SIMPLIFIED MODEL EVALUATION OF COOLING RATES FOR GLASS-CONTAINING LUNAR COMPOSITIONS. D. R. Uhlmann, H. Yinnon, Chih-yao Fang, Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Mass. 02139

The occurrence of glasses in samples returned from the lunar surface has been used to estimate the rates at which various samples cooled and to gain insight into their thermal histories. In estimating the cooling rates, use has been made of the formal theory of transformation kinetics to construct time-temperature-transformation (TTT) curves corresponding to the observed degree of partial crystallinity. The use of this approach requires information on the viscosity and crystal growth rate over a wide range of temperature, as well as detailed kinetic treatments to evaluate critical cooling rates from the experimental data.

While extensive data on viscous flow and crystallization kinetics have been obtained for a number of lunar samples of interest, measurements of this type are quite time-consuming, with the result that the necessary data are not available for many additional samples of potential interest.

In the basic approach for calculating critical cooling rates from TTT curves (Uhlmann 1972), use is made only of information at the nose of the curve—specifically, the time at the nose, \( T_N \), and the temperature of the nose, \( T_N \). According to this approach, the critical cooling rate, \( R_c \), is approximated by the relation:

\[
R_c = \frac{T - T_E}{T_N} \tag{1}
\]

where \( T_E \) is the equilibrium temperature.

In a previous paper (Uhlmann et al., 1979), a model was developed which allows estimates of \( T_N \) and \( T_E \) to be made based on limited information about the materials; and using this model together with the appropriate (but limited) data, critical cooling rates can be estimated for a large number of lunar compositions.

Application of the detailed treatment of crystallization statistics to a range of glass-forming materials has shown that the temperature at the nose of TTT curves, \( T_N \), scales approximately with the liquidus temperature, \( T_E \). In particular, for a variety of silicate compositions, one finds: \( T_N = 0.77 T_E \).

Hence knowing the liquidus temperature, it is possible to estimate the temperature of the nose of the TTT curve.

The critical cooling rate to obtain a glass is obtained from the expressions for the nucleation frequency and crystal growth rate as:

\[
R_c = \frac{A T_E^2}{\eta_N} \exp (-0.2117 B) (1 - \exp [-\frac{\Delta H_m}{RT_E}]) \tag{2}
\]

where \( A \) is a numerical constant equal to \( 1.2 \times 10^6 \) ergs \( m^3 \) \( K \); \( B \), the nucleation barrier, is expressed in units of \( kT \); \( T_E \) is the viscosity at \( T_N \); \( \Delta H_m \) is the molar heat of fusion.

Eq. (2) involves four unknowns: the viscosity at \( T_N \), the liquidus temperature, the nucleation barrier, and the molar heat of fusion. To estimate the relation between the nucleation barrier \( B \) and the heat of fusion, available data on nucleation behavior and heats of fusion for a wide variety of materials were compared. The results indicate that \( B \) and \( \Delta H_m \) are related by: \( B \approx 12.6 \Delta H_m/RT_E \).
To estimate the viscosity at $T_N$, the glass transition temperature was used as a corresponding states parameter and a least squares fit for the appropriate Vogel-Fulcher relation was obtained for flow data previously obtained on 13 lunar compositions. This resulted in an expression which described the viscosity of lunar compositions within an order of magnitude of that interpolated from measurements. This expression can be used to estimate the viscosity of a given liquid composition from a knowledge of its glass transition temperature.

In the present work, seven lunar compositions (10060, 15028, 15086, 15101, 15301, 60255 and 77017) were melted in an electric furnace in a forming gas atmosphere (95% $N_2$-5% $H_2$) at temperatures between 1400 and 1450°C. The melts were quenched on a graphite block under the same atmosphere.

The glassy bodies obtained were analyzed by differential thermal analysis to determine the liquidus and glass transition temperatures. The results are shown in Table 1, where each value represents the average of 2 to 4 separate DTA runs.

<table>
<thead>
<tr>
<th>Composition Code</th>
<th>$T_g$ (K)</th>
<th>$T_N$ (K)</th>
<th>$\eta_N$ (poise)</th>
<th>$R_c$ K sec$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>10060</td>
<td>1461</td>
<td>1125.0</td>
<td>1.6x10$^6$</td>
<td>0.78</td>
</tr>
<tr>
<td>15028</td>
<td>1468</td>
<td>1130.3</td>
<td>2.7x10$^6$</td>
<td>0.45</td>
</tr>
<tr>
<td>15086</td>
<td>1473</td>
<td>1134.2</td>
<td>7.3x10$^5$</td>
<td>1.68</td>
</tr>
<tr>
<td>15101</td>
<td>1495</td>
<td>1151.2</td>
<td>1.7x10$^6$</td>
<td>0.75</td>
</tr>
<tr>
<td>15301</td>
<td>1495</td>
<td>1151.2</td>
<td>5.0x10$^5$</td>
<td>2.55</td>
</tr>
<tr>
<td>60255</td>
<td>1668</td>
<td>1284.4</td>
<td>1.1x10$^5$</td>
<td>14.2</td>
</tr>
<tr>
<td>77017</td>
<td>1701</td>
<td>1310.0</td>
<td>5.2x10$^4$</td>
<td>31.7</td>
</tr>
</tbody>
</table>

The method used to estimate the viscosity at the nose temperature is somewhat different from that originally proposed by Uhlmann et al. (1979). The semi-empirical model of Bottinga and Weill (1972) was used to calculate viscosity values at temperatures between 1473 and 1823 K based on the compositions of the systems studied. This was justified by the very good agreement observed between viscosities calculated using the Bottinga-Weill parameters and those measured for all the lunar compositions examined in our laboratory.

A separate data point was obtained by taking the viscosity at the glass transition temperature as $10^{13}$ poise. All the viscosity points were then fitted to a Vogel-Fulcher expression using $T_g$ as a corresponding states parameter:

$$\log_{10} \eta = A + \frac{B}{T/T_g - \alpha}$$

where $A$, $B$ and $\alpha$ are constants. The best fit to the data was obtained by varying $\alpha$ from 0.6 to 1.2 and obtaining $A$ and $B$ as the linear least squares parameters for each value of $\alpha$. The $\alpha$, $A$ and $B$ values which yielded the best fit of the data points were later used to calculate the viscosity at $T_N$. 

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A detailed experimental investigation of the barrier to crystal nucleation in lunar glasses (Yinnon, et al., 1980) indicated that B values range between 60 and 76 kT*. A uniform value of 68 kT* was assumed for all systems included in this study. Using the experimentally determined relation between B and ∆H_m outlined above, ∆H_m was estimated as: 10.8 T_E cal mole⁻¹ (∆S_m ≈ 5.4R).

A summary of the estimated cooling rates for seven lunar compositions is given in Table 1. The implications of these results and comparison with previous results on other lunar compositions will be discussed in detail in the formal presentation.

REFERENCES