

VISCOSITIES AND NUCLEATION BEHAVIORS IN THE SYSTEM ALBITE-ANORTHITE,
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A significant fraction of the lunar surface consists of anorthositic materials. Besides their direct and considerable geological interest, some of these materials have notable potential for providing the raw materials which might be used in lunar-based production of glassy objects. Indeed, some samples returned from the lunar surface (e.g., the matrix composition of the 67975 breccia) are close to those of commercial aluminosilicate glasses. As noted previously (1), the 67975 matrix composition has a usefully wide working range, and would make a fine, rather refractory commercial glass for applications where the optical absorption due to the presence of 2.5% FeO would not present a limitation.

Results obtained more recently (2), using simple differential thermal analysis with a new treatment of crystallization statistics which describes the development of crystallinity on reheating a glass, have suggested an exceptionally large barrier to crystal nucleation for anorthite, as well as for the anorthite-rich lunar composition 65016. This suggestion is based on measurements of the temperature of recrystallization upon reheating an initially-formed glass at different heating rates. The data suggest a barrier to crystal nucleation in the range of 70-75 kT at a relative undercooling ($\Delta T/T_L$) of 0.2. For comparison, the barriers to crystal nucleation directly measured for most other materials fall in the range of 45-60 kT at $\Delta T/T_L = 0.2$.

Because of the general significance of anorthite-rich lunar compositions, in areas ranging from lunar and planetary science to space manufacturing, as well as for its own terrestrial importance, an investigation has been carried out of the system anorthite-albite. This investigation has focussed attention on two areas, both of which are important in considering processes and phenomena such as glass formation, rheology, and melt vs. crystal structure. In particular, attention has been directed to the viscous flow and crystal nucleation behavior of a series of compositions in the anorthite-albite system.

The viscous flow behavior of pure anorthite has been reported (3) over a wide range of temperature (800-1600°C), and limited data are available (4) on pure albite and several anorthite-albite compositions. The data on pure anorthite are well described by the semi-empirical models of Bottinga and Weill (5) and Shaw (6). The present study was carried out on four compositions: Anorthite, An₇₅-Ab₂₅, An₅₀-Ab₅₀ and An₂₀-Ab₈₀. The crystal growth behavior of these same compositions has been determined in a companion study (7). The experimental data on liquid viscosity were obtained in the molten range using a rotating-cylinder viscosimeter; and viscosities greater than about 10⁹ poise were determined using a bending-viscosimeter. Both instruments have been described in detail previously (8), and both were calibrated using NBS reference materials. To obtain data in the fluid range at temperatures below the liquidus, the samples were superheated above the liquidus to melt out retained crystalline embryos.

The results obtained in this way indicate:

- (1) The viscosity-temperature relation for each composition.
- (2) The viscosity-temperature relation for each composition does not exhibit a simple Arrhenian temperature dependence; rather, pronounced

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curvature is seen in each of the log viscosity vs. $1/T$ relation.

(3) The viscosity-temperature relations in the fluid range for all of the compositions are well described by the semi-empirical models of Bottinga and Weill and of Shaw.

(4) The variation of viscosity with composition is relatively mild but by no means insignificant; and the pronounced differences in crystallization kinetics and ease of glass formation in this system are apparently associated in large measure with the change of liquidus temperature or melting point with composition.

The determination of the barrier to crystal nucleation for these compositions has been carried out using a technique introduced at a previous Lunar Science Conference (9). This technique is based on a determination of the times required at various temperatures to obtain detectably crystalline bodies from amorphous materials. These times-at-temperatures are used to construct curves representing loci of approximately constant volume fraction crystallized. Such data are combined with measurements of crystal growth rate vs. temperature on the same compositions to obtain the desired data on the rates of crystal nucleation.

The magnitude of the nucleation rate in each case is determined from the relation:

$$V_c/V = 1 - \exp\left(-\frac{\pi}{3} I_v u^3 t^4\right) \quad (1)$$

where V_c/V is the volume fraction of the material crystallized in a time t , I_v is the nucleation rate, and u is the crystal growth rate.

According to the classical theory of crystal nucleation, the nucleation rate for a system with a free energy of forming the critical nucleus of BkT at a relative undercooling ($\Delta T/T_L$) of 0.2 can be expressed:

$$I_v \sim \frac{a}{\eta} \exp\left(-\frac{0.0205B}{T_r^3 T_L^2}\right) \quad (2)$$

where $a \approx 10^{32} \text{ cm}^{-3} \text{ sec}^{-1}$ poise; η is the viscosity; $\Delta T_r = \Delta T/T_L$; $T_r = T/T_L$; ΔT is the undercooling ($T_L - T$); and T_L is the melting point or liquidus temperature.

Previous application of this analysis to the matrix composition of lunar breccia 70019 (9) indicate good agreement between experimental data and predictions of the classical theory of homogeneous nucleation. The barrier to crystal nucleation determined in this way was about 55 kT at a relative undercooling of 0.2. For comparison, application of the analysis to sodium disilicate indicated a smaller nucleation barrier, in the range of 45 kT at $\Delta T_r = 0.2$.

In the present study, the An-Ab samples were superheated to a temperature well above the liquidus temperature to remove any retained crystalline embryos which may be present. Following this initial heating, the samples were rapidly transferred to a second furnace maintained at a desired temperature below the liquidus and held at that temperature for a specified period of time. After the desired hold time, the samples were rapidly quenched to ambient, broken open and examined microscopically for evidence of internal heterogeneous nucleation. When such nucleation was not observed, any crystallized layer on the surface was removed and the remaining portion of the sample was crushed and analyzed using X-ray diffraction techniques. The resulting patterns were grouped into three classes with respect to the breadth of the principal diffraction peaks: (1) non-crystalline; (2) detectably crystalline; and (3) partly crystalline. Specific values of the volume fraction crystallized were assigned to each of the three classes.