

Nucleation in laboratory charges of basaltic composition

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Abstract

Isothermal nucleation experiments using liquid beads suspended in 5 mm-diameter platinum-wire loops were carried out on several compositions near the thermal minima in the system diopside–anorthite–forsterite. Homogeneous nucleation was never observed, at temperatures from 400° C to the liquidi. Crystals of diopside, anorthite and forsterite all nucleate predominantly on the platinum wire. Nucleation on the surface of the bead occurs less often and is apparently promoted by mechanical stress. Similar isothermal experiments on a natural diabase also did not show homogenous nucleation, nor did dynamic crystallization experiments in nickel and alumina crucibles. Homogeneous nucleation probably never occurs in the laboratory or in nature in basaltic compositions. The principal question concerning natural basaltic rocks is whether nucleation in each case was internal, on suspended crystals, or external, on wall rocks or other surfaces.

Introduction

Dynamic crystallization experiments have recently become an important tool in volcanic petrology (Lofgren, 1980). In these experiments a molten rock is crystallized by cooling at a programmed rate, the purpose being to obtain direct information on textures and actual crystallization sequences of minerals. Understanding the results of such experiments, as well as the textures of natural rocks, requires knowledge of the kinetic processes of crystal nucleation and growth. The theory of crystal growth rates is fairly well known (Kirkpatrick, 1974), and it is reasonably easy to measure growth rates in the laboratory; indeed, there is a surprising amount of data on growth rates in basaltic systems (Dowty, 1980a). On the other hand, nucleation is a much more difficult phenomenon to deal with theoretically and experimentally (Dowty, 1980a; Kirkpatrick, 1981). In principle, there are two basic mechanisms, homogeneous nucleation, in which the new crystal forms by itself in the liquid, and heterogeneous nucleation, in which the new crystal forms on another phase, usually a solid.

Previous experience of many investigators had suggested that most nucleation in the laboratory is heterogeneous, usually on container walls. Recent dynamic crystallization experiments have also shown that textures of some natural basalts are best reproduced when the starting material is not completely molten, implying that suspended crystals often act as heterogeneous nucleation centers. However, some recent experiments (*e.g.*, Lofgren *et al.*, 1974; Donaldson *et al.*, 1975b; Donaldson, 1979) in which the starting material was completely molten were interpreted in terms of internal nucleation (not on the container or surface), which under such circumstances would presumably be homogeneous. Many of these experiments were carried out in samples suspended in platinum-wire loops, a technique which minimizes the area of the interface between melt and solid container.

If homogeneous nucleation were predominant in any rocks, it would simplify theoretical modeling of crystallization. This study began as experiments on simple synthetic compositions, for testing and calibration of numerical models of crystallization

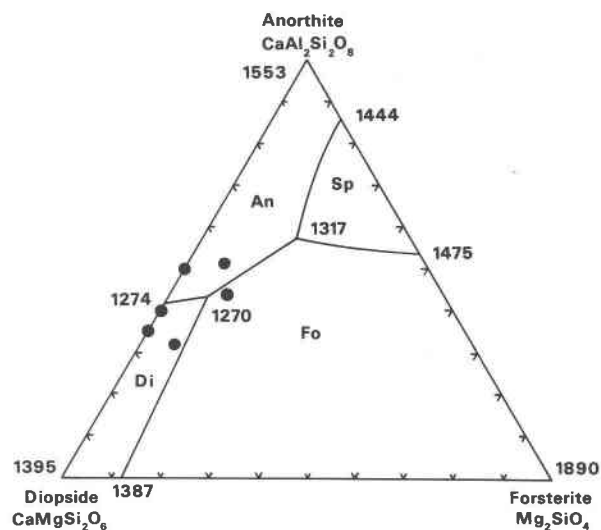


Fig. 1. Compositions studied in the system diopside-anorthite-forsterite (in weight percent). Numbers give temperatures of invariant points.

(Dowty, 1980a), on the implicit assumption that nucleation would be homogeneous if the charge were completely molten. However, no homogeneous nucleation was observed in the synthetic compositions or in a natural basalt melt. Instead, nucleation took place by a variety of heterogeneous mechanisms, depending on sample treatment.

Experimental methods

Furnaces were made of 2-inch diameter alumina muffles with SiC heating elements. The furnaces cool at about 0.5°/second and heat at 0.1 to 0.5°/second. For dynamic crystallization runs, temperature was controlled by a microcomputer. Runs in Pt-wire loops were carried out largely as described by Donaldson *et al.* (1975a), but instead of pressing powdered material into pellets as these authors did, it was found to be easier to make glass beads by a pre-melting process. To do this, holes of about 0.6 mm in diameter were drilled in a graphite block and weighed amounts of glass or rock powder, normally about 140 mg, were inserted. The block was then placed in the furnace at 1350–1400° C in a Pt crucible for 2–5 minutes. The spherical beads thus produced were tacked onto Pt wire loops as described by Donaldson *et al.* (1975a). All beads of synthetic compositions were annealed at 1350–1400° C in air for at least one hour prior to crystallization at lower temperature. Any graphite on the beads is rapidly burned off in air at these temperatures.

Synthetic compositions were weighed out in 10 g

batches from reagent-grade MgO and CaCO₃, spectroil glass, and Al₂O₃ powder originally supplied by Frank Schairer of the Geophysical Laboratory. In order to form homogeneous glass, the mixes were cycled at least twice through a process of melting in a Pt crucible and grinding in a silicon carbide ball mill. Most compositions were checked by atomic absorption analysis.

Photographs of whole synthetic glass beads shown in this paper were taken by immersion of the bead in a transparent cell containing liquid with a refractive index close to that of the glass. All runs on synthetic compositions were examined in this cell both under the binocular microscope in incident light, and under the petrographic microscope in transmitted light.

Nucleation mechanisms—synthetic compositions

The synthetic compositions chosen in the diopside-anorthite-forsterite (Di–An–Fo) system (Fig. 1) constitute simplified analogs of various types of basalt, with clinopyroxene, plagioclase or olivine as the initial liquidus phase. It will be noted in the following descriptions that the sequence of phases crystallizing is sometimes not that expected if equilibrium were always maintained during cooling. The determining factor in nucleation and growth rates under real conditions is the supercooling, ΔT , with respect to the liquidus of the phase in question, whether this liquidus is stable or only metastable; normally only stable liquidi are shown in phase diagrams such as Figure 1. For example, in a eutectic system such as Di–An, the metastable diopside liquidus must be visualized as an extension of the stable liquidus past the eutectic to lower temperature and higher An content. If a liquid with An content greater than that of the eutectic is suddenly brought to a temperature below the metastable diopside liquidus, diopside may crystallize in addition to or instead of anorthite. More detailed discussions of the theory of metastable crystallization are given by Baker and Cahn (1974) and Dowty (1980a).

In the present experiments, nucleation was found to be rather sporadic and unpredictable (the number of crystals did not follow a Poisson distribution) at supercoolings of less than about 60°. This is similar to the findings of Fenn (1977) and Swanson (1977) on nucleation in granitic systems and Gibb (1974) on nucleation of plagioclase in basalt, but contrasts with the findings of Donaldson (1979) on nucleation of olivine in natural basalts.

Table 1. Nucleation and morphology data for simple isothermal crystallization experiments

Composition	# of runs	ΔT range	Phases	Locus of Nucleation	Rate (#/hr)	Morphology
Di ₆₀ An ₄₀	18	10-60	Di	on wire	0-3	(110) prisms; hollow (pyramidal reentrants). Crystals become longer and more hollow with increasing ΔT .
		60-120	Di	on wire	2-10	Dendrites; initially long and pointed, they become stouter with increasing ΔT .
		120-260	Di	on wire	4+	Spherulites.
Di ₅₀ An ₅₀	9	10-55	An	on wire	0-4	Plates on (010); polygonal at low ΔT , become rectangular hour-glass, then dendritic with increasing ΔT .
		65-285	An, Di	on wire	0-4	An dendrites, Di spherulites.
Di ₄₄ An ₄₄ Fo ₁₂	12	20-33	Fo	on wire	0-0.5	Euhedral; typical igneous shape.
		40-140	Fo	wire, surf. 1-6		Rectangular plates; become hourglass, then dendritic with increasing ΔT .
		240-640	Fo	wire, surf. 10-20		Dendrites and spherulites.

ΔT ranges are approximate; morphologies overlap considerably in some cases.

Distinctly different modes of nucleation were observed in isothermal runs on synthetic compositions in Pt-wire loops, depending on whether the bead was (1) subjected to a simple isothermal treatment, being taken directly from the annealing temperature of 1350–1400° C to the crystallization temperature without removal from the furnace; (2) subjected to more complex thermal treatment, still without removal from the furnace, or (3) removed from the furnace at the annealing temperature and quenched to room temperature before being reinserted at a crystallization temperature.

(1) Synthetic compositions—*isothermal runs, no quench*

In simple isothermal experiments, the predominant mechanism of nucleation of all three phases, and the only one for diopside and anorthite, was heterogeneous on the Pt wire. The results are summarized in Table 1 and Figure 2. The morphologies are somewhat similar to those observed in previous studies (see Lofgren, 1980, for review), although the rectangular hour-glass and dendritic plates of anorthite and forsterite which we found to be common at moderate ΔT do not seem to be observed in natural basaltic compositions.

Although nucleation on the wire was always dominant, forsterite also nucleated sometimes on

the surface of the bead, the plates usually lying flat. The proportion of nucleation on the wire to that on the surface was quite variable from run to run. In some cases the crystals on the surface can be seen to have originated from a foreign particle, often a Pt fragment, but in others there is no obvious seed material.

(2) Synthetic compositions—*complex thermal history, no quench*

In several previous studies of synthetic glass-forming systems (James, 1974; Kalinina *et al.*, 1980; Klein *et al.*, 1977; Strnad and Douglas, 1973; Klein and Uhlmann, 1976), internal, presumably homogeneous nucleation was observed, but at supercoolings of 200° to over 700°. It is known that the growth rates of diopside and anorthite maximize at about 100° and decrease at larger ΔT 's (Leonteva, 1948, 1949; Kirkpatrick *et al.*, 1979). It is possible, then, that nuclei generated at very high ΔT may not grow to visible size in reasonable times. Therefore, the compositions Di₆₅An₃₅, Di₅₀An₅₀ and Di₄₄An₄₄Fo₁₂, after annealing at 1350–1400° C, were held for 20 to 50 hours at temperatures of 400°, 500°, 600°, 700°, 800° and 900° C, then brought back near the liquidus for growth of any nuclei produced at the lower temperatures. The charges were not removed from the furnace until final quench and examination.

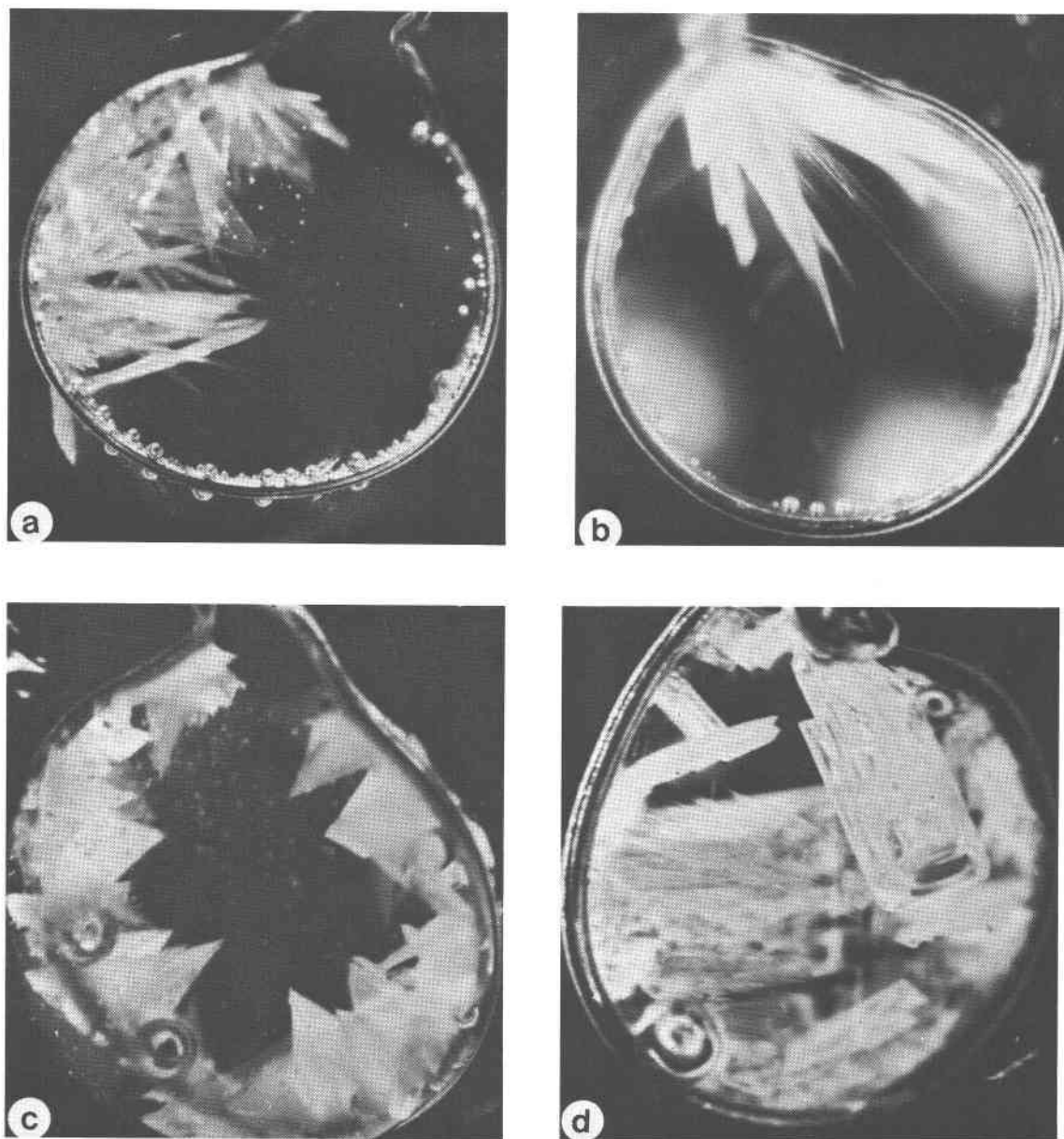


Fig. 2. Simple isothermal runs. The diameter of the wire loop is always about 5 mm. The small spherical objects adhering to the wire are air bubbles. (a) Pointed needles of diopside in $\text{Di}_{60}\text{An}_{40}$ held for 1.5 hours at 1200°C ($\Delta T = 65^\circ$). (b) Diopside crystals, transitional from pointed needles to dendrites, in $\text{Di}_{65}\text{An}_{35}$ held for 3 hours at 1160°C ($\Delta T = 115^\circ$). (c) Wedge-shaped diopside dendrites in $\text{Di}_{60}\text{An}_{40}$ held for 1/2 hour at 1140°C ($\Delta T = 125^\circ$). (d) Forsterite plates in $\text{Di}_{44}\text{An}_{44}\text{Fo}_{12}$ run for 15 hours at 1250°C ($\Delta T = 60^\circ$).

None of these runs showed internal nucleation, although they all produced crystals of the liquidus phase on the Pt wire. These crystals were probably generated during heating and cooling—the beads must have spent the better part of an hour in the ΔT ranges at which nucleation and growth are rapid. Runs of 20 hours or longer were thus not possible at temperatures of 1000° and higher, because rapid nucleation and growth of crystals on the wire

causes essentially complete crystallization. Many runs were made in this temperature range for shorter times with the same result, *i.e.*, no internal nucleation.

For a bead of 4 mm diameter, a 20 hour run time thus establishes the maximum rate of homogeneous nucleation for the temperature interval $400\text{--}900^\circ\text{C}$ at about $2 \times 10^{-4} \text{ cm}^{-3} \text{ sec}^{-1}$. For temperatures above 900° , rates could be as much as an order of

magnitude greater, since our observation times were shorter. These inferred maximum rates are considerably less than the measured maximum rate of 4×10^3 at 480°C in $\text{Li}_2\text{Si}_2\text{O}_5$ (James, 1974).

Although a complex thermal history did not produce homogeneous nucleation, it did result in some additional modes of heterogeneous nucleation. In the compositions $\text{Di}_{60}\text{An}_{40}$ and $\text{Di}_{65}\text{An}_{35}$ crystals of diopside sometimes grew on the surface during the period of holding at low ΔT for growth. If there was little previous growth of diopside on the wire, such surface nucleation was rare and resulted in a few isolated crystals. This type of growth may in some cases be due to surface impurities, perhaps dust particles generated by friction between the furnace tube and the upper ceramic plug during heating and cooling. However, several observations suggest that nucleation on the surface may be produced by mechanical stress. If a large volume of diopside crystals is generated on the wire, which may occur if the initial supercooling for "nucleation" is up to about 250° , the additional diopside crystals which grow on the surface during the second period of "growth" at lower ΔT usually occur in quasi-linear arrays, in which the grain size increases away from the larger diopside crystals. This mode of growth may be due to the accumulation of stress near the surface, due either to volume changes on crystallization or to differential thermal expansion of crystals and liquid. This in turn may lead to cracks or dislocations in the glass which facilitate nucleation. Stresses are undoubtedly great in quenched beads which consist partly of crystals and partly of glass; such beads are usually observed to be cracked, and in some cases the cracking occurs hours or days after the bead is removed from the furnace.

Somewhat similar behavior was observed in $\text{Di}_{44}\text{An}_{44}\text{Fo}_{12}$. Crystals of forsterite, sometimes in stellate clusters, grew on the surface in the two-stage runs. These surface crystals were usually sparse and did not form linear arrays like diopside. When the temperature of the first stage was about $900\text{--}1000^\circ\text{C}$, abundant dendritic or spherulitic forsterite grew on the wire. If beads containing such growth were brought back to near the liquidus, in some cases cracks developed in the interior of the bead and additional forsterite crystals nucleated on the cracks. Although some crystals were seen in the interior which did not obviously nucleate on cracks, in no case did crystals grow in the interior unless there was already a significant volume of growth on the wire. Again, differential volume effects are strongly indicated.

In $\text{Di}_{50}\text{An}_{50}$, if the bead was held at over $100^\circ\Delta T$, diopside sometimes crystallized instead of anorthite, usually in the form of spherulites. If the charge was then held just below the anorthite liquidus, anorthite plates nucleated on the diopside spherulites (Fig. 4a). This temperature is above the metastable diopside liquidus, as shown by the fact that the diopside would dissolve in due course, leaving the anorthite plates suspended in the interior of the bead. No anorthite or diopside was observed to crystallize on the surface under these conditions, nor did any other type of thermal history ever cause anorthite to crystallize on the surface if the bead was not removed from the furnace.

Some experiments were made specifically to test for crystals nucleating on one another. The possibility of diopside nucleating on anorthite was presumably tested in the composition $\text{Di}_{60}\text{An}_{40}$. First, to test for the nucleation of diopside and anorthite on forsterite, the composition $\text{Di}_{44}\text{An}_{44}\text{Fo}_{12}$ was held at a temperature at or just below the ternary eutectic (1270°) for fairly long periods (over 12 hours). A limited amount of forsterite crystallized on the wire under these conditions, usually in the form of large skeletal crystals or hopper plates. Then the charge was taken to about 40° lower than the eutectic, causing the crystallization of diopside and anorthite. Most of the diopside seemed to nucleate independently on the wire, but in several cases small pointed dendrites of anorthite grew on the forsterite. Two special compositions were made up in order to test the possibility of nucleation of forsterite on other phases: $\text{Di}_{42}\text{An}_{51}\text{Fo}_7$, in which the metastable forsterite liquidus should be just below the stable anorthite liquidus; and $\text{Di}_{62}\text{An}_{32}\text{Fo}_6$, in which the metastable forsterite liquidus should be just below the stable diopside liquidus. At moderate supercoolings, forsterite nucleated independently on the wire in both compositions (in addition to the stable liquidus phase), but no clear cases of forsterite nucleating on diopside or anorthite were seen.

(3) Synthetic compositions—removed from the furnace

Nucleation of all three phases could be induced by removing the bead from the furnace at the annealing temperature and then reinserting it at some small ΔT . If the bead was not touched, and if it contained no crystals already, crystals formed by this mode of nucleation were rather sparse, there usually being less than about fifteen new crystalliza-

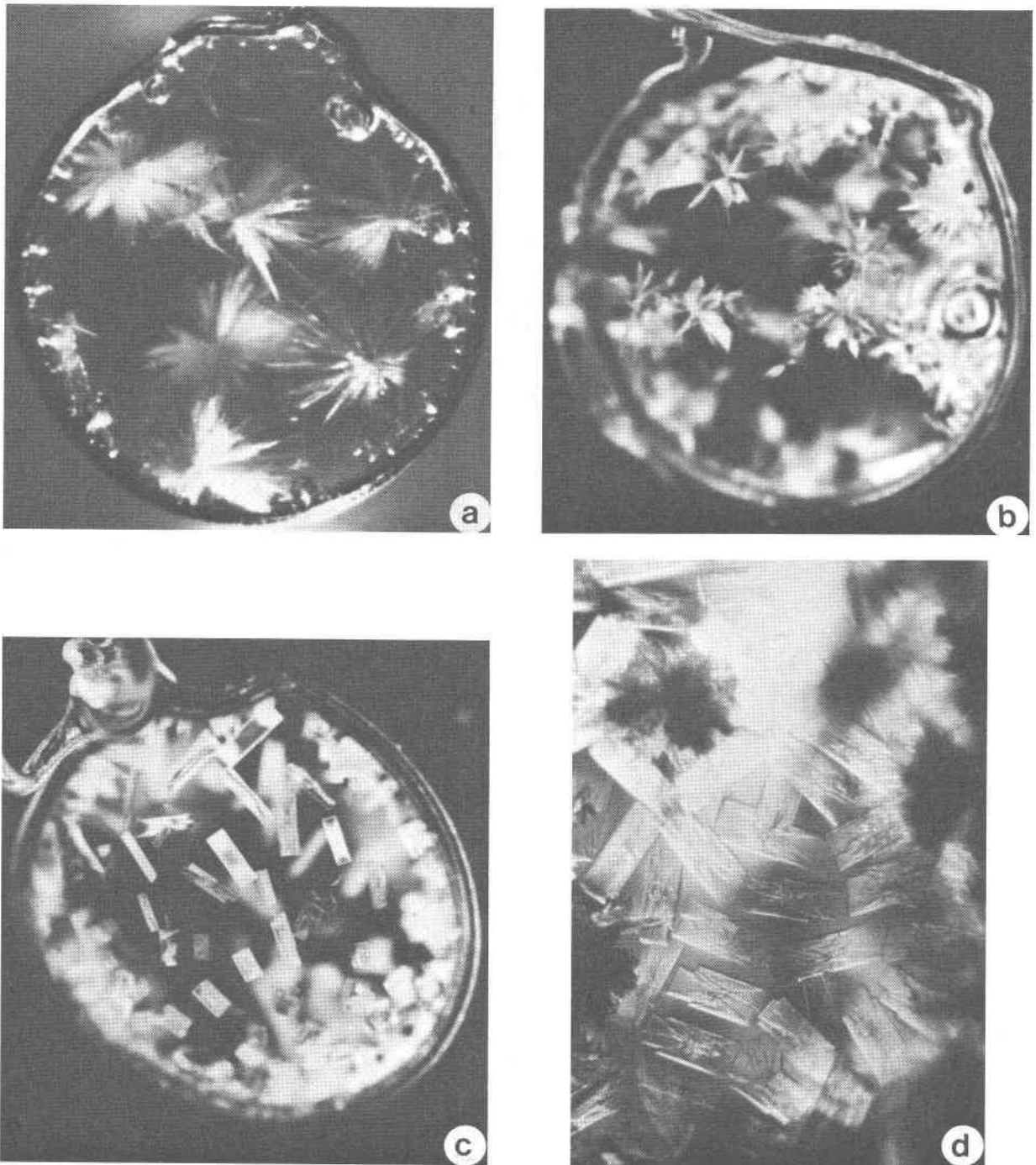


Fig. 3. Runs quenched to room temperature, without handling, then reinserted in the furnace for crystallization. All crystals in the beads are on the surface. (a) Diopside in $\text{Di}_{60}\text{An}_{40}$ held for 3 hours at 1240°C ($\Delta T = 25^\circ$). (b) Anorthite in $\text{Di}_{50}\text{An}_{50}$ held for 45 minutes at 1260°C ($\Delta T = 25^\circ$). (c) Forsterite in $\text{Di}_{44}\text{An}_{44}\text{Fo}_{12}$ run for 10 hours at 1270°C ($\Delta T = 40^\circ$). (d) Close-up taken in polarizing microscope (crossed polars) of forsterite plates and sparse diopside (?) stars in $\text{Di}_{44}\text{An}_{44}\text{Fo}_{12}$ run for 10 minutes at 1240°C ($\Delta T = 70^\circ$). Height of the field of view is about 2 mm.

tion centers on the surface. The dominant phase which grew was in all cases the stable liquidus phase, although in the composition $\text{Di}_{44}\text{An}_{44}\text{Fo}_{12}$, diopside sometimes grew in addition to forsterite at

moderate ΔT (Fig. 3d). Anorthite and diopside have a tendency to form stellate clusters (Fig. 3a,b), while forsterite is normally in the form of individual skeletal or hopper plates (Fig. 3c,d). This type of

nucleation is most likely caused by the adherence of dust particles, generated by friction between the upper plug and the muffle, but mechanical stress may also be involved.

More abundant nucleation was caused if the bead was touched with a finger before reinsertion. This led to dense crystallization over the entire surface, usually consisting of individual crystals at low ΔT , and stellate clusters at higher ΔT . Possibly the salts in perspiration cause some chemical change in the supercooled liquid, or act as a mineralizer. Even at temperatures below the liquidus, surface diffusion of NaCl or other substances must be rapid enough to spread them over the surface within minutes. Another possibility is that the water from perspiration may act as a surfactant. In experiments on alkali feldspar compositions, Fenn (1977) showed that the presence of water in the melt greatly reduced the ΔT needed for nucleation.

Dependence of nucleation rate on superheating

Much incidental information on the effect of annealing time at 1375–1400° C on nucleation was accumulated. There seems to be a tendency for nucleation to become more difficult as time goes on in beads that are recycled through many crystallization runs, or otherwise annealed for long periods at high temperature. The time necessary for this process is usually on the order of a hundred hours total at annealing temperatures. It seems most likely that this behavior can be attributed to changes in the physical state of the wire. Wires in beads which have been recycled many times or otherwise held at annealing temperatures for long times develop pronounced grooves on their surfaces, which apparently represent grain boundaries. Thus it is apparent that some annealing of the platinum is taking place.

In contrast with the findings of Donaldson (1979) on nucleation of olivine, no evidence was found for short-term effects of annealing time or temperature on nucleation rate. However, the number of our experiments pertaining to this problem is not sufficient to allow any firm conclusions to be drawn.

Experiments on natural basalt

To verify that the nucleation phenomena described above, in particular the absence of homogeneous nucleation, are not a peculiarity of synthetic compositions, experiments were carried out on a natural diabase from Rocky Hill, New Jersey, a typical Triassic-basin basaltic rock. Analyses are given by Dowty and Berkebile (1982). The sample

used had original grain size of about 2 mm diameter and contained no olivine.

Experiments were carried out both in 20 ml crucible and in Pt-wire loops. For most of the Pt-wire experiments, the starting material was basalt melted at 1350° C and ground repeatedly to obtain a homogeneous glass. All preparation and crystallization runs were carried out in a furnace atmosphere of 10 parts CO₂ to one part CO, which gives an oxygen fugacity between the quartz–magnetite–fayalite and magnetite–wüstite buffers at the temperatures of interest. The beads are brown and opaque to incident light, so sections were cut parallel to the wire loop and ground until translucent—usually to a thickness of about 0.5 mm.

When beads were quenched from 1350° and touched before reinsertion at supercoolings of up to 50°, abundant pyroxene needles grew on the surface, and they persisted if the bead was annealed at up to 1200°. This temperature is presumably the liquidus and pyroxene the primary liquidus phase. However, when the beads were annealed at 1350° and taken directly to the crystallization temperature without being removed from the furnace, olivine was at least as common as pyroxene (Fig. 4b–d). Both phases nucleated exclusively on the wire under these conditions. Morphologies are similar to those previously observed in crystallization experiments on natural basalts (*e.g.* Donaldson, 1976; Lofgren, 1980), rather than those seen in the synthetic compositions (Table 1). When the starting material was homogeneous glass, plagioclase was not observed unless the bead had essentially completely crystallized. Plagioclase nucleated on the wire at the top of beads when sintered powdered basalt was the starting material (Fig. 4d); such runs differentiate during melting (Dowty and Berkebile, 1982).

In order to test the possibility that the high ratio of surface area (both wire and air interfaces) to volume in the Pt-wire beads causes an artificial predominance of heterogeneous nucleation, several runs were made on the Rocky Hill composition in 30 ml nickel crucibles. Most of these runs were dynamic cooling experiments, at cooling rates from 2° to 50° per hour. Some were made in an atmosphere of argon and some in the 10/1 mixture of CO₂/CO. The furnace atmosphere seemed to make no difference in the phases crystallized or the texture, and it is likely that the bulk of the liquid did not come to redox equilibrium with the atmosphere (see Dowty and Berkebile, 1982). These runs were actually done before the experiments in platinum-

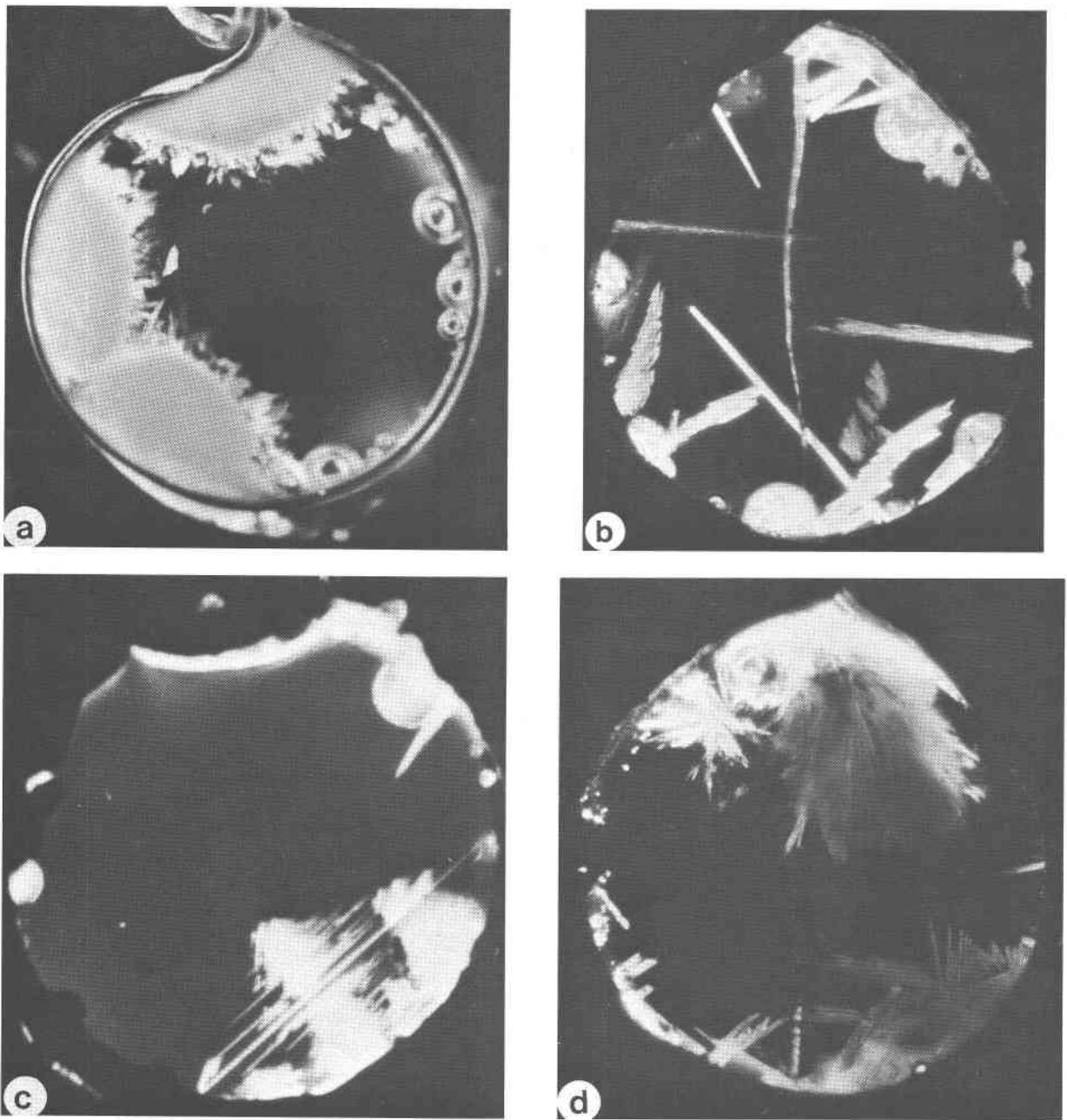


Fig. 4. (a) Anorthite plates growing on diopside spherulites in $\text{Di}_{50}\text{An}_{50}$ held for $\frac{1}{2}$ hour at 900°C ($\Delta T = 385^\circ$), then $\frac{1}{2}$ hour at 1270°C ($\Delta T = 15^\circ$). (b) Thick section of bead of Rocky Hill diabase, transmitted light, uncrossed polars. All crystals in this bead are olivine. Starting material homogenized glass, held for 16 hours at 1125°C ($\Delta T = 75^\circ$). The long thin bright object running vertically through the center is a crack in the section. Air bubbles appear as bright circles. (c) Same, held for 6 hours at 1100°C ($\Delta T = 100^\circ$). One large, wedge-shaped olivine dendrite is present on the lower part of the wire to the right of center. (d) Starting material crushed rock, held for 2 hours at 1150°C ($\Delta T = 50^\circ$). Olivine crystals are all in the lower half and have elongated, chain-like shape, as in (b). Pyroxene crystals appear dark and feathery and occur in the right half of the bead, both top and bottom. The bright, feathery cluster just below the top and to the left of center is plagioclase.

wire loops described above; initial runs used large chunks of the rock, while later ones were made from homogenized glass. There were very important differences between these two types of runs, in

that the runs made from rock chunks differentiated during melting (Dowty and Berkebile, 1982), but the nucleation behavior seems to be the same.

In all these runs, olivine clearly nucleated on the

walls and bottom of the crucible, and grew inward as long skeletal blades (See Dowty and Berkebile, Fig. 1). Pyroxene usually crystallized as curved, feathery dendrites and it fills in the interstices between olivine crystals. The morphologies of olivine and pyroxene are very similar to those observed previously in laboratory experiments on basalts (e.g. Donaldson, 1976; Lofgren, 1980). In the runs made from glass, and in the lower parts of runs made from rock chunks, only olivine and pyroxene are present. In the runs made from rock chunks, the liquid became enriched in the plagioclase component in the upper part (Dowty and Berkebile, 1982), and this part shows only plagioclase and pyroxene. The plagioclase is usually in the form of hollow prisms, as observed previously in natural basalts (e.g. Crawford, 1973) and synthetic charges (Lofgren, 1974). Some plagioclase certainly nucleates on the wall, but other crystals appear, in thin section, to be coming down from the surface (gas interface). It is not clear whether these crystals actually nucleated directly on the surface, or whether crystallization spread across the surface or near it from an origin on the walls.

One run was made from homogenized glass in an alumina crucible at $10^\circ/\text{hour}$. In this run, olivine was entirely absent, and long plagioclase and pyroxene needles grew inward from the walls and bottom surface of the crucible (the appearance is somewhat similar to Figure 1c of Dowty and Berkebile, 1982). The difference between alumina and nickel crucibles may be due in part to Al_2O_3 and NiO respectively being incorporated in the liquid adjacent to the walls. However, slow diffusion rates imply that such compositional differences could not have extended very far from the walls, and the persistence of the difference in phases crystallizing all the way to the center of the charges demonstrates that either plagioclase or olivine is metastable.

Summary of nucleation results—implications for laboratory studies

In detail the observations on nucleation form a large and confusing mass; in many cases we have insufficient data to elucidate all the phenomena encountered, and many of our interpretations are speculative. Nevertheless, the most important result is quite unambiguous; no clear example of homogeneous nucleation was observed in any run on synthetic or natural basalt compositions, despite concerted efforts to cause it under a wide variety of conditions. When the charges were completely mol-

ten, and not subjected to mechanical stresses or contamination, pyroxene, feldspar and olivine nucleated almost exclusively on the Pt-wire, or Ni or Al_2O_3 crucible, and when not nucleating on the container they nucleated on the gas interface. Annealing the charge for very long periods (ca. 100 hours) seemed to depress the rate of nucleation on the wire, but did not cause any other mechanism to appear; indeed, longer annealing seemed to eliminate the nucleation of forsterite on the surface, which is perhaps understandable if the latter is due to impurity particles on the surface.

In previous dynamic crystallization experiments in which the charge was not completely molten, nucleation probably occurred in most cases on suspended crystals. However, if no actual remnant crystals were present, we infer that nucleation probably occurred on the container. Except for the study of synthetic diopside composition by Kirkpatrick *et al.* (1981), in which forsterite was observed to nucleate on the wire, none of the recent dynamic crystallization studies acknowledged the likelihood of nucleation on the container. It seems that the nature of the nucleation mechanism was simply not observed in these studies. There are two probable reasons for this. (1) The natural basalt compositions studied previously, being opaque, were examined only in thin section, which in the case of the beads in Pt wire loops was usually cut perpendicular to the wire. Our results indicate that nucleation may originate from only a few points on the wire (e.g. Fig. 2b) and the probability of observing these points in a thin section is small. (2) Most runs were examined only after essentially complete crystallization, which further tends to obscure nucleation relations.

In some studies (e.g. Lofgren *et al.*, 1978) it was suggested that there may be sub-microscopic incipient nuclei which can exist stably or metastably above the liquidus, and which can cause internal, but not strictly homogeneous nucleation. Since our experiments show that there is no internal nucleation if the charge is completely molten, this hypothesis appears very improbable.

It is perhaps understandable that previous investigators would in some cases have reserved judgment on the nature of nucleation mechanism, but the problem is one which simply cannot be evaded; reproduction of the crystallization of natural rocks in the laboratory obviously depends on duplication of all conditions, and if the nucleation mechanism is different, inferences derived from comparison of natural and laboratory textures may not be valid. In

particular, quantitative cooling rates of the natural rocks derived by comparison of grain sizes cannot be expected to be accurate.

Some previous nucleation results require special comment. Donaldson *et al.* (1975b) did suggest that the relatively minor differences in texture between their runs from glass in Pt wire loops and those of Walker *et al.* (1976) on a similar composition in iron capsules, were due to heterogeneous nucleation on iron droplets *within* the liquid in the runs of the latter, but Donaldson *et al.* (1975b) concluded that nucleation in their own runs was probably "spontaneous" or internal. Nabelek *et al.* (1978) nucleated plagioclase from glass which had been homogenized, then ground and pressed into pellets and inserted into the furnace at a temperature below the liquidus. They concluded that unmelted glass particles acted as nucleation sites for plagioclase. However, it seems more likely that the mechanism of nucleation in these runs was the same as that in our runs in which the glass bead was quenched from above the liquidus, *i.e.* crystals nucleated in the glass as a result either of mechanical stress or contamination. The grinding of the glass by Nabelek *et al.* could have introduced both stress and contaminants. Bianco and Taylor (1977) likewise inserted pressed pellets of homogenized and ground glass into the furnace below the liquidus for annealing before starting dynamic crystallization runs. Despite rather small supercooling at these temperatures, the prior treatment of the glass must have caused near-instantaneous nucleation, probably throughout the bead. Donaldson (1979) suggested that olivine probably nucleated homogeneously in his isothermal experiments in Pt-wire loops on natural basaltic and ultramafic compositions. However, he did not make thin sections, but only crushed the beads and examined the fragments in oil to determine if crystallization had taken place. There is no strong theoretical reason to believe that the systematic effects of annealing temperature which he found could not be a result of heterogeneous as well as homogeneous nucleation.

Since our own experiments did not produce homogeneous nucleation, and we do not find convincing evidence for it in previous experiments, we therefore tentatively conclude that homogeneous nucleation has not been observed in isothermal or dynamic crystallization of laboratory charges of basaltic or ultramafic composition. There is always some danger in making such generalizations in kinetic studies, but it seems clear at least that our

observations shift the burden of proof on to anyone who contends that he has observed homogeneous nucleation. Such observations will have to meet two main criteria; it must be shown *in three dimensions* (not in thin sections only) that there is no connection of the crystals with the container or surface; and it must be shown that the liquid was homogeneous and contained no remnant crystals, or at least the liquid must have been annealed at a temperature which was definitely above the liquidus for several hours.

Nucleation mechanisms in natural rocks

Our results, combined with previous studies of synthetic and natural silicate compositions, suggest that homogeneous nucleation is not to be expected in natural basaltic rocks. The chief uncertainty at present seems to be whether nucleation in basaltic rocks is primarily external, with crystallization originating on wall rocks or other surfaces, or internal heterogeneous nucleation, on crystals or other material suspended in the melt. Perhaps the least ambiguous situation is that in which the texture is dominated by elongated "quench" crystals growing inward from the walls or upward from apparent cumulate crystals, as found in the "perpendicular feldspar", crescumulate and harrisitic textures of layered intrusions (Wager and Brown, 1968; Donaldson, 1977), the spinifex textures of ultramafic extrusive rocks (Pyke *et al.*, 1973; Donaldson, 1974) and the comb or Willow-Lake layering of granodioritic rocks (Lofgren and Donaldson, 1975). These textures have well-characterized laboratory analogs and may be considered to arise from heterogeneous, external nucleation.

In some cases, external nucleation may not be so obvious. The textures of lunar pyroxene-phyric or quartz-normative basalts were fairly closely reproduced by dynamic crystallization experiments using glass as starting material (Lofgren *et al.*, 1974). It seems likely from the results of our own experiments that the prominent pyroxene phenocrysts in the dynamic crystallization experiments nucleated on the Pt wire. This inference is reinforced by the fact that using iron capsules (Grove and Walker, 1977) instead of Pt-wire loops in dynamic crystallization experiments on similar compositions led to significantly different grain sizes. Some of our experiments show that crystallization which originates on the wire or surface does not always yield crystal arrays which are perpendicular to the nucleating surface. The examples shown in Figure 5a and

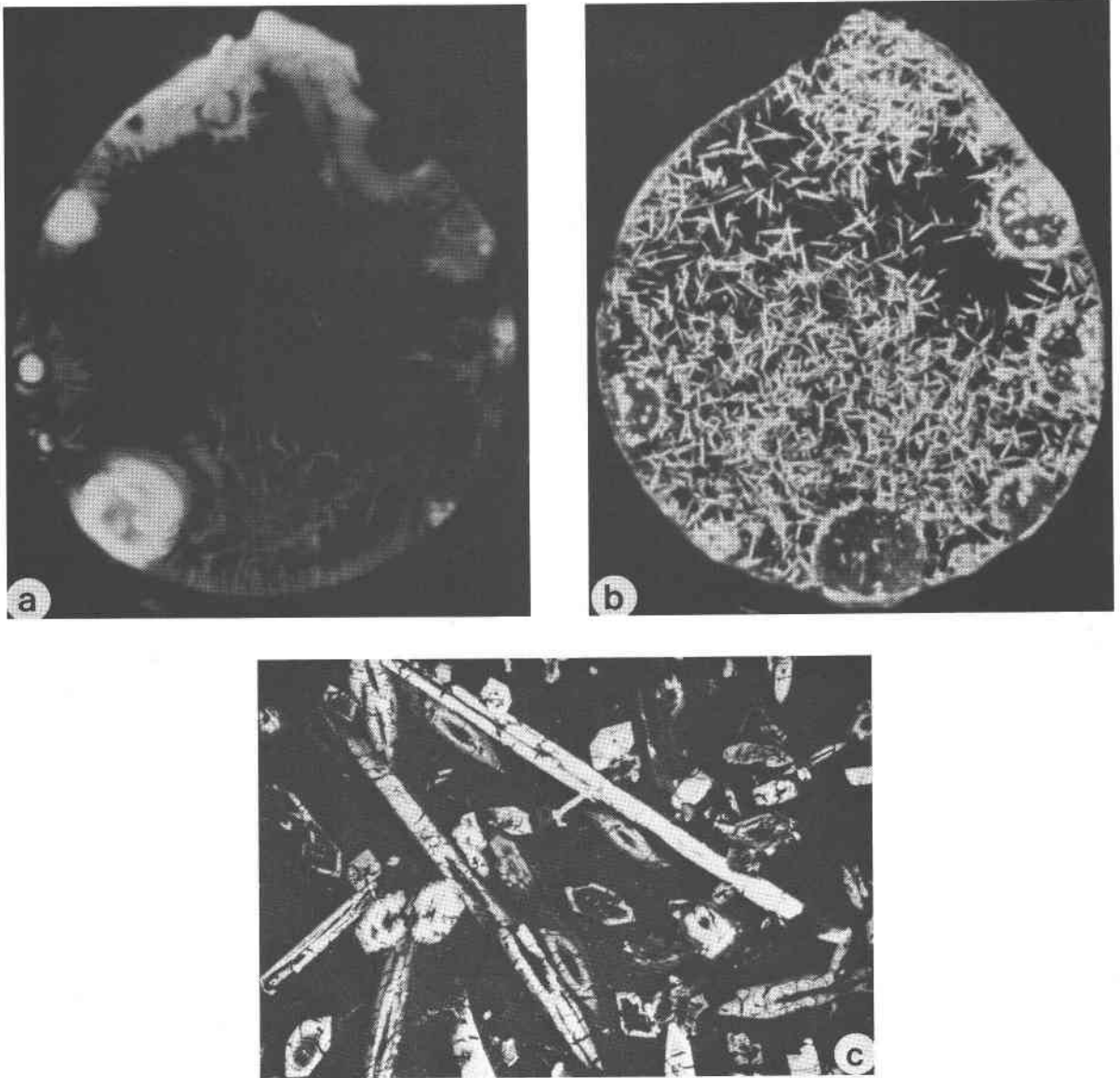


Fig. 5. Thick section of bead of Rocky Hill diabase, starting material homogenized glass, quenched to room temperature, touched and held at 1190° C for 1 hour. (b) Similar, held at 1185° C for 1 hour. (c) Thin section of lunar sample 15125, crossed polars. Width of the field of view is 3 mm.

b were produced by growth at rather low supercooling in beads which had been quenched and touched. Under these circumstances, growth seems to proceed inward by continued heterogeneous nucleation with a more-or-less random orientation of the elongated pyroxene crystals. There seems to be considerable resemblance between such arrays of crystals and the phenocrysts in the lunar basalts (Fig. 5c). This mechanism of external nucleation is certainly more plausible than homogeneous nucleation of the phenocrysts which was suggested by Dowty *et al.*

(1974). However, internal heterogeneous nucleation, on previously existing crystals (chromite) or iron droplets (Donaldson *et al.*, 1975) is also a distinct possibility.

Laboratory crystallization experiments on basaltic compositions very often produce porphyritic textures, perhaps more often than observed in natural basalts (*e.g.* Walker *et al.*, 1979; Lofgren, 1980). It certainly seems significant that such textures are more common when controlled cooling is initiated from a temperature above the liquidus than

from one below it. Our experiments permit the specific suggestion that in some cases, laboratory-produced porphyritic textures are due to external nucleation on the container. It would not be warranted, however, to conclude that porphyritic texture in synthetic or natural rocks in general is an indication of external nucleation.

Most basalts and gabbros show neither obvious elongated quench crystals at the margins, nor the rather dense interlocking fabric of elongated pyroxene phenocrysts of the lunar pyroxene-phyric basalts. They tend to have fairly equant crystals right up to the margins, the crystals simply becoming smaller in most cases. Such observations, combined with the fact that basalt textures are generally most closely reproduced in dynamic crystallization experiments when the melt is annealed below the liquidus, or for only a limited time above the liquidus (Usselman and Lofgren, 1976; Bianco and Taylor, 1977; Lofgren, 1977; Lofgren *et al.*, 1978; Nabelek *et al.*, 1978; Walker *et al.*, 1978), have led Lofgren (1980), among others, to suggest that in most cases crystals in basaltic and intermediate rocks nucleate on pre-existing crystals within the liquid. The study by Kirkpatrick (1977) of partially crystalline Hawaiian lava lakes, in which crystals were usually found in clusters and nucleation was inferred to be continuous, is at least consistent with this conclusion, although since these lakes appear to be crystallizing from the top, it also seems quite possible that nucleation was originally external.

The phenomenon of "lateral accretion" proposed for batholithic rocks (Bateman and Chappell, 1976), while not absolutely requiring external nucleation, would certainly seem to be facilitated by it. For the bulk composition of a pluton to change as it crystallizes inward requires extensive material exchange over long distances. Diffusion in molten silicates is too slow to accomplish this unaided, so that some sort of convection or other liquid motion is required. This in turn seems to require that the newly accreted crystals be rather firmly attached to the walls. The generally greater facility of mafic crystals to nucleate may assist in this type of differentiation (Naney and Swanson, 1981).

The conclusion that homogeneous nucleation is absent or very rare in basaltic rocks is not necessarily applicable to magmas of granitic composition, in which laboratory experiments have produced internal nucleation. For example, Swanson (1977) shows photographs of quartz crystals, grown in synthetic granite, which are clearly isolated plates with no

connection to other crystals or to the container. The reason for the difference between basaltic and granitic compositions may be the presumably slower diffusion rates of Si and Al in the granite, which might have a more drastic effect on growth than nucleation, or the considerably higher water contents of the granitic liquids. Quartz and feldspar phenocrysts in porphyritic granitic rocks sometimes form in clusters, which has often been interpreted as evidence for synneusis (Vance, 1969), but is more simply explained as the result of heterogeneous nucleation (Dowty, 1980b). However, euhedral crystals also commonly occur in isolation. A good example is the occurrence of orthoclase phenocrysts in a rhyolitic rock near Goodsprings, Nevada, originally described by Drugman (1938). We collected and examined a suite of phenocrysts from this locality and qualitatively verified Drugman's conclusion that the great majority are single untwinned crystals of a remarkably uniform euhedral habit. The remainder of the crystals are twins, almost all of which consist of two individuals with reasonably symmetric development and which probably grew from twinned nuclei (Buerger, 1945). These facts tend to suggest homogeneous nucleation for this particular rock.

Conclusions

Most recent studies of nucleation seem to have raised more questions than they have answered, and our work is no exception. However, our conclusion that nucleation occurs exclusively on external surfaces when the charge is completely molten is a firm one, and it is clear that some previous results should be reinterpreted or reinvestigated. Our results also provide further confirmation that homogeneous nucleation in natural basaltic rocks is improbable. We find that heterogeneous nucleation mechanisms in the laboratory are quite varied, and varied (though probably different) mechanisms evidently operate in nature.

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