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Viscosity–temperature relationships at 1 atm in the system diopside–anorthite

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Abstract

Laboratory measurements of the viscosities of nine compositions on the diopside–anorthite join were made with a concentric-cylinder viscometer at temperatures between approximately 1200 and 1600°C in air. Viscosities were measured both above the liquidus and in the supercooled liquid region. Viscosities were independent of shear rate, indicating Newtonian viscous behavior for the melts. Viscosities decreased with increasing temperature and, at constant temperature, they decreased with increasing amounts of diopside component in the mixtures. The temperature dependence of the viscosity above the liquidus was fitted to an Arrhenius relationship from which activation energies for viscous flow, ranging from 61 kcal/mole for a melt of anorthite composition to 38 kcal/mole for a melt of diopside composition, were derived. Viscosities over the entire range of melt and supercooled liquid temperatures were fitted by the method of least squares to the Fulcher equation. The fit was better than 0.02 in log viscosity.

The present experimental results are systematically lower at any temperature than the earlier measurements of Kozu and Kani (1935). Viscosity is strongly dependent on the amount of alumina in the melt and on temperature. As diopside is added to anorthite melt, there is a modification of the three-dimensional network structure in favor of a more depolymerized structure. Activation energies for viscous flow, however, suggest that this change does not take place gradually across the join and that there are fundamental differences in the flow properties of liquids of diopside composition compared to alumina-bearing melts along the join.

Introduction

Bowen (1915) selected the ternary system diopside–anorthite–albite to illustrate the crystallization of haplobasaltic and haplodioritic magmas. Since that time considerable attention has been given to the phase relationships (*e.g.*, Osborn, 1942; Schairer and Yoder, 1960; Wyllie, 1963; Kushiro and Schairer, 1969; Kushiro, 1973) and more recently to the thermochemistry (*e.g.*, Weill *et al.* 1980; Navrotsky *et al.*, 1980; Hon *et al.*, 1981) of this classic system. In contrast, much less attention has been focused on other petrologically-important properties such as the viscosity and density of melts in the system.

A knowledge of the viscosity of silicate melts and magmas is important to the understanding of the generation, transport and emplacement of igneous rocks (*e.g.*, Shaw, 1965; Spera, 1980). Melt viscosities can also provide information about melt structure (*e.g.*, Bockris and Lowe, 1954; Bottinga and Weill, 1972; Kushiro, 1980; Mysen *et al.*, 1980). For these reasons, and because viscosities for this system by Kozu and Kani (1935) appeared to be systematically high (Scarfe *et al.*, 1979), a study of viscosity–temperature relationships along the binary joins and in the ternary system was begun in conjunction with structural investigations on quenched melts (glasses) with Raman and infrared spectroscopy. This paper describes viscosity results for the join diopside–anorthite over the temperature range 1200–1600°C, which for all compositions includes both the region above the liquidus and part of the supercooled region below the liquidus. The objectives were to obtain improved data over a wider temperature range than results previously published, and to attempt to interpret the results in terms

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of structural changes in the melts as a function of temperature and composition.

Experimental method

Starting mixtures were prepared in 650 g batches from reagent grade oxides, carbonates and purified quartz sand. Melts free from bubbles and crystals were obtained by melting at approximately 100°C above the liquidus temperature of each composition. Melts were made in platinum crucibles in an electrically-heated furnace with SiC resistance elements, and were stirred for approximately two hours to assure homogeneity. The melts were then poured directly into a 10.5 × 5.5 cm diameter crucible, which was used for viscosity measurements. The homogeneity and compositions of the quenched melts (glasses) were verified by electron microprobe analysis.

Viscosities were measured with a concentric-cylinder viscometer, which uses a platinum–10% rhodium inner cylinder 5 cm long and 1.2 cm in diameter, with conical ends. The inner cylinder rotates and the resultant torque is measured and converted to a millivolt signal. The apparatus was calibrated with NBS standard lead-silica glass SRM 711, for which the viscosity–temperature relationship is accurately known. The viscosities are accurate to ±5% with a precision of ±1%, and temperatures have uncertainties of ±1°C. Further details of the design, calibration procedure and operation of the viscometer are being published elsewhere.

Measurements were usually taken at 25 or 50°C intervals after a stabilization time at each point of approximately one hour. Measurements were routinely performed during cooling from 1600 to 1200°C, but some measurements were also made during heating. There were no measurable differences in the viscosities determined along these two thermal paths. Viscosities were independent of the rotational speed of the inner cylinder, indicating Newtonian viscous behavior. This conclusion is in accord with the observation that most silicate melts of geological interest show Newtonian behavior at temperatures above their liquidi (Shaw, 1969; Murase and McBirney, 1973; Scarfe, 1973, 1977).

Results

The results are shown in Figure 1 and Table 1 for nine compositions along the join diopside–anorthite. Viscosities were measured over a range of temperatures above the liquidus and in the supercooled liquid region until significant crystallization intervened and measurements became time dependent. Viscosities for all compositions decrease with increasing temperature and the curves are sub-parallel to each other. For each composition, the viscosities at the liquidus temperature and at 1600°C are summarized in Table 2. At constant temperature, there is

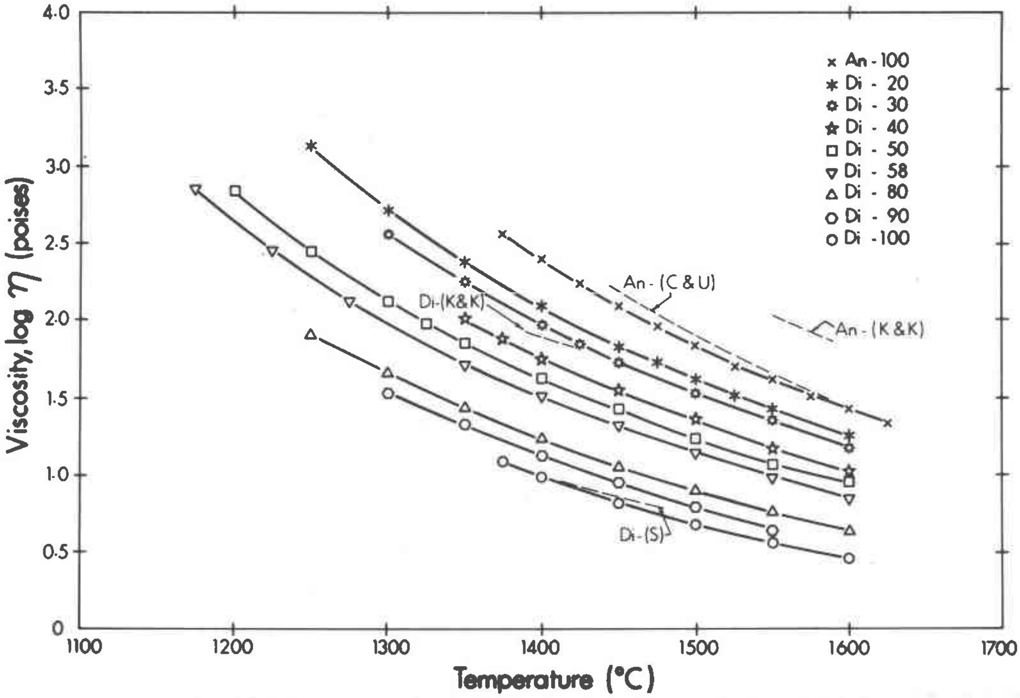

Fig. 1. Viscosity–temperature plot for compositions in the system diopside–anorthite. Dashed lines are previous determinations by Kozu and Kani (1935), Cukierman and Uhlmann (1973), and Scarfe *et al.* (1979). Liquidus temperatures for each composition are given in Table 2.

Table 1. Results of viscosity experiments for the join diopside–anorthite in logη (poises) and wt.% diopside

Temp (°C)	Di	90Di	80Di	58Di	50Di	40Di	30Di	20Di	An
1625	--	--	--	--	--	--	--	--	1.333
1600	0.465	--	0.636	0.851	0.956	1.029	1.179	1.252	1.433
1575	--	--	--	--	--	--	--	--	1.513
1550	0.559	0.648	0.759	0.990	1.074	1.194	1.358	1.434	1.625
1525	--	--	--	--	--	--	--	1.522	1.711
1500	0.678	0.800	0.898	1.146	1.240	1.370	1.531	1.625	1.841
1475	--	--	--	--	--	--	--	1.738	1.968
1450	0.821	0.957	1.057	1.329	1.432	1.553	1.730	1.836	2.101
1425	--	--	--	--	--	--	1.848	--	2.246
1400	0.992	1.128	1.237	1.518	1.630	1.756	1.980	2.098	2.402
1375	1.086	--	--	--	--	1.883	--	--	2.567
1350	--	1.327	1.442	1.721	1.854	2.015	2.258	2.384	--
1325	--	--	--	--	1.989	--	--	--	--
1300	--	1.539	1.660	--	2.132	--	2.575	2.730	--
1275	--	--	--	2.134	--	--	--	--	--
1250	--	--	1.909	--	2.457	--	--	3.140	--
1225	--	--	--	2.468	--	--	--	--	--
1200	--	--	--	--	2.846	--	--	--	--
1175	--	--	--	2.859	--	--	--	--	--

a systematic decrease in viscosities from anorthite to diopside. However, because of the temperature effect along the liquidus, viscosities at the liquidus increase away from both end-member melts to a maximum at the eutectic composition.

Compositions across the join have constant mole% SiO_2 and CaO but varying molar contents of Al_2O_3 and MgO. When the results are plotted against mole% alumina in the starting compositions (Fig. 2), for any temperature there is a linear relationship between log viscosity and alumina to 16% alumina. Beyond 16% alumina, the data for anorthite lie somewhat below the linear extrapolation. It should also be noted that the slope increases as temperature decreases, indicating that alumina has a greater effect on viscosity as temperatures approach those of the liquidus.

Viscosities above the liquidus were fitted to an Arrhenius relationship of the form

$$\log\eta = \log\eta_0 + E\eta/(2.3RT) \qquad (1)$$

where η_0 is a constant, $E\eta$ the activation energy for viscous flow, R the gas constant, and T the absolute temperature. Activation energies range from 61 kcal/mole for anorthite to 38 kcal/mole for diopside (Table 3). Because of the notable curvature in logη *vs.* $1/T$ (Fig. 3), however, the experimental data are better fitted by the method of least squares to the Fulcher (1925) equation

Table 2. Liquidus temperatures and viscosities in the diopside–anorthite system

NBS #	Diopside, wt %	Liquidus, °C	Log η (T_ℓ), poises	Log η (1600 °C), poises
K-1532	100	1391.5	1.03	0.47
K-1756	90	1368	1.25	0.52
K-1542	80	1343	1.46	0.64
K-1540*	58	1274	2.14	0.85
K-1554	50	1323	2.00	0.96
K-1545	40	1388	1.82	1.03
K-1560	30	1438	1.79	1.18
K-1547	20	1488	1.67	1.25
K-1538	0	1553	1.61	1.43

*Eutectic composition. Liquidus temperatures from phase diagram by Osborn (1942); see also Yoder (1976).

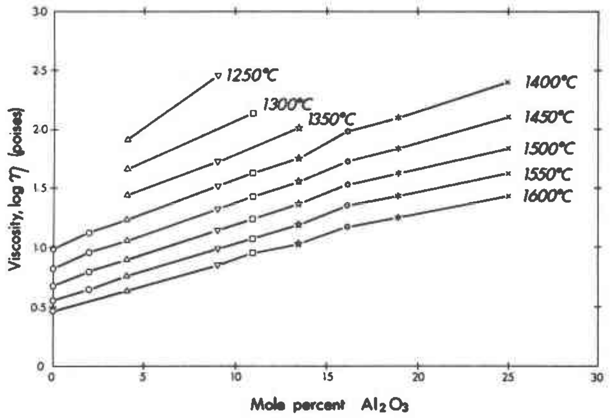

Fig. 2. Plot of logη *vs.* mole% Al_2O_3. Isotherms at 50°C intervals between 1250–1600°C.

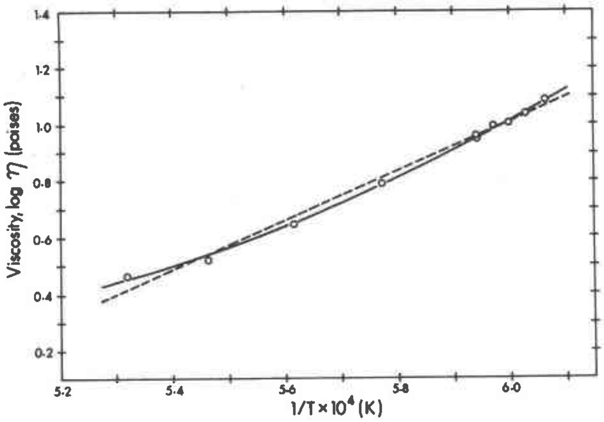

Fig. 3. Plot of $\log\eta$ *vs.* $1/T$ for diopside melt. Broken line is Arrhenius fit and solid line is Fulcher fit. Circles are experimental data points. Additional data points for diopside at 1410°C(0.942, 0.959), 1395°C(1.003) and 1385°C(1.038) are not included in Table 1 and Fig. 1.

$$\log\eta = A + B/(T - T_0) \qquad (2)$$

where T is the temperature in degrees centigrade and A, B and T_0 are constants. The Fulcher equation reproduces the experimental data for each melt to better than 0.02 in $\log\eta$ throughout the entire range of melt and supercooled liquid temperatures. An example of this fit is given in Figure 3 and the Fulcher and Arrhenius constants for all compositions are given in Table 3. By using the Fulcher constants and temperature, activation energies can be recalculated by differentiating $\log\eta$ with respect to $1/T$, which yields the expression

$$d(\log\eta)/d(1/T) = B(T/(T - T_0))^2 \qquad (3)$$

Table 3. Arrhenius and Fulcher equation constants

Diopside, wt %	$\log\eta_0$	E_η	A	B	T_0
100	-3.971	37.9	-0.729	778.7	946.6
90	-4.700	44.6	-2.642	3871	374.3
80	-4.614	44.8	-1.938	2703	548.2
58	-5.235	51.9	-1.587	2304	656.5
50	-5.143	52.0	-1.394	2093	706.4
40	-5.042	52.0	-1.945	3024	585.4
30	-5.113	53.9	-1.472	2319	727.5
20	-5.324	56.4	-1.615	2540	715.5
0	-5.637	60.5	-1.343	2123	833.0

Arrhenius constants calculated from data above the liquidus in table 1 (E_η in kcal/mole). Fulcher constants calculated from complete data set in table 1.

The activation energy may be obtained from the instantaneous slope (S_f) at any temperature by using

$$E\eta = 2.3RS_f \qquad (4)$$

Activation energies for viscous flow calculated in this way for all compositions are plotted in Figure 4. The change in the activation energy for diopside as a function of temperature is significantly different from the activation energy changes for other compositions. A more pronounced change in the structure of diopside melt as a function of temperature compared with other compositions is therefore inferred. When activation energies are plotted against mole% alumina there is a smooth increase in activation energy between 4–25 mole% alumina (Fig. 5). Diopside and the composition with 2 mole% alumina, however, do not complete this linear trend, reinforcing the observation that there is a major break between the behavior of diopside melt and alumina-bearing melts along the join.

Discussion

The present data are compared in Figure 1 with some previous determinations. For the same compositions the present results are lower than the measurements of Kozu and Kani (1935). Bottinga and Weill (1972), in a discussion of their model for the viscosities of silicate melts, noted similar discrepancies between their calculations and the results of Kozu and Kani (1935). There is, however, agreement between the present results for diopside and those of Scarfe *et al.* (1979). Results for anorthite are also in agreement with the work of Cukierman and Uhlmann (1973) and Cranmer and Uhlmann (1981).

The dependence of viscosity on the content of alumina is striking (Fig. 2). This relationship may be used to predict viscosities in the system from the mole% of alumina in the starting composition. The results indicate increased resistance to flow as the alumina content increases. Similar systematic changes have been observed in the system Na_2O–Al_2O_3–SiO_2 with replacement of Na_2O by Al_2O_3 (Riebling, 1966; Kou *et al.*, 1978).

Mysen *et al.* (1980) interpreted Raman spectroscopic data for diopside to mean that diopside melt consists primarily of chains (SiO_3^{2-}) with some monomers (SiO_4^{4-}) and sheets ($Si_2O_5^{2-}$). When alumina is added, aluminum goes into tetrahedral positions in the melt and calcium and magnesium provide charge balance (Mysen *et al.*, 1981). Under these circumstances polymerization of the melt takes places, leading to the observed viscosity increases. In contrast, spectroscopic evidence (Virgo *et al.*, 1979) suggests that anorthite melt is a completely polymerized three-dimensional structure having two types of network unit, one containing more Al than the other. Furthermore, the X-ray data of Taylor and Brown (1979) suggest that the structure of anorthite melt consists of four-membered rings of SiO_4 and AlO_4 tetrahedra.

Consequently, melt structures along the join should be a mixture of highly polymerized, three-dimensional, network structures and relatively depolymerized chain, sheet and monomer structures.

The data plotted in Figures 4 and 5 strongly suggest fundamental differences in the flow properties of diopside *vs.* alumina-bearing melts along the diopside–anorthite join. This behavior in turn implies that the structure of melts along the join changes radically where Al_2O_3 is present as a component. It is assumed, of course, throughout this discussion that the activation energy for viscous flow is a structure-sensitive parameter and that glasses do, in fact, fully represent the structure of their corresponding melts (Mysen *et al.*, 1980; Seifert *et al.*, 1981). Unfortunately, at present it is difficult to go beyond these qualitative statements because the mechanism of viscous flow in silicate melts is poorly understood.

In addition to the compositional dependence of the melt structure, it is clear that temperature-induced structural changes also occur. This latter effect is most pronounced in the case of diopside where the activation energy calculated from the Fulcher equation changes dramatically between 1400 and 1600°C (Fig. 4). This type of behavior suggests significant structural reorganization and possible polymerization of the melt as temperature decreases. It should be noted that similar effects in the anorthite-rich melts are less pronounced, suggesting that the degree of reorganization in these highly polymerized melts is small. These observations suggest caution regarding the quenching of silicate melts to glass without concern for thermal history. It may be possible to quench significantly different structures depending on the degree of superheating and thermal treatment above the liquidus.

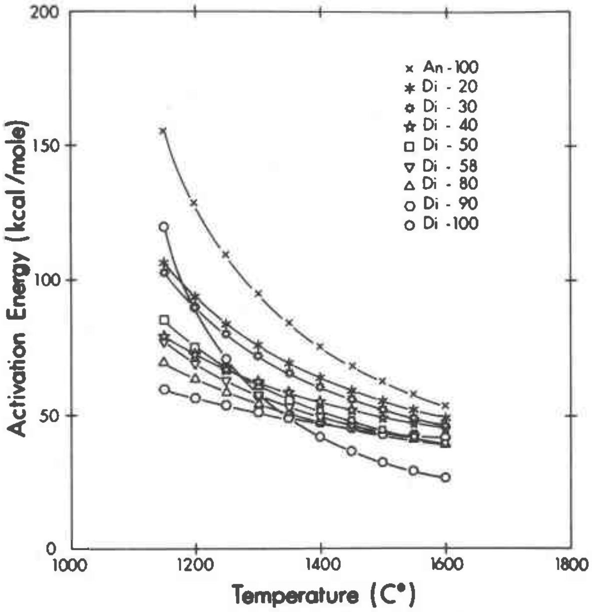

Fig. 4. Activation energy for viscous flow *vs.* temperature.

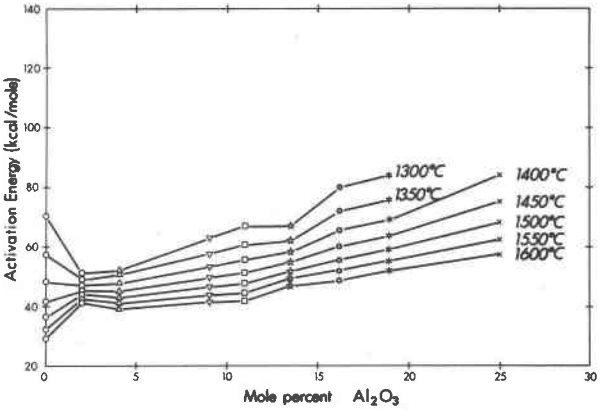

Fig. 5. Activation energy for viscous flow *vs.* mole% Al_2O_3. Isotherms at 50°C intervals between 1300–1600°C.

The present results suggest that these effects will occur more readily in relatively depolymerized melts such as diopside.

Conclusions

Viscosity–temperature relationships for the binary join diopside–anorthite show that the earlier work by Kozu and Kani (1935) requires revision. We have shown that viscosity is strongly dependent on the mole% alumina in the melt and is also temperature dependent. Structurally, the effect of adding diopside to anorthite melt is the modification or elimination of the three dimensional network structure in favor of a more depolymerized melt. As a function of temperature, implied changes in the structure of diopside melt are much larger than changes in melts with a feldspathic component. These data, along with viscosity and structural information presently being obtained on other parts of the ternary system diopside–albite–anorthite, will provide a suitable data base for the understanding of the relationship between melt structure and properties in this classic petrological system.

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