American Mineralogist, Volume 71, pages 767–771, 1986

Viscosity-temperature relationships of melts at 1 atm in the system diopside-albite

CHRISTOPHER M. SCARFE,* DAVID J. CRONIN
Center for Materials Science, National Bureau of Standards,
Washington, D.C. 20234

ABSTRACT

The viscosities of six melt compositions have been measured along the join diopside-albite with a concentric-cylinder viscometer. Measurements were made between 1600 and 1150°C; viscosities were independent of shear rate, indicating Newtonian viscous behavior. 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 88 kcal/mol for a melt of albite composition to 38 kcal/mol for a melt of diopside composition, were derived. Viscosities over the entire range of the melt and supercooled liquid temperatures were fitted by the method of least squares to the Fulcher equation. Viscosity is strongly dependent upon the mole fractions of silica and alumina and on the number of nonbridging oxygens (NBO/T) in the melt. Addition of diopside to albite melt probably causes a reorganization of the three-dimensional network in favor of a more depolymerized structure. Furthermore, activation energies indicate significant differences in the flow properties of diopside versus alumina-bearing melts across the join.

INTRODUCTION

A knowledge of the viscosity of silicate melts and magmas is important to our understanding of the generation, transport, and emplacement of igneous rocks. Melt viscosities can also provide information about melt structure.

One of the important systems of petrological interest is the system diopside-anorthite-albite. This ternary system has been extensively investigated for its phase relationships (e.g., Osborn, 1942; Schairer and Yoder, 1960; Wyllie, 1963; Kushiro and Schairer, 1969; Kushiro, 1973) and its thermochemistry (e.g., Weill et al., 1980; Navrotsky et al., 1980; Hon et al., 1981; Henry et al., 1982, 1983). However, much less attention has been paid to other petrologically important properties such as the viscosity and density of melts in the system. For these reasons, and because viscosities for this system by Kozu and Kani (1935) have been shown to be systematically high (Scarfe et al., 1983), 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. A previous paper (Scarfe et al., 1983) describes viscosity results for the join diopside-anorthite, and the present paper describes results for the join diopside-albite.

Measurements were made over the temperature range 1600–1150°C, which for all compositions includes 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 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. Melts were made in platinum crucibles in an electrically heated furnace with SiC resistance elements and were stirred for approximately 2 h to assure homogeneity. The homogeneity and composition 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 crucible used to contain the melt is 10.5 cm long by 5.5 cm in diameter. 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%; temperatures have uncertainties of ±1°C. Further details of the design, calibration procedure, and operation of the viscometer will be published elsewhere.

---

* Visiting scientist, permanent address: Experimental Petrology Laboratory, Department of Geology and Institute of Earth and Planetary Physics, University of Alberta, Edmonton T6G 2E3, Canada.

0003–004X/86/0506–0767$02.00

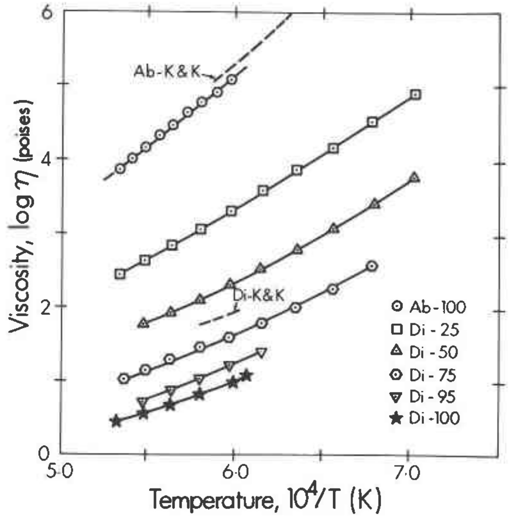

Fig. 1. Log η versus $1/T$ (in kelvins) plot for compositions in the system diopside-albite. Previous determinations for diopside and albite by Kozu and Kani (1935).

Measurements were usually taken at 25 or 50°C intervals after stabilization times of 1 h at each point. Measurements were routinely performed during cooling from 1600 to 1150°C, but some measurements were also made during heating; however, 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 geologic interest show Newtonian behavior at temperatures above their liquidi (e.g., Shaw, 1969; Murase and McBirney, 1973; Scarfe, 1973, 1977).

RESULTS

The results are shown in Figure 1 and Table 1 for six compositions along the join diopside-albite. Viscosities were measured over a range of temperatures above the liquidus and in the supercooled region until significant crytallization occurred and measurements became time dependent. Viscosities for all compositions decrease with increasing temperature, and the curves are subparallel to each other. For each composition, the viscosities at the liquidus temperature are summarized in Table 2.

Table 1. Results of viscosity experiments (log η) for the join Di-Ab (compositions in mole percent; viscosities measured in poises)

Temp (°C)	Di	95 Di	75 Di	50 Di	25 Di	Ab
1600	0.465	-	-	-	2.435	3.862
1590	-	-	1.027	-	-	-
1575	-	-	-	-	-	3.999
1550	0.559	0.724	1.148	1.760	2.627	4.151
1525	-	-	-	-	-	4.313
1500	0.678	0.884	1.290	1.927	2.833	4.460
1475	-	-	-	-	-	4.624
1450	0.821	1.040	1.465	2.103	3.064	4.775
1425	-	-	-	-	-	4.922
1400	0.992	1.211	1.590	2.305	3.306	5.080
1375	1.086	-	-	-	-	
1350	-	1.405	1.791	2.516	3.587	
1300			2.007	2.790	3.870	
1250			2.269	3.070	4.178	
1200			2.576	3.418	4.535	
1150				3.782	4.922	

Table 2. Log viscosities of melts (viscosities in poises) at liquidus temperatures in the system Di-Ab

NBS#	Diopside mole %	Liquidus* °C	Log η
K-1532	100	1391.5	1.02
K-2104	95	1378	1.30
K-1752	75	1324	1.91
K-1754	50	1272	2.94
K-1757	25	1217	4.41
K-2093	0	1118	7.5+

* from Schairer and Yoder (1960); + obtained by extrapolation. The pseudoeutectic or piercing point occurs at 10.8 mole % diopside.

For any temperature there is a smooth relationship between log viscosity and the mole fractions of SiO_2 and Al_2O_3 (Figs. 2a, 2b). Both plots, however, show a break in slope between the diopside and diopside–95 compositions. The slope also increases more sharply at the albite end and increases slightly as temperature decreases toward the liquidus; the isotherms have a closer spacing at higher temperatures.

Viscosities above the liquidus have been fitted to an Arrhenius relationship of the form

$$\log \eta = \log \eta_0 + E_\eta/(2.303RT), \qquad (1)$$

where η_0 is a constant, E_η the activation energy for viscous flow, R the gas constant, and T the absolute temperature. Activation energies range from 88 kcal/mol for albite to 38 kcal/mol for diopside (Table 3). Because of the curvature in log η versus $1/T$ for all compositions other than albite (Fig. 1), the experimental data are better fitted by the method of least squares to the Fulcher (1925) equation

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

where T is the temperature in degrees Celsius and A, B, and T_0 are constants. The Fulcher equation reproduces the experimental data for each melt to better than 0.02 log units throughout the entire range of melt and supercooled liquid temperatures. The Fulcher and Arrhenius constants are given in Table 3.

By using the Fulcher constants and temperature, activation energies can be recalculated by differentiating log η with respect to $1/T$, which yields the expression

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

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

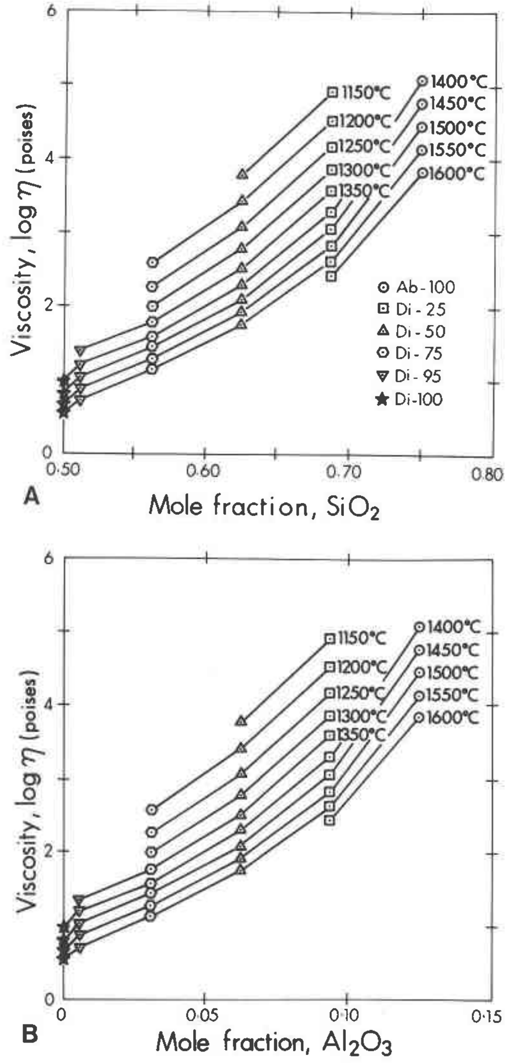

Fig. 2. Log η versus mole fraction of SiO_2 (a) and Al_2O_3 (b). Isotherms at 50°C intervals between 1600 and 1150°C.

for all compositions are plotted in Figure 3. Because of the lack of curvature of the line showing the dependence of the viscosity of albite composition on temperature (Fig. 1), the activation energy for albite does not depend on temperature (Fig. 3). The most striking difference, however, is between the change in the activation energy of diopside melt and other compositions along the join.

DISCUSSION

The present data are compared in Figures 1 and 4 with some previous determinations. For albite and diopside melts, the present results are lower than the measurements of Kozu and Kani (1935). All the data for albite melt (Fig. 4) are very close at the highest temperatures but depart appreciably at lower temperatures. Because of the systematically high values of Kozu and Kani for other compositions along this join and in the diopside-anorthite join (Scarfe et al., 1983), we believe that the higher viscosities at the lower temperatures obtained by Kozu and Kani (1935) and Urbain et al. (1982) for albite melt may need revision. The present results for albite are almost identical to those of Riebling (1966). Rotational viscometers were used in all studies except that of Riebling, where a counterbalanced sphere method was used. The results for diopside appeared in an earlier paper (Scarfe et al., 1983) and were discussed in the light of previous work at the time.

Table 3. Arrhenius and Fulcher equation constants

Diopside Mole %	log η_o	E_η	A	B	T_o
100	-3.97	37.86	-0.729	778.7	946.6
95	-4.68	45.13	-3.226	5415	180.7
75	-4.06	43.39	-1.304	2325	600.0
50	-4.67	53.54	-1.374	3191	532.3
25	-5.20	65.27	-2.859	7443	193.3
0	-6.39	87.94	-	-	-

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

The dependence of viscosity on the mole fractions of SiO_2 and Al_2O_3 is shown in Figures 2a and 2b. These relationships may be used to predict viscosities in the system, and in addition, they indicate increasing resistance to flow both with increasing SiO_2 and Al_2O_3 content and with temperatures closer to the liquidus.

According to Mysen et al. (1980, 1982), NBO/T (nonbridging oxygens to tetrahedrally coordinated cations, Si^{4+} and Al^{3+}) decreases from 2 at the diopside composition to 0 at albite. Starting from a relatively depolymerized anionic structure dominated by chains in diopside melt, with compositions increasingly rich in the albite component, the melts become more polymerized and domi-

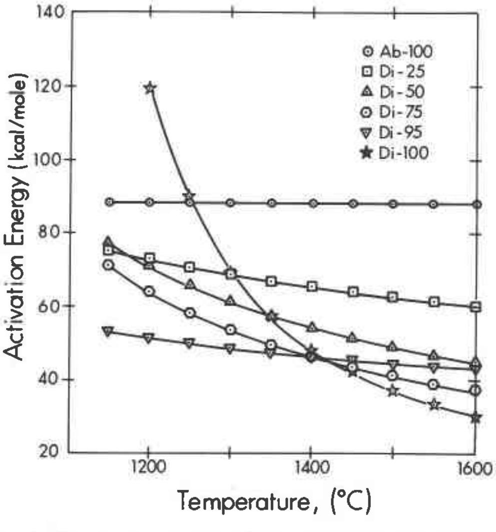

Fig. 3. Activation energy for viscous flow versus temperature.

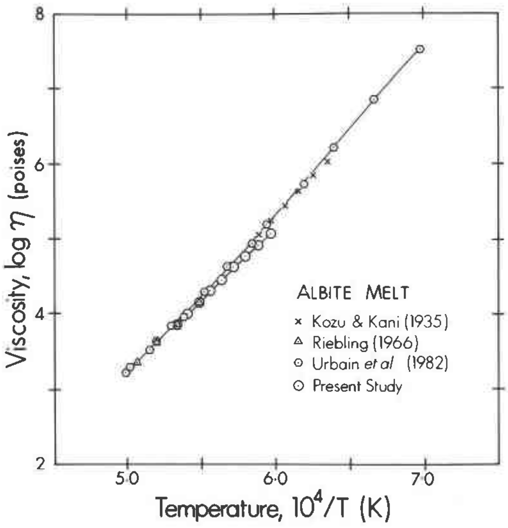

Fig. 4. Comparison of results from several studies of the viscosity of albite melt.

nated by the three-dimensional network structure of feldspar melt. These structural changes should lead to increases in melt viscosity for albite-rich melts. As expected, Figure 5 shows that there is indeed a good correlation between the structure-composition parameter NBO/T and the viscosity of melts across the join. The data plotted in Figures 2, 3, and 5, however, also suggest fundamental differences in the flow properties of diopside versus alumina-bearing melts along the diopside-albite join. Similar trends were observed in our previous paper on the diopside-anorthite join (Scarfe et al., 1983).

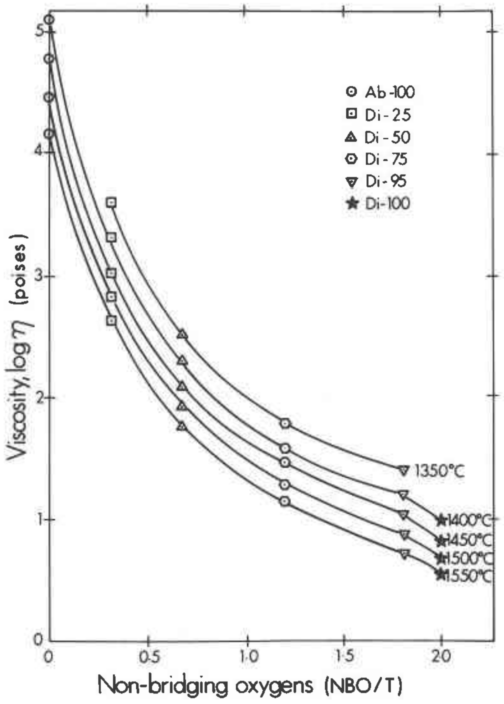

Fig. 5. Log η versus NBO/T. Isotherms at 50° intervals between 1350 and 1550°C.

In addition to the compositional dependence of melt structure, it is possible that temperature-induced structural changes also occur. Judging by the activation energies (Fig. 3), the effects are more pronounced in the case of diopside melt than they are for the albite end of the join. This type of behavior suggests significant structural reorganization and possible polymerization of the melt as temperature decreases. Furthermore, the departure from Arrhenian behavior by all melts except albite may indicate significantly different flow mechanisms for fully polymerized, 3-dimensional network liquids such as albite compared to other compositions along the join. The exceptional Arrhenian behavior of albite and its similarities with SiO_2 and GeO_2 have been discussed by Cranmer and Uhlmann (1981) and Urbain et al. (1982) and will not be discussed further here. Unfortunately, at present it is difficult to go beyond these qualitative statements because the mechanisms of viscous flow in silicate melts are poorly understood.

CONCLUSIONS

The viscosities of melts along the diopside-albite join decrease with increasing temperature and diopside component. Specifically, viscosities are dependent on the mole fractions of SiO_2 and Al_2O_3 and on the number of non-bridging oxygens (NBO/T) in the melts. All melts other than albite are slightly non-Arrhenian, and activation energies suggest different flow properties for diopside versus alumina-bearing melts along the join. The present results are systematically lower at any temperature than the earlier results of Kozu and Kani (1935).

ACKNOWLEDGMENTS

Scarfe acknowledges the hospitality of the Center for Materials Science, National Bureau of Standards, Washington, D.C. Financial support for this project was provided by NBS and Canadian NSERC grant A8394. Dale Kauffmann carried out some of the viscosity measurements, and K. Montgomery assisted with the preparation of the manuscript. D. B. Dingwell, W. Haller, and B. O. Mysen are thanked for reviews that improved the final manuscript. Experimental Petrology Laboratory, University of Alberta, publication number 120.

REFERENCES

Cranmer, D., and Uhlmann, D.R. (1981) Viscosities in the system albite-anorthite. Journal of Geophysical Research, 86, 7951–7956.

Fulcher, G.S. (1925) Analysis of recent measurements of the viscosity of glasses. American Ceramic Society Journal, 8, 339–355.

Henry, D.J., Navrotsky, A., and Zimmermann, H.D. (1982) Thermodynamics of plagioclase-melt equilibria in the system albite-anorthite-diopside. Geochimica et Cosmochimica Acta, 46, 381–391.

Henry, D.J., Mackinnon, I.D.R., Chan, I., and Navrotsky, A. (1983) Subliquidus glass-glass immiscibility along the albite-diopside join. Geochimica et Cosmochimica Acta, 47, 277–282.

Hon, R., Henry, D.J., Navrotsky, A., and Weill, D.F. (1981) A thermochemical calculation of the pyroxene saturation surface in the system diopside-albite-anorthite. Geochimica et Cosmochimica Acta, 45, 157–161.

Kozu, S., and Kani, K. (1935) Viscosity measurements of the ternary system diopside-albite-anorthite at high temperatures. Imperial Academy of Japan Proceedings, 11, 383–385.

Kushiro, I. (1973) The system diopside-anorthite-albite: Determination of compositions of coexisting phases. Carnegie Institution of Washington Year Book, 72, 502–507.

Kushiro, I., and Schairer, J.F. (1969) Diopside solid solutions in the system diopside-anorthite-albite at 1 atm. and at high pressures. Carnegie Institution of Washington Year Book, 68, 222–226.

Murase, T., and McBirney, A.R. (1973) Properties of some common igneous rocks and their melts at high temperatures. Geological Society of America Bulletin, 84, 3563–3592.

Mysen, B.O., Virgo, D., and Scarfe, C.M. (1980) Relations between the anionic structure and viscosity of silicate melts—A Raman spectroscopic study. American Mineralogist, 65, 690–710.

Mysen, B.O., Virgo, D., and Seifert, F.A. (1982) The structure of silicate melts: Implications for chemical and physical properties of natural magma. Reviews of Geophysics and Space Physics, 20, 353–383.

Navrotsky, A., Hon, R., Weill, D.F., and Henry, D.J. (1980) Thermochemistry of glasses and liquids in the systems $CaMgSi_2O_6$-$CaAl_2Si_2O_8$-$NaAlSi_3O_8$, SiO_2-$CaAl_2Si_2O_8$-$NaAlSi_3O_8$, and SiO_2-Al_2O_3-CaO-Na_2O. Geochimica et Cosmochimica Acta, 44, 1409–1423.

Osborn, E.F. (1942) The system $CaSiO_3$-diopside-anorthite. American Journal of Science, 240, 751–788.

Riebling, E.F. (1966) Structure of sodium aluminosilicate melts containing at least 50 mole% SiO_2 at 1500°C. Journal of Chemical Physics, 44, 2857–2865.

Scarfe, C.M. (1973) Viscosity of basic melts at varying pressure. Nature, 241, 101–102.

——— (1977) Viscosity of a pantellerite melt at one atmosphere. Canadian Mineralogist, 15, 185–189.

Scarfe, C.M., Cronin, D.J., Wenzel, J.T., and Kauffman, D.A. (1983) Viscosity-temperature relationships at 1 atm in the system diopside-anorthite. American Mineralogist, 68, 1083–1088.

Schairer, J.F., and Yoder, H.S., Jr. (1960) The nature of residual liquids from crystallization, with data on the system nepheline-diopside-silica. American Journal of Science, 258A, 273–283.

Shaw, H.R. (1969) Rheology of basalt in the melting range. Journal of Petrology, 10, 510–535.

Urbain, G., Bottinga, Y., Richet, P. (1982) Viscosity of liquid silica, silicates and alumino-silicates. Geochimica et Cosmochimica Acta, 46, 1061–1072.

Weill, D.F., Hon, R., and Navrotsky, A. (1980) The igneous system $CaMgSi_2O_6$-$CaAl_2Si_2O_8$-$NaAlSi_3O_8$; Variations on a classic theme by Bowen. In R.B. Hargraves, Ed. Physics of magmatic processes, 49–92. Princeton University Press, Princeton, New Jersey.

Wyllie, P.J. (1963) Effects of the change in slope occurring on the liquidus and solidus paths in the system diopside-anorthite-albite. Mineralogical Society of America Special Paper 1, 204–212.

MANUSCRIPT RECEIVED JUNE 27, 1985
MANUSCRIPT ACCEPTED JANUARY 14, 1986