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Densities of melts in the CaO-MgO-Al_2O_3-SiO_2 system

PHILIPPE COURTIAL* AND DONALD B. DINGWELL

Bayerisches Geoinstitut, Universität Bayreuth, D-95440 Bayreuth, Germany

ABSTRACT

Density measurements have been performed on 4 Mg-aluminosilicate melts and 4 melts in the CaO-MgO-Al_2O_3-SiO_2 system (including stoichiometries corresponding to the mineral compositions åkermanite, diopside, enstatite, and cordierite) in the temperature ranges from their respective melting points up to 1800 °C, using the very precise Ir-based double-bob Archimedean method. The measured densities of the melts range from 2.67 to 2.42 g/cm^3.

Together with our previous density measurements in the CaO-Al_2O_3-SiO_2 system, the present results were analyzed using a regression equation, including a non-ideal mixing term between CaO and SiO_2, from which the partial molar volume of each oxide liquid component was obtained by the method of least squares. This procedure yields partial molar volumes of 12.66, 20.66, 36.67, 27.30 cm^3/mol at 1873 K for MgO, CaO, Al_2O_3, and SiO_2, respectively. A calculation scheme for melts in the CaO-MgO-Al_2O_3-SiO_2 system is proposed, involving an excess volume term between SiO_2 and CaO that is capable of reproducing the liquid molar volumes to within 1% except for extremely Ca-, Mg-, and Al-rich compositions. Better constraints on melt volumes in those extreme composition ranges requires new very high-temperature data.

The volume of fusion of various minerals was calculated and implications for the structure of their respective melts are also discussed. In addition, the volumes of fusion from this study are also compared to that obtained using the Clausius-Clapeyron equation.

INTRODUCTION

As the density of silicate melts is an important variable involved in many geological problems associated with the petrogenesis of magmatic rocks, the knowledge of such a physico-chemical property is essential. Densities of silicate melts are also an essential contribution to the description of the thermodynamics of magmatic systems. They may even be the key to understanding the geophysical and geochemical evolution of the Earth's interior as well as those of other terrestrial planets.

During the ten past years, efforts have been made to extend the database on density of silicate melts to various multicomponent systems (e.g., Stein et al. 1986; Lange and Carmichael 1987; Dingwell et al. 1988; Dingwell and Brearley 1988; Taniguchi 1989; Knoche et al. 1992a, 1992b; Dingwell et al. 1993; Courtial and Dingwell 1995; Knoche et al. 1995; Courtial et al. 1997). However, silicate melts occur naturally over a very wide range of compositions and temperatures, so that a complete investigation of all magmatic liquids of interest to geoscientists is experimentally unrealistic. To cope with this situation, precise models are required to estimate the variation of the density in response to the temperature and composition changes occurring in magmas. Bottinga and Weill (1970) suggested that density of melts in two- or three-components systems could be used to refine variables in a model equation for volumes of naturally occurring melts. Since Bottinga and Weill (1970), the literature contains several models based on the partial molar properties, which are applicable to natural melts (e.g., Nelson and Carmichael 1979; Bottinga et al. 1982, 1983; Lange and Carmichael 1987). Lange and Carmichael (1990) present a summary and review of these models.

In this paper, we present a re-determination of densities of melts over a large temperature range in the CaO-MgO-Al_2O_3-SiO_2 system, using the Ir-based double-bob Archimedean method. In addition to previous density determinations on liquids covering a very wide compositional range in the CaO-Al_2O_3-SiO_2 system (Courtial and Dingwell 1995), this study reports new density measurements in the MgO-Al_2O_3-SiO_2 and CaO-MgO-Al_2O_3-SiO_2 systems.

During this study, compositions were investigated along pseudo-binary joins where the ratios of all components, except one, are constant, using systematically the method described by Darken (1950). In this way, the compositional dependence of the molar volume can be analyzed directly. The molar volumes were also analyzed using a regression equation, which is defined based on the previous step, from which the partial molar volume of each oxide was obtained. In doing so, we aim to establish a structurally based model of melt densities in

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* E-mail: philippe.courtial@uni-bayreuth.de

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TABLE 1. Comparison between nominal and analysed compositions (in weight percent), and liquidus temperatures (T_l) of the investigated materials

		SiO_2	Al_2O_3	CaO	MgO	Total*	gfw	T_l (°C)†
Mg 60.10	Nom.	62.00	17.50	00.00	20.50		58.406	1355
	Anal.	62.46	18.12	00.18	19.02	99.80	58.958	
Mg 38.15	Nom.	40.00	27.50	00.00	32.50		57.411	1650
	Anal.	40.51	27.59	00.22	31.84	100.15	57.605	
Mg 50.00	Nom.	59.85	00.00	00.00	40.15		50.194	1557
	Anal.	60.43	00.91	00.29	38.09	99.72	50.750	
Mg 55.22	Nom.	51.00	35.00	00.00	14.00		64.959	1550
	Anal.	51.33	34.77	00.12	13.41	99.62	65.110	
CaMg 50.00	Nom.	55.49	00.00	25.90	18.61		54.138	1391
	Anal.	55.43	00.92	26.74	16.78	99.88	54.731	
CaMg 40.00	Nom.	44.00	00.00	41.00	15.00		54.478	1454
	Anal.	43.44	00.64	41.68	14.17	99.93	54.784	
CaMg 44.13	Nom.	43.61	21.40	20.37	14.61		60.182	1400
	Anal.	43.33	20.92	20.76	14.06	99.08	60.211	
CaMg 37.26	Nom.	33.29	40.00	15.55	11.16		66.642	1625
	Anal.	33.77	38.68	16.04	10.20	98.69	66.660	

* Analyses made with an automated Cameca electron microprobe operated at 15 kV and 15 nA.
† Levin et al. (1964).

CaO-MgO-Al_2O_3-SiO_2 system, because the variation of the volume reflects the macroscopic consequences of the microscopic changes taking place in the melt structure in response to variation of composition. A structurally based model of a simple system represents a basic skeleton for extrapolations to different temperature and composition conditions to predict more complex, geologically relevant systems. In the long term, we are confident that such an approach will likely bring new insights into the prediction of physico-chemical properties.

EXPERIMENTAL METHODS

Sample preparation

The synthetic starting materials investigated in this densitometry study were synthesized from a mixture of SiO_2 (Fluka Quartz-ignition loss <0.3%), Al_2O_3 (Merck γ-alumina), MgO (Alfa, 99.5%), and $CaCO_3$ (Merck extra pure). These powders were held at 120 °C in a drying oven for 24 h prior to the weighing. They were ground, mixed, and then fused in a platinum crucible between 1550 and 1650 °C depending on the melting point of the sample. The melts were held for more than 1 h in this temperature range in a $MoSi_2$ box furnace and were poured onto a stainless steel plate for cooling. A comparison between the weight of the samples before and after the melting serves as a check of the complete volatilization of CO_2 from $CaCO_3$ powder. For the more viscous compositions, this cycle of grinding and fusion was repeated three times in order to obtain a homogeneous glass (i.e., Mg 60.10, Mg 50.00, Mg 55.22).

The samples that quenched to glasses were analyzed with the electron microprobe to check the composition and for homogeneity. They are labeled CaMg Y.x or Mg Y.x, where Y and x give the nominal mole fraction of SiO_2 and Al_2O_3, respectively. Some of these glasses were not excellent glass-formers, such as Mg 50.00, Mg 38.15, and CaMg 40.00. In those cases, the glasses that were analyzed were obtained by a rapid quenching of a small amount of liquid. Electron microprobe analyses were repeated after the density experiments to check whether volatilization occurred during the time that the samples were held at high temperatures. The results of the analyses of the starting materials, together with the nominal compositions, are presented in Table 1.

The compositions investigated in this study were selected to lie along various series of pseudo-binary joins (e.g., SiO_2-$Mg_3Al_2O_6$, SiO_2-$MgAl_2O_4$, SiO_2-MgO, $MgSiO_3$-$CaSiO_3$, and $CaMgSi_2O_6$-Al_2O_3) and include several important mineral compositions (Fig. 1). Moreover, compositions generally close to eutectics were chosen to investigate a temperature range as wide as possible, in such

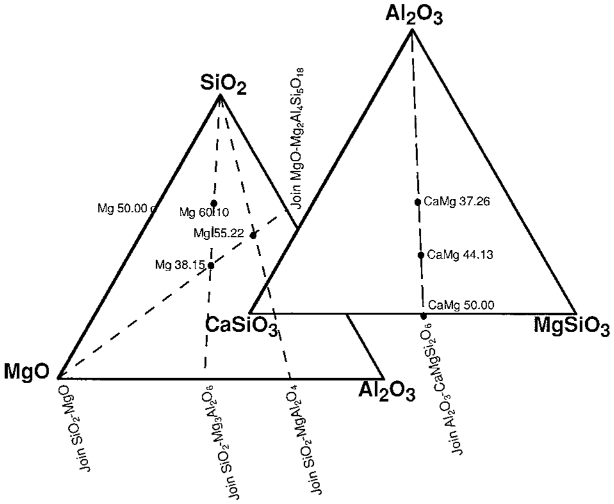

FIGURE 1. Compositions (in weight percent) investigated in the MgO-Al_2O_3-SiO_2 and $CaSiO_3$-$MgSiO_3$-Al_2O_3 systems. The compositions have been selected to lie on pseudo-binary joins (SiO_2-MgO, SiO_2-$Mg_3Al_2O_6$, SiO_2-$MgAl_2O_4$, SiO_2-$Mg_2Al_4Si_50_{18}$, and Al_2O_3-$CaMgSi_2O_6$). Note that CaMg 40.00 is not reported on the figure.

TABLE 2. Experimental density results (g/cm³)

No.	T (K)	ρ	Std. Dev.	No.	T (K)	ρ	Std. Dev.
		Mg 60.10				CaMg 50.00	
1	1823	2.452	(0.011)	1	1773	2.577	(0.007)
2	1873	2.436	(0.015)	2	1873	2.561	(0.006)
3	1973	2.439	(0.010)	3	1973	2.553	(0.009)
4	2073	2.423	(0.005)	4	2073	2.530	(0.014)
		Mg 38.15				CaMg 40.00	
1	1923	2.595	(0.003)	1	1823	2.668	(0.007)
2	1973	2.589	(0.015)	2	1873	2.651	(0.008)
3	2023	2.574	(0.003)	3	1973	2.637	(0.012)
4	2073	2.566	(0.004)				
		Mg 50.00				CaMg 44.13	
1	1873	2.509	(0.006)	1	1773	2.593	(0.009)
2	1923	2.502	(0.011)	2	1873	2.588	(0.007)
3	1998	2.497	(0.001)	3	1948	2.592	(0.004)
4	2073	2.491	(0.007)	4	2073	2.564	(0.005)
		Mg 55.22				CaMg 37.26	
1	1848	2.500	(0.005)	1	1923	2.603	(0.015)
2	1923	2.498	(0.016)	2	1973	2.597	(0.015)
3	1973	2.496	(0.007)	3	2023	2.593	(0.016)
4	2023	2.496	(0.007)	4	2073	2.591	(0.020)
5	2073	2.493	(0.009)				

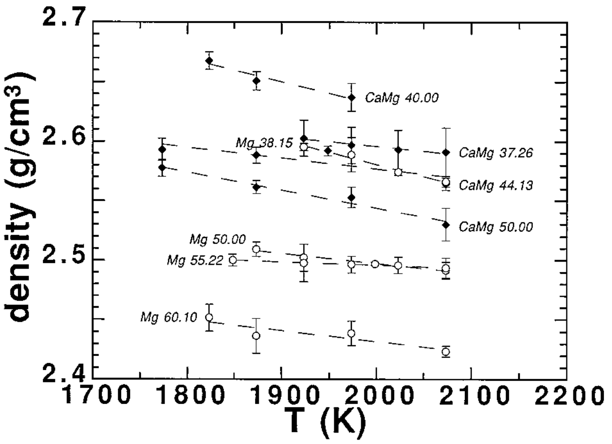

FIGURE 2. Compilation of the density data of this study as function of temperature obtained for the $MgO-Al_2O_3-SiO_2$ (open circles) and $CaO-MgO-Al_2O_3-SiO_2$ (solid diamonds) systems. The error bars correspond to the standard deviation in the buoyancy determinations propagated through Equation 1.

a manner that important mineral compositions were also included (e.g., åkermanite, diopside, enstatite, and cordierite). The accessible range is controlled by the temperature of the liquidus surface and by the immiscibility area (e.g., Levin et al. 1964).

Densitometry

The fused starting materials (75 g) were loaded and remelted in rigid cylindrical crucibles and bottom-loaded into the furnace. The densities of melts were determined by using the double-bob Archimedean method. This technique is based on two bobs of Iridium with different volumes (fabricated in the form of spindles) that are immersed in the liquid. The bobs are suspended from a wire that extends out of the furnace. The masses of the bobs in air, corrected to vacuum, were measured at regular time intervals between the buoyancy determinations. The submerged volume of the bobs was computed from their masses, using a volume-temperature relationship for the metal, geometric considerations of the immersed length of leader wire, and the melt height displacement of the submerged bob. These buoyancy data were entered into Equation 1 to solve for density:

$$\rho = (B_1 - B_2)/(V_1 - V_2) \tag{1}$$

where B_1 and B_2 are the buoyancies and V_1 and V_2 are the submerged volumes of the large and small bobs, respectively.

Measurements of densities were conducted until 1800 °C or more, using the device described previously by Dingwell (1991, 1992). The precision of the present density measurements was obtained by propagating the standard deviations of the buoyancy determinations through Equation 1. The experiments were conducted in sets of three or four immersions for each bob (large and small) at each temperature to compute mean and standard deviation values of the replicate buoyancy determinations for both bobs (i.e., large and small). Each re-immersion of the bobs involved all the intermediate steps required between different samples (e.g., removing the wire and bob assembly, cleaning the bob in 40% HF, re-suspending the bob, and re-taring the balance).

Temperatures were measured with an infrared optical pyrometer situated 30 cm from the crucible by viewing the crucible through a window in the wall of the furnace. It is important to note that the pyrometer reads directly from the surface of the Ir crucible with no intervening surface. This pyrometer, which also controls the temperature of the furnace, is calibrated regularly for several temperatures between 1450 and 1650 °C using a Pt_{94}/Rh_6-Pt_{70}/Rh_{30} (Type 8) thermocouple. With such methods, the temperature errors involved are estimated to be about 10 °C. This temperature uncertainty is estimated to contribute an imprecision of $<0.1\%$ to the density data.

The accuracy of the Ir-based double bob Archimedean method can be appreciated by comparison to the Pt-based technique. The accuracy of the Pt-based double-bob Archimedean technique was tested previously by Dingwell et al. (1988) by determining the density of molten NaCl, prior to their study. Since the volume-temperature relationship of Ir is less well known than that of Pt, a good agreement of such an Ir-based system is essential as emphasized previously by Courtial and Dingwell (1995).

RESULTS

Experimental results

Density measurements on four Mg-aluminosilicate melts and four melts in the $CaO-MgO-Al_2O_3-SiO_2$ system at different temperatures are listed in Table 2. The variation of density with temperature in the investigated samples is shown in Figure 2. Within the uncertainties of the determinations, a linear relationship was found between

TABLE 3. Density of experimental melts [$\rho = a + b\,T(K)$]

	a	10^4b	ΔT (K)	R
Mg 60.10	2.6169	−0.9268	1823–2073	0.88979
Mg 38.15	2.9903	−2.0480	1923–2073	0.98857
Mg 50.00	2.6654	−0.8414	1873–2073	0.98784
Mg 55.22	2.5490	−0.2662	1848–2073	0.98618
CaMg 50.00	2.8456	−1.5090	1773–2073	0.98452
CaMg 40.00	3.0193	−1.9443	1823–1973	0.96881
CaMg 44.13	2.7583	−0.9074	1773–2073	0.83808
CaMg 37.26	2.7497	−0.7700	1923–2073	0.97521

the density and the temperature for each composition from its respective melting point up to 1800 °C. The parameters of this linear fit and the correlation coefficient for each composition are reported in Table 3. The melt densities range from 2.67 to 2.42 g/cm^3 and decrease with increasing SiO_2 content along the same join (Fig. 2). In the same way, the density of melts in the CaO-MgO-Al_2O_3-SiO_2 system is generally greater than the density of Mg-aluminosilicate melts.

The precision of the density determinations, which derives only from the precision of replicate buoyancy determinations, is individually reported in Table 2 and plotted in Figure 2 for each temperature and composition. In addition, the mean precision of the density determinations resulting from all the measurements conducted in this study is ~0.36% and the standard deviations range from 0.06 to 0.67%.

Using the present density measurements and melt compositions, the molar volume of each melt was calculated by following Equation 2:

$$\rho = M/V \tag{2}$$

where ρ is the measured density of the liquid, M its gfw, and V its molar volume. At this point, it is useful to assess the errors involved in the volume calculation. The mean error in the precision of the density measurements is 0.36% (see above), and additional errors in the electron microprobe analyses propagate into a mean error <1% in the molar volumes of the melts.

Composition dependence of the molar volume

The density measurements of the present melts were analyzed via the molar volume as a function of composition along several pseudo-binary joins. In Figure 3, the molar volumes calculated at 1973 K are plotted as a function of SiO_2 content along joins radiating from SiO_2 to various stoichiometric compositions on the Mg-aluminate binary (e.g., SiO_2-$MgAl_2O_4$, SiO_2-$Mg_3Al_2O_6$, and SiO_2-MgO). In addition, the value of pure liquid SiO_2 extrapolated linearly to 1973 K from Bacon et al. (1960) is also reported, which is fairly close to the partial molar volume of SiO_2 obtained by Courtial and Dingwell (1995) for Ca-aluminosilicate melts. Figure 3 illustrates first that the molar volume of the present melts increases from SiO_2-MgO to the SiO_2-$MgAl_2O_4$ joins; in other words, it increases with increasing Al_2O_3 content. Despite a larger error involved in the measurements of Bacon et al. (1960), probably due to the high viscosity of SiO_2 melts, the data plotted in Figure 3 suggest that the molar volume behaves ideally along these three joins and in the composition range investigated here; in other words, a linear variation of the molar volume of these melts as a function of SiO_2 content is exhibited from the value of pure SiO_2 from Bacon et al. (1960) down to the most Si-poor composition we were able to investigate. In fact, if a nonideal behavior with respect to the molar volume may be observed in the alkaline earth aluminosilicate melts, it might be expected for Si-poor melts, as previously observed (e.g., Lange and Carmichael 1987; Courtial and Dingwell 1995) for Ca-aluminosilicate melts, resulting from an interaction between SiO_2 and the alkaline earth element. Unfortunately, such an Si-poor composition range was not accessible in the MgO-Al_2O_3-SiO_2 system because of the very high temperatures required.

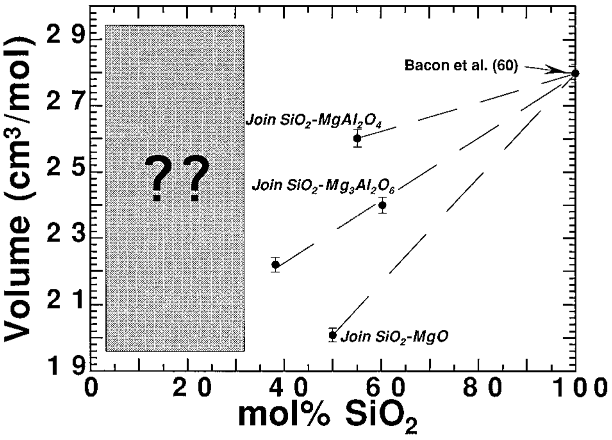

FIGURE 3. Molar volumes calculated at 1973 K from the individual fits of Table 3 along the joins SiO_2-MgO, SiO_2-$Mg_3Al_2O_6$, and SiO_2-$MgAl_2O_4$ shown in Figure 1. The molar volume of pure liquid SiO_2 extrapolated to 1973 K from Bacon et al. (1960) also has been plotted. The shadowed box represents the compositional range unfortunately not investigated because of the very high temperatures required, where a linear extrapolation is made for the rest of the study. However, we are aware that such an extrapolation remains open to criticism (see text).

In Figure 4, the variation of the molar volume calculated at 1973 K is plotted for melts in the CaO-MgO-Al_2O_3-SiO_2 system along the $MgSiO_3$-$CaSiO_3$ join. The molar volume decreases gradually from Ca 50.00 to Mg 50.00 or, in other words, the substitution of Ca for Mg leads to an increase of the molar volume. The difference between enstatite melt (i.e., Mg 50.00) and pseudowollastonite melt (i.e., Ca 50.00), where Mg is fully substituted by Ca, is about 9%. Moreover, a linear variation of the molar volume is clearly observed along the entire join, which may suggest that no interaction occurs between the alkaline earth metals themselves (i.e., CaO and MgO) in the present aluminosilicate melts.

In Figure 5, the molar volumes calculated at 1973 K along joins extrapolated to Al_2O_3 are plotted as a function of Al_2O_3 content (i.e., $MgSiO_3$-Al_2O_3 and $CaMgSi_2O_6$-

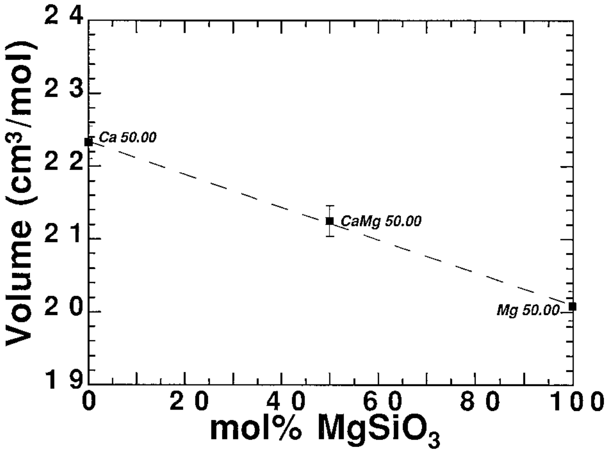

FIGURE 4. Molar volumes calculated at 1973 K from the individual fits of Table 3 along the join $CaSiO_3$-$MgSiO_3$.

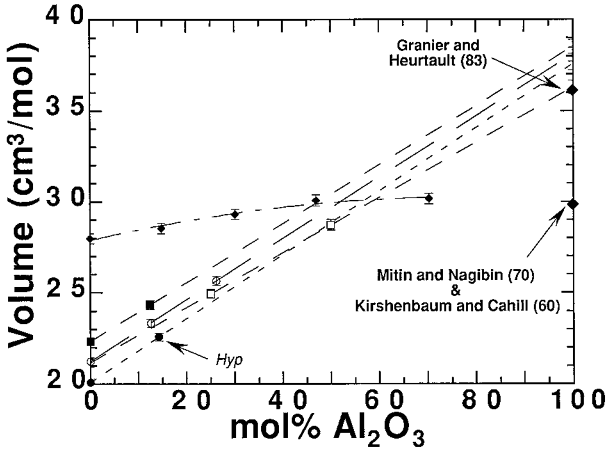

FIGURE 5. Molar volumes calculated at 1973 K from the individual fits of Table 3 along joins extrapolated to Al_2O_3 [$CaMgSi_2O_6$-Al_2O_3 (open circles), $MgSiO_3$-Al_2O_3 (solid circles)]. Molar volumes along the $CaSiO_3$-Al_2O_3 and CaO-Al_2O_3 joins (solid squares and open squares, respectively) from Courtial and Dingwell (1995) also have been plotted. All these joins suggest a linear extrapolation to the value, or relatively close to the value of pure liquid Al_2O_3 from Granier and Heurtault (1983). On the other hand, molar volumes along the SiO_2-Al_2O_3 join (small solid diamonds) from Aksay et al. (1979) are more consistent with the values of pure liquid Al_2O_3 given by Mitin and Nagibin (1970) or Kirshenbaum and Cahill (1960). Mg 38.15 does not perfectly lie on the $MgSiO_3$-Al_2O_3 join; therefore, the molar volume of a hypothetical composition lying on this join (Hyp) was calculated from a linear interpolation between the molar volume of Mg 38.15 and Mg 60.10 in order to shift that composition on the join.

Al_2O_3 joins). In addition, CaO-Al_2O_3 and $CaSiO_3$-Al_2O_3 joins from Courtial and Dingwell (1995) also have been reported in Figure 5. The data span a small composition range, so that they define initial slopes that are poorly constrained. However, a linear extrapolation of the data along the joins $CaMgSi_2O_6$-Al_2O_3, $MgSiO_3$-Al_2O_3, $CaSiO_3$-Al_2O_3, and CaO-Al_2O_3 yields an estimate of the partial molar volume of pure Al_2O_3 liquid of 38.1, 37.6, 38.5, and 36.3 cm^3/mol, respectively; in other words, the extrapolations from four different joins in the MgO-Al_2O_3-SiO_2, CaO-Al_2O_3-SiO_2, and CaO-MgO-Al_2O_3-SiO_2 systems converge to a similar value for Al_2O_3 (i.e., 37.6 ± 2% cm^3/mol). This may indicate that the partial molar volume of Al_2O_3 is composition independent for melts in the CaO-MgO-Al_2O_3-SiO_2 system in the composition range investigated.

The molar volume of pure liquid Al_2O_3 has been investigated mainly in the ceramic literature (for a review, see Granier and Heurtault 1983). Unfortunately, values of the molar volume span a large range, ~20%. For example, plotted in Figure 5 are the molar volumes measured by Granier and Heurtault (1983) by an aerodynamic levitation technique using argon gas, as well as the values obtained by Mitin and Nagibin (1970) and Kirshenbaum and Cahill (1960) by the single-bob Archimedean method in an argon atmosphere using a tungsten sinker and a molybdenum crucible. Our estimate of the partial molar volume of Al_2O_3 agrees well with that of Granier and Heurtault (1983) extrapolated to 1973 K, but largely disagrees with the measurements of Mitin and Nagibin (1970) and Kirshenbaum and Cahill (1960). In fact, unpublished density measurements on Al_2O_3 using the same contactless technique as Granier and Heurtault (1983) seem to confirm the values of Granier and Heurtault (1983) (Rifflet and Coutures, personal communication).

Density measurements along the SiO_2-Al_2O_3 join extrapolated to 1973 K from Aksay et al. (1979) exhibit a partial molar volume of Al_2O_3 quite different from that estimated in this study (Fig. 5). Despite the difficulty in investigating such a join resulting from the very high melting temperatures, this difference does not seem to result from errors involved in the X-radiographic technique. Courtial and Dingwell (1995), using the precise double-bob Archimedean method, conducted one high-temperature measurement along this join, which agrees with the previous work of Aksay et al. (1979). If we accept the molar volume of pure Al_2O_3 given by Granier and Heurtault (1983), the measurements of Askay et al. (1979) suggest that the partial molar volume of Al_2O_3 depends on composition along the SiO_2-Al_2O_3 join and that an interaction exists between SiO_2 and Al_2O_3 for Al-rich melts along this join. In fact, this macroscopic observation reflects microscopic changes occurring in the melt structure along the SiO_2-Al_2O_3 join, which have already been noted in the spectroscopic literature. Poe et al. (1992a, 1992b) have thus proposed the coexistence of Al in fourfold, fivefold, and sixfold coordination for melts along the SiO_2-Al_2O_3 join.

The results shown in Figure 5 also suggest that the molar volume increases strongly with increasing Al_2O_3 content in both MgO-Al_2O_3-SiO_2, CaO-Al_2O_3-SiO_2, and CaO-MgO-Al_2O_3-SiO_2 systems, except along the SiO_2-Al_2O_3 join where the molar volume increases slightly with

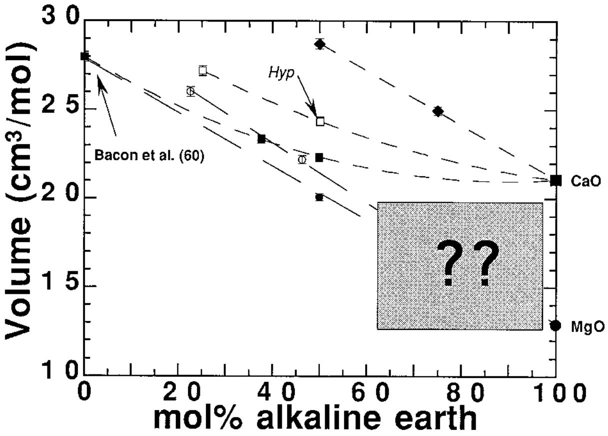

FIGURE 6. Molar volumes calculated at 1973 K from the individual fits of Table 3 along SiO_2-MgO (solid circles) and $Mg_2Al_4Si_5O_{18}$-MgO (open circles) joins. The molar volume of pure liquid SiO_2 extrapolated to 1973 K from Bacon et al. (1960) also has been plotted. A possible linear extrapolation along these two joins allows us to determine the partial molar volume of MgO liquid. On the other hand, molar volumes from Courtial and Dingwell (1995) in the CaO-Al_2O_3-SiO_2 system along the SiO_2-CaO (solid squares), $CaAl_2Si_2O_8$-CaO (open squares) and Al_2O_3-CaO (solid diamonds) joins do not exhibit a similar trend. Ca 36.16 does not perfectly lie on the $CaAl_2Si_2O_8$-CaO join; therefore, the molar volume of a hypothetical composition lying on this join (Hyp) was calculated by a slight linear interpolation between the molar volume of Ca 36.16 and Ca 09.23.

increasing Al_2O_3 content, at least in the Al-content investigated by Aksay et al. (1979). Another feature evident in Figure 5 is that the molar volume of Ca-aluminosilicate melts is larger than Mg-aluminosilicate melts, as previously mentioned.

In Figure 6, the variation of the molar volume calculated at 1973 K is plotted as a function of alkaline earth content along joins extrapolated to alkaline earth end-members (e.g., SiO_2-MgO and $Mg_2Al_4Si_5O_{18}$-MgO). In addition, joins extrapolated to CaO from Courtial and Dingwell (1995) are also shown in Figure 6. Once again, Figure 6 illustrates that the molar volume of Ca-aluminosilicate melts is generally larger than Mg-aluminosilicate melts. Another feature evident in Figure 6 is the decrease of the molar volume with increasing alkaline earth content. In contrast to the Ca-aluminosilicate melts, which exhibit a Ca-Si interaction, a similar Mg-Si interaction is not observed here. By investigating specifically the joins MgO-SiO_2 and CaO-SiO_2, Tomlinson et al. (1958) made similar observations (i.e., deviation from additivity along CaO-SiO_2 join, in contrast to melts along MgO-SiO_2 join). If such an MgO-SiO_2 interaction exists, it may be restricted to MgO-rich melts. But, such extreme compositions are difficult to investigate because of their very high melting temperatures.

Model

Using the metallurgical database of available densities, Bottinga and Weill (1970) were the first to apply and extend the binary and ternary components resource to geological systems following the simple equation:

$$V_{\mathrm{Liq}}(T) = \Sigma\, X_i\, V_i\,(T) \tag{3}$$

where V_{Liq} is the measured liquid molar volume, X_i the mole fraction of the oxide (i), and V_i the partial molar volume of the oxide (i). Equation 3 embodies the assumption that molar volume follows a linear variation with composition. In the CaO-MgO-Al_2O_3-SiO_2 system, Lange and Carmichael (1987) suggested a linear model for the molar volume of silicate melts having compositions that are geologically relevant, whereas an excess volume term between CaO and SiO_2 was identified for melts that have a $X_{\mathrm{CaO}} > 0.5$. In the same way, the molar volume data of Tomlinson et al. (1958) along the CaO-SiO_2 join exhibit a non-ideal volume of mixing between CaO and SiO_2, whereas a non-ideal volume of mixing between MgO and SiO_2 was not observed along the MgO-SiO_2 join for melts ranging from 42 to 54 mol% of MgO. In the $CaSiO_3$-$CaMgSi_2O_6$-$Ca_2MgSi_2O_7$ system, Licko and Danek (1982) also inferred a small deviation from linearity for the molar volume. More recently, Courtial and Dingwell (1995) clearly observed an excess volume term between CaO and SiO_2 for Ca-aluminosilicate melts at low SiO_2 content (i.e., <30 mol% of SiO_2). A similar excess term between CaO and SiO_2 was also reported by Dingwell and Brearley (1988) and Dingwell (1990) for melts in the CaO-FeO-Fe_2O_3-SiO_2 system. In addition, Kress and Carmichael (1989) also suggested a non-ideal volume of mixing between CaO and SiO_2 for melts with very low silica content ($CaO/SiO_2 < 0.3$) in the same system.

Taking into account possible excess terms, Equation 3 thus becomes:

$$V_{\mathrm{Liq}}(T) = \Sigma\, X_i\, V_i\,(T) + XS \tag{4}$$

where XS is the excess volume term corresponding to the interaction between SiO_2 and CaO (e.g., Courtial and Dingwell 1995). Courtial and Dingwell (1995) clearly identified and defined this excess volume term between SiO_2 and CaO ($XS_{\mathrm{SiO_2\text{-}CaO}}$) as:

$$XS_{\mathrm{SiO_2\text{-}CaO}} = X_{\mathrm{SiO_2}} X_{\mathrm{CaO}} V_{\mathrm{SiO_2\text{-}CaO}} \tag{5}$$

where $X_{\mathrm{SiO_2}}$ and X_{CaO} are the mole fractions of SiO_2 and CaO, respectively, and $V_{\mathrm{SiO_2\text{-}CaO}}$ is the corresponding excess volume term. Accordingly, the combination of Equations 4 and 5 leads to the model Equation 6:

$$\begin{aligned} V_{\mathrm{Liq}}(T) = {} & \Sigma X_i[V_{i,1873} + (\partial V_i/\partial T)(T - 1873)] \\ & + X_{\mathrm{SiO_2}} X_{\mathrm{CaO}}[V_{\mathrm{SiO_2\text{-}CaO},1873} + (\partial V_{\mathrm{SiO_2\text{-}CaO}}/\partial T) \\ & \times (T - 1873)]. \end{aligned} \tag{6}$$

Using the previous density measurements of Courtial and Dingwell (1995) for the CaO-Al_2O_3-SiO_2 system obtained from the same laboratory, together with the results for eight melts in the MgO-Al_2O_3-SiO_2 and CaO-MgO-Al_2O_3-SiO_2 systems, the partial molar volume of each ox-

TABLE 4. Calculated values of partial molar volumes

	V_i	Std. Err.	$(\partial V_i/\partial T)$ $\times 10^3$	Std. Err.
SiO_2	27.297	(0.152)	1.157	(0.0007)
Al_2O_3	36.666	(0.196)	−1.184	(0.0009)
CaO	20.664	(0.123)	3.756	(0.0005)
MgO	12.662	(0.181)	1.041	(0.0008)
SiO_2-CaO	−7.105	(0.509)	−2.138	(0.0023)
R^2	0.997			
Adjusted R^2	0.996			
S	0.1453			
F-ratio	287 487			

Notes: Fit parameters derived from separate regressions using Equation 6 for eight melts in the $MgO-Al_2O_3-SiO_2$ and $CaO-MgO-Al_2O_3-SiO_2$ systems, respectively, together with 10 melts in the system $CaO-Al_2O_3-SiO_2$ from Courtial and Dingwell (1995).

ide component (i.e., SiO_2, Al_2O_3, CaO, and MgO) was obtained using regression Equation 6. Such calculations were made using the analyzed compositions of the samples. The regressions were made simultaneously and not separately as a function of composition and temperature over the temperature range from 1773 to 2273 K. The results of these regressions following the model of Equation 6 are reported in Table 4. The uncertainties in the quality of these fits are indicated by the standard error of each fit coefficient (in parentheses in Table 4). The relative standard error of the fit, when compared with our experimental uncertainties, indicates whether the fit can reproduce the data adequately within our best estimate of experimental uncertainties. The coefficient of determination (R^2), the adjusted R^2 statistic, the relative standard error of the fit (S), and the F-ratio are also included in Table 4. Note that the adjusted R^2 is used most often in multiple regression because it accounts for the number of variables in the regression equation.

In view of the fact that the molar volume of melts behaves non ideally in the $CaO-Al_2O_3-SiO_2$ system, it is tempting to speculate that the molar volume of Mg-aluminosilicate melts may vary non ideally with composition as well. As noted above, the lack of experiments on Si-poor melts in the $MgO-Al_2O_3-SiO_2$ system does not allow us to check such an assumption. However, if we suppose for the moment that the compositional dependence of the molar volume may be similar in form for all the alkaline earth-aluminosilicate melts, then an excess volume term between MgO and SiO_2 must be included in this model, assuming the same variation as the one defined between CaO and SiO_2, even if such a behavior was not observed in this study. Use of this new excess volume term between MgO and SiO_2 yields similar partial molar volumes, except for MgO (i.e., 8% larger), but it does not markedly improve the quality of the regression. On the other hand, an ideal regression was also attempted to our data, which yields a larger relative standard error of the fit (i.e., three time more) and a smaller F-ratio (i.e., five times less).

Molar volumes of melts in the $CaO-MgO-Al_2O_3-SiO_2$ system calculated according to the model Equation 6 conform to experimentally measured volume with a standard error of 0.3 cm^3/mol in the temperature range investigated. The present model reproduces quantitatively (within 1%) volume data of liquids in this system, except probably for Ca-, Mg- and Al-rich melts. The difficulty in constraining the model for such extreme compositions comes from the very high temperatures required and, consequently, the calculation of the molar volume for such composition ranges results in large extrapolations.

DISCUSSION

Comparison with previous literature density data

A comparison between the literature data of several authors in the $CaO-MgO-Al_2O_3-SiO_2$ system (e.g., Tomlinson et al. 1958; Riebling 1964; Licko and Danek 1982; Lange and Carmichael 1987; Taniguchi 1989; Knoche et al. 1992a, 1992b) and the present experimental measurements has been made for some similar compositions. Using the double-bob Archimedean method, Tomlinson et al. (1958) obtained data along the SiO_2-MgO join that are lower than for our enstatite melt. Similar differences between our results and those from Tomlinson's laboratory were noted previously by Courtial and Dingwell (1995) along the SiO_2-CaO join. This systematic difference may be interpreted as temperature uncertainties stemming from the use of the Mo/W thermocouples by Tomlinson et al. (1958). A good agreement is found with the data of Licko and Danek (1982) for åkermanite melt (i.e., 1.3%) as well as for diopside melt (i.e., 0.6%). The present experiments for diopside melt were also compared with the works of Lange and Carmichael (1987), Taniguchi (1989), and Knoche et al. (1992a, 1992b), which exhibit values lower than ours of about 1.5%, likely due to the slight deviation from the nominal composition of our sample (i.e., 1.1%). Finally, the data from Riebling (1964) in the $MgO-Al_2O_3-SiO_2$ system match ours within 1.5%.

Among the different models that describe the molar volumes of natural silicate melts as a function of temperature and chemical composition (for a complete review of these models see Lange and Carmichael 1990), some are ideal, i.e., the partial molar volumes of the liquid oxide components are independent of the composition [e.g., Bottinga and Weill 1970; Nelson and Carmichael 1979; Bottinga et al. 1983 (restricted to the Al-free silicate melts); Lange and Carmichael 1987 (with the exception of some Ti-bearing melts], whereas others are nonideal, i.e., Bottinga et al. (1982) the partial molar volume of Al_2O_3 is composition dependent. Taking the most recent one (i.e., Lange and Carmichael 1987), we compared the volume data it yields with the data measured in this present study. Their ideal model reproduces our experimental data to within 1.6%.

In addition, recent molecular dynamics (MD) simulations have been conducted on melts in the $CaO-MgO-Al_2O_3-SiO_2$ system (e.g., Matsui 1996). The simulated molar volumes calculated at 1900 K compare quite well with the present observed values, with the differences of

TABLE 5. Volume of fusion of some minerals in the CaO-MgO-Al_2O_3-SiO_2 system

Minerals	T_f (K)	V (298K) crystals* (cm³/mol)	V (T_f) crystals† (cm³/mol)	V (T_f) liquids‡ (cm³/mol)	ΔV_f (cm³/mol)
SiO_2 cristobalite	1999	25.925	26.191	27.462	1.271§
α-Al_2O_3 corundum	2323	25.577	27.076	36.206	9.130§
CaO lime	2843	16.762	18.880	24.339	5.459§
MgO periclase	3073	11.244	12.894	13.983	1.089§
$Ca_2MgSi_2O_7$ åkermanite	1727	18.524	19.428	20.301	0.873
$Mg_2Al_4Si_5O_{18}$ cordierite	1740‖	25.913	26.010	25.956	−0.054
$CaMgSi_2O_6$ diopside	1665	16.510	17.279	20.868	3.589
$CaSiO_3$ pseudowollastonite	1817	20.040	21.148	22.032	0.884
$MgSiO_3$ protoenstatite	1834#	16.220	16.641	19.989	3.348
$CaAl_2Si_2O_8$ anorthite	1830	25.243	25.810**	27.003	1.193

* Data from Peacor (1973) (cristobalite); Newnham and Dehaan (1962) (corundum); Wyckoff (1963) (lime); Hazen (1976) (periclase); Kimata and Ii (1981) (åkermanite); Robie et al. (1979) (cordierite); Cameron et al. (1973) (diopside); Robie et al. (1979) (pseudowollastonite); Vaughan and Bass (1983) (protoenstatite); Carpenter (1992) (anorthite).

† Calculated from the Eq. $V = V_{298}\exp[\alpha_0(T - 298) + \alpha_1/2(T^2 - 298^2) - \alpha_2(T^{-1} - 298^{-1})]$, where α_0, α_1, and α_2 are listed in Fei (1995).

‡ Molar volume of the molten minerals derived from this study, except for molten pseudowollastonite and anorthite, which are from Courtial and Dingwell (1995).

§ Molar volume of these liquids results from the fit of all experimental data from the present study and Courtial and Dingwell (1995).

‖ Incongruent melting.

Metastable congruent melting.

** Despite the Al/Si disorder at high temperature occurring in anorthite crystals, the molar volume at the melting point has been estimated from a linear extrapolation of the data of Carpenter (1992).

6.5, 1.2, 2.3, and 4.2% for molten enstatite, diopside, pseudowollastonite, and anorthite, respectively.

Partial molar volumes

The partial molar volume of SiO_2 derived from this study is in agreement with that obtained by Courtial and Dingwell (1995) for melts in the CaO-Al_2O_3-SiO_2 system. In addition, the partial molar volume from the linear model of Lange and Carmichael (1987) and the non-linear model of Dingwell and Brearley (1988) agrees well with our value. When compared to the molar volume of pure liquid SiO_2 extrapolated from Bacon et al. (1960), a larger disagreement of about 2.5% is found over the temperature range investigated in this work. However, although an error of greater than 2.5% seems unlikely from the counter-balanced sphere method they used, it probably stems from the difficulty in conducting density measurements on such a highly viscous liquid.

The partial molar volume of Al_2O_3 obtained in this study was also compared to various estimates from previous studies. For example, it agrees with the partial molar volume proposed by Courtial and Dingwell (1995), whereas a slightly higher value was obtained by Lange and Carmichael (1987). The present partial molar volume of Al_2O_3 is also in agreement with the measurements made on Al_2O_3 liquid by Granier and Heurtault (1983), at least for temperatures ranging from 1750 to 2300 K. [Note however the large errors involved in the measurements of the study of Granier and Heurtault (1983) (i.e., 5%)]. In contrast, the molar volume of Al_2O_3 liquid measured by Mitin and Nagibin (1970) or Kirshenbaum and Cahill (1960) has a completely different value, as mentioned previously. One can note that the present partial molar volume of Al_2O_3 exhibits a negative coefficient of thermal expansion, in disagreement with all the literature data (for a review, see Granier and Heurtault 1983). This proves, once again, that our model requires more constraints at high-Al_2O_3 content. Indeed, another regression was performed after weighting our data set with the molar volume of pure Al_2O_3 from Granier and Heurtault (1983); a new positive thermal expansion coefficient for Al_2O_3 resulted from such a fit.

The partial molar volumes of the alkaline earth metals derived from this study, compared to those of Lange and Carmichael (1987), exhibit the largest differences amongst all the oxides studied. The discrepancy is about 6% at 1873 K for MgO and it is more important for CaO (i.e., 18%). This disagreement most likely results from the large extrapolations needed. In addition, the difference in the partial molar volume of CaO stems also from the excess term between CaO and SiO_2 we used, whereas Lange and Carmichael (1987) used an ideal model. On the other hand, Courtial and Dingwell (1995) obtained a similar partial molar volume for CaO. Dingwell and Brearley (1988) obtained a value 4% lower than the present one in the CaO-FeO-Fe_2O_3-SiO_2 system.

Volume of fusion

The volume of fusion (ΔV_f) can be calculated by combining the molar volume of the crystal (the variation of which as a function of temperature is well known) with the molar volume of the liquid at the melting point (T_f) according to Equation 7:

$$\Delta V_f = V_{\mathrm{Crys}}(T_f) - V_{\mathrm{Liq}}(T_f) \qquad (7)$$

where $V_{\mathrm{Crys}}(T_f)$ and $V_{\mathrm{Liq}}(T_f)$ represent the molar volume of the crystalline and molten phases at the melting point, respectively. The volume of fusion is listed in Table 5 for a variety of minerals in the CaO-MgO-Al_2O_3-SiO_2 system. The volume of fusion expresses, at the melting temperature, the volumetric changes that occur within the structure of the molten phase with respect to its crystalline counterpart. Given a small ΔV_f, the structure of a melt will likely be close to that of its corresponding crystal at the melting point. This simplification may bring some insights into the structure of the melts by comparison with that of the crystals.

Pseudowollastonite, anorthite, cordierite, åkermanite, cristobalite, and periclase exhibit a small volume of fusion, so that the structure of their respective liquids may remain similar to that of the crystals at their respective melting temperature. In fact, spectroscopic investigations on pseudowollastonite melts (e.g., Yin et al. 1986; Waseda and Toguri 1990; Gaskell et al. 1991) have suggested the same Ca- and Si-environment as in crystals (i.e., sixfold and fourfold coordinated, respectively). In the same way, structural studies on anorthite melts (e.g., Taylor and Brown 1979; Okuno and Marumo 1982; Oestrike et al. 1987) have revealed the presence of Si and Al in the same coordination as in crystals (i.e., fourfold coordinated), whereas the coordination number of Ca in the melt and glass varies from 6 to 8 (7 in the crystal) depending on the studies (e.g., Okuno and Marumo 1982; Binstead et al. 1985; Combes et al. 1991). The structure of cordierite melt may be related closely to that of its respective crystalline form at the melting temperature since its volume of fusion is small. Surprisingly, the volume of fusion for cordierite is slightly negative, which results in a negative $\partial T_f/\partial P$ slope (e.g., Newton 1972). Although, cordierite has a high-temperature polymorph (indialite), the volume of the crystalline phase listed in Table 5 was calculated for cordierite. Thus, the effects of polymorphism could contribute to the observed negative volume of fusion. For cristobalite, Si still remains in fourfold coordination in the network of SiO_2 glasses and melts like in crystals (for a review, see Brown et al. 1995). In the same way, the high-temperature ^{17}O and ^{25}Mg NMR study by Fiske et al. (1994) on solid MgO up to 1300 °C suggested that subtle changes occur in bonding with increasing temperature (i.e., an increase in orbital overlap due to thermal vibrations with increasing temperature). As these authors claimed, this simple bond expansion is not likely to be analogous to changes in coordination number. Given the small volume of fusion calculated here and in light of the work of Fiske (1994), it is likely that MgO liquid has a structure close to that of the crystal.

On the other hand, the pyroxene minerals (i.e., protoenstatite and diopside), corundum, and lime are characterized by a large volume of fusion, which may reflect some differences between the structure of the crystal and the corresponding melt. In protoenstatite crystals, Mg is in sixfold or eightfold coordination but mainly fourfold coordinated Mg sites were observed in $MgSiO_3$ melts by X-ray scattering studies (Waseda and Toguri 1990). Recent MD simulations by Kubicki and Lasaga (1991) also suggest a mean coordination number for Mg close to 4, whereas Matsui (1996) proposed a number of about 5. In the same way, lower coordination numbers of the network-modifying cations (i.e., Ca and Mg) have been observed in diopside glass, in contrast to crystal (e.g., Henderson et al. 1992; Combes et al. 1991; Binstead et al. 1985). In addition, MD simulations by Matsui (1996) also suggested lower mean coordination numbers for Ca and Mg in the diopside melt compared to crystals. In contrast to corundum, various coordination numbers have been proposed for Al in molten Al_2O_3 by ^{27}Al NMR spectroscopy (e.g., Coutures et al. 1990; Poe et al. 1992a, 1992b). In the same way, the large volume of fusion calculated for lime suggests that the structure of its melt at the melting point is rather different from that of the crystalline phase; perhaps Ca is surrounded by more or less neighboring O atoms. However, the lack of spectroscopic data on amorphous lime does not allow us to make further comments.

We are aware that the interpretation of the volumes of fusion of cristobalite, corundum, lime, and periclase are more tentative because they are not based on direct measurements. Instead, the volume of their liquid phase results from extrapolations. In particular, the volume of fusion of periclase might be different from the present value if the molar volume of the melt does not behave ideally for Al-poor Mg-silicate melts. The volume of fusion of cristobalite and lime are likely to be more reliable because the molar volume of their melt phase results from extrapolations over a wide range of composition. Moreover, the discrepancy of the molar volume of SiO_2 liquid obtained from this study compared with that obtained from Bacon et al. (1960) at 1999 K leads to a difference of ~4.5% for the volume of fusion. The volume of fusion of corundum also has been calculated with the data on Al_2O_3 liquid provided by Granier and Heurtault (1983) and the disagreement between both data sets is ~10%.

Volumes of fusion are also determined from the Clausius-Clapeyron equation:

$$\partial T_f/\partial P = \Delta V_f/\Delta S_f = T\Delta V_f/\Delta H_f \quad (8)$$

where ΔS_f and ΔH_f represent the entropy and enthalpy of fusion, respectively, and $\partial T_f/\partial P$ the experimentally determined slopes of melting curves at 1 bar pressure. In Table 6, the volume of fusion from this study is compared to that calculated with the Clausius-Clapeyron equation. In addition, ΔS_f data from the literature used for such a calculation are included in Table 6. Both calculations give consistent volume of fusion for pseudowollastonite, anorthite, protoenstatite, and åkermanite, whereas diopside exhibits a greater discrepancy. Most experimental $\partial T_f/\partial P$ values have inaccuracies of a few kelvins per bar stemming from the error involved in temperature and pressure measurements, the extrapolation of higher pressures data to one bar (which exhibit a large pressure interval between the measurements), the large temperature bracketing between each experiment (i.e., generally larger than 25 K), and the possible pollution by gaseous material in high-pressure apparatus. For the minerals considered here, the entropy of fusion is known accurately. On the other hand, uncertainties in determining the volume of

TABLE 6. Comparison between the volumes of fusion for some minerals in the CaO-MgO-Al_2O_3-SiO_2 system, obtained in the present study and calculated with the Clausius-Clapeyron equation

Minerals	$\partial T_f/\partial P$	ΔS_f (J/mol·K)	ΔV_f (cc)* (cm^3/mol)	ΔV_f† (cm^3/mol)	ΔV‡ (cm^3/mol)
$Ca_2MgSi_2O_7$ åkermanite	2(2)	71.7(3)	1.4	0.873	0.5
$CaMgSi_2O_6$ diopside	13.0(4)	82.5(5)	10.7	3.589	7.1
	15.4(6)		12.7		9.1
	14.6(7)		12.0		8.4
	16.0(8)		13.2		9.6
$CaSiO_3$ pseudowollastonite	3.3(9)	31.5(10)	1.0	0.884	0.1
	2.0(11)		0.6		0.3
$MgSiO_3$ protoenstatite	12.8(12)	39.9(1)	5.1	3.348	1.7
$CaAl_2Si_2O_8$ anorthite	2.7(13)	72.7(5)	2.0	1.193	0.8
	2.5(14)		1.82		0.6

Notes: (1) = Richet and Bottinga (1986); (2) = Kushiro (1964a); (3) = Bell and Roseboom (1969); (4) = Yoder (1952) and Boettcher et al. (1982); (5) = Richet and Bottinga (1984); (6) = Boyd and England (1963); (7) = Williams and Kennedy (1969); (8) = Eggler and Rosenhauer (1978); (9) = Kushiro (1964b); (10) = Adamkovicova et al. (1980); (11) = Huang and Wyllie (1975); (12) = Boyd et al. (1964); (13) = Hariya and Kennedy (1968); (14) = calculated from the data of Goldsmith (1980).

* Volume of fusion calculated with the Clausius-Clapeyron equation.

† Volume of fusion obtained in the present study (e.g., Table 5).

‡ ΔV represents the difference between the Clausius-Clapeyron ΔV_f and ΔV_f obtained in the present study.

fusion via volume measurements of both phases result mainly from a poor knowledge of the molar volume of crystalline phases at their melting point. Fortunately, premelting effects, which have been observed calorimetrically for the present minerals by Ziegler and Navrotsky (1986), Lange et al. (1991), Richet and Fiquet (1991), and Courtial et al. (unpublished manuscript), take place within a scale much smaller than a few tens of angstroms (i.e., Richet et al. 1998). In other words, the premelting of silicate minerals does not produce anomalous changes in the volume so far, so that the extrapolation of the volume data of crystals up to the melting point is not affected by such an earlier stage of the fusion.

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