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## Thermal expansivities of supercooled haplobasaltic liquids

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**Abstract**—The thermal expansion of supercooled liquids in the haplobasaltic (anorthite–diopside) system have been determined via methods of container-based dilatometry. The expansivity data obtained in this study agree well with estimates provided by previous dilatometric determinations in the system that have relied on alternative experimental strategies. The data have been combined with high-temperature, superliquidus determinations of melt density to obtain expressions for the volume–temperature (V–T) relationships of liquids in the anorthite–diopside system. The V–T data clearly indicate a nonlinear temperature dependence of volume for all melts investigated. The variation is most striking for diopside, where the coefficient of volume thermal expansion decreases ~56% from temperatures near the glass transition to superliquidus temperatures. With increasing anorthite content, the degree of variation appears to decrease.  $An_{42}Di_{58}$  exhibits a decrease of 39% of its coefficient of thermal expansion and  $An_{98}Di_{02}$  of 33%, respectively. The expansivities obtained in this study cannot be reproduced by means of published models that are based on linear V–T relationships. They require instead a reanalysis of existing pressure–V–T equations of state models for silicate melts. Copyright © 2002 Elsevier Science Ltd

### 1. INTRODUCTION

Knowledge of the expansivity of silicate melts is a vital component in the construction of accurate pressure–volume–temperature equations of state. Accordingly, various workers (e.g., Bottinga and Weill, 1970; Bottinga et al., 1982; Lange and Carmichael, 1987, 1990; Knoche et al. 1992a,b; Lange, 1997) have contributed to the generation of thermal expansivity data and models for temperatures extant during igneous petrogenesis (see Gottsmann and Dingwell, 2000, for a summary).

During the last decade, significant experimental interest focused on the haplobasaltic system anorthite–diopside. Knoche et al. (1992a,b), by use of dilatometric techniques, proposed a nonlinear variation of liquid volume with temperature. That unexpected observation represented a challenge to our ability to predict melt volumes on the basis of multicomponent linear volume–temperature (V–T) models (Bottinga and Weill, 1970; Lange and Carmichael, 1987; Lange, 1997). Recently, newly developed dilatometric techniques (Sipp, 1998; Gottsmann et al., 1999) have been applied to derive directly the supercooled thermal expansivities of the haplobasaltic system (Gottsmann and Dingwell, 2000; Toplis and Richet, 2000). Despite the major differences between these experiments, the thermal expansivities of supercooled diopside liquids—resulting from all three methods—are entirely consistent with each other. Moreover, the combination of these low temperature expansivity data with thermal expansivities obtained at superliquidus conditions (Lange and Carmichael, 1987; Knoche et al., 1992a,b) has clearly confirmed the nonlinear temperature dependence of diopside liquid expansivities. As such, the results of all direct dilatometric investigations of diopside melt expansivity stand in clear contrast to the predictions of linear V–T relationships.

The present study is a further contribution in directly determining supercooled liquid expansivities by container-based dilatometry. Here we provide data on two further compositions within the system anorthite–diopside (AnDi): the 1-bar eutectic composition  $An_{42}Di_{58}$  and  $An_{98}Di_{02}$ , which were chosen to complete our picture of melt expansivities in the haplobasalt system.

We compare our results to existing thermal expansivity data to determine the V–T relationship from superliquidus through supercooled liquid to near-glass transition temperatures.

### 2. EXPERIMENTAL METHODS

#### 2.1. Sample Preparation

Anorthite and diopside starting glasses were synthesized from  $SiO_2$ ,  $CaCO_3$ ,  $MgCO_3$ , and  $Al_2O_3$  mixes. These powders were dried at 120°C for 24 h before weighing. They were subsequently ground and mixed, then fused in a platinum crucible at 1650°C for anorthite and 1500°C for diopside. After fusion, the melts were poured onto a stainless steel plate for cooling. Weighing of the samples before and after melting provided a check on the complete volatilization of  $CO_2$  from the carbonate powders. The cycle of grinding and fusion was repeated three times to ensure homogeneous starting glasses.

$An_{42}Di_{58}$  and  $An_{98}Di_{02}$  glasses were generated by mechanically mixing powders of anorthite and diopside starting glasses, melting them, and pouring the resultant melt onto a stainless steel plate. These glass samples were then analyzed by electron microprobe to check their composition and homogeneity. The electron microprobe analyses of the materials before the experiments (all within error of the nominal compositions) are listed in Table 1, together with the chemical compositions of those samples investigated within the system anorthite–diopside by other authors. Because of subtle chemical variations of the samples investigated by individual workers, the results from our dilatometric investigations are reported both as molar and specific units.

Glass samples for the experiments were carefully drilled with a diamond corer. The cores measured 8 mm in diameter and were cut to lengths of ~8 mm to obtain right cylinders. The ends of the drilled and cut cylinders were then ground and polished to 5- $\mu$ m surface roughness to ensure good initial mechanical contact with the container at room temperature. Samples thus prepared were dried at 90°C and stored in a desiccator until use in the dilatometers.

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Table 1. Chemical composition (wt%) of investigated samples.

Study	SiO <sub>2</sub>	CaO	MgO	Al <sub>2</sub> O <sub>3</sub>	Total	gfw <sup>a</sup>
<b>Diopside</b>						
Gottsmann and Dingwell (2000) reanalyzed	56.38 (0.67)	25.67 (0.20)	17.68 (0.13)	0.28 (0.02)	1.1.43	54.426
Knoche et al. (1992a,b) <sup>a</sup>	56.46 (0.24)	25.54 (0.11)	18.00 (0.16)	—	99.81	54.297
Lange (1997) <sup>b</sup>	55.23 (0.08)	26.51 (0.04)	18.25 (0.06)	—	—	54.208
Toplis and Richet (2000)	55.91 (0.16)	25.27 (0.24)	18.83 (0.12)	—	100.01	54.140
Stoichiometric	55.5	25.9	18.6	—	—	54.141
<b>Anorthite<sub>42</sub>-diopside<sub>58</sub></b>						
This study <sup>a</sup>	50.37 (0.24)	23.57 (0.11)	10.46 (0.14)	15.53 (0.09)	99.65	59.840
Toplis and Richet (2000)	49.63 (0.29)	24.59 (0.18)	10.08 (0.17)	14.80 (0.07)	100.01	54.140
Stoichiometric	50.3	23.5	10.8	15.4	—	59.695
<b>Anorthite<sub>98</sub>-diopside<sub>02</sub></b>						
This study	43.32 (0.29)	20.41 (0.22)	0.44 (0.02)	35.83 (0.10)	98.85	69.099
Stoichiometric	43.45	20.31	0.37	35.97	—	69.165

<sup>a</sup>Gram formula weight.

<sup>a</sup> Data from microprobe analysis normalized to 100 wt%, accelerating voltage 15 kV (15 nA), peak count time 10 s, 5- $\mu$ m defocused beam; glass/mineral standards: olivine–melilite basanite glass (Si, Al, Mg), synthetic wollastonite (Ca). Total quoted as original analysis total.

<sup>b</sup> Data from Lange (1997) based on wet chemical analysis.

## 2.2. Dilatometry

Container-based dilatometry (Gottsmann et al., 1999) using two different experimental setups was employed to derive the supercooled liquid expansivities of the compositions investigated. During all measurements, the sample resided within a cylindrical metal container composed of a cylindrical sleeve and two end pieces (Gottsmann et al., 1999; Gottsmann and Dingwell, 2000). Experiments on An<sub>42</sub>Di<sub>58</sub> were performed with a Netzsch TMA 402 quartz-rod dilatometer in a vertical configuration. The dilatometer components have been described in detail previously (Webb et al. 1992; Gottsmann et al. 1999; Gottsmann and Dingwell, 2000). The dilatometer was calibrated against a standard single crystal of corundum. The reference expansivity data are taken from the National Institute of Standards and Technology data sheet.

Investigations on An<sub>98</sub>Di<sub>02</sub> were performed with a NETZSCH DIL 402 C dilatometer in a horizontal configuration. The sample assembly is supported on a polycrystalline Al<sub>2</sub>O<sub>3</sub> tube-type sample holder connected to a measuring head. The push rod (manufactured from polycrystalline Al<sub>2</sub>O<sub>3</sub>) maintains continuous contact with the sample assembly during the measurement. The push rod is fixed and mounted into a horizontally movable metal block that passes through a horizontally mounted, linear variable displacement transducer. The latter has been calibrated against a polycrystalline Al<sub>2</sub>O<sub>3</sub> standard. The push rod is supported by a spring, which can be adjusted to control the force exerted onto the surface of the sample assembly. This “loading” prevents the liquid from expanding without fully filling the hollow cylinder. To maintain a cylindrical geometry of the expanding liquid, we set the force to equal 30 cN. After the experiments the sample assemblies were cut to confirm complete container wetting of the sample and the absence of crystallization and vesiculation.

The precision and accuracy of the measured volumes are  $\pm 0.1$  and  $\pm 0.2\%$ , respectively. These result in an error of less than 4.0% for the quoted thermal expansivities. All experiments were conducted under an inert gas atmosphere with a constant argon flow.

## 2.3. Container Setup, Sample Assembly, and Measurement Protocols

The container materials and experimental setups used for investigations on An<sub>42</sub>Di<sub>58</sub> exactly match those reported in Gottsmann and Dingwell (2000). For experiments on An<sub>98</sub>Di<sub>02</sub> we used containers machined from 99.9 wt% Ni metal (see Gottsmann et al., 1999). The coefficients of thermal expansion of the container materials in use were individually determined with the same dilatometers.

Figure 1 shows the two different experimental setups used during the present study. The inner diameter of the hollow metal cylinder in both

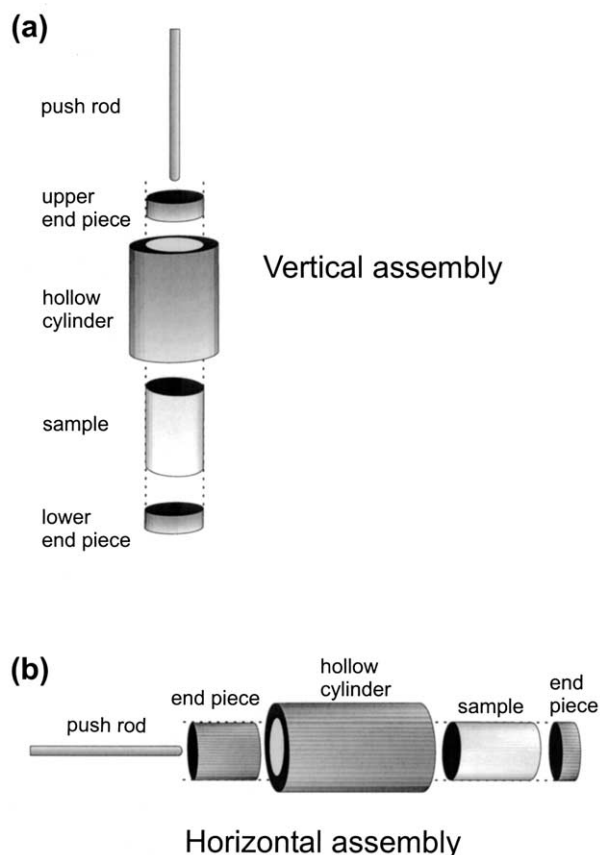


Fig. 1. Schematic illustration of the container assemblies used for the containment of liquid samples during the determination of their liquid thermal expansivity. The inner dimensions of the metal container precisely matches those of the ground and polished sample cylinder at room temperature. The end pieces are free to move and record as an assembly length change the combined expansion of the sample and the container as a function of temperature above the glass transition curve. (a) Sample assembly during vertical dilatometry. (b) Sample assembly during horizontal dilatometry. See text for details.

setups matches precisely the diameter of the sample and of the two end pieces at room temperature. The total assembly length at room temperature was  $\sim 12$  mm for experiments on  $An_{48}Di_{52}$  and  $\sim 16$  mm for  $An_{98}Di_{02}$ . Both cylindrical end pieces used for investigations on  $An_{48}Di_{52}$  measured  $\sim 2$  mm (Fig. 1a). For experiments on  $An_{98}Di_{02}$  we enlarged the end piece on which the push rod rests during the measurement, to 6 mm in length (Fig. 1b).

This modification in the sample assembly is an improvement of our method applying horizontal dilatometric techniques to prevent the end piece from possible tilting and blocking the sample expansion. It has no further effects on the precision or accuracy of the method.

Container-based dilatometry benefits from sample collapse at super- $T_g$  temperatures, which is precisely the feature whereby unconstrained sample dilatometry, taken in isolation, fails, in the determination of supercooled silicate liquid expansivities. At temperatures within the glass transition, the constrained sample starts to collapse gravitationally, trying to fill the space provided by the temperature-dependent expansion of the cylinder. To allow total and quantifiable sample collapse in experimental temperature and time, a temperature–time window had to be found in which the sample viscosity was low enough to allow intimate space-filling wetting of the sample to the container-walls within experimental time frames. In addition, the temperature had to be low enough to prevent sample crystallization. For  $An_{42}Di_{58}$  a maximum temperature of  $\sim 975^\circ\text{C}$  was found to be adequate because the sample viscosities are  $< 10^{5.5}$  Pa s (Tauber and Arndt, 1987) and the time interval for total sample collapse is on the order of tens of minutes. For  $An_{98}Di_{02}$ , a maximum temperature of  $930^\circ\text{C}$  run during dilatometry could be attained without any signs of crystallization during the run time of the experiment. In addition, further V-T data was derived for both compositions at significantly higher viscosities and lower temperatures. Further details are provided in the following sections.

### 2.3.1. $An_{42}Di_{58}$

Two different isothermal collapse experiments were conducted using the  $An_{42}Di_{58}$  composition. Experiment 1 consisted of a 30-min dwell experiment at  $973^\circ\text{C}$  after a 5-K/min heating procedure from room temperature into the supercooled liquid state. The sample volume was calculated from the constant elongational signal after a 15-min dwell time.

Experiment 2 involved the heating of the assembly at 5 K/min into the supercooled region to  $940^\circ\text{C}$  followed by a isothermal segment of 60 min dwell time. Then the assembly was rate cooled at 5 K/min to  $804^\circ\text{C}$ , again followed by a isothermal segment of 60 min. The volumes at 940 and  $804^\circ\text{C}$  were calculated from constant elongational signals obtained toward the end of both dwell segments. Both experiments were repeated to estimate the precision of the expansivity data.

Our study and that of Toplis and Richet (2000) involve the same sample material for  $An_{42}Di_{58}$ . Hence, for the first time, it is possible to cover a temperature interval of more than 210 K within the supercooled liquid range to determine liquid expansivities by applying two different techniques at two independent laboratories on the precisely the same composition.

### 2.3.2. $An_{98}Di_{02}$

Initial attempts to determine anorthite supercooled liquid expansivities failed as a result of crystallization during the experimental runs. We decided to circumvent this problem by doping the An with a few percent of Di. Thus, the  $An_{98}Di_{02}$  composition was chosen to prevent crystallization during the course of our experiments. After heating the assembly at 5 K/min across the glass transition a first isothermal collapse experiment was conducted at a temperature of  $872^\circ\text{C}$ . A constant elongational signal approached after  $\sim 18.5$  h of isothermal run time. The sample volume at this temperature was calculated from the elongation data acquired after another 7 h of isothermal dwelling during which no change in the constant elongational signal was observed. Subsequent to this first isothermal hold, the assembly was rate-heated at 1 K/min to a temperature of  $897^\circ\text{C}$  followed by a second isothermal experiment. After 10 h of isothermal run time, a constant signal was obtained. Again, the volume was calculated from the elongational data after another 11 h dwell. A third isothermal experiment was conducted after heating the assembly at 1 K/min subsequent to the

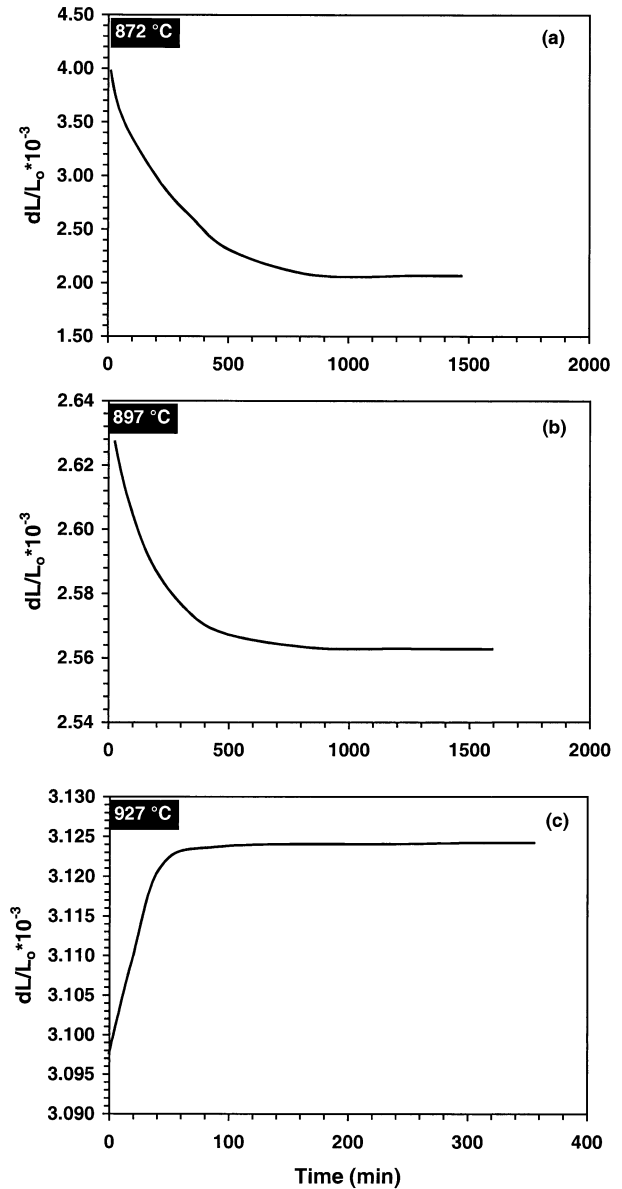


Fig. 2. The evolution of the sample assembly expansion with time during the three isothermal experiments on  $An_{98}Di_{02}$ . The thermal expansion is expressed as a dimensionless length change ( $dL$ ) with respect to the initial assembly length at room temperature ( $L_0$ ). With increasing temperature from  $872^\circ\text{C}$  (a) to  $927^\circ\text{C}$  (c), both the degree of sample collapse and the time required to completely fill the space provided by the container expansion are decreasing.

second isothermal step to  $927^\circ\text{C}$ . Because of the lower viscosity and higher temperature, a constant signal was obtained after less than a 1.5-h dwell. The volume was calculated from the elongational signal extant after another 6 h of isothermal dwell. For reproducibility, checks the measurements were repeated.

## 2.4. Supercooled Liquid Volume Calculation

The intimate space-filling wetting of the supercooled liquid to the container walls during isothermal dwells yields accurate and reproducible data between  $804$  and  $973^\circ\text{C}$  for  $An_{42}Di_{58}$  and  $872$  and  $927^\circ\text{C}$  for  $An_{98}Di_{02}$ . Because the volume calculations are based on directly ac-

Table 2. The volume (V), volume thermal expansivity ( $\Delta V/\Delta T^*$ ), and coefficient of volume thermal expansion ( $\alpha$ ) of the investigated composition.<sup>a</sup>

T (°C)	Molar units			Specific units			Source
	V (cm <sup>3</sup> /mol)	$\Delta V/\Delta T \times 10^{-4}$ (cm <sup>3</sup> /mol K) <sup>b</sup>	$\alpha \times 10^{-6}$ (K <sup>-1</sup> )	V (cm <sup>3</sup> /g)	$\Delta V/\Delta T \times 10^{-6}$ (cm <sup>3</sup> /g K) <sup>b</sup>	$\alpha \times 10^{-6}$ (K <sup>-1</sup> )	
Anorthite <sub>42</sub> -Diopside <sub>58</sub>							
804	87.68 ± 0.18	88.2 ± 3.0	100.6 ± 3.7	0.36711 ± 0.0007	36.9 ± 1.3	100.6 ± 3.3	This study
940	88.88 ± 0.18	72.7 ± 2.7	81.7 ± 3.0	0.3724 ± 0.0007	30.5 ± 1.1	81.8 ± 3.1	This study
973	89.12 ± 0.18			0.37314 ± 0.0007			This study
750	87.11	92.6	106.3	0.36500	38.8	106.3	TR2000
804	87.64	59.0	67.3	0.36639	24.7	67.4	L1997
1522	91.87	59.0	64.2	0.38411	24.7	64.3	L1997
Anorthite <sub>98</sub> -Diopside <sub>02</sub>							
872	104.41 ± 0.21	55.5 ± 2.2	53.1 ± 2.7	0.37776 ± 0.0009	20.1 ± 0.9	53.1 ± 2.3	Thisstudy
897	104.55 ± 0.22	56.6 ± 2.0	54.1 ± 2.6	0.37827 ± 0.0009	20.5 ± 0.9	54.1 ± 2.0	Thisstudy
927	104.72 ± 0.22			0.37888 ± 0.0009			Thisstudy
870	103.73	63.8	61.5	0.37530	23.1	61.5	TR 2000
1500	107.10	44.6	41.6	0.38749	16.1	41.6	TR 2000
850	104.51	47.0	45.0	0.37812	17.0	45.0	KDW 1995
870	104.80	38.7	36.9	0.37917	14.0	36.9	L 1997
1500	107.23	38.7	36.1	0.38787	14.0	36.1	L 1997

<sup>a</sup> The thermal properties were calculated on a molar and specific unit basis. The specific values allow direct comparison of the data sets from this study and the studies of Knoche et al. (1995), Lange (1997), and Toplis and Richet (2000), irrespective of slight chemical or analytical variations of the investigated compositions.

<sup>b</sup> Expansivities are calculated over temperature intervals of tens of Kelvin and should therefore be referred as  $\Delta V/\Delta T$ .

quired sample elongation signals supercooled liquid expansivities can be constrained covering a temperature interval of 170 K for An<sub>42</sub>Di<sub>58</sub> and 55 K for the An<sub>98</sub>Di<sub>02</sub> composition.

The total assembly elongation during container-based dilatometry contains contributions of the sample, of both metal end pieces (simple elongation or contraction) and the container (radial expansion and contraction as a result of its geometry). The dilatometric signal hence needs to be corrected to derive true sample volumes and expansivities.

In all experiments, the coefficient of linear thermal expansion of the metals used for the containment as a function of temperature was measured with the same dilatometers with identical thermal procedures applied to the loaded container assemblies.

The molar volume are calculated from the elongational signal at the specific supercooled liquid dwell temperatures  $T_x$  and the area expansion of the base of the metal container by

$$V_{T_x} = l_x \times A_{T_0} \times (1 + 2\alpha_c \times \Delta T) \times \frac{gfw}{m_{T_0}}, \quad (1)$$

where  $l_x$  is the length of the sample at  $T_x$  derived from the total elongational signal of the assembly from which the elongational contribution of the two metal end pieces has to be subtracted.  $A_{T_0}$  is the base area of the sample which exactly matches the inner base area of the hollow cylinder at room temperature  $T_0$ .  $\alpha_c$  is the average coefficient of linear thermal expansion of the metal container at  $T_x$ ,  $\Delta T$  is ( $T_x - T_0$ ),  $m_{T_0}$  is the mass of the sample, and  $gfw$  is the gram formula weight of the sample.

Supercooled liquid expansivities are calculated over a specific temperature interval  $\Delta T_x$  with the determined V-T points  $V(T)$

$$\frac{\Delta V}{\Delta T} = \frac{V_{T_x'} - V_{T_x}}{T_x' - T_x}, \quad (2)$$

with  $T_x' > T_x$ . The combination of Eqn. 1 and Eqn. 2 gives

$$\alpha_v = \frac{\Delta V}{V_y \times \Delta T} \quad (3)$$

to determine the average coefficient of volume thermal expansion.  $V_y$  is the average of both volumes, defined by the specific temperature interval  $\Delta T_x$ .

### 3. RESULTS

Figure 2 displays the evolution of the sample assembly expansion with time during the three isothermal experiments on An<sub>98</sub>Di<sub>02</sub>. The thermal expansion is expressed as a dimensionless length change ( $dL$ ) with respect to the initial assembly length at room temperature ( $L_0$ ). With increasing temperature from 872 (cf. Fig. 2a) to 927°C (cf. Fig. 2c), both the degree of viscous sample deformation and the time required to fill the space provided by the container expansion are decreasing. The constant elongational signal expresses the complete sample collapse inside the container.

At the lower end of the temperature range covered during the experiments, total sample collapse occurs within 1000 min. An increase in temperature by 55 K is accompanied by a more than one order of magnitude faster sample collapse. The collapse behavior during the experiments on An<sub>42</sub>Di<sub>58</sub> is exactly the same as on An<sub>98</sub>Di<sub>02</sub>, although the time required for complete sample collapse at the lower end of the supercooled liquid interval is significantly smaller, as the sample already wets the container wall while being cooled down from 940°C.

The supercooled liquid volumes, expansivities, and coefficients of volume thermal expansion derived from container-based dilatometry are listed in Table 2.

An<sub>42</sub>Di<sub>58</sub> molar volumes are 87.68 cm<sup>3</sup>/mol at 804°C, 88.88 cm<sup>3</sup>/mol at 940°C and 89.12 cm<sup>3</sup>/mol at 973°C. The resulting liquid expansivities calculated via Eqn. 2 are  $88.24 \times 10^{-4}$  cm<sup>3</sup>/mol K between 804 and 940°C,  $72.73 \times 10^{-4}$  cm<sup>3</sup>/mol K between 940 and 973°C. The average liquid expansivities calculated over the entire temperature range is  $85.21 \times 10^{-4}$  cm<sup>3</sup>/mol K.

Molar volumes for An<sub>98</sub>Di<sub>02</sub> were found to be 104.41 cm<sup>3</sup>/mol at 872°C, 104.55 cm<sup>3</sup>/mol at 897°C and 104.72 cm<sup>3</sup>/mol at

927°C. The resultant average thermal expansivity over the investigated 55 K is  $56.4 \times 10^{-4} \text{ cm}^3/\text{mol K}$ .

#### 4. DISCUSSION

##### 4.1. Liquid Expansivities of the System Anorthite–Diopside

Figure 3 displays the change in molar volume ( $\Delta V$ ) as a function of a change in temperature ( $\Delta T$ ) for the supercooled liquids of the haplobasaltic system anorthite–diopside investigated by container-based dilatometry. The  $\Delta V$  and  $\Delta T$  data for diopside ( $\text{Di}_{100}$ ) is recalculated from our previous study (Gottsmann and Dingwell, 2000). The V-T relationship for all three compositions may be fitted via a linear expression reflecting a temperature-independent expansivity over the investigated temperature ranges. It is, however, noteworthy that the expansivity data (Table 2) derived for  $\text{An}_{42}\text{Di}_{58}$  yields of a smooth negative temperature dependence of supercooled liquid expansivity over the large temperature range of 170 K investigated.

Combining V-T data derived from dilatometric investigations performed within the supercooled liquid region with superliquidus volume determinations forces the consideration of a temperature dependence of liquid expansivities within the investigated haplobasaltic system anorthite–diopside.

Figure 4 is derived from of figure 4b from Gottsmann and Dingwell (2000) inasmuch as it incorporates recently published data on diopside by Toplis and Richet (2000). The specific V-T relationship of  $\text{Di}_{100}$  is displayed from the metastable liquid (Knoche et al. 1992a,b; Lange, 1997; Gottsmann and Dingwell, 2000; Toplis and Richet, 2000) to the superliquidus (Lange and Carmichael, 1987; Knoche et al., 1992a,b). The available volume and expansivity data across the liquid temperature range is best fitted by a linear function of the logarithm of temperature (°C) (Toplis and Richet 2000), resulting in a temperature dependence of diopside liquid expansivity, as proposed earlier by Knoche et al. (1992a,b). A discussion of this nonlinear dependence and reasoning regarding the apparent mismatch with data proposed by Lange (1997) was already presented in Gottsmann and Dingwell (2000). The resultant log natural fit (following Toplis and Richet, 2000) to the available specific V-T data yields

$$V(\text{cm}^3/\text{g}) = 0.1151 + 0.0364 \times \ln T (\text{°C}) \quad R^2 = 0.9935. \quad (4)$$

Figure 5a shows a combination of supercooled liquid specific volumes and expansivities of  $\text{An}_{42}\text{Di}_{58}$  derived from this study, by Toplis and Richet (2000) and by calculation from Lange's (1997) model. Volume data for  $\text{An}_{42}\text{Di}_{58}$  published by Knoche et al. (1992a,b), unfortunately cannot be compared to the present results as close inspection of their chemical data reveals that their "anorthite<sub>42</sub>–diopside<sub>58</sub>" composition does not correspond well to the 1-bar eutectic.

Despite the fact that the specific volume calculated for anorthite<sub>42</sub>–diopside<sub>58</sub> at 804°C using the model by Lange (1997) matches remarkably well with our V-T determination, there appears to be a mismatch of resultant expansivities of our data and that of Toplis and Richet (2000) with expansivities calculated from Lange (1997). The model of Lange (1997) is based on a linear expression to fit stable liquid volumes with a single

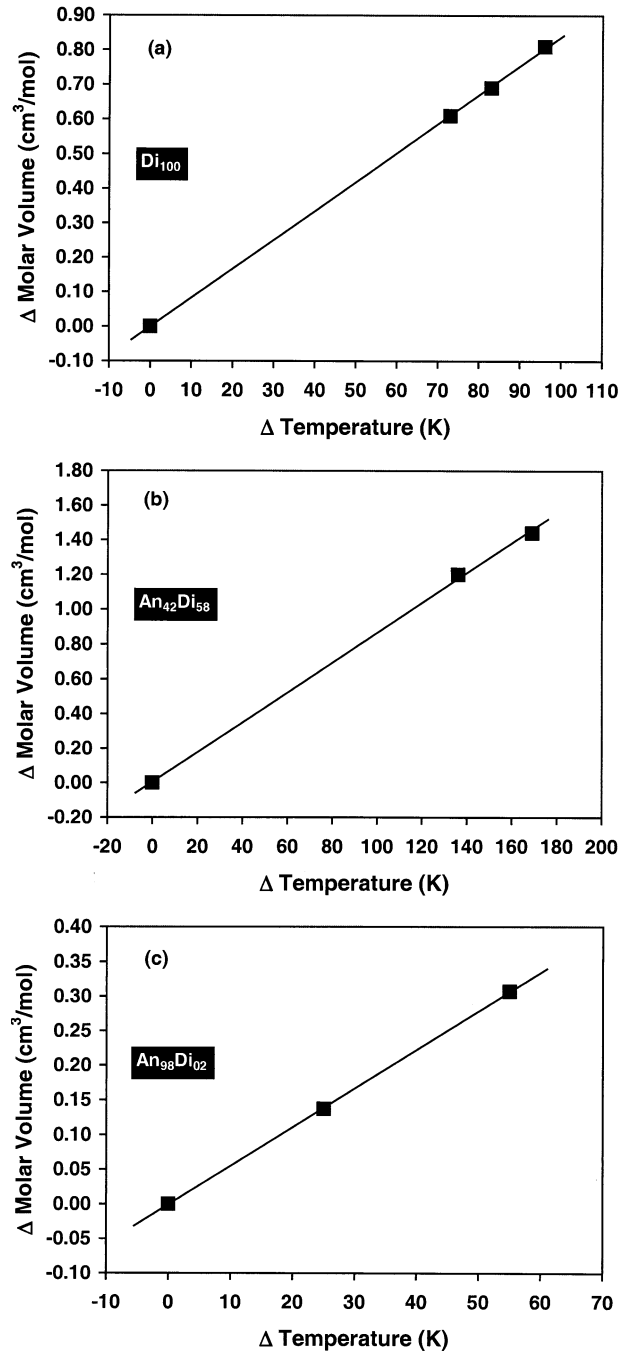


Fig. 3. The change in molar volume ( $\Delta V$ ) as a function of a change in temperature ( $\Delta T$ ) for the supercooled liquids of the haplobasaltic system anorthite–diopside investigated by container-based dilatometry. The volume and temperature changes were calculated relative to the volume determined during the lowest isothermal temperature experiment performed (cf. Table 2). (a) The data for diopside ( $\text{Di}_{100}$ ) is recalculated from our previous study (Gottsmann and Dingwell, 2000). (b) Data for  $\text{An}_{42}\text{Di}_{58}$ . (c) Data for  $\text{An}_{98}\text{Di}_{02}$ . The V-T relationship for all three compositions may, within error, be fitted via a linear expression reflecting a temperature-independent expansivity over the investigated temperature ranges. It is, however, of note that the data for  $\text{An}_{42}\text{Di}_{58}$  gives the impression of a smooth negative temperature dependence of supercooled liquid expansivity over the investigated temperature range of 170 K.

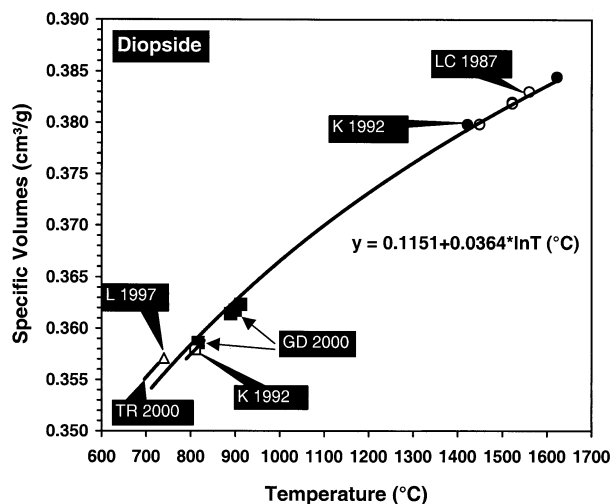


Fig. 4. The available data on specific V-T relationship of  $\text{Di}_{100}$  displayed from the metastable liquid (Lange, 1997 [L]; Knoche et al. 1992a,b [K]; Gottsmann and Dingwell, 2000 [GD]; Toplis and Richet, 2000 [TR]) to the superliquidus (Lange and Carmichael, 1987 [LC]; Knoche et al., 1992a,b). Both volume and expansivity data across the liquid temperature range are best fitted by a linear function of the logarithm of temperature (Toplis and Richet, 2000). Note that the agreement in expansivities is better than in volumes. The determination of expansivity is more direct than the determination of volume in container-based dilatometry. Modified from Gottsmann and Dingwell (2000), their figure 4b.

volume determination close to the glass transition (see discussion in Gottsmann and Dingwell, 2000). However, both our and that of Toplis and Richet (2000) include the direct determination of volume changes with temperature within the supercooled liquid and close to the glass transition, respectively. Fitting the V-T data points of both studies requires a nonlinear expression. The thermal expansivity for supercooled  $\text{An}_{42}\text{Di}_{58}$  liquid appears to decrease smoothly over a temperature range of more than 220 K covered by the dilatometric experiments by Toplis and Richet (2000) and our study (cf. Table 2). Extending the V-T relationship of liquid  $\text{An}_{42}\text{Di}_{58}$  to higher temperatures (Fig. 5b) by calculating superliquidus volumes from Lange (1997) yields the observation that the linear dependence of thermal expansivity with temperature proposed by Lange (1997) may be invalid for this composition. In contrast, a temperature-dependent expansivity appears to be a more accurate description to combine our V-T data and that by Toplis and Richet (2000) with superliquidus data (Lange and Carmichael, 1987; Lange, 1997). The specific volumes of  $\text{An}_{42}\text{Di}_{58}$  are fitted by a linear function of the logarithm (see Toplis and Richet, 2000) of temperature from the supercooled liquid to the superliquidus via

$$V(\text{cm}^3/\text{g}) = 0.1893 + 0.0267 \times \ln T (\text{°C}) \quad R^2 = 0.9979. \quad (5)$$

Comparing both V-T and expansivity data for supercooled  $\text{An}_{98}\text{Di}_{02}$  liquids from our study with data calculated from the model of Lange (1997) displays a marked discrepancy (cf. Fig. 6). The temperature-independent liquid expansivity of  $36.4 \times 10^{-4} \text{ cm}^3/\text{mol K}$  from Lange (1997) is  $\sim 35\%$  lower than our

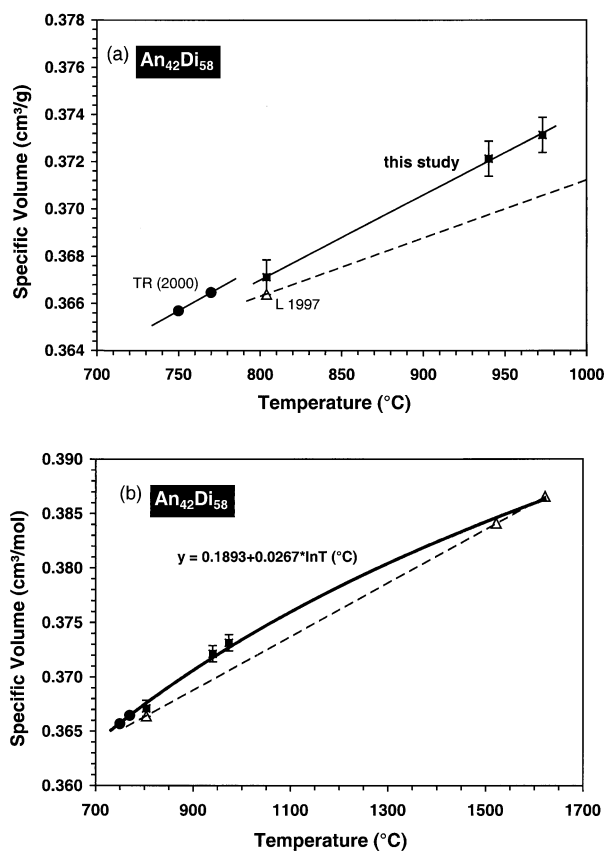


Fig. 5. Volumes of supercooled  $\text{An}_{42}\text{Di}_{58}$  melts derived by container-based dilatometry (solid squares). Also shown are preexisting data from Toplis and Richet (2000, solid circles) and the model by Lange (1997, open triangle). (a) Specific volumes and expansivities of the supercooled liquid. (b) Combination of specific supercooled liquid volumes with superliquidus data calculated from Lange (1997). The directly determined volume data from our study, from Toplis and Richet (2000), and the superliquidus volumes may be best fitted by a linear expression of the logarithm of temperature ( $^{\circ}\text{C}$ ), reflecting a temperature-dependent expansivity for  $\text{An}_{42}\text{Di}_{58}$ . The linear thermal expansivity calculated from the model by Lange (1997, broken line) poorly constrains the directly determined supercooled V-T data.

directly determined expansivity for the temperature range 872 to 927 $^{\circ}\text{C}$ . In the absence of directly determined superliquidus expansivity data for  $\text{An}_{98}\text{Di}_{02}$ , we must assume that expansivities calculated from Lange (1997) are the best estimate for the stable liquid because her high temperature model is based on direct buoyancy-based determinations by Lange and Carmichael (1987). Moreover, for diopside those data match those presented in Knoche et al. (1992a,b). Thus, we surmise a slight temperature dependence of liquid expansivities of  $\text{An}_{98}\text{Di}_{02}$ . Moreover, comparison to volume temperature data available from multicomponent models by Knoche et al. (1995) and Toplis and Richet (2000) reveal a good agreement with our supercooled liquid expansivity data (Fig. 6; Table 2).

#### 4.2. Variations of Coefficients of Volume Thermal Expansion

Figure 7 shows a compilation of coefficients of volume thermal expansion as a function of temperature for  $\text{Di}_{100}$ .

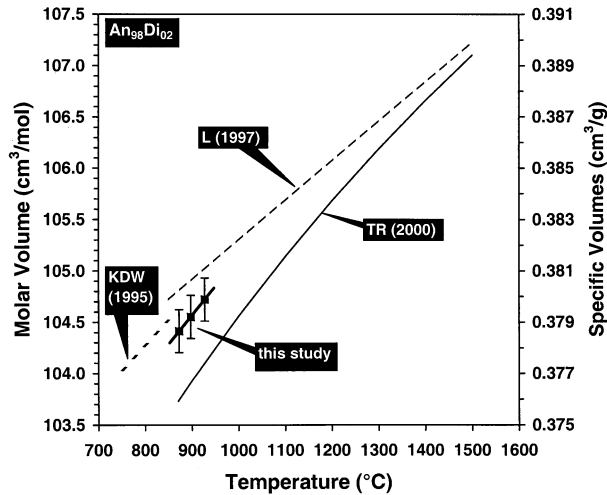


Fig. 6. A comparison of both V-T and expansivity data for supercooled  $An_{98}Di_{102}$  liquids from our study with data calculated from models by Lange (1997), Knoche et al. (1995), and Toplis and Richet (2000). The supercooled liquid expansivity data from Lange is  $\sim 35\%$  lower than our directly determined data. The expansivities of the supercooled liquid calculated from both Knoche et al. (1995) and Toplis and Richet (2000) are in good agreement to our data. Assuming that superliquidus expansivities calculated from Lange (1997) are currently the best estimate for the stable liquid because her high-temperature model is based on direct V-T determinations by Lange and Carmichael (1987), we infer a temperature dependence of liquid expansivities of  $An_{98}Di_{102}$ .

$An_{42}Di_{58}$ , and  $An_{98}Di_{102}$ . On the bases of the available data, there appears to be compelling evidence for a variation of thermal expansivity with temperature within the investigated system. The variation is most striking for  $Di_{100}$  (cf. Knoche et al. 1992a,b; Gottsmann and Dingwell, 2000; Toplis and Richet 2000), where the coefficient of volume thermal expansion decreases  $\sim 56\%$  from temperatures near the glass transition to superliquidus temperatures and stands in sharp contrast to the constant value of thermal expansivity proposed by Lange (1997) (e.g., Gottsmann and Dingwell, 2000; Toplis and Richet, 2000). With increasing anorthite content, the degree of variation appears to decrease (cf. Fig. 8.  $An_{42}Di_{58}$  exhibits a decrease of 39% of its coefficient of thermal expansion and  $An_{98}Di_{102}$  of 33%, respectively. Both values are based on the difference of directly measured coefficients of thermal expansion (this study and Toplis and Richet, 2000) and the superliquidus data proposed by Lange (1997). The decrease proposed for  $An_{98}Di_{102}$  is very similar to the decrease calculated for  $An_{100}$  by comparing data by Toplis and Richet (2000) with the model of Lange (1997). A log natural fit to combine our specific supercooled liquid volumes of  $An_{98}Di_{102}$  with superliquidus data calculated from the model by Lange (1997) data yields

$$V(\text{cm}^3/\text{g}) = 0.2586 + 0.0176 \times \ln T (\text{°C}) \quad R^2 = 0.9991.$$

(6)

## 5. CONCLUSIONS

The combination of directly determined supercooled liquid expansivities (our studies and those of Toplis and Richet, 2000)

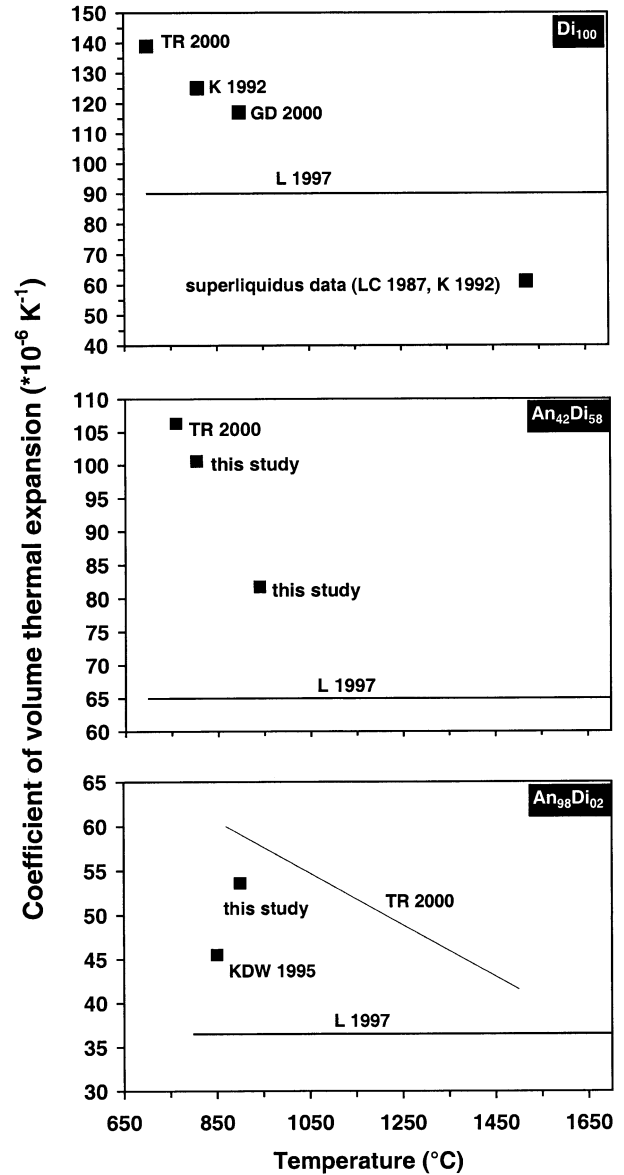


Fig. 7. Available data on coefficients of volume thermal expansion of the investigated compositions. Data on diopside,  $An_{42}Di_{58}$ , and  $An_{98}Di_{102}$  are from this study; Gottsmann and Dingwell (2000) (GD), Toplis and Richet (2000) (TR), Knoche et al. (1992) (K), Knoche et al. (1995) (KDW), Lange and Carmichael (1987), and Lange (1997). The discrepancy of low and high temperature data for  $Di_{100}$  is clearly visible and was discussed in detail in Gottsmann and Dingwell (2000) and Toplis and Richet (2000). Data on  $An_{42}Di_{58}$  also show a pronounced negative temperature dependence of liquid expansivities from glass transition to superliquidus temperatures. The temperature-independent thermal expansivity proposed by the model of Lange (1997) for  $An_{98}Di_{102}$  cannot reproduce our directly determined supercooled liquid expansivity. Comparison of our expansivity data to data derived from the models by Knoche et al. (1995) and Toplis and Richet (2000) reveals good agreement.

and superliquidus data for the haplobasaltic system anorthite–diopside confirms the marked temperature dependence of liquid expansivities as proposed by Knoche et al. (1992a,b) a decade ago. Combining container-based dilatometry (this study) and annealing techniques (Toplis and Richet, 2000) with buoyancy-

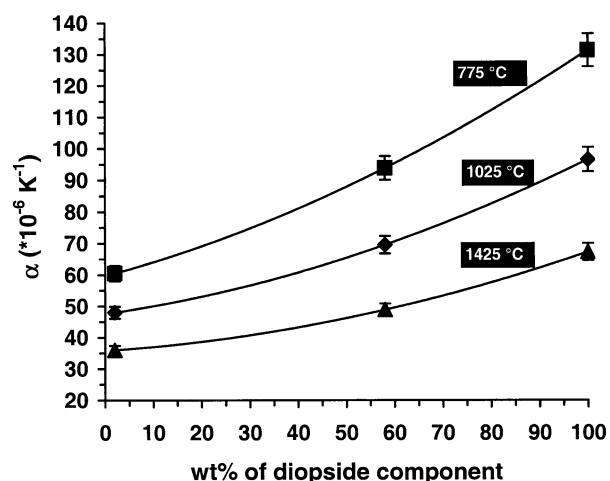


Fig. 8. The variation of the coefficient of volume thermal expansion ( $\alpha$ ) within the system anorthite–diopside. The data are calculated from our log natural fits to available V-T data (Eqns. 4 to 6) at three reference temperatures from the supercooled liquid to superliquidus temperatures (775, 1025, and 1425°C). There seems to be a positive correlation of the coefficient with increasing diopside content at the respective reference temperatures. In addition, on the bases of these data, we propose an increasing temperature dependence of liquid expansivities with increasing diopside content within the haplobasaltic system anorthite–diopside, as suggested earlier by Knoche et al. (1992a,b) and recently confirmed by Toplis and Richet (2000).

based superliquidus determination is hence proposed as an appropriate means to directly quantify the V-T relationship of silicate melts over the temperature range relevant for magmatic processes. The direct quantification of thermal expansivities over substantial temperature intervals results in a decrease of errors associated with the extrapolation of V-T data beyond their calibration from superliquidus to glass transition temperatures. We propose that multicomponent models that are based on linear V-T relationships for silicate melts be carefully re-evaluated. Low-temperature expansivities cannot be ignored because many volcanic processes occur at temperatures far below liquidus. For example, the vitrification and fragmentation of basaltic magma during submarine eruptions may take place at temperatures as low as 700°C (e.g., Wilding et al., 2000). Accurate knowledge of the V-T relationship of supercooled basaltic liquids is of great importance to precisely determine melt rheology during such processes and construct their equations of state. Toward this end, container-based dilatometric investigations on the thermal expansivities of supercooled basaltic liquids are currently under way.

Finally, knowledge of the structural processes responsible for the temperature dependence of thermal expansivity would clearly help to clarify the kinetics of nonlinear expansion of the investigated melts. Unfortunately, such a theoretical framework has not yet been forthcoming.

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