CRYSTALLIZATION BEHAVIOR OF ALBITE. D. R. Uhlmann, H. Yinnon and D. Cranmer, Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Mass. 02139.

The mineral albite is an important component of the earth's crust and has, accordingly, been the subject of numerous investigations. In their classic study of phase equilibria in the Na₂O-Al₂O₃-SiO₂ system, Schairer and Bowen(1) noted the difficulty of crystallizing albite from the melt. They subjected albite samples to heat treatments at several temperatures for long time durations but obtained no crystallization. One of their samples was held at 1025°C for 5 years without crystallizing. They were able to obtain crystallization by subjecting the material to an "acclimation" treatment. This treatment consisted of holding the glass at progressively lower temperatures above the melting point for periods of days to months, with daily cooling, crushing and reheating.

The usual practice of homogeneously crystallizing a difficult-to-crystallize glass involves first subjecting it to prolonged heat treatments in the temperature range of large undercooling (ΔT/ΔTₐ< 0.2 to 0.3) to effect nucleation of the crystalline phase. This is followed by heating the material to the range of smaller undercooling where the nucleation rate is low but the crystal growth rate is relatively high. Such a procedure is followed in the commercial production of glass-ceramic materials, which have the complicating factor of a distinct nucleating phase but otherwise illustrate the principles.

The importance of the nucleation treatment at large undercoolings can be appreciated from the standard expression (2) for the frequency of homogeneous nucleation per unit volume, Iₐ:

\[ Iₐ = \frac{K}{\eta} \exp \left( -\frac{0.0205B}{\Delta T/\Delta Tₐ} \right) \]

Here K is a constant, \( 10^{30} \) cm⁻³ sec⁻¹ poise; \( \eta \) is the viscosity; the nucleation barrier is \( BkT^* \); \( T^* = 0.8 \) \( T_E \); \( T_E \) is the melting point; \( T_T = T/\Delta T_E \); and \( \Delta T_T = \Delta T/\Delta T_E \).

Experimental studies of nucleation on a variety of materials have indicated nucleation barriers in the range of 40-80 kT^*. For An, the barrier is \( 80kT^* \) (3). For such nucleation barriers, the rate of homogeneous nucleation at small undercoolings—such as \( \Delta T/\Delta T_E = 0.07 \)—would be negligibly small. As an example, for albite at 1025°C, for a nucleation barrier of even 50 kT^*, the calculated nucleation rate is only \( 10^{-96} \) cm⁻³ sec⁻¹—or one nucleation event in a 1 cm³ sample in \( 10^{89} \) years!

Viewed from a different perspective, homogeneous nucleation of crystals would be seen in 5 years at 1025°C for a 1 cm³ sample of albite only if the nucleation barrier were about 13 kT^*, an excessively small value. The observation of crystallization would then depend completely on heterogeneous nucleation associated with adventitious impurities, or on exposure of the sample to the range of larger undercoolings for appropriate periods.

In the present work, plates of albite glass were dusted with a thin layer of natural albite crystals and heat treated at temperatures between 1000°C and 1075°C for times between 6 days and 19 days. The albite crystals provided effective crystal nucleation on the dusted surface. After removal from the furnace, the samples were fractured in half and mounted in a polyester resin; and the fracture surfaces were polished and examined in a scanning electron microscope.
At all temperatures, crystal growth was observed to proceed inward from the nucleated surfaces. No internal nucleation of crystals was observed. The thickness of the crystalline layer was measured, and the rate of crystal growth was calculated from the slopes of the crystal thickness vs. time plots. The crystal growth rates determined in this way are shown in Figure 1. The rates measured are approximately two orders of magnitude slower than the crystal growth rates measured in 80Ab-20An (4) and six orders of magnitude slower than the maximum growth rates measured in pure anorthite (5).

At all crystallization temperatures, the crystal-liquid interface was faceted. Such faceted morphologies are expected for materials with entropies of fusion like that of albite (6), and have also been observed for the crystallization of anorthite (5), which has an even-higher entropy of fusion.

The growth rate data shown in Figure 1 were combined with viscosity data on albite (7, 8) to construct the reduced growth rate vs. undercooling relation. The reduced growth rate, \( u_R \), can be expressed:

\[
\frac{u}{u_R} = \frac{u_n}{[1 - \exp(-\Delta H/R T_E) - 1]}
\]

Here \( u \) is the crystal growth rate; \( \Delta H \) is the heat of fusion; and \( R \) is the gas constant.

The \( u_R \) vs \( \Delta T \) relation for anorthite is a curve with positive curvature which passes through the origin. The form of \( u_R \) vs \( \Delta T \) relation suggests that growth may be taking place by a surface nucleation process. To test
this suggestion, the log \( \log(u) \) vs \( (TAT)^{-1} \) relation was constructed. This relation is shown in Figure 2.

In accord with predictions of the standard model for nucleation-controlled growth, the log \( \log(u) \) vs \( (TAT)^{-1} \) relation is seen to be a straight line of negative slope.

In summary, it has been shown that albite, once nucleated, will crystallize from the melt at measurable rates. The rate of crystal growth is, however, quite small—much smaller than that of various plagioclase compositions or even of pure SiO\(_2\). The form of the \( uR \) vs \( AT \) and log \( \log(u) \) vs \( (TAT)^{-1} \) relations suggests growth by a surface nucleation mechanism.

REFERENCES