low viscosities, in contrast to the large structural changes assumed to be seen in the low temperature (high viscosity) calorimetry measurements of Richet and Bottinga (1985) and Lange and Navrotsky (1993) on alkali-titanosilicate melt compositions. Richet and Bottinga (1985) and Lange and Navrotsky (1993) pointed out that at temperatures some 400 °C above the glass transition temperature (T_g) the heat capacity of their titanosilicate melts was no longer anomalously temperature dependent, and they assumed that all of

Table 3 Relaxed longitudinal velocity, c, and relaxed bulk modulus, K, as a function of temperature, T, together with the shear viscosity, η, and density, ρ, of the alkali-titanosilicate and alkali-silicate melts and frequency, f, of the ultrasonic signal.

T °C	η^a $\log_{10}$ Pa s	ρ^b g cm^{-3}	f MHz	c m s^{-1}	K GPa	c m s^{-1}	K GPa
Li_2TiSiO_5							
1375	−1.272	2.4360	2.920	2420.2	14.27	2439.8 ± 18.3	14.50 ± 0.22
			5.010	2443.1	14.54		
			5.010	2432.4	15.41		
			6.830	2463.4	14.78		
1450	−1.384	2.4138	2.920	2400.2	13.91	2404.0 ± 20.0	13.95 ± 0.23
			4.995	2392.8	13.82		
			5.115	2389.7	13.78		
			6.830	2433.3	14.29		
1525	−1.487	2.3916	2.915	2382.0	13.57	2380.0 ± 17.4	13.56 ± 0.20
			4.995	2379.8	13.54		
			6.830	2359.4	13.31		
			6.830	2402.0	13.80		
1600	−1.581	2.3694	4.960	2337.3	12.94	2337.3 ± 20.0	12.94 ± 0.21
Na_2TiSiO_5							
1025	−0.536	2.5277	3.040	2272.7	13.06	2273.4 ± 16.9	13.08 ± 0.19
			5.115	2286.6	13.22		
			6.950	2269.4	13.02		
			6.950	2293.4	13.29		
			6.950	2249.8	12.79		
1075	−0.693	2.5008	3.040	2273.6	12.93	2297.4 ± 28.4	13.20 ± 0.33
			5.115	2289.7	13.11		
			6.950	2328.9	13.56		
1150	−0.907	2.4606	3.015	2275.6	12.74	2288.9 ± 16.3	12.89 ± 0.18
			5.100	2284.0	12.84		
			6.950	2307.1	13.10		
K_2TiSiO_5							
950	0.084	2.4270	3.025	2122.6	10.93	2117.9 ± 11.6	10.89 ± 0.12
			3.045	2103.3	10.74		
			5.115	2130.6	11.02		
			6.950	2115.0	10.86		
1050	−0.235	2.3933	3.030	2093.1	10.49	2115.2 ± 25.1	10.71 ± 0.25
			5.105	2094.1	10.50		
			5.105	2140.2	10.96		
			6.950	2133.5	10.89		
1150	−0.510	2.3598	3.025	2091.8	10.33	2092.0 ± 11.1	10.33 ± 0.11
			5.105	2103.2	10.44		
			6.950	2081.0	10.22		
Rb_2TiSiO_5							
875	0.696	3.0393	3.030	1895.2	10.92	1936.0 ± 36.1	11.40 ± 0.42
			4.990	1948.6	11.54		
			6.950	1954.1	11.73		
950	0.338	3.0222	3.010	1877.1	10.65	1875.5 ± 24.7	10.63 ± 0.28
			5.000	1863.4	10.49		
			5.110	1852.2	10.37		
			6.950	1909.3	11.02		
1015	0.062	3.0074	3.005	1805.4	9.80	1852.1 ± 45.1	10.32 ± 0.51
			3.025	1836.0	10.14		
			5.090	1854.6	10.34		
			6.950	1912.5	11.00		
1085	−0.207	2.9914	3.025	1792.8	9.62	1832.5 ± 38.8	10.05 ± 0.43
			5.065	1834.3	10.07		
			6.950	1870.4	10.47		
1150	−0.432	2.9766	3.045	1842.1	10.10	1858.5 ± 14.3	10.28 ± 0.16
			5.105	1864.8	10.35		
			6.950	1868.6	10.40		
Cs_2TiSiO_5							
875	0.794	3.5252	3.010	1742.4^c	10.70^c	–	–
			5.115	1884.8^c	12.52^c		
			6.950	1926.7^c	13.09^c		
950	0.440	3.5085	3.010	1656.3	9.63	1655.8 ± 7.8	9.62 ± 0.09
			5.115	1657.5	9.64		
			5.115	1645.3	9.50		
			6.950	1664.2	9.72		

Table 3 (continued)

T °C	η^a $\log_{10}$ Pa s	ρ^b g cm^{-3}	f MHz	c m s^{-1}	K GPa	c m s^{-1}	K GPa
1015	0.166	3.4941	3.010	1606.4	9.02	1605.0 ± 5.9	9.00 ± 0.07
			5.115	1598.5	8.93		
			6.950	1610.0	9.06		
1085	− 0.099	3.4785	3.010	1568.9	8.56	1566.7 ± 2.0	8.54 ± 0.02
			5.115	1566.3	8.53		
			6.950	1565.0	8.52		
1150	− 0.322	3.4641	3.010	1535.0	8.16	1535.0 ± 2.7	8.16 ± 0.03
			3.010	1537.9	8.19		
			5.115	1535.5	8.16		
			5.115	1536.1	8.17		
			6.950	1530.5	8.11		
Rb_2SiO_3							
950	–	3.0541	3.010	1860.8	10.51	1905.1 ± 41.2	11.09 ± 0.61
			5.115	1912.4	11.17		
			6.900	1942.1	11.52		
1000	–	3.0240	3.010	1820.4	10.02	1847.0 ± 23.3	10.32 ± 0.34
			5.115	1856.8	10.43		
			6.900	1863.9	10.51		
1050	–	2.9940	3.010	1791.2	9.61	1802.8 ± 16.5	9.72 ± 0.33
			5.115	1793.4	9.63		
			6.900	1820.8	9.93		
Cs_2SiO_3							
900	–	3.6800	3.015	1517.7	8.48	1510.3 ± 13.0	8.40 ± 0.27
			3.015	1505.5	8.34		
			5.115	1523.6	8.54		
			5.115	1494.3	8.22		
1000	–	3.6078	3.015	1447.0	7.55	1448.2 ± 2.0	7.57 ± 0.21
			5.115	1450.5	7.59		
			6.910	1447.1	7.56		
NTS1							
1100	− 0.165	2.3211	2.995	2744.5	17.48	2474.7 ± 14.8	17.52 ± 0.19
			4.940	2725.8	17.25		
			5.015	2745.3	14.49		
			5.015	2763.4	17.72		
			6.885	2759.4	17.67		
1200	− 0.467	2.2910	3.040	2701.11	6.72	2689.5 ± 24.5	16.58 ± 0.30
			5.045	2718.5	16.93		
			5.045	2667.9	16.31		
			6.885	2670.6	16.34		
1300	− 0.731	2.2610	3.040	2642.8	15.79	2644.5 ± 11.3	15.81 ± 0.14
			5.045	2660.9	16.01		
			5.045	2638.6	15.74		
			6.885	2635.6	15.71		

[a] Dingwell (1992b)

[b] Dingwell (1992a)

[c] Non-relaxed velocities and moduli

[d] The metasilicate densities were measured at 1000 °C and combined with the data of Rivers and Carmichael (Fig. 8). The resulting densities were extrapolated in temperature assuming $d\rho/dT = 6 \times 10^{-4}$ g cm^{-3} °C^{-1}

the configurational changes take place in the temperature interval within 400 °C above T_g. Based on the T_g data of Lange and Navrotsky (1993), the present compressibility measurements are performed at temperatures more than 500 °C above the respective T_gs of the titanosilicate melts. Therefore the present observation of no anomalous temperature dependence of the compressibility is not inconsistent with the normal temperature dependence of heat capacity observed by Richet and Bottinga (1985) and Lange and Navrotsky (1993) at temperatures more than 400 °C above the melt T_g.

Isostructural Melts

In order to investigate the structural changes occurring in these melts as a function of composition, the bulk modulus has been plotted as a function of the molar

Table 4 Relaxed longitudinal velocity, *c*, and relaxed bulk modulus, *K*, as a function of temperature, *T*, together with the shear viscosity, η, and density, ρ, of the alkaline-earth titanosilicate and silicate melts, and frequency, *f*, of the ultrasonic signal

T °C	η $\log_{10}$ Pa s	ρ^a g cm^{-3}	*f* MHz	*c* m s^{-1}	*K* GPa	*c* m s^{-1}	*K* GPa
BaTiSiO$_5$							
1375	– 0.815^b	3.8085^c	3.060	2196.8	18.38	2212.9 ± 14.7	18.65 ± 0.25
			5.055	2225.7	18.87		
			6.950	2216.2	18.71		
1450	– 0.999^b	3.7863^c	3.015	2172.0	17.86	2172.3 ± 11.6	17.87 ± 0.19
			5.055	2156.8	17.61		
			5.055	2175.6	17.92		
			6.950	2184.7	18.07		
1525	– 1.167^b	3.7641^c	3.060	2158.0	17.53	2174.7 ± 14.0	17.80 ± 0.23
			5.055	2191.7	18.08		
			5.055	2171.9	17.76		
			6.950	2177.0	17.84		
1600	– 1.321^b	3.7419^c	3.060	2138.7	17.12	2153.9 ± 15.0	17.36 ± 0.24
			5.055	2154.2	17.36		
			6.950	2168.7	17.60		
CaTiSiO$_5$							
1400	– 0.930^b	2.9211^c	2.920	2708.6	21.43	2710.8 ± 8.1	21.47 ± 0.13
			5.055	2700.3	21.30		
			5.055	2716.8	21.56		
			6.840	2717.5	21.57		
1450	– 1.039^b	2.9033^c	2.920	2674.9	20.77	2705.0 ± 52.5	21.25 ± 0.83
			2.920	2727.2	21.59		
			3.060	2661.8	20.57		
			5.055	2644.3	20.30		
			5.055	2735.2	21.72		
			6.840	2694.0	21.07		
			6.840	2797.6	22.72		
1500	– 1.142^b	2.8855^c	2.920	2682.1	20.75	2690.5 ± 15.7	20.92 ± 0.19
			2.920	2700.2	21.03		
			5.055	2706.9	21.14		
			6.840	2682.9	20.77		
1550	– 1.239^b	2.8677^c	2.920	2674.9	20.52	2691.9 ± 12.7	20.78 ± 0.20
			5.055	2697.2	20.86		
			5.055	2704.7	20.98		
			6.840	2690.5	20.76		
1600	– 1.330^b	2.8499^c	2.900	2693.8	20.68	2687.9 ± 42.5	20.59 ± 0.65
			5.055	2636.8	19.81		
			6.840	2740.6	21.40		
			6.840	2681.1	20.49		
SrTiSiO$_5$							
1500	– 1.106^b	3.3896^c	3.020	2451.6	20.37	2449.3 ± 7.4	20.34 ± 0.12
			5.070	2441.1	20.20		
			6.950	2455.3	20.43		
1550	– 1.205^b	3.3694^c	3.045	2431.2	19.92	2441.1 ± 7.4	1.87 ± 0.13
			5.070	2419.5	19.72		
			6.950	2434.5	19.97		
1600	– 1.297^b	3.3492^c	3.050	2413.1	19.50	2441.1 ± 7.4	19.56 ± 0.12
			5.070	2424.9	19.69		
			6.950	2411.2	19.47		
SrSiO$_3$							
1625	melt + crystals			–	–	–	–
BaSiO$_3$							
1600	– 0.556^d	3.949^e	3.020	2449.6	23.70	2442.8 ± 9.8	23.57 ± 0.19
			5.070	2431.7	23.35		
			5.070	2447.3	23.65		
1605	– 0.565^d	3.948^e	3.020	2419.9	23.12	2456.8 ± 32.5	23.83 ± 0.63
			5.090	2480.8	24.30		
			5.090	2469.8	24.08		
1625	– 0.602^d	3.942^e	5.090	2458.3	23.82	2478.6 ± 28.7	24.22 ± 0.57
			5.090	2498.9	24.62		
1600					calculated value →		23.86 ± 0.49

Table 4 (continued)

T °C	η $\log_{10}$ Pa s	ρ^a g cm^{-3}	*f* MHz	*c* m s^{-1}	*K* GPa	*c* m s^{-1}	*K* GPa
$BaSi_2O_5$							
1450	0.587^d	3.4531^e	3.040	2429.9	20.49	2434.05 ± 6.1	20.56 ± 0.10
			3.040	2433.5	20.55		
			5.015	2430.0	20.50		
			6.970	2442.8	20.71		
1500	0.420^d	3.4410^e	3.040	2421.9	20.28	2428.50 ± 9.4	20.39 ± 0.16
			5.015	2424.3	20.32		
			6.970	2439.3	20.58		
1550	0.261^d	3.4290^e	3.040	2419.8	20.08	2408.0 ± 12.1	19.88 ± 0.20
			5.015	2395.7	19.68		
			6.970	2408.5	19.89		

[a] 3% error in metasilicate densities
[b] Dingwell (1992b)
[c] Dingwell (1992a)
[d] Bockris et al. (1955)
[e] Tomlinson et al. (1958)

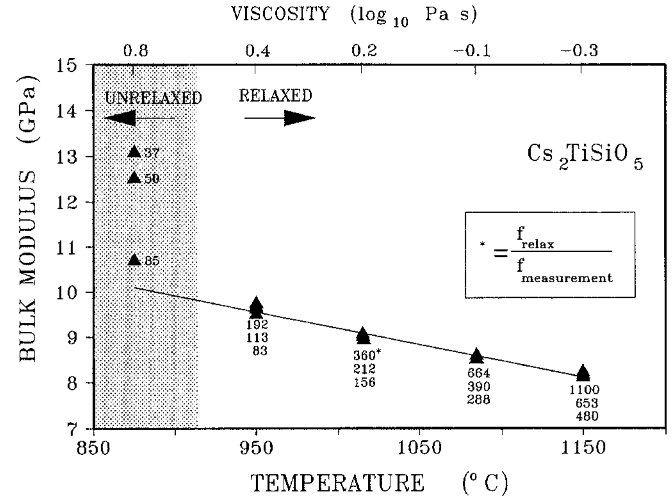

Fig. 1 The relaxed and unrelaxed bulk modulus of Cs_2TiSiO_5 melt as a function of temperature and frequency. The numbers indicate the ratio of the period of the applied signal to the calculated relaxation time

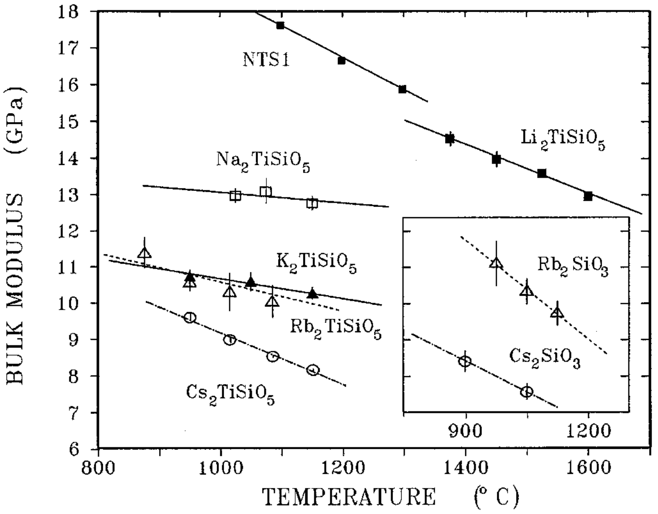

Fig. 2 The relaxed bulk moduli of the alkali-titanosilicate melts as a function of temperature (see Table 3)

volume of the melt. A semi-empirical relationship between the bulk modulus, K, and the molar volume, V, (or the volume per ion pair, V_{pair}) for isostructural crystalline materials has been developed from classical ionic physics:

$$K \propto V^{-4/3} \qquad (4)$$

(Bridgman 1923; Anderson and Nafe 1965). This relationship has been found to apply in general to isostructural oxides and silicates. Recently Rivers and Carmichael (1987) and Herzberg (1987) have applied this relationship in discussions of the compressibility of silicate melts. Both of these studies pointed out that this relationship is applicable to simple binary alkali-silicate melts but not to alkaline-earth compositions. Figure 4 illustrates the applicability of this relationship for octahedrally co-ordinated crystalline oxides where the slope of a straight line fitted to the data is − 1.3 ± 0.1. Data for SiO_2 are taken from Anderson and Anderson (1970) and Weidner et al. (1982); for TiO_2 from Manghnani (1969) and Anderson and Anderson (1970), for GeO_2 from Wang and Simmons (1973), and for SnO_2 from Chang and Graham (1975). The bulk moduli of a series of melts which have the same instantaneous average structure independent of composition and for which the same component of the structure determines the bulk compression independent of composition will also follow the $KV^{4/3}$ relationship presented in Eq. 4.

Figure 5 is a log/log plot of the relaxed bulk modulus versus molar volume for the alkali-metasilicate

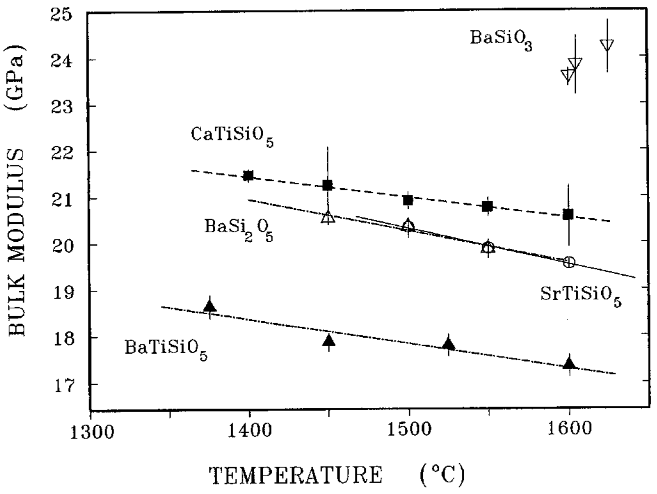

Fig. 3 The relaxed bulk moduli of the alkaline earth-titanosilicate melts as a function of temperature (see Table 4)

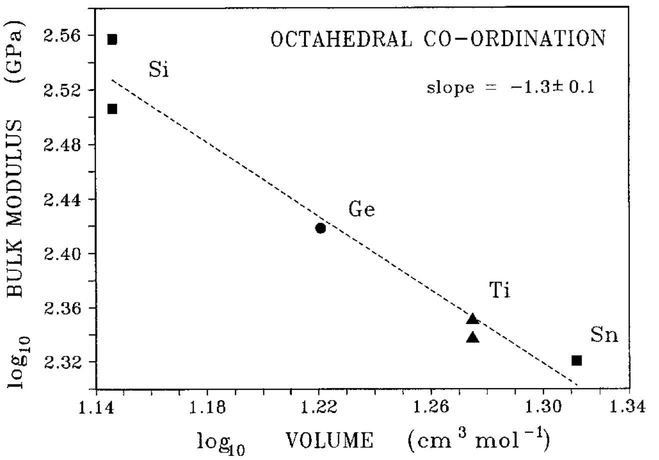

Fig. 4 KV$^{4/3}$ relationship for octahedrally co-ordinated crystalline XO$_2$ compounds at 23 °C

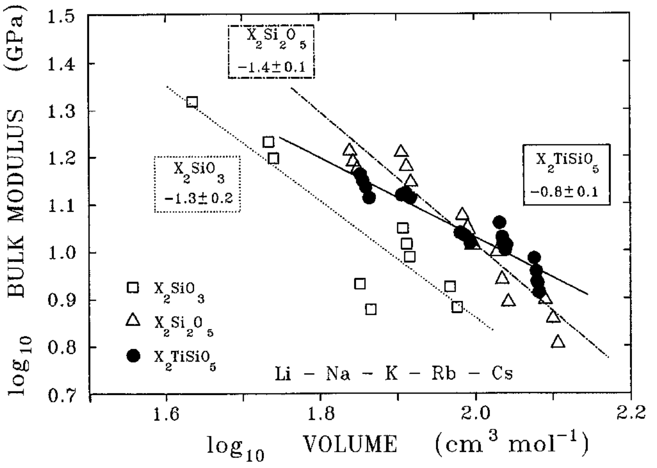

Fig. 5 KV$^{4/3}$ relationship for X$_2$SiO$_3$, X$_2$Si$_2$O$_5$ and X$_2$TiSiO$_5$ (X = Li, Na, K, Rb, Cs) melts at temperatures from 875 to 1600 °C

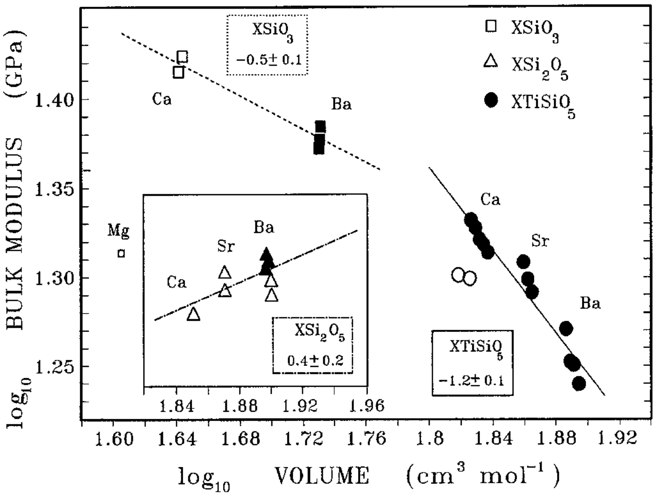

Fig. 6 KV$^{4/3}$ relationship for XSiO$_3$, XSi$_2$O$_5$ and XTiSiO$_5$ (X = Ca, Sr Ba) melts at temperatures from 1375 to 1600 °C

(950–1400 °C) alkali-disilicate (1100–1400 °C) and alkali-titanosilicate melts (950 °C–1600 °C). The slope of the straight lines fitted to the alkali-metasilicate (− 1.3 ± 0.2) and alkali-disilicate (− 1.4 ± 0.1) melt compositions is − 4/3 implying that the melts in each of these series are compressionally isostructural. The slope of the straight line fitted to the alkali-titanosilicate data is − 0.8 ± 0.1, suggesting that the structure of the melts changes as a function of composition. As the titanium-free alkali-metasilicate and -disilicate melts are isostructural within each series it is assumed that the structural changes occurring in the Ti-bearing melts are due to the presence of Ti. Thus the evidence is for a change in the structural role of Ti as a function of alkali identity on the basis of these modulus-volume systematics.

Figure 6 is a log/log plot of the relaxed bulk modulus versus molar volume for the alkaline earth-metasilicate and -disilicate melts and the alkaline earth-titanosilicate melts. The alkaline earth-silicate melts are not isostructural as a function of the cation identity, as the slope of the straight lines fitted to the metasilicate (− 0.5 ± 0.1) and disilicate (0.4 ± 0.2) compositions are not − 4/3. The slope of the straight line fitted to the alkaline earth-titanosilicate data is (− 1.2 ± 0.1) − 4/3, implying that these titanium-bearing melts are isostructural independent of cation identity.

Linear extrapolation to K(TiO$_2$)

Selecting data for the metasilicate and titanosilicate melt compositions at temperatures of 1000 °C (alkali melts) and 1600 °C (alkaline-earth melts), one can attempt to linearly extrapolate as a function of vol.%

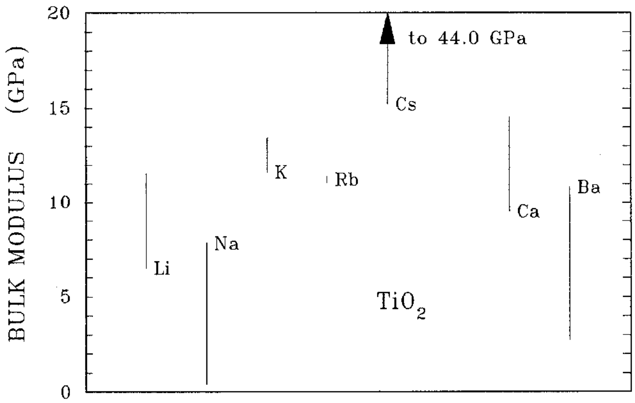

Fig. 7 Bulk moduli for the TiO_2 component of the titanosilicate melts (at 1000 °C and 1600 °C) extrapolated as a function on volume fraction TiO_2 (see Tables 5 and 6)

TiO_2 in the melt to the bulk modulus of the TiO_2 component. It has been shown by Watt et al. (1976) for crystalline materials that the bulk modulus (K^*) of a mixture is bounded by the sum of the bulk moduli (K_i) as a function of volume fraction (v_i) and the sum of the compressibilities (K_i^{-1}) as a function of volume fraction

$$K^*_R = \left(\sum_{i=1}^{n} v_i/K_i\right)^{-1} \leq K^* \leq \sum_{i=1}^{n} v_i K_i = K^*_V. \tag{5}$$

The Reuss bound (K^*_R) is calculated for the case of equal stress throughout an isotropic mixture and the Voigt bound (K^*_V) is calculated for uniform strain in an isotropic aggregate. As the real condition for a melt lies somewhere between the ideal conditions of uniform stress and uniform strain in the structure, the upper and lower bounds on the bulk modulus of the TiO_2 component are calculated from the present data.

Figure 7 illustrates the range of bulk moduli calculated for TiO_2 in these melts as a linear function of the volume fraction and Tables 5 and 6 show the range of values (0.7–40 GPa at 1000 °C and 3–15 GPa at 1600 °C) of the bulk modulus of the TiO_2 component calculated from Eq. 5 for each of the compositions. This wide range of calculated bulk moduli for the TiO_2 component in these melts is inferred to be a consequence of the compositional dependence of Ti co-ordination in these melts (and the non-isostructural nature of the alkaline-earth silicate melts). Such a variation in the structural role and compressibility of the titanium component in silicate melts makes it impossible to

Table 5 Alkali-titanosilicate and alkali-silicate melt density, relaxed bulk modulus and molar volume at 1000 °C.

	ρ 10^3 g cm^{-3}	K GPa	$\partial K/\partial T$ MPa° C^{-1}	vol% TiO_2	volume cm^3 mol^{-1}
Li_2SiO_3	2.1469[a]	22.38 ± 1.08[c]	− 7.3		41.91
Na_2SiO_3	2.3103[a]	19.09 ± 0.88[d]	− 11.3		52.83
K_2SiO_3	2.2768[a]	9.63 ± 0.47[d]	− 5.0		67.76
Rb_2SiO_3	3.0240 ± 0.0120	10.36 ± 0.47	− 13.6 ± 2.6		81.69
Cs_2SiO_3	3.6078 ± 0.0144	7.57 ± 0.23	− 7.5 ± 0.8		94.76
Li_2TiSiO_5	2.5470[b]	16.94 ± 0.20	− 6.57 ± 0.79	34.2	68.09
Na_2TiSiO_5	2.5411[b]	13.16 ± 0.24	− 1.43 ± 1.39	32.2	80.08
K_2TiSiO_5	2.4102[b]	10.16 ± 0.18	− 2.72 ± 0.67	30.8	96.54
Rb_2TiSiO_5	3.0108[b]	10.56 ± 0.42	− 3.96 ± 1.08	25.4	108.57
Cs_2TiSiO_5	3.4974[b]	9.20 ± 0.08	− 7.18 ± 0.27	21.4	119.70
NTS1	2.3511[b]	18.35 ± 0.21	− 8.55 ± 0.71	7.1	55.01
TiO_2(Li)		6.47 − 11.54			24.27
TiO_2 (Na)		0.35 − 7.84			27.03
TiO_2(K)		11.59 − 13.35			28.54
TiO_2(Rb)		11.15 − 11.19			26.89
TiO_2(Cs)		15.19 − 44.00			25.84
$Li_2Si_2O_5$	2.19[a]	16.93 ± 0.07[d]	− 4.61		68.32
$Li_2Si_2O_5$		17.93 ± 0.90[c]			
$Na_2Si_2O_5$	2.30[a]	17.26 ± 0.17[d]	− 7.72		79.58
$K_2Si_2O_5$	2.26[a]	12.66 ± 0.24[d]	− 5.61		95.33
$K_2Si_2O_5$		11.11 ± 0.44[c]			
$Rb_2Si_2O_5$	2.93[d]	10.87 ± 0.58[d]	− 7.38		104.87
$Cs_2Si_2O_5$	3.30[d]	8.41 ± 0.90[d]	− 4.92		121.76

[a] Bockris et al. (1956)
[b] Dingwell (1992a)
[c] Baidov and Kunin (1968)
[d] Rivers and Carnmichael (1987)

Table 6 Alkaline-earth titanosilicate and alkaline-earth silicate melt density, relaxed bulk modulus and molar volume at 1600 °C

	ρ g cm^{-3}	K GPa	K GPa	$\partial K/\partial T$ MPa° C^{-1}	vol% TiO_2	Volume cm^3 mol^{-1}
$CaSiO_3$	2.639[a]	26.5 ± 1.33[e]				44.02
$CaSiO_3$	2.65[b]	27.1 ± 0.64[f]				43.84
$SrSiO_3$			–	–		
$BaSiO_3$	3.949[a]		23.86 ± 0.49	–		54.05
$MgSiO_3$	2.52[c]	20.6 ± .04[f]				40.27
$CaTiSiO_5$	2.850[d]	19.8 ± 0.09[f]	20.55 ± 0.56	– 4.46 ± 0.17	35.0	68.72
$SrTiSiO_5$	3.349[d]		19.53 ± 1.48	– 7.80 ± 0.35	33.1	73.29
$BaTiSiO_5$	3.742[d]		17.33 ± 2.01	– 5.25 ± 0.56	30.9	78.39
TiO_2(Ca)			9.49–14.49			24.1
TiO_2 (Sr)						24.2
TiO_2(Ba)			2.73–10.75			24.2
$CaSi_2O_5$	2.486[a]	19.1 ± 0.96[e]				70.94
$SrSi_2O_5$	3.000[a]	19.0 ± 0.16[f]				74.78
$BaSi_2O_5$	3.417[a]	18.9 ± 0.06[f]	19.60 ± 0.17	– 6.80 ± 0.74		79.69

[a] Tomlinson et al. (1958)
[b] Rivers and Carmichael (1987) at 1563 °C
[c] Rivers and Carmichael (1987) at 1640 °C
[d] Dingwell (1992a)
[e] Baidov and Kunin, (1968)
[e] Rivers and Carmichael (1987)

calculate the bulk modulus of TiO_2 liquid. Calculation of the bulk modulus of titanium-bearing silicate melts must in general contain excess terms, a conclusion arrived at by those previously attempting the inclusion of TiO_2 in linear models (Kress and Carmichael 1991).

Structural role of TiO_2

The addition of TiO_2 to the metasilicate melts results, for the Li-, Na-, Ca-, and Ba-bearing melts, in a decrease in bulk modulus, but for the K-, Rb-, and Cs-bearing melts, in an increase in bulk modulus. Similar trends are observed for the addition of SiO_2 to the metasilicate stoichiometry in the simple alkali- and alkaline earth-silica binaries (Fig. 8). As there is no evidence for a co-ordination shift of Si from metasilicate to disilicate stoichiometry we cannot draw the simple conclusion from Fig. 8 that the cation specific differences in the shift of the bulk modulus are a direct consequence of a co-ordination shift of Ti (i.e. relatively incompressible TiO_2 tetrahedra versus relatively compressible TiO_2 octahedra). The modulus/volume systematics for the alkali- and alkaline earth-titanosilicate melts along with data from the literature for the alkali- and alkaline earth-silicate melts are presented in Figs. 5 and 6. For the case of the alkali-bearing melts, the bulk modulus-volume data for both the metasilicate and the disilicate melts exhibit slope values within error of the – 4/3 value expected for isostructural materials on theoretical grounds (Bridgman 1923). The titanosilicates in contrast exhibit a slope significantly less than this value (slope = – 0.8). In Fig. 5 it is apparent that this lower slope indicates anomalously high bulk moduli for the large cation alkali melts, or conversely anomalously low values for the small cation alkali melts. This trend is in general consistent with the notion that an increasing component of tetrahedrally co-ordinated TiO_2 present in the large cation alkali melts results in increasingly incompressible behavior. Comparison of the disilicate and titanium-metasilicate

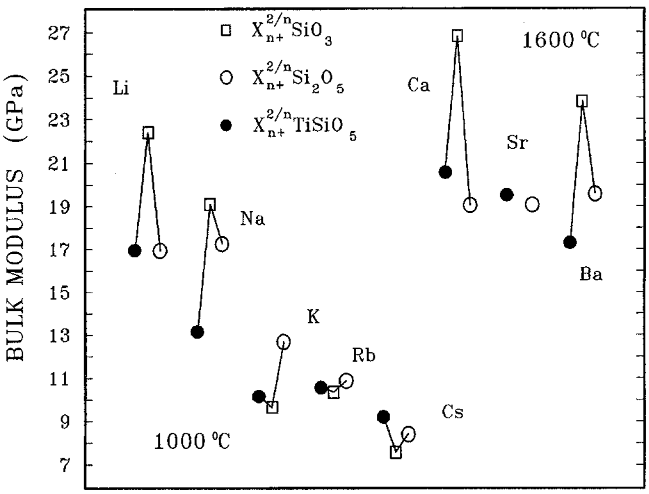

Fig. 8 Relaxed bulk moduli for X_2SiO_3, $X_2Si_2O_5$ and X_2TiSiO_5 (X = Li, Na, K, Rb, Cs) melts at 1000 °C and for $XSiO_3$, XSi_2O_5 and $XTiSiO_5$ (X = Ca, Sr, Ba) melts at 1600 °C

trends in Fig. 5 illustrates that the exchange operator $TiSi_{-1}$ can decrease or increase the compressibility in these melts on the disilicate-titanium metasilicate join. Structural evidence from X-ray absorption spectra of these melts also indicates a shift in co-ordination with alkali cation identity consistent with the non-isostructural slope value for the alkali titanium-metasilicates in Fig. 5 (Dingwell et al. 1994).

The alkaline earth-silicate and -titanosilicate melts present a completely different set of volume-modulus systematics. The alkaline-earth titanium-metasilicate melts present an isostructural value of the slope (slope = -1.2) of the straight line fitted to the bulk modulus/volume data. This observation alone is consistent with the structural evidence from X-ray absorption spectroscopy for glasses quenched from these melts which are quite similar for all alkaline earth-titanosilicates. As has been previously noted, however, (e.g. Rivers and Carmichael 1987) the alkaline earth-silicate melts themselves exhibit slopes in modulus/volume plots which do not follow the $-4/3$ rule for isostructural compounds. This indicates that for the alkaline earth-silicate melts either the instantaneous average structure varies as a function of composition, or different parts of the structure deform under stress as a function of changing composition. The trends in the alkaline earth-silicate melts might be related to a shift in the average co-ordination number of Ti or distribution of the alkaline-earth cations throughout the melt structures at high temperatures. These are both structural parameters for which insufficient data are available. If this hypothesis holds then the logical conclusion is that Ti somehow regularizes the co-ordination number of the alkaline-earths presumably by the formation of alkaline earth-titanium complexes. This "ordering" effect of Ti on the co-ordination of alkaline-earths and/or structure of the alkaline earth-silicate melts could help to explain the relatively high viscosities exhibited by the alkaline earth-titanosilicate melts compared with the alkali-titanosilicates (Dingwell 1992b).

Conclusion

The modulus/volume systematics of Ti-bearing silicate melts investigated in this study are consistent with an isostructural role of Ti in the alkaline earth-titanosilicate melts and a non-isostructural role in the alkali-titanosilicate melts. The structural parameter causing the shift in melt modulus/volume systematics is likely to be the shift in average co-ordination number of Ti inferred from X-ray absorption studies of glasses quenched from these melts (Paris et al. 1993; Dingwell et al. 1994). This correlation indicates that a decrease in the average co-ordination number of Ti causes a stiffening of the melt structure. This observation is consistent with limited evidence for the behavior of Al and Fe in silicate melts (Kress et al. 1988; Kress and Carmichael 1991). The wide range of values calculated for the bulk modulus of the TiO_2 component in these melts is inferred to be a consequence of the compositional dependence of Ti co-ordination in these melts (and the non-isostructural nature of the alkaline-earth silicate melts). Such a variation in the structural role and compressibility of the titanium component makes it impossible to calculate the bulk modulus of TiO_2 liquid from the compressibility data for titanosilicate melts by linear extrapolation. The origin of strongly non-isostructural trends for the alkaline earth-silicate melts remains a challenge for further structural investigations.

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