

SINTERING, CRYSTALLIZATION, AND BRECCIA FORMATION

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Abstract. The process of breccia formation by viscous sintering in the absence of pressure, advanced forcefully by Simonds (1973), is examined in detail. The limitations on the standard model for such sintering are considered. The competing process of crystallization is analyzed kinetically in terms of time-temperature-transformation curves corresponding to various degrees of crystallinity. The analysis is applied to Lunar Composition 15418 to illustrate the approach. The results indicate that close constraints can be placed on the thermal histories of lunar breccias, particularly breccias with modest degrees of crystallinity, from microstructural observations and kinetic measurements.

1. Introduction

Clastic or fragmental breccias represent an important and abundant rock type at landing sites on the lunar surface. The breccias returned from the Moon have substantial degree of porosity, ranging from 15 to 40 or 45%, with the pores typically about a few microns in extent. The matrix material – i.e., the material characterized by grain sizes smaller than 25μ (Chao *et al.*, 1971) – generally comprises about 20 to 60% of the breccias. In addition to the matrix, there is generally an abundance of clasts consisting of single mineral grains, fragments of igneous rocks, glass, or other breccias.

Breccias have been classified by Warner (1972) in terms of the degree of crystallization and the state of metamorphism of the matrix. According to Warner's classification, these range from low grade breccias, which have a sizable glass component and little recrystallization, to high grade breccias, which have extensive or nearly complete recrystallization and little or no glass.

Some early work, based on the results of Short (1966) and others on shock lithification in artificial explosions, suggested that the welding of lunar breccias took place by a shock lithification of unconsolidated material in the presence of relatively high dynamic shock pressures. The suggested shock pressures for such a process were in the range of 100–200 kbars.

Subsequent work by McKay *et al.* (1970), McKay and Morrison (1971), Waters *et al.* (1971) and others have indicated difficulties with this interpretation. These difficulties include the high porosity of many breccias, the absence of extensive fracturing and shock damage in most crystals, the frequent presence of original shapes and structures including some highly friable ones, and the presence of clearly accretionary structures bonded together by lightly sintered glass. It was suggested that the coherency of the breccias resulted from sintering of the fine grain matrix in a stress-free environment, rather than from a shock lithification process.

This concept was notably advanced by Simonds (1973) who adopted the standard model for viscous (liquid phase) sintering due originally to Frenkel (1945). Simonds estimated the times required for significant development of necks between particles

for different particle sizes and different viscosities. In doing this, he took an estimate of the surface tension together with the limited viscosity data available at the time for a typical Apollo 14 glass, fit the viscosity data with an Arrhenius relation to represent the viscosity at intermediate temperatures, and estimated that significant sintering would be achieved in minutes at 800°C but would require days to months or longer at temperatures of 700°C or less.

Simonds also carried out laboratory experiments on synthetic Apollo 14 glass and obtained results which were in qualitative agreement with the predictions of Frenkel's model. In particular, it was found that firmly lithified material, texturally similar to the Apollo 14 breccias, could be produced at temperatures in the range of 795–850°C. The materials produced under these conditions were cohesive solids with porosities in the range of 25% or more and slight devitrification. Higher temperatures produced materials with fewer pores and more devitrification. Devitrification took place readily at temperatures only 50°C above those needed for significant sintering in reasonable times.

Simonds also carried out some hot pressing experiments on the synthetic glass at pressures of about 500 bars. He produced materials of low porosity (0 to 5%) at 600°C and only loose powder at 560°C. The textures of the hot pressed samples did not resemble those of the lunar breccias.

Taken as a whole, the paper by Simonds presents strong evidence for stress free sintering as the mechanism of lithification of the lunar breccias. Ambiguity was left, however, concerning the time and temperature of lithification, since a given degree of sintering could be achieved by holding for different times at different temperatures.

The present study was undertaken to reduce this ambiguity. It builds upon previous work in our laboratory concerned with the crystallization behavior of representative lunar materials and the formation of lunar glasses; and uses combined information on crystallization and sintering kinetics to help elucidate the thermal histories of lunar breccias. The results described below are preliminary in character, but illustrate a promising approach to the conditions of formation of lunar breccias.

2. Model of Viscous Sintering

As noted above, the standard model of viscous sintering, due to Frenkel (1945), has been used by Simonds (1973) to describe the lithification of lunar breccias; this model will also be used in the calculations to follow. It seems appropriate, therefore to examine critically the physical assumptions of the model and to estimate the accuracy of its predictions.

It should be recognized at the outset that the Frenkel model is an approximation to the physical situation. The initial geometries of the particles are rarely known in detail; and even when the geometries are known, the hydrodynamic problem of the flows involved in sintering is a very difficult one. Further, the shapes do not remain geometrically similar as sintering proceeds, even for spherical particles; hence the

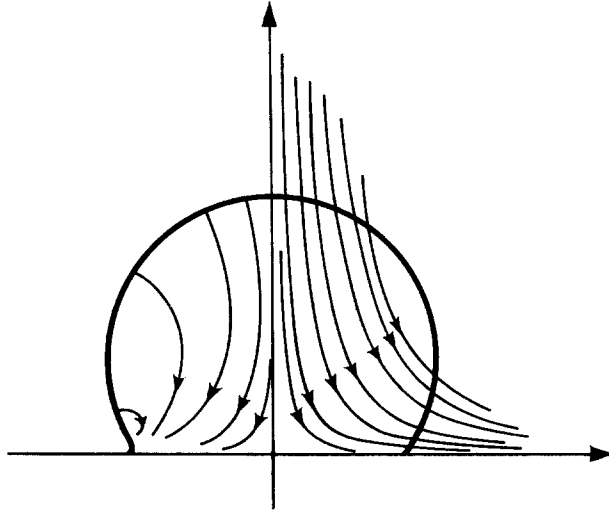


Fig. 1. Flow fields for viscous sintering (schematic). Right-hand side, uniaxial contraction assumed in standard model; left-hand side, form expected in real situations.

solutions must be repeated iteratively to obtain the time dependence of the coalescence process.

Such a procedure was not adopted by Frenkel, who displayed impressive physical insight with a clever but highly approximate theoretical attack on the problem. In particular, he considered the viscous sintering of two spheres and *assumed* a very simple form for the flow field – *viz.*, simple uniaxial contraction. The form of this flow field is illustrated in the right hand side of Figure 1. For comparison, the left hand side of the figure illustrates the expected form of the flow field. The assumption of Frenkel is obviously much in error near the regions of high curvature at the neck. Frenkel also assumed that the shape remains that of two intersecting spheres as sintering proceeds, and obtained an expression for the rate of thickening of the neck by equating the rate of change of the surface energy with the rate of energy dissipation in viscous flow calculated for the assumed flow field. The result was expressed as

$$\frac{X}{R} = \left[\frac{3\gamma t}{2\pi\eta R} \right]^{1/2}, \quad (1)$$

where X is the radius of the neck; R is the radius of the particles; γ is the surface tension; η is the viscosity; and t is the time. This result indicates that significant sintering will occur in a time t_s of the order of

$$t_s \approx \frac{\eta R}{\gamma}. \quad (2)$$

Because of the approximations used in the analysis, these expressions should be regarded as providing order-of-magnitude estimates rather than an exact description

of the sintering process. A more precise description can be obtained using the techniques of numerical analysis; but until such an analysis becomes available, use will be made of the Frenkel treatment, despite the approximations involved.

3. Crystallization and Glass Formation

The application of the sintering model to the problem of breccia formation can be particularly fruitful when combined with treatments of the competing process of crystallization. As will be seen, such a combined approach can place close constraints on the thermal histories of many breccias, particularly those which are low-grade or medium-grade in Warner's classification scheme.

The kinetics of crystallization are included in the analysis as suggested by Uhlmann (1972) in a kinetic treatment of glass formation. This treatment has been applied with success to the formation of many different glasses (Davies *et al.*, 1974), including a number of lunar compositions (Uhlmann *et al.*, 1974). In the analysis, the volume fraction, V_c/V , of a material crystallized in a time t at a given temperature is related to the kinetic constants describing the rates of crystal nucleation and growth as

$$\frac{V_c}{V} \approx \frac{\pi}{3} I_v u^3 t^4, \quad (3)$$

where I_v is the rate of nucleation per unit volume and u is the growth rate.

The nucleation rate can be measured experimentally; but its determination is not simple. In most cases, therefore, I_v is estimated theoretically. A convenient form for such estimation is

$$I_v \approx \frac{10^{31}}{\eta} \exp\left(-\frac{1.229}{\Delta T_r^2 T_r^3}\right), \quad (4)$$

where $T_r = T/T_E$, $\Delta T_r = (T_E - T)/T_E$, and T_E is the liquidus temperature. This expression assumes a nucleation barrier of 60 kT at $\Delta T_r = 0.2$, which is in accord with experimental results on a variety of liquids and inferences drawn about a number of lunar compositions (Uhlmann *et al.*, 1974; Hopper *et al.*, 1974). Implicit in Equation (4) is a neglect of nucleating heterogeneities, which seems appropriate for many breccias and is in accord with the results obtained in our laboratory on a number of lunar glasses (Hopper *et al.*, 1974). The crystal growth rate can be estimated theoretically; but in most cases, it is convenient to determine u experimentally for the particular composition of interest.

With such information about the nucleation and growth rates as functions of temperature, one can evaluate the time required at any temperature to reach a given fraction crystallized. By carrying out the evaluations for different temperatures, one can construct time-temperature-transformation (TTT) curves corresponding to a given fraction crystallized. Examples of such TTT curves corresponding to a just-detectable degree of crystallinity ($V_c/V = 10^{-6}$), constructed for nucleation barriers of 50, 60 and 70 kT at $T/T_E = 0.2$, are shown in Figure 2. The noses in such curves, representing the

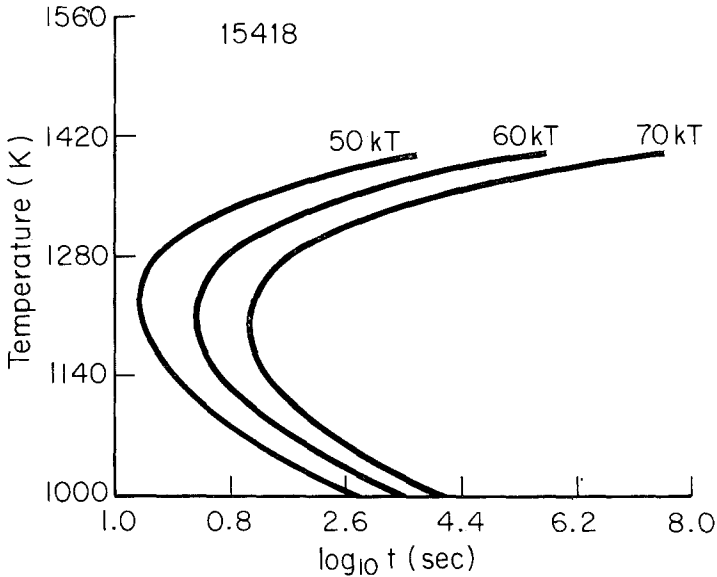


Fig. 2. Time-temperature-transformation curves for Lunar Composition 15418 calculated from measured growth rate and viscosity data together with assumed barriers to crystal nucleation at $\Delta T/T_E=0.2$ of 50 kT, 60 kT and 70 kT.

shortest times at any temperature to achieve the assumed fraction crystallized (10^{-6} in this case), reflect a competition between the driving force for crystallization (which increases with decreasing temperature) and the molecular mobility (which decreases with decreasing temperature).

Previous work in our laboratory (e.g., Uhlmann *et al.*, 1974) has used TTT curves representing a just-detectable degree of crystallinity to estimate the minimum cooling rates required to form glasses of various materials. In the present application, they will be constructed for various degrees of crystallinity and used to delineate the regions of time and temperature where materials with such degrees of crystallinity can be formed.

4. Formation of Lunar Breccias

The present kinetic approach to the problem of breccia formation involves combining the treatment of crystallization kinetics, represented by TTT curves, with that of sintering kinetics. The approach will be illustrated by the data for Lunar Composition 15418. This is a highly crystalline breccia with a very complex structure. It weighs a little more than 1 kg and is composed of about 60% matrix material and 35% clasts. The viscosity and crystal growth rate for this composition had previously been determined over wide ranges of temperature (Cukierman and Uhlmann, 1972; Uhlmann *et al.*, 1974). It was selected as a composition containing about 26% Al_2O_3 (see Table I), whose kinetic behavior should be useful for understanding the more feldspathic breccias.

TABLE I
Lunar composition 15418 (components listed in wgt pct)

SiO ₂	45.0	Al ₂ O ₃	26.7	CaO	16.1
Cr ₂ O ₃	0.1	FeO	5.4	Na ₂ O	0.3
TiO ₂	0.3	MgO	5.4	MnO	0.3

The TTT curves for this material were constructed from Equation (3) for various values of V_c/V using measured values for the crystal growth rate and a nucleation rate evaluated from Equation (4) with the measured viscosity data. The curve representing the condition of significant sintering was constructed from Equation (2) using measured viscosity data together with $\gamma = 300 \text{ erg cm}^{-2}$ and $R = 15\mu$. The results are shown in Figure 3 for $V_c/V = 10^{-6}$, corresponding to a just-detectable degree of crystallinity.

As shown in Figure 3, the kinetic analysis has delineated several regions in which different types of bodies are produced. In the first, amorphous matrix breccias are formed. In this region, there is sufficient time for the matrix material to sinter, but not sufficient time for it to develop a detectable degree of crystallinity. In the second region, the material will form partly or completely crystalline matrix breccias. In this region, the time is not only sufficient to produce a sintered matrix, it is also sufficient for detectable degrees of crystallinity to develop. In the third region, unshaded in Figure 3, no breccia should be formed from the material. In this region, either

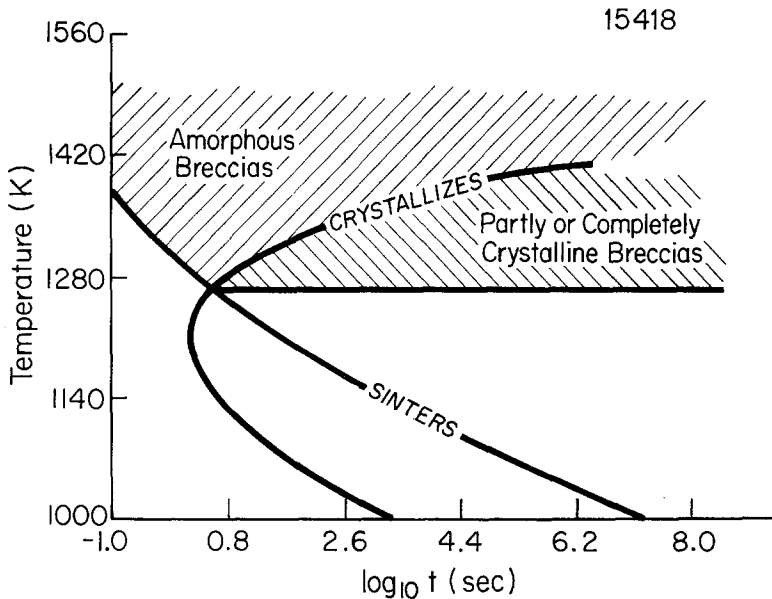


Fig. 3. Curve for significant sintering and time-temperature-transformation curve corresponding to a just-detectable degree of crystallinity for Lunar Composition 15418. Regions indicate where amorphous breccias and breccias with detectable crystallinities are formed.

insufficient time is allowed for the sample to sinter, or the material will crystallize prior to the occurrence of significant sintering. (The sintering of crystalline ceramic bodies in the absence of pressure requires times which are longer by many orders of magnitude than those needed for the coalescence of molten silicate bodies with typical viscosities.)

By considering the development of partial crystallinity in breccias, even tighter constraints can be placed on their thermal histories. This is illustrated by the results in Figure 4, also for the 15418 composition, in which TTT curves have been constructed for volume fractions crystallized of 10^{-6} , 10^{-2} and 1. As indicated there, breccias with partly crystalline matrices—with crystallinities in the range of 1 to 100%—are expected to have formed in the relatively narrow range of temperature and time indicated in the figure.

In both cases, the data for Composition 15418 have been used for illustrative purposes to indicate the kinetic approach to determining the time and temperature range for breccia formation. The approach is presently being extended to other breccias, particularly those which have modest degrees of crystallinity in the matrix and are low-grade or medium-grade in Warner's classification scheme. Such breccias should be particularly well suited for determinations of thermal history.

The approach outlined above seems to offer significant promise for setting close limits on the thermal history of lunar breccias. The estimates of temperatures and times provided by a combined treatment of sintering and crystallization kinetics can be refined using better models of viscous sintering and more reliable determinations of the rates of crystal nucleation. Even without such improved information, however, the

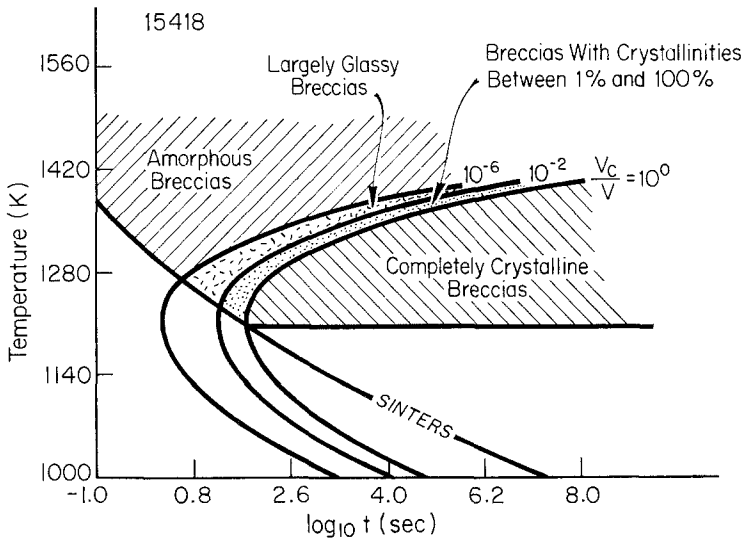


Fig. 4. Curve for significant sintering and time-temperature-transformation curves corresponding to volume fractions crystallized of 10^{-6} , 10^{-2} and 1 for Lunar Composition 15418. Regions indicated where amorphous breccias, completely crystalline breccias and various partly crystalline breccias are formed.

approach seems to be quite powerful. It should be particularly informative when used in combination with other data such as magnetic measurements for single-domain vs. multi-domain iron, rare gas loss, etc., together with detailed heat flow calculations for various assumed geometries of interest.

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References

- Chao, E. C. T., Boreman, J. A., and Desborough, G. A.: 1971, *Proc. Second Lunar Sci. Conf.*, 797–816.
- Cukierman, M. and Uhlmann, D. R.: 1972, *The Apollo 15 Lunar Samples*, 57–59, Lunar Sci. Inst., Houston Tex., U.S.A.
- Davies, H. A., Aucote, J., and Hull, J. B.: 1974, *Scripta Met.* **8**, 1179–1190.
- Frenkel, J.: 1945, *J. Phys. (U.S.S.R.)* **9**, 385–391.
- Hopper, R. W., Onorato, P., and Uhlmann, D. R.: 1974, *Proc. Fifth Lunar Sci. Conf.*, 2257–2273.
- McKay, D. S., Greenwood, W. R., and Morrison, D. A.: 1970, *Proc. Apollo 11 Lunar Sci. Conf.*, 673–694.
- McKay, D. S. and Morrison, D. A.: 1971, *J. Geophys. Res.* **76**, 5658–5669.
- Simonds, C. H.: 1973, *Am. J. Sci.* **273**, 428–439.
- Uhlmann, D. R.: 1972, *J. Non-Cryst. Solids* **7**, 337–348.
- Uhlmann, D. R., Klein, L., Kritchevsky, G., and Hopper, R. W.: 1974, *Proc. Fifth Lunar Sci. Conf.*, 2317–2331.
- Warner, J. L.: 1972, *Proc. Third Lunar Sci. Conf.*, 623–643.
- Waters, A. C., Fisher, R. V., Garrison, R. E., and Wax, D.: 1971, *Proc. Second Lunar Sci. Conf.*, 893–907.