

Supercooling and the crystallization of plagioclase, olivine, and clinopyroxene from basaltic magmas

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ABSTRACT. Effects of supercooling have been studied in a range of basaltic melts by isothermal and constant cooling rate experiments at one-atmosphere, using the wire-loop container method. The nucleation of plagioclase in these melts is systematically controlled by supercooling ($-\Delta T$), time below the liquidus temperature, and initial superheating ($+\Delta T$). The temperature at which the melt is initially superheated prior to supercooling controls the temperature at which crystal nucleation first takes place in a supercooled melt undergoing cooling; the greater the $+\Delta T$ the larger the degree of supercooling required prior to nucleation of the liquidus phase during cooling. In all six compositions investigated there are at least two fields in time-temperature space, one in which the liquidus phase always fails to nucleate on supercooling (favoured by small $-\Delta T$) and one (favoured by large $-\Delta T$) in which it always nucleates. These two fields may be separated by another in which the liquidus phase may or may not crystallize. Supercooling phenomena are not restricted to the liquidus phase but can also occur when the melt becomes saturated with subsequent phases. It is shown that the composition of plagioclase varies systematically with $-\Delta T$ and it is demonstrated that isothermal supercooling 'lines' can be used with a relatively high degree of accuracy to predict when nucleation of the liquidus phase will take place during constant cooling rate experiments.

It is generally recognized (Gibb, 1974; Lofgren, 1974; Lofgren and Donaldson, 1975; Walker *et al.*, 1976; Swanson, 1977; Donaldson, 1979) that it is possible for a silicate liquid (anhydrous or hydrous) to be cooled substantially below its equilibrium liquidus temperature without crystallization of the liquidus phase. The present work is an extension of that of Gibb (1974) who showed that a single basaltic composition could be cooled from above its liquidus temperature such that the liquidus phase (plagioclase) sometimes failed to crystallize depending on the degree of supercooling ($-\Delta T$) and the duration of the experiment. The study is also an extension to the work of Donaldson (1979), who showed that the delay in the nucleation of

olivine in basaltic melts varies systematically with $-\Delta T$, superheating ($+\Delta T$), and cooling rate.

Five main topics have been investigated: (1) isothermal supercooling behaviour in a range of basaltic rocks; (2) the relationship between initial superheating and the temperature at which plagioclase nucleates on supercooling; (3) the effect of supercooling on the crystallization of subsequent phases; (4) the compositions of plagioclase feldspars produced during isothermal supercooling, and (5) the validity of using isothermal supercooling diagrams to predict when nucleation will be initiated during constant rate cooling, as proposed by Gibb (1974).

Samples and experimental method. Supercooling phenomena have been investigated in seven mafic rocks: a hawaiite (028) from Oldugigar 10 km west of Hekla, South Iceland; a basanite (331) from Cangreja, Tenerife in the Canary Islands; an ankaramite (336) from Montana Dornajo, Tenerife; a trachy-basalt (339) from west of the Garachico Teno Peninsula, Tenerife, and two olivine tholeiites (G. 1 and G. 60) and a tholeiite (G. 18) from dykes on the Island of Arran in south-west Scotland. The chemical compositions of these rocks are given in Table I.

All experiments were made at one-atmosphere using a 30 mm bore, Pt-wound, vertical, quench furnace. The oxygen pressure of the furnace was controlled by a

TABLE I. *Chemical analyses of samples used (wt. %)*

Sample number	336	G. 1	G. 60	331	G. 18	339	028
SiO ₂	42.41	45.39	46.33	47.31	48.94	51.32	54.06
Al ₂ O ₃	15.14	17.46	17.10	17.10	13.25	16.26	14.66
TiO ₂	4.16	1.55	1.53	3.31	2.19	2.63	2.06
Fe ₂ O ₃	8.27	4.39	4.53	3.63	4.68	5.01	2.08
FeO	5.09	7.24	6.44	6.28	10.59	5.29	9.94
MnO	0.23	0.19	0.25	0.18	0.21	0.20	0.28
MgO	5.75	6.20	7.33	4.35	5.24	3.56	2.81
CaO	10.97	10.69	10.55	8.82	9.71	7.40	6.87
Na ₂ O	2.15	2.75	2.39	5.05	2.58	5.10	4.09
K ₂ O	1.44	0.17	0.22	2.08	0.64	1.82	1.21
P ₂ O ₅	0.89	0.15	0.15	1.33	0.18	1.07	1.07
S	0.01	0.09	0.04	0.01	0.12	0.04	0.02
CO ₂	n.d.	2.73	1.71	n.d.	0.41	n.d.	n.d.
H ₂ O ⁺	3.18	1.38	1.98	0.61	0.97	0.81	0.12
Total	99.69	100.38	100.55	100.06	99.71	100.51	99.27

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method essentially the same as that of Darken and Gurry (1945), in which CO_2 and H_2 were mixed before being passed upwards through the furnace in predetermined proportions necessary to give an oxygen fugacity (f_{O_2}) of 10^{-8} atmospheres for samples 028, 331, 336, 339, and G. 18, and 10^{-9} atmospheres for samples G. 1 and G. 60 (most basalts are thought to crystallize in the 10^{-6} – 10^{-8} atmospheres range (Hamilton and Anderson, 1967)). In all the melts studied, plagioclase is the equilibrium silicate liquidus phase and the liquidus temperatures together with the temperatures at which subsequent phases 'go out' on heating are given in Table II.

TABLE II. Liquidus temperatures ($^{\circ}\text{C}$) and temperatures ($^{\circ}\text{C}$) at which subsequent phases 'go out' on heating for the samples used

Sample	Liquidus	2nd phase	3rd phase
028	1166	n.d.	n.d.
331	1168	n.d.	n.d.
336	1210 ± 3	1155 ± 4 (Ol)	1147 (Cpx)
339	1176	n.d.	n.d.
G. 1	1258 ± 5	n.d.	n.d.
G. 18	1166	1147 ± 4 (Cpx)	n.d.
G. 60	1237 ± 6	n.d.	n.d.

Ol = Olivine Cpx = Clinopyroxene

The temperatures for samples 028, 331, 336, 339, and G. 18 were determined at an f_{O_2} of 10^{-8} atmospheres and those for samples G. 1 and G. 60 at 10^{-9} atmospheres. The furnace temperature measurements are considered accurate to $\pm 2^{\circ}\text{C}$. The \pm figures constitute the range of error in the determination of these temperatures.

Prior to the isothermal supercooling experiments pellets of powdered rock were attached to Pt wire-loops (using 0.2 mm diameter wire), and in later experiments to $\text{Ag}_{40}\text{Pd}_{60}$ wire-loops (using 0.2 mm and 0.15 mm diameter wire) in order to reduce iron losses from the sample to the container (Corrigan and Gibb, 1979). The pellets were then partly fused to form beads, by heating them in a muffle furnace to temperatures substantially above their solidus temperatures for a short interval. The beads were then suspended at the 'hot spot' of the furnace (see Corrigan, 1980, for a full description of the method used). The charges were then heated above their liquidus temperatures for 12–24 hours at set $+\Delta T$ values to permit equilibration with the furnace atmosphere (Fudali, 1965). This flexibility in the duration of superheating is probably acceptable since Gibb (1974) and Donaldson (1979) concluded that supercooling was not affected by the duration of heating above the liquidus. Subsequent to superheating the temperature was lowered as rapidly as possible to a predetermined sub-liquidus isotherm, taking care to avoid undershoot, and held within 2°C of this temperature for the desired run time before quenching into water at room temperature. During each run the gas mixture was adjusted to appropriate values for the new thermal conditions so that the oxygen fugacity remained

constant. Using this method the time required for plagioclase nucleation over a range of supercooling was determined.

Plagioclase nucleation was studied during cooling-rate experiments using sample G. 18 beads in which, after initial superheating, the charges were cooled at constant rates (0.3–11.8 $^{\circ}\text{C}/\text{hr}$) and quenched from various temperatures below the liquidus. In these constant rate cooling experiments the temperature was lowered by using a variable speed electro-mechanical stepping device to regularly increase the output from a DC millivolt source by extremely small increments (either 4.5×10^{-5} mv or 1.39×10^{-6} mv). This signal was added to that from the control thermocouple in the furnace to simulate a gradual rise in the furnace temperature, thus inducing the control system to cool the furnace at the required rate by attempting to maintain the total signal at a constant level. This method was used as manual or mechanical

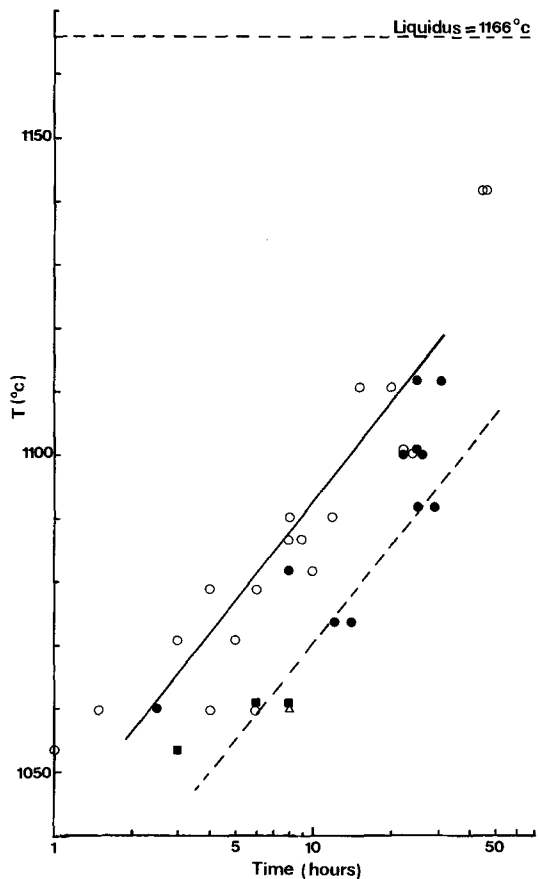


FIG. 1. Isothermal supercooling 'line' for plagioclase (solid line) for sample 028 determined using Pt wire-loops. The initial superheating was $+\Delta T = 24 \pm 2^{\circ}\text{C}$. The dashed line refers to the inferred lower limit of the Unpredictable Zone. Open circle = glass; solid circle = glass + plagioclase; solid square = glass + plagioclase + clinopyroxene; open triangle = glass + plagioclase + olivine.

adjustments of the set point of the controller could not give the precision required and, in any case were liable to give 'overshoot'.

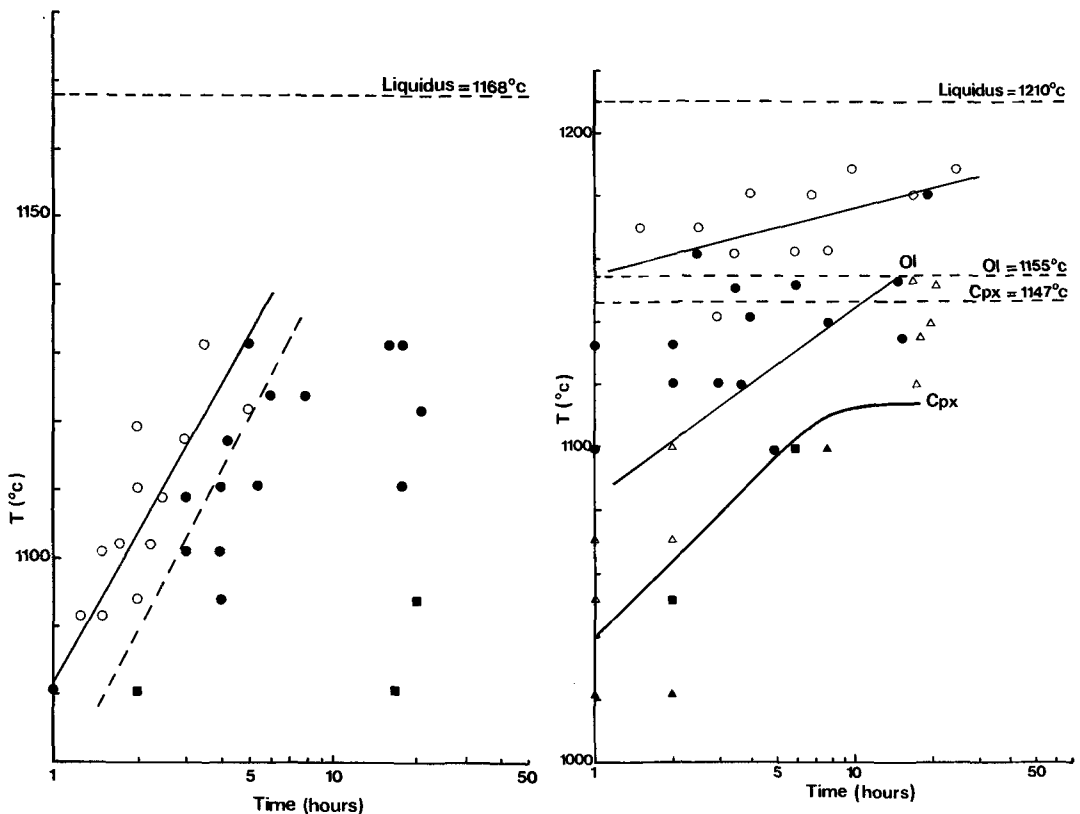
During the initial superheating the gas mixture was set to give an f_{O_2} of 10^{-8} atmospheres. The charges were then cooled rapidly to 10–15°C above the liquidus temperature, with an adjustment in the gas mixture to give the same f_{O_2} at the liquidus temperature. The charges were then cooled at the predetermined rates through the liquidus temperature to various degrees of $-\Delta T$ and quenched. The $CO_2:H_2$ ratio in the atmosphere was not altered during the runs, so that the f_{O_2} decreased slightly with cooling. This procedure is justifiable since Hamilton and Anderson (1967) have shown that anhydrous basaltic magma cooling under conditions of constant total composition will have a small decrease in f_{O_2} , with the amount depending on how much cooling has occurred.

After quenching, in the case of shattered beads, a small amount of the charge was coarsely ground and mounted for optical identification of the phases. This expedited preliminary identification of the silicate phases and the consequent decisions regarding the conditions necessary

for subsequent experiments. Thin sections were made from the remainder of each of the charges. Where beads remained intact they were cut horizontally, i.e. perpendicular to the suspending wire and either made into ordinary thin sections or polished for use on the electron microprobe.

Results

Isothermal supercooling studies. As in the case of the Columbia River basalt investigated by Gibb (1974), it has been found that when samples 028, 331, 336, and 339 (contained in Pt wire-loops) are cooled from above their liquidus temperatures, after initially being superheated respectively to $24 \pm 2^\circ C$, $21 \pm 2^\circ C$, $27 \pm 2.5^\circ C$, and $25.5 \pm 3.5^\circ C$, the liquidus phase (plagioclase) may fail to nucleate depending on the degree of supercooling and the duration of the run (figs. 1–4). A field in time-temperature space in which plagioclase fails to nucleate (Non-Nucleation Zone) is separated from



FIGS. 2 and 3. FIG. 2 (left). Isothermal supercooling 'line' for plagioclase (solid line) for sample 331 determined using Pt wire-loops. The initial superheating was $+\Delta T = 21 \pm 2^\circ C$. The dashed line refers to the inferred lower limit of the Unpredictable Zone. FIG. 3 (right). Isothermal supercooling 'lines' for plagioclase (upper solid line), olivine (Ol) and clinopyroxene (Cpx) for sample 336. The initial superheating was $+\Delta T = 27 \pm 2.5^\circ C$. Symbols as for fig. 1 and also solid triangle = glass + plagioclase + clinopyroxene + olivine.

another in which plagioclase may or may not crystallize (Unpredictable Zone), which is itself separated from a field in which plagioclase always nucleates (Nucleation Zone). In contrast to the results of the isothermal supercooling experiments of Donaldson (1978, 1979) show that olivine nucleation is a predictable event to within a few minutes. No Unpredictable Zone was found to exist for the composition used, which is presumably because olivine nucleates very readily once its saturation level has been reached because of its simple neso-silicate structure.

Since very short times, i.e. rapid cooling or quenching, are likely to result in complete suppression of nucleation the supercooling line must be asymptotic to the temperature axis. The line must

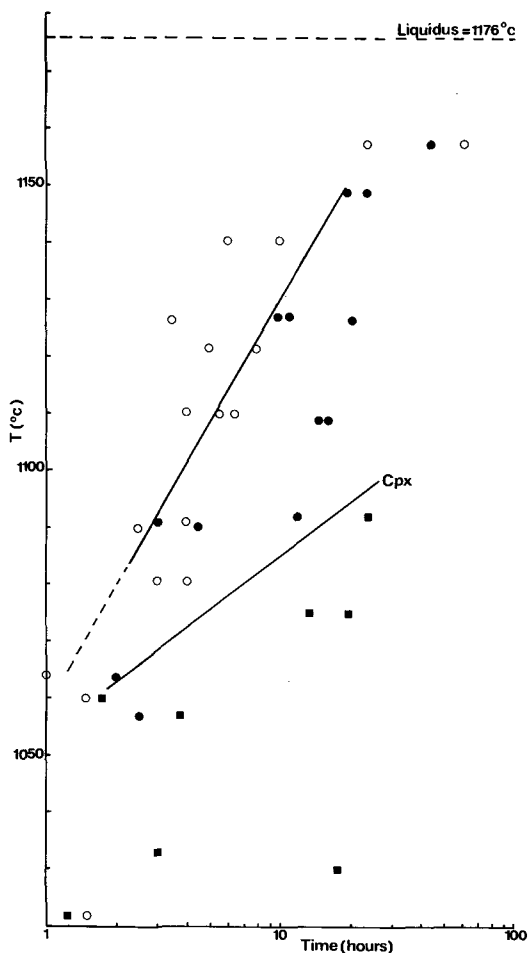


FIG. 4. Isothermal supercooling 'lines' for plagioclase (solid/dashed line) and clinopyroxene (Cpx) for sample 339 determined using Pt wire-loops. The initial superheating was $+\Delta T = 25 \pm 3.5^\circ\text{C}$. Symbols as for fig. 1.

also be asymptotic to the time axis at the liquidus temperature since at infinitely small $-\Delta T$ values no crystals will nucleate (Gibb, 1974). In reality, therefore, the line is a curve which is asymptotic to the temperature and time axes (Gibb, 1974). Throughout this work, when referring to these isothermal supercooling diagrams, the boundary between the Non-Nucleation Zone and the Unpredictable Zone or the Nucleation Zone will be referred to as a 'line' since most of the data collected from the rock compositions refer to the almost linear portion of the 'curve'.

The Non-Nucleation Zone. The fact that these silicate melts can be supercooled could be due to one or more of three main factors. First, the delay in plagioclase nucleation could be attributed to the slow growth of embryos into nuclei in the melt (Turnbull, 1948), or plagioclase nuclei may form but growth is so slow that crystals do not reach observable sizes in times of the order used in these experiments. Secondly, diffusion rates of elements such as Si or Al in the liquid adjacent to a plagioclase crystal could be the rate-determining factor in the growth of crystals but, as stressed by Gibb (1974), it is difficult to envisage how the liquid adjacent to a plagioclase embryo could be so depleted in significant amounts of the essential elements as to prevent growth. Finally, time is necessary at any temperature for the structural ordering in the melt of the complex tectosilicate framework of plagioclase. This final factor seems to be the most likely explanation as substances with simple structural configurations appear to crystallize more readily than complex structures (Goldsmith, 1953; Donaldson, 1978, 1979). Although the Non-Nucleation Zone could be accounted for in this way, the existence of the Unpredictable Zone in an area where plagioclase is a stable phase is problematical.

The Unpredictable Zone. It is shown that mechanical effects such as agitation, shock (Mullin, 1972) or vibration (Chalmers, 1964) of a liquid can induce crystallization, since the mechanical motion so produced can facilitate the rearrangement of the atoms necessary to produce an embryo. The work of Mullin and Raven (1961, 1962), however, on aqueous salt solutions showed that an increase in the intensity of agitation did not always lead to an increase in nucleation. Although gentle agitation causes nucleation in solutions that are otherwise stable and vigorous agitation considerably enhances nucleation, the transition between the two conditions may not be continuous. A plot of critical supersaturation versus the intensity of agitation is not a single smooth curve, but rather a portion of the curve may have a reversed slope, indicating a region where an increase in the agita-

tion actually reduces the tendency to nucleate. This could be explained by assuming that agitation could also lead to the disruption of crystal embryos, as well as facilitating their growth and further development. As a result of either or both effects, variable intensities of such phenomena could produce an Unpredictable Zone. It is thought, however, that such effects, if any, are slight, as the laboratory in which the experiments reported here were performed was viewed as being more or less free from vibrations.

As the internal configuration of Pt wire within each rock pellet is unlikely to be identical, the probability of heterogeneous nucleation (i.e. nucleation on the wire-loop) will be slightly greater in some charges than in others and such an effect could give rise to the irregular crystallization pattern in the Unpredictable Zone when wire-loops are used, if the crystals are not recognized as having grown heterogeneously. It has been shown (Corrigan, 1980) that the actual surface area of the container in contact with the sample can substantially alter the $-\Delta T$ required for homogeneous nucleation (i.e. spontaneous nucleation directly from the melt) at any given time, since the Unpredictable Zone was found to be smaller when using $\text{Ag}_{40}\text{Pd}_{60}$ capsules than when using Pt wire-loops. It must, however, be realized that such an effect could also be due to the different iron and alkali losses incurred when using the different containers, which would cause changes in the bulk compositions.

If the time the charge has been heated above its liquidus temperature is too short to allow complete melting, there could be 'relics' (i.e. 'domains' in the liquid which retain long-range order) of the liquidus phase present which could influence the subsequent crystallization on supercooling. Hence variation in the initial heating period could result in crystals nucleating in the area of otherwise 'non-nucleation' and so give rise to the Unpredictable Zone. This seems unlikely as Gibb (1974) showed that the duration of melting above the liquidus temperature did not appear to affect the subsequent extent of supercooling attained.

The speed of cooling to the subliquidus isotherm would seem unlikely to affect plagioclase crystallization in the Unpredictable Zone, since the total variation in the cooling rate is small as all runs were lowered to their subliquidus temperature as quickly as possible (the speed of cooling was of the order of 300 °C/hr).

It must be realized that where there are only a very few crystals present they may not appear in the plane of the thin section especially if the initial bead had a heterogeneous distribution of crystals.

The effect of superheat. Although Gibb (1974)

concluded that superheating of a silicate melt above its liquidus temperature by amounts ranging from 50 °C to more than 100 °C for periods of up to 20 hours had no 'observable' effect on the extent to which the crystallization of plagioclase was inhibited, it has been observed by Schairer (1959) that crystallization may be inhibited where melts have been severely overheated. It has been implied by Biggar *et al.* (1971) that the structure of the liquid exerts some control over crystallization, as when glasses are used as the initial starting material in experiments and crystallization of plagioclase is inhibited possibly in favour of 'simpler structures'. There is also some evidence to support the contention that the structure of a silicate liquid changes with heating above its liquidus temperature (*cf.* with molten sulphur [Gingrich, 1965]). The fact that glasses quenched from various temperatures show variation in such physical properties as density and refractive index (Lillie and Ritland, 1954) suggests (Morey, 1954) that such a relationship also exists for silicate liquids. Further, Donaldson (1978, 1979) has quantified the effect of $+\Delta T$ on olivine nucleation and has shown that the delay in nucleation is systematically increased by increasing the amount of superheat on melting.

To evaluate the effect of superheating on the supercooling of plagioclase in sample 028, diagrams like fig. 1 have been determined for other $+\Delta T$ values and the positions of the supercooling lines are compared with the one from fig. 1 on fig. 5. From fig. 5 it is clear that $+\Delta T$ does indeed have a definite effect on supercooling and subsequent crystallization, since, for any given time, greater supercooling is required prior to nucleation as $+\Delta T$ increases. The presence of an Unpredictable Zone (like that in fig. 1) for each $+\Delta T$ value shows that variation in $+\Delta T$ is not responsible for its existence. Variation in $+\Delta T$ could, however, be partially responsible for the apparent extent of the Unpredictable Zone in diagrams based on experimental data in which $+\Delta T$ varied, since it is almost certainly going to make it seem very much larger if $+\Delta T$ is ignored (e.g. Gibb (1974) fig. 3). The erroneous observation of Gibb (1974) that $+\Delta T$ does not affect the extent of supercooling and subsequent crystallization could be explained by his failure to recognize the individuality of supercooling 'lines' for different $+\Delta T$ values, because of the limited data used and the masking effect of the Unpredictable Zone; these zones having been aggregated by him into a simple much larger Unpredictable Zone.

As shown in fig. 6 the time of delay in plagioclase nucleation at a given value of $-\Delta T$ increases systematically with increasing superheat, which presumably reflects the higher entropy and greater

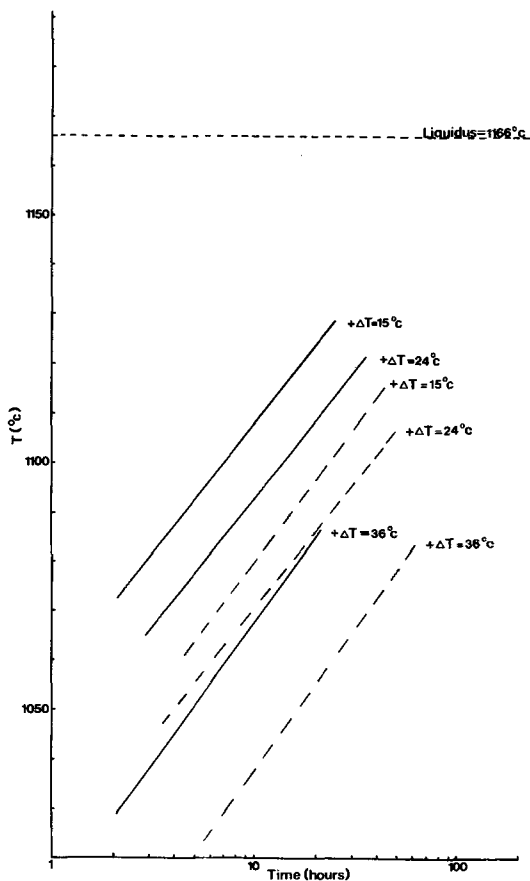


FIG. 5. Isothermal supercooling 'lines' for plagioclase (solid lines) for sample 028 determined using Pt wire-loops. The dashed 'lines' refer to the inferred lower limits of the Unpredictable Zone. Each 'line' was constructed for different $+\Delta T$ values.

structural disorder of the melt with increasing temperature.

For sample 028 melted at $+\Delta T = 24 \pm 2^\circ\text{C}$ a plot of $\log -\Delta T$ against $\log t$ (where t = time delay in nucleation) (fig. 6) is linear ($\log -\Delta T = -0.2942 \log t + 2.1461$) over the range of $-\Delta T = 57 - 120^\circ\text{C}$ for 1 to 20 hours. If it is linear over a wider range of $-\Delta T$ values then either extrapolation or solving the above equation for t can be used in calculating the incubation period necessary for nucleation at smaller values of $-\Delta T$. For example at $-\Delta T = 5^\circ\text{C}$ there would have to elapse 9.47 years before nucleation commenced. Extrapolation of the supercooling line (fig. 1) to 1161°C (i.e. $-\Delta T = 5^\circ\text{C}$) shows that nucleation would commence after 8.75 days. The disparity between these two values could be explained by either the $\log -\Delta T$ versus $\log t$ plot not being linear at smaller $-\Delta T$ values

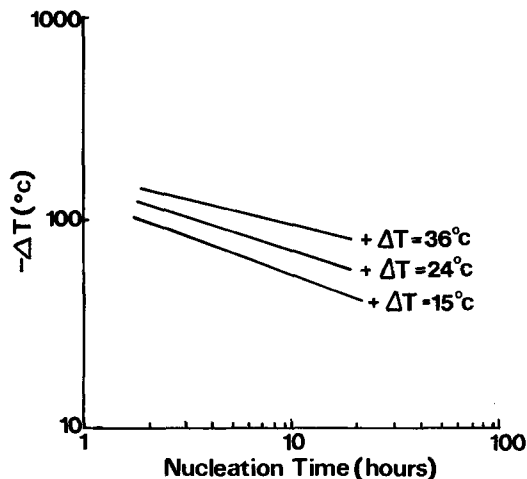


FIG. 6. Linear relationship between $\log -\Delta T$ and \log nucleation time for sample 028 determined at three values of $+\Delta T$.

or the supercooling 'line' (fig. 1) not projecting linearly to the liquidus temperature but being asymptotic to the time axis (or both).

Fig. 7 plots the length of the incubation period at three isotherms against the melt viscosity in poises (Shaw, 1972) at the determined $+\Delta T$ values. It is evident that the length of the incubation period increases with decreasing melt viscosity (at the $+\Delta T$ value), which again reflects the increasing disorder of the melt with rise in temperature. The decreasing melt viscosity with larger $+\Delta T$ values will lead to enhanced destruction of 'relic' structures in the melt and thus the larger the initial $+\Delta T$ the greater the amount of supercooling which will occur.

After initial superheating at a constant $+\Delta T$

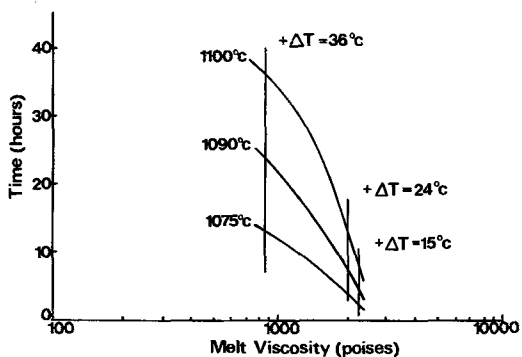
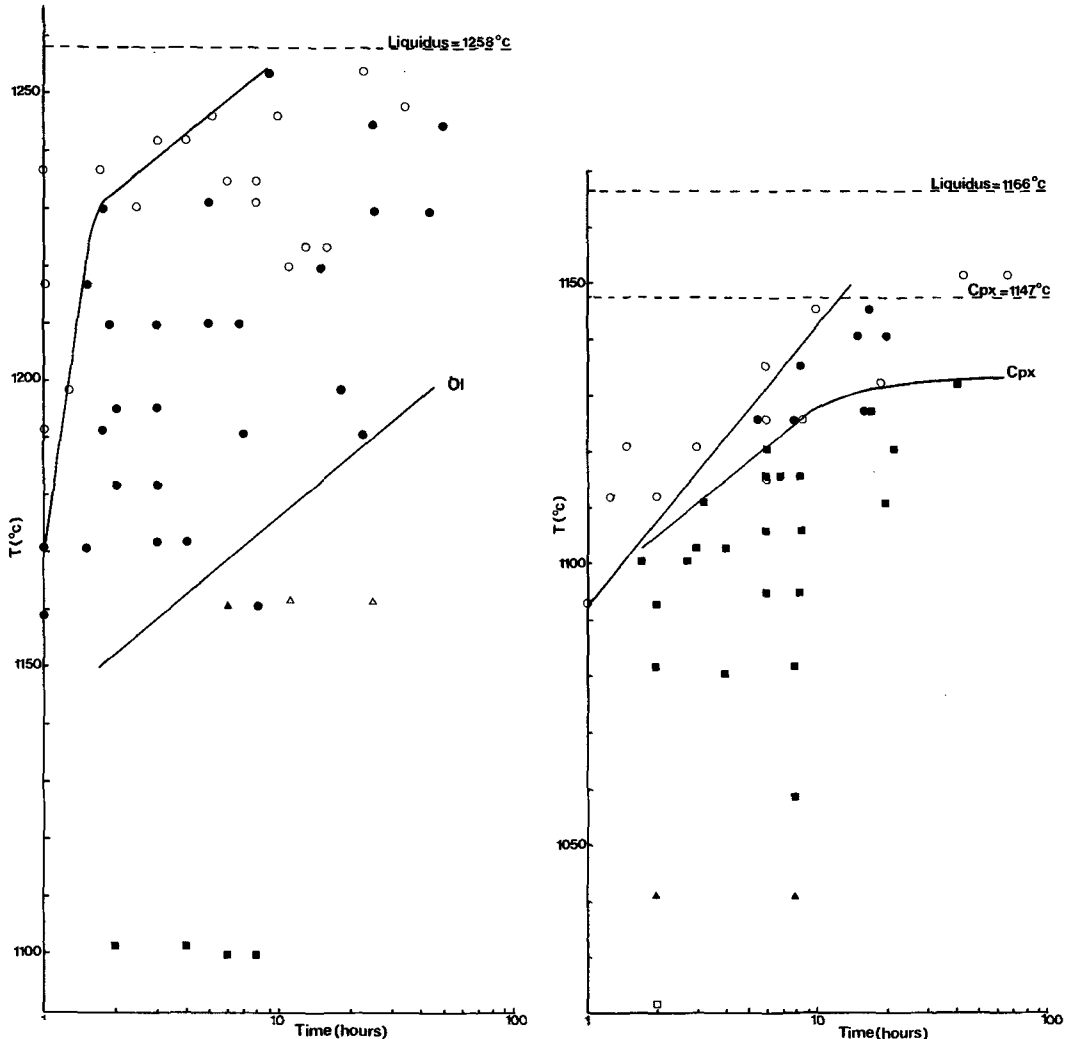


FIG. 7. Relationship between the time needed for nucleation on the 1075°C , 1090°C , and 1100°C isotherms and melt viscosity calculated at the $+\Delta T$ values for sample 028.

value the incubation period decreases as $-\Delta T$ increases (i.e. temperature decreases) showing that the increasing viscosity of a melt does not seriously inhibit nucleation (or if it does it is overcome by the supersaturation effect). This is contrary to what one might expect since, in a partially solidified medium, molecular-scale movements necessary to facilitate nucleation would be slower.

The delay in plagioclase nucleation with increasing $+\Delta T$ could be due to a variety of factors. First, embryo size could be important in determining the

delay since it is thought that the greater the amount of $+\Delta T$ the smaller the size of the embryos in the melt due to progressive destruction of the structural order of the melt and this would result in longer times being required at a given $-\Delta T$ (Donaldson, 1978, 1979). Secondly, if relic structures do persist in the liquid, the greater the amount of $+\Delta T$ the more likely supercooling is to occur and the greater its extent. If such local chemical concentrations of the elements from the melted plagioclase are built up and preserved in the melt because of its relatively



FIGS. 8 and 9. FIG. 8 (left). Isothermal supercooling 'lines' (solid lines) for plagioclase and olivine (Ol) for sample G. 1, determined using $\text{Ag}_{40}\text{Pd}_{60}$ wire-loops. The initial superheating was $+\Delta T = 22.5^\circ\text{C} \pm 2.5^\circ\text{C}$. Symbols as for fig. 1 and also solid triangles = glass + plagioclase + clinopyroxene + olivine. FIG. 9 (right). Isothermal supercooling 'lines' for plagioclase (unlabelled solid line) and clinopyroxene (Cpx) for sample G. 18. The initial superheating was $+\Delta T = 34.5 \pm 2.5^\circ\text{C}$. Symbols as for fig. 1 and also solid triangles = glass + plagioclase + clinopyroxene + olivine; open squares = plagioclase + clinopyroxene.

high viscosity impeding diffusion, then these may aid plagioclase nucleation, providing the melt is cooled quickly enough before they have had time to disperse (Gibb, 1974).

The effect of supercooling on other phases. Isothermal supercooling diagrams have also been constructed for samples G. 1 ($+\Delta T = 22.5 \pm 2.5^\circ\text{C}$), G. 18 ($+\Delta T = 34.5 \pm 2.5^\circ\text{C}$) and G.60 ($+\Delta T = 45 \pm 3.5^\circ\text{C}$) (figs. 8, 9, and 10) to supplement the data on the other samples so that the effect of supercooling on the crystallization of olivine and clinopyroxene could be investigated in more detail. To further reduce Fe loss the experiments were conducted using 0.2 mm diameter $\text{Ag}_{40}\text{Pd}_{60}$ wire in preference to the Pt wire used for samples 028, 331, 336, and 339 (Pt wire was initially used for these four samples because it was not known until later on in the experimental programme that $\text{Ag}_{40}\text{Pd}_{60}$ wire reduced Fe losses to a greater extent than Pt wire of the same diameter [Corrigan and Gibb, 1979]). The two sets of data, however, cannot be directly compared as compositionally different container wires and a range of $+\Delta T$ values were used for the two sets of experiments, but the basic effects are the same in both. The crystallization of olivine and clinopyroxene will be discussed in detail for samples 336 and G. 18.

It is evident from the isothermal supercooling diagrams for samples 336 and G. 18 (figs. 3 and 9) that the phenomena of supercooling and non-nucleation of crystals is not restricted to the liquidus phase but can also occur when the melt becomes saturated with the second and third phases (Biggar *et al.*, 1971; Gibb, 1974).

1. *Clinopyroxene nucleation.* The effects of isothermal supercooling on second phase (clinopyroxene) nucleation are seen in fig. 9 where $T_{\text{Cpx-out}} = 1147 \pm 4^\circ\text{C}$. The chain structure of clinopyroxene is simpler than the feldspar framework and it might therefore be expected to nucleate more readily than plagioclase. The shorter incubation period at the same degree of undercooling for clinopyroxene than for plagioclase (fig. 11) suggests that this is the case. Further, the lack of any suggestion of an Unpredictable Zone (except for one run at 1127°C for 16 hours in fig. 9) could be attributed to a similar structural control (*cf.* Kirkpatrick *et al.* 1976).

2. *Olivine and clinopyroxene nucleation.* The effects of isothermal supercooling on the nucleation of second phase olivine ($T_{\text{Ol-out}} = 1155 \pm 4^\circ\text{C}$) and third phase clinopyroxene ($T_{\text{Cpx-out}} \approx 1147 \pm 3^\circ\text{C}$) as shown by sample 336 (figs. 3 and 12) are more complicated. It is clear (fig. 12) that for values of $-\Delta T$ less than 46.5°C , olivine nucleates more readily than plagioclase but that at greater $-\Delta T$

values olivine nucleates less readily. Clinopyroxene, over the entire range of $-\Delta T$ values investigated, needs more time to nucleate than plagioclase or olivine once its supersaturation level has been reached. However, if the line for the clinopyroxene data is extrapolated to smaller $-\Delta T$ values the relationship between clinopyroxene and plagioclase will be reversed (*cf.* plagioclase and olivine). That clinopyroxene nucleates less readily than plagioclase could be due to olivine growth depleting the melt in some of the components (i.e. Mg and Fe) necessary for clinopyroxene growth. If three runs in which olivine was not observed,

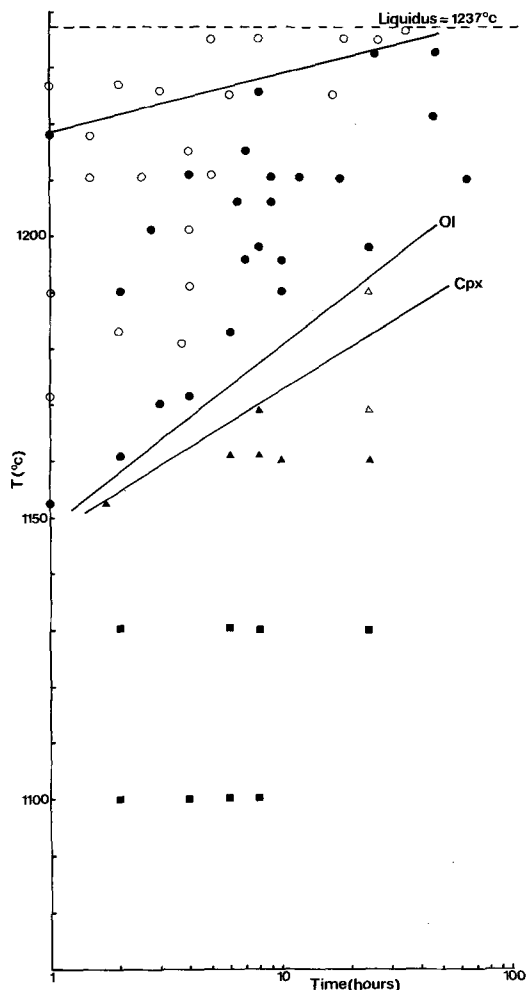
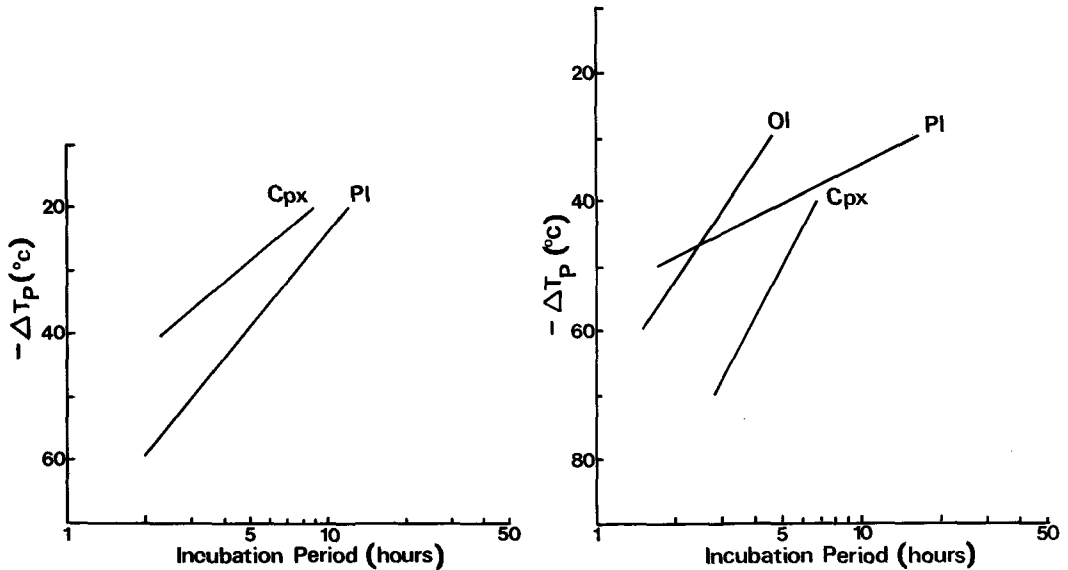


FIG. 10. Isothermal supercooling 'lines' for plagioclase (unlabelled solid line) olivine (Ol) and clinopyroxene (Cpx) for sample G. 60 determined using $\text{Ag}_{40}\text{Pd}_{60}$ wire-loops. The initial superheating was $+\Delta T = 45 \pm 3.5^\circ\text{C}$. Symbols as for fig. 1 and also solid triangles = glass + plagioclase + clinopyroxene + olivine.



FIGS. 11 and 12. FIG. 11 (left). Variations in the incubation periods of plagioclase and clinopyroxene as functions of their respective $-\Delta T$ s for sample G. 18. P = plagioclase or clinopyroxene. FIG. 12 (right). Variations in the incubation periods of plagioclase, clinopyroxene, and olivine for sample 336. P = plagioclase, clinopyroxene, or olivine.

although it might have been present are ignored (one at 1135 °C for 15.5 hours, another at 1099 °C for 5 hours and another at 1155 °C for 15 hours [fig. 3]) no Unpredictable Zone was found in the field of olivine nucleation. This provides evidence that olivine nucleates more readily than plagioclase. It is suggested that the reason olivine nucleates less readily than plagioclase when $-\Delta T$ is greater than 46.5 °C is because by this stage clinopyroxene is nucleating abundantly in the melt and is competing for the Mg and Fe necessary for olivine growth. The suggestion that olivine actually nucleates more readily than clinopyroxene and is not just a result of competition for ions in the melt is supported by the fact that although the difference between T_{Ol-out} and $T_{Cpx-out}$ temperatures is only 8 °C, it takes about twice as long for clinopyroxene to nucleate at any given $-\Delta T$ as it does for olivine (fig. 12). This evidence that olivine can be supercooled substantially is in agreement with the work of Donaldson (1979), who observed significant supercooling of olivine during a series of isothermal supercooling experiments on an alkali olivine basalt.

3. *Conclusions.* The observed differences in the ease of nucleation of clinopyroxene compared to plagioclase in sample G. 18 and olivine relative to clinopyroxene in sample 336 could be attributed to fundamental differences in the powers of nucleation between different minerals (Goldsmith, 1953; Wager, 1959; Hawkes, 1967; Wager and Brown,

1968; McBirney and Noyes, 1979). In this way minerals of simple structure, e.g. olivine, would nucleate before phases of more complex structure, e.g. clinopyroxene and plagioclase. For sample 336 the relationship of plagioclase, olivine, and clinopyroxene is not wholly consistent with this view, although it is at $-\Delta T$ less than 30 °C, if the clinopyroxene line is extended upwards. Indeed the reversal in the nucleation sequence of olivine and plagioclase for different $-\Delta T$ values suggests that the relative powers of nucleation are not simply related to structural control alone. Further, in sample G. 18 clinopyroxene embryos could have smaller critical radii compared with plagioclase embryos or they could grow faster (or both) and similarly in sample 336 olivine could have the same sort of relationship with both plagioclase and clinopyroxene. This reversal of the ease of nucleation of some minerals relative to others suggests the possibility that in some melts under different cooling conditions differences in the order of nucleation may well occur. It would be of interest in this respect to investigate a melt in which plagioclase was the liquidus phase and olivine the second phase with its melting point only a few degrees below the liquidus temperature.

Evidence from the melts investigated suggests that it is likely that plagioclase initially nucleates homogeneously, but that later crystallization frequently involves plagioclase apparently nucleating on plagioclase, or on subsequent phases as

'crystallization space' in the melt is reduced. In the case of sample G. 18, clinopyroxene sometimes nucleates freely in the melt, but more often it apparently nucleates on a plagioclase substrate or else it is intimately intergrown with acicular plagioclase. Similarly in sample 336 olivine and clinopyroxene nucleate freely in the melt or apparently heterogeneously on plagioclase. It must be pointed out that surface tension effects could cause crystals to stick together and give the appearance of heterogeneous nucleation.

Feldspar compositions produced during isothermal supercooling. The compositions of plagioclase feldspars produced during the isothermal supercooling of sample G. 60 have been determined by electron microprobe analyses for Si, Al, Ca, Na, K, and Fe using the Microscan 9 Electron Microprobe and the results are given in fig. 13. Over the range of $T = 1234\text{--}1100^\circ\text{C}$ and time = 1–65 hours the plagioclase composition varies from An_{83} at 1234°C (i.e. $-\Delta T = 3^\circ\text{C}$) to An_{69} at 1130°C (i.e. $-\Delta T = 107^\circ\text{C}$). It appears that over the range of supercooling studied the plagioclase composition is generally a direct function of $-\Delta T$ and, at any $-\Delta T$ value, it is constant with time. This is, however, not the case for the point labelled 'A' on fig. 13, which is anomalous in that it has a larger range of composition than any of the other points on the figure. For each analysed charge the range of compositions found is usually less than $\pm\text{An}_2$. The range within each charge suggests that the crystals are slightly zoned. No strong evidence of reversed zoning was found in the crystals (contrast Lofgren, 1974). Donaldson (1979), as a result of his experimental investigation of the delay in the nucleation of olivine in mafic magmas, suggested that continuous zoning may form under isothermal conditions due to the slow attainment of equilibrium of the melt structure following supercooling. Thus as changes in the melt structure proceed crystal/melt partition coefficients might also change and as a result zoned crystals may well form under isothermal conditions.

Prediction of incubation times. Gibb (1974) used one-atmosphere supercooling data on the nucleation times of plagioclase in a basaltic melt to predict plagioclase nucleation times during constant rate cooling experiments. This method has been applied to the isothermal supercooling diagram for sample G. 18 to predict when nucleation will be initiated during constant rate cooling experiments.

The supercooling line for plagioclase for sample G. 18 is a curve with the general form $T = T_L - (\log t_m - \log t)^n$ where T = temperature ($^\circ\text{C}$), T_L = the liquidus temperature ($^\circ\text{C}$) and t_m = the time required for plagioclase to nucleate at the tempera-

ture T (in hours) (Gibb, 1974). As the plagioclase supercooling 'line' (fig. 9) is nearly linear over the range of times for which it has been determined experimentally (time is on a log scale) n approaches one. Such curves are asymptotic to T_L at $t = t_m$ and also asymptotic to the temperature axis at small values of t (the present work indicates that these values would usually be substantially less than one hour). This latter relationship simply reflects the fact that if a charge is held for a short enough period at any sub-liquidus temperature, nucleation will never be initiated and that quenching of such charges would produce glasses. No attempt was made to conduct experiments at very short cooling times (less than half an hour) since considerable difficulties arise due to the thermal inertia of the furnace. Fig. 9 shows that over the

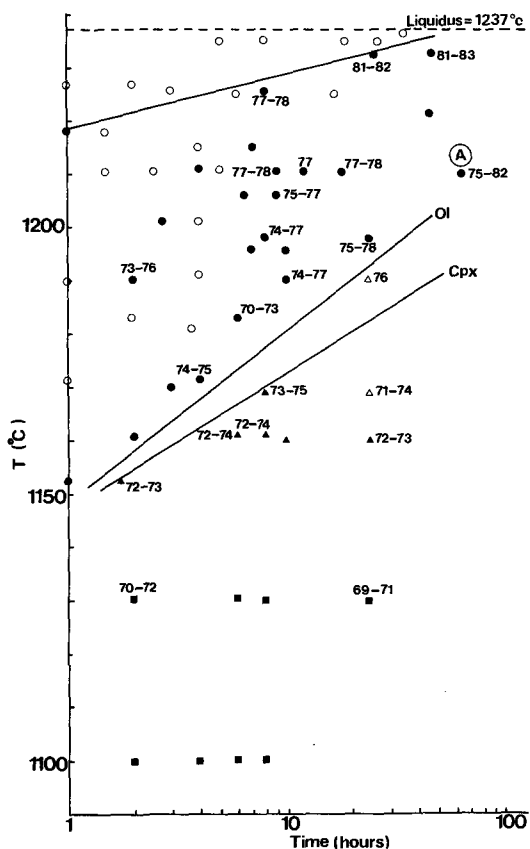


FIG. 13. Plagioclase crystal compositions determined by electron microprobe studies of crystals from charges of sample G. 60 as a function of T ($^\circ\text{C}$) and time. The range of composition (anorthite wt. %) from each charge is given, and the range at point 'A' is discussed in the text. For the initial superheating and the key to the symbols used see fig. 10.

range of temperature and time for which the plagioclase supercooling 'line' has been determined experimentally it is in fact linear, so that as a first approximation the 'line' can be represented by the equation $T = 49.25 \log t + 1092.5$. Although constant rate cooling is unlikely in nature as the cooling of an igneous body is a non-linear process, magmatic cooling over a limited range of temperature below the liquidus temperature can be regarded as linear, an approximation whose accuracy improves inversely with the cooling rate. Gibb (1974) indicated that when the cooling curve intersects the supercooling 'line' the nucleation of the liquidus phase will be possible and such a condition will first be satisfied when a cooling rate curve is tangential to the supercooling 'line'. Applying this method of Gibb (1974) to sample G. 18 it is shown that at a cooling rate of $1^\circ\text{C}/\text{hour}$ this condition is fulfilled at $T = 1158^\circ\text{C}$; first attained 8.8 hours after falling below T_L and after a further 21.4 hours at and below this temperature the nucleation of plagioclase is possible. Similar solutions for a range of cooling rates are given in Table III.

To test the validity of the theory put forward by Gibb (1974) and the results it yielded for G. 18, and to observe whether the experimentally observed times at which plagioclase first nucleates coincides with the total times at which plagioclase should first nucleate as predicted by the model, this sample was cooled from above its liquidus temperature at a number of different cooling rates and total cooling times. In fig. 14 it is clear that the experimentally determined curve (curve A) does not coincide exactly with the theoretical curve

TABLE III. Cooling times and nucleation temperatures for a range of constant cooling rates for sample G. 18

R ($^\circ\text{C}/\text{hour}$)	T ($^\circ\text{C}$)	H (hours)	t (hours)
10	1108	7.9	2.1
9	1111	8.6	2.4
8	1113	9.3	2.7
7	1116	10.3	3.1
6	1119	11.4	3.6
5	1123	12.9	4.3
4	1128	14.9	5.4
3	1134	17.9	7.1
2	1143	22.5	10.7
1	1158	30.2	21.4

R = Cooling rate.

T = Nucleation temperature.

H = Total cooling time.

t = Time at or below the nucleation temperature.

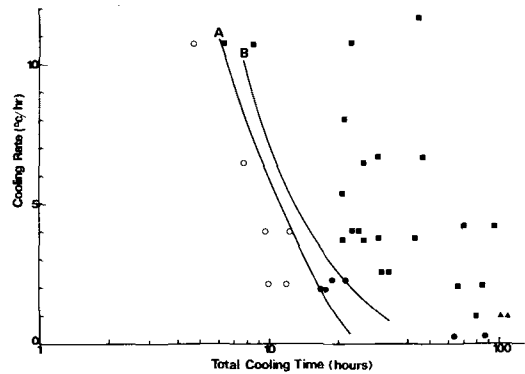


FIG. 14. Results of runs on sample G. 18 at different cooling rates (initial superheating = $34.5 \pm 4^\circ\text{C}$). The line 'A' separates runs in which plagioclase nucleated (solid symbols) from those in which it did not (open symbols). 'B' is the corresponding theoretically predicted line. Symbols as for fig. 1 and also solid triangles = glass + plagioclase + clinopyroxene + olivine.

(curve B). For example, the model predicts that for a cooling rate of $2^\circ\text{C}/\text{hour}$, a temperature of 1143°C should be attained 11.8 hours after falling below T_L and not until a further 10.7 hours at or below 1143°C had elapsed would the nucleation of plagioclase be possible. After a total experimental cooling time of 16.7 hours at a cooling rate of $2^\circ\text{C}/\text{hour}$, however, plagioclase did nucleate. At this cooling rate no plagioclase nucleated after 12.1 hours. Thus the discrepancy between the theoretical and experimental nucleation times must be at least 5.7 hours. Fig. 14 does suggest that as the cooling rate increases the discrepancies between the theoretical and experimental curves decrease, for example at a cooling rate of $10^\circ\text{C}/\text{hour}$ the theory predicts that nucleation would be possible after 7.9 hours but the experimental result indicates that nucleation occurs after 6.6 hours. Such discrepancies between the theoretical and the experimental results (lines A and B, fig. 14) could be due to the fact that during the constant-rate cooling experiments the $\text{CO}_2:\text{H}_2$ ratio was not changed (for practical purposes) to accommodate the continuously changing thermal conditions, but instead it remained set at the liquidus temperature so that the f_{O_2} decreases slightly with the falling temperature, whereas in the isothermal supercooling experiments the $\text{CO}_2:\text{H}_2$ ratio was adjusted in accordance with the new thermal regime and hence the f_{O_2} remained constant. Work on the delay in nucleation during isothermal supercooling studies and constant rate cooling studies over a range of f_{O_2} values might help to elucidate this problem, but it is likely that any change due to variations in f_{O_2} would be very small. A more likely source

of the discrepancies between lines A and B (fig. 14), such that nucleation takes place more rapidly at a given cooling rate experimentally than that predicted by the model, may be due to the fact that during cooling once the nucleation temperature has been reached the temperature does not remain constant as it does in isothermal supercooling, but it does in fact continue to fall. Such lower temperatures would aid nucleation. The error introduced by this factor is also likely to be small. In view of these two possible sources of error it is surprising how similar the position of the lines are. Hence constant rate cooling predictions calculated from the linear portion of a supercooling 'line' can be used with a fair degree of confidence.

Conclusion

The delay in the nucleation of liquidus plagioclase in basaltic melts varies systematically with $-\Delta T$, time below the liquidus temperature and $+\Delta T$. $+\Delta T$ significantly affects the extent to which plagioclase crystallization can be suppressed during supercooling, such that greater $+\Delta T$ gives greater supercooling prior to nucleation. To some extent the growth of silicates in a supercooled melt is governed by the structural complexity of the phases. Once the melt supersaturation level has been reached for a subsequent phase (e.g. olivine or clinopyroxene), with a simpler structure than liquidus plagioclase, the nucleation and growth of such a phase may well proceed more rapidly than that of plagioclase crystallizing at the same time. The composition of plagioclase varies systematically with $-\Delta T$. Isothermal supercooling 'lines' can predict when nucleation will be initiated during constant rate cooling at greater than approximately $1^\circ\text{C}/\text{hr}$.

This study has further emphasized the fact that supercooling phenomena are undoubtedly of great importance in the nucleation and crystallization of igneous rocks. It demonstrates that the order of nucleation could vary in the same melt, depending on the cooling rate, and this would be of great importance in the non-equilibrium crystallization of quickly cooled volcanic rocks and their more slowly cooled dyke rocks.

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REFERENCES

- Biggar, G. M., O'Hara, M. J., Peckett, A., and Humphries, D. J. (1971) *Proc. Second Lunar Sci. Conf., Geochim. Cosmochim. Acta*, **1**, 617-43.
- Chalmers, B. (1964) *Principles of solidification*. Wiley, New York.
- Corrigan, G. M. (1980) Ph.D. Thesis, University of Sheffield.
- and Gibb, F. G. F. (1979) *Mineral. Mag.* **43**, 121-6.
- Darken, L. S., and Gurry, R. W. (1945) *J. Am. Chem. Soc.* **67**, 1398-412.
- Donaldson, C. H. (1978) *Prog. Exp. Petrol.* **4** (NERC), 13-16.
- (1979) *Contrib. Mineral. Petrol.* **69**, 21-32.
- Fudali, R. F. (1965) *Geochim. Cosmochim. Acta*, **29**, 1063-75.
- Gibb, F. G. F. (1974) *Mineral. Mag.* **39**, 641-53.
- Gingrich, N. S. (1965) In: T. J. Hughel: *Liquids; Structure, properties, solid interactions*, 172-200. Elsevier, Amsterdam.
- Goldsmith, J. R. (1953) *J. Geol.* **61**, 439-51.
- Hamilton, D. L., and Anderson, G. M. (1967) In: H. H. Hess and A. Poldervaart: *Basalts*, 445-82. Wiley, New York.
- Hawkes, D. D. (1967) *Geol. Mag.* **104**, 473-86.
- Kirkpatrick, R. J., Robinson, G. R., and Hays, J. F. (1976) *Geophys. Res.* **81**, 5715-20.
- Lillie, H. R., and Ritland, H. N. (1954) *J. Am. Ceram. Soc.* **37**, 466-73.
- Lofgren, G. E. (1974) *Am. J. Sci.* **274**, 243-73.
- and Donaldson, C. H. (1975) *Trans. Am. Geophys. Union* **56**, 468.
- McBirney, A. R., and Noyes, R. M. (1979) *J. Petrol.* **20**, 487-554.
- Morey, G. W. (1954) *The properties of glass*. Reinhold, New York.
- Mullin, J. W. (1972) *Crystallisation*. Butterworths, London.
- and Raven, K. D. (1961) *Nature Phys. Sci.* **190**, 251.
- (1962) *Ibid.* **195**, 35-8.
- Schairer, J. F. (1959) In *Physicochemical measurements at high temperatures*. Butterworths, London.
- Shaw, H. R. (1972) *Am. J. Sci.* **272**, 870-93.
- Swanson, S. E. (1977) *Am. Mineral.* **62**, 966-78.
- Turnbull, D. (1948) *Trans. AIME* **175**, 744-83.
- Wager, L. R. (1959) *Geol. Mag.* **96**, 75-80.
- and Brown, G. M. (1968) *Layered igneous rocks*. Oliver and Boyd, Edinburgh.
- Walker, D., Kirkpatrick, R. J., Longhi, J., and Hays, J. F. (1976) *Geol. Soc. Am. Bull.* **87**, 646-56.

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