

Supercooling and the crystallization of plagioclase from a basaltic magma

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SUMMARY. The liquidus temperature (1198 °C) and equilibrium phase relations of a sample of Columbia River basalt from the Picture Gorge section have been determined at 1 atmosphere by heating in a controlled atmosphere. When this basalt is cooled from above its liquidus temperature the liquidus phase (plagioclase) may fail to crystallize depending on the degree of undercooling and the duration of the experiment. A field in temperature-time space in which plagioclase fails to crystallize on cooling is separated from another in which plagioclase always crystallizes by a third in which the nucleation of plagioclase is unpredictable in terms of temperature and time. The extent to which this basaltic liquid can be supercooled without the crystallization of plagioclase is independent of the time it is held above the liquidus or the temperature in excess of the liquidus to which it is heated.

The exceptionally long times required to ensure the nucleation of plagioclase at or near the liquidus temperature suggest that many so-called 'equilibrium' phase relations determined from experiments of a few hours' duration could be in serious error if the 'equilibration' involves a nucleation process.

It is demonstrated that, over a range of cooling rates, the temperature at which plagioclase begins to crystallize on cooling varies markedly and the temperature and times required for both possible and certain nucleation of plagioclase are calculated for a range of constant cooling rates. The range of cooling rates over which the nucleation temperature of plagioclase varies is likely to occur in nature only in certain lava flows and small minor intrusions. In such cases this could lead to changes in the order in which the minerals appear on cooling and other petrologically significant effects.

MANY silicate liquids can be cooled below their equilibrium liquidus temperature without crystallization of the liquidus phase. This tendency to supercool is generally recognized (Schairer, 1959) and necessitates some caution in interpreting crystal-liquid relations in experimental charges that have been above the intended equilibration temperature at any time before or during the experiments.

Whether or not a silicate liquid can be supercooled below its liquidus temperature seems to depend largely on the composition of the liquid and the nature of the liquidus phase. For example, in systems where forsteritic olivine is the liquidus phase there are no recorded instances of supercooling: on the contrary, olivine appears to crystallize very readily as soon as its saturation level is reached, as evidenced by the difficulties encountered in quenching Mg-rich liquids (Yoder, 1952; Kushiro and Yoder, 1969; Green, 1973). On the other hand, there are several examples of silicate melts failing to crystallize pyroxene or feldspar below the temperature at which the solid phase is in equilibrium with the liquid. In studying the melting relations of some calc-alkaline volcanic rocks Brown and Schairer (1968) completely melted their samples at 1300 °C in order to eliminate 'residual grains' of plagioclase that persisted above 1200 °C and, having done so, found that the liquids would not nucleate crystals as low as 900 °C

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even after 7 days. During an investigation of inclusions of silicate liquid trapped in olivine crystals from some Apollo 11 lavas, Roedder and Weiblen (1970) observed that after completely melting inclusions, which had initially contained plagioclase and pyroxene crystals as well as glass, holding them in 'appropriate temperature ranges' for many hours failed to re-nucleate crystals.

Supercooling and the non-nucleation of crystals is not restricted to the liquidus phase but can also occur when the melt becomes saturated with the second or subsequent phases. Supercooling of this latter type has recently been invoked by Biggar *et al.* (1971) to account for discrepancies between the values reported by different investigators for the temperature at which plagioclase begins to crystallize from certain lunar basalts. In support of their argument they cite a number of experiments on Apollo 12 basalts, which demonstrate that after heating the samples above the temperature at which plagioclase was presumed to be in equilibrium with the liquid they could be cooled below this temperature—in some cases by more than 50 °C—without precipitating plagioclase.

Despite the evidence that basic silicate liquids can supercool, there appears to have been no detailed study of the phenomenon in a petrological context and the present investigation is an attempt to evaluate whether or not this phenomenon might be significant in the crystallization of igneous rocks.

TABLE I. *Analyses of basalt FG 10104 and basalt/olivine mixture FG 10104-OL*

Wt %	FG 10104	FG 10104-OL	Wt %	FG 10104	FG 10104-OL
SiO ₂	48.74	47.84	CaO	10.66	9.65
TiO ₂	1.68	1.52	Na ₂ O	2.60	2.34
Al ₂ O ₃	15.00	13.56	K ₂ O	0.42	0.38
Fe ₂ O ₃	3.09	2.81	P ₂ O ₅	0.26	0.23
FeO	8.40	8.87	H ₂ O+CO ₂	1.33	1.20
MnO	0.24	0.23			
MgO	7.58	11.33	Total	100.00*	99.96

* The total of FG 10104 is normalized to 100 % (see text).

Heating experiments

A specimen of Columbia River basalt (FG 10104) from flow 14 of the Picture Gorge section (Waters, 1961) was studied, as it has plagioclase as its liquidus phase. An analysis of this material is given (Table I) in which FeO and Fe₂O₃ were determined chemically and the total H₂O+CO₂ by ignition loss at 1000 °C. The remaining values were determined by X-ray fluorescence analysis and normalized to 100 %—(FeO+Fe₂O₃+H₂O+CO₂).

All experiments were made at 1 atmosphere on finely crushed rock in containers of Ag₄₀Pd₆₀ alloy. The furnace atmosphere was a mixture of CO₂ and H₂ in the proportions necessary to give an oxygen fugacity (*f*O₂) of 10^{-6.4} atmospheres at 1200 °C; this *f*O₂ being specifically selected as it is the magmatic oxygen fugacity determined experimentally for a similar sample of Picture Gorge basalt (Fudali, 1965). During all experiments in the temperature range 1100–1275 °C the CO₂:H₂ ratio was kept constant, as this gives a better approximation to natural magmatic conditions on cooling than maintaining a constant *f*O₂ (Hamilton and Anderson, 1967).

Two different sample-thermocouple configurations were employed in the experiments; one using a single thermocouple (fig. 1A) and the other using three thermocouples (fig. 1B). At 1200 °C vertical

temperature gradients in the furnace hot spot were less than 1 °C over 2 cm but radial gradients of up to 4 °C were measured over a distance of 1 cm. Consequently, temperatures recorded using the three thermocouple configurations are believed to be in error by less than 1 °C whereas those from single thermocouple experiments may be in error by up to 4 °C. Single and triple thermocouple experiments are represented by circular and square symbols respectively in the figures.

In the experiments referred to as 'heating experiments' samples were raised to within 30 °C of run temperature and held for 15 to 20 hours to permit equilibration with the furnace atmosphere (Fudali, 1965). The samples were then raised to run temperature, taking great care to avoid any overshoot; held within 1 °C of this temperature for a predetermined time and then quenched. Fragments from the top, middle, and bottom parts of each of the quenched charges were examined optically to determine whether or not plagioclase crystals were present in the glass.

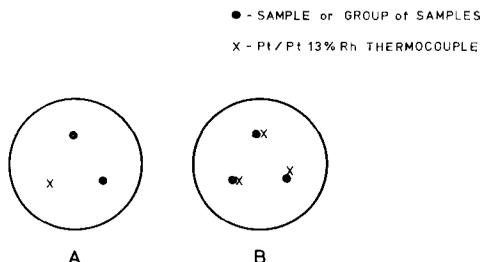
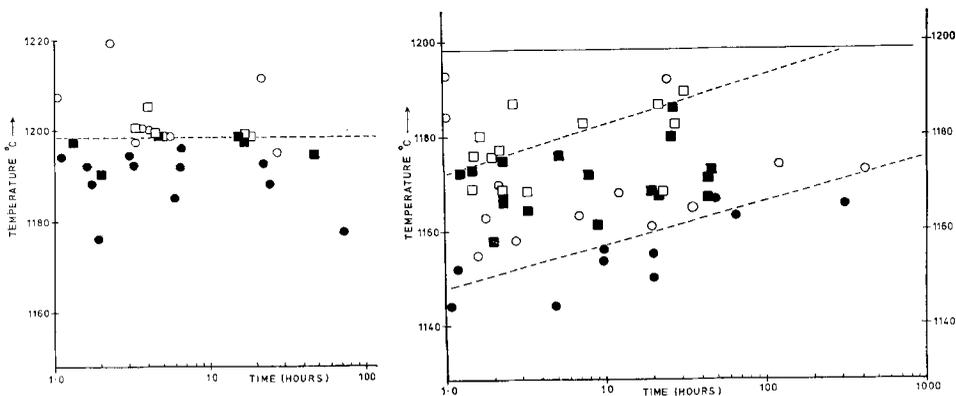


FIG. 1. Schematic cross-sections of the furnace tube illustrating the sample-thermocouple configurations used in the experiments.

The results of these heating experiments on basalt FG 10104 are shown in fig. 2, in which one axis represents the time the sample was at run temperature. It is apparent



FIGS 2 and 3: FIG. 2 (left). Results of 'heating' experiments on basalt FG 10104 (see text). Solid symbols = glass+plagioclase; open symbols = glass only. FIG. 3 (right). Results of 'cooling' experiments on basalt FG 10104 (see text). Symbols as in fig. 2.

from fig. 2 that, with one exception, experiments below 1198 (± 1) °C contain plagioclase whereas those above this temperature do not. The exception is a 27-hour run at 1195 °C in which no plagioclase was observed but this could be an anomaly due either to a near maximum error in the temperature measurement or to the failure to observe a few small plagioclase fragments in the charge. It is also notable that the division between plagioclase-bearing experiments and those resulting in complete melting (shown by the dashed line in fig. 2) is horizontal, i.e. the duration of the experiment is immaterial. Indeed, it is significant that while experiments of less than one hour's duration above 1198 °C produce complete melting, those longer than a day only a few

degrees lower fail to eliminate plagioclase crystals. Some of the very shortest runs above 1198 °C actually contain clusters of very small rounded grains of olivine (or possibly pyroxene) but it is presumed that these are metastable relics due to the refractory nature of magnesian olivine (and pyroxene) and that plagioclase, which is the last phase to melt in longer experiments, is the true liquidus phase.

Cooling experiments

The techniques employed in the 'cooling' experiments were identical to those used in the heating experiments except that the initial equilibration with the furnace atmosphere was at a temperature between 1199 and 1210 °C, i.e. under conditions where the sample was entirely liquid. The sample was then cooled as rapidly as possible to the temperature of the experiment taking care to avoid undershoot and held within 1.5 °C of this temperature for a predetermined time before quenching into cold water.

The results of a series of cooling experiments on basalt FG 10104 are shown in fig. 3 in which the dashed line of fig. 2 is shown as a solid line. In experiments above the upper dashed line the quenched charges were found to consist entirely of glass, whereas those below the lower dashed line invariably contained small lath-shaped, usually twinned crystals of plagioclase. In experiments falling between the two dashed lines in fig. 3 the quenched charges sometimes contained well-formed crystals of plagioclase and sometimes were entirely glass.

Interpretation

Below the solid line two dashed lines in fig. 3 define three temperature-time fields. In the uppermost field plagioclase crystals coexisting with liquid will not melt and yet a liquid of the same bulk composition will not precipitate plagioclase. In the field between the two dashed lines plagioclase may or may not crystallize from the liquid on cooling. Since the lower boundaries of both fields are obviously time-dependent the only possible candidate for an equilibrium boundary is the solid line in fig. 3. This must be either the true liquidus temperature of FG 10104 or a temperature higher than the liquidus because superheating is necessary to melt the plagioclase. If it is merely that feldspar is difficult to melt it should be possible to effect complete melting at lower temperatures in long experiments than in very short ones. There is no evidence of this with plagioclase (although in some *very* short experiments olivine fails to melt completely). Also, it is noteworthy that in many of the *heating* experiments of more than 20 hours' duration below 1198 °C the plagioclase crystals have a lath-shaped habit and are decidedly larger than the angular feldspar fragments in the starting material. The implication is that at temperatures just below 1198 °C plagioclase crystals have grown in the melt and are therefore unlikely to be relics or a metastable phase. It appears likely, therefore, that 1198 (± 1) °C is the true liquidus temperature of basalt FG 10104 at the f_{O_2} of the experiments.

The absence of plagioclase in experiments where it is a stable phase could be due to failure of the plagioclase nuclei to form in the liquid or it could be that nuclei do form, but crystal growth is so slow that crystals do not reach observable size in times of the order used in the experiments.

Nucleation of crystals in silicate melts is a complex and little-understood process although recent research into the production of glass ceramics has stimulated interest in the related problems of nucleation in quenched glasses (Rogers, 1970). It is well known (Rogers, 1970; De Vekey and Majumdar, 1970) that the number of nuclei formed during heat treatment of glasses increases with time and it appears likely that this should also be true of nucleation from silicate melts.

It has been demonstrated (Bottinga *et al.*, 1966) that diffusion, probably of Si or Al, in the liquid adjacent to a plagioclase crystal is the rate-determining factor in the growth of the crystal. While an imbalance between growth and diffusion rates might account for zoning phenomena such as those described by Bottinga *et al.* (1966), it is difficult to see how the liquid adjacent to a plagioclase embryo could be so depleted in one or more of the essential elements as to prevent growth when no significant growth had already occurred to deplete the liquid. Low diffusion rates could result eventually in slow or inhibited growth but should not play a significant part in the initial growth of the crystal. If diffusion, or the lack of it, is to be invoked to account for the absence of plagioclase crystals in the experiments described above, this 'initial' stage of growth would have to terminate before the crystals became readily observable: this seems unlikely. Furthermore, it has been observed that during some of the heating experiments in the 'supercooled' region many of the smaller angular plagioclase fragments present in the starting material grew into larger lath-shaped crystals, thus suggesting an absence of diffusion-controlled impedance to the growth of reasonably large crystals under the conditions of the experiments. The above arguments, together with the fact that diffusion cannot account for the irregular crystallization behaviour of plagioclase in the field between the two dashed lines (fig. 3) render it unlikely that diffusion and growth rate are responsible for the absence of plagioclase in experiments below liquidus temperature. Consequently, the explanation favoured is nucleation failure, i.e. supercooling (*sensu stricto*).

It is evident from the results of the experiments (fig. 3) that the principal factors controlling plagioclase crystallization are time and the degree of supercooling. However, the existence of a time-temperature field in which plagioclase may or may not crystallize implies the operation of at least one other factor.

Mechanical effects. It is known that effects such as agitation or vibration can induce supercooled liquids to crystallize due to the mechanical motion facilitating the rearrangement of the atoms necessary to produce an embryo. The possibility that vibration may be important in influencing plagioclase crystallization in experiments between the two dashed lines in fig. 3 has not been investigated due to the difficulties of obtaining a vibration-free environment in a busy laboratory, but it may be more than a coincidence that during a period in which construction work was being carried out in the laboratory (resulting in considerable vibration) a markedly higher proportion of the experiments in this field crystallized feldspar.

Wall effects. Optical examination of charges that contained only small amounts of plagioclase revealed a tendency for the crystals to be more abundant near the walls of the container thus suggesting that the surface of the alloy presents a source of nuclei on which plagioclase growth might occur. Consequently the smoothness of the

container walls might affect the appearance or non-appearance of crystals although all the container walls seemed equally smooth and were thoroughly cleaned prior to use.

Time above liquidus. As the last feldspar crystals melt at the liquidus their structure must change from that of plagioclase to that of the liquid. However, because of the relatively high viscosity, it is possible that this change is not instantaneous and relics of the plagioclase structure persist in the liquid for some time after complete melting is achieved. If this is so, subsequent crystallization could be strongly influenced by the extent to which these relic structures have persisted. The longer the sample is above the liquidus temperature the more likely the relic structures are to be destroyed and the less likely plagioclase is to crystallize on subsequently cooling. In most of the cooling experiments the samples were held above the liquidus for between 15 and 25 hours but no obvious relationship between this interval and the crystallization of plagioclase has been detected. An additional set of experiments in which the time above the liquidus was varied from 1 to 48 hours gave the same result.

Cooling rate. It is possible to supercool a silicate melt so far and so quickly that, while technically it is still a liquid, its viscosity and the ensuing kinetic problems become so great that nucleation is inhibited. Although this is a possible explanation for exceptionally large degrees of supercooling it is not applicable to the relatively small amounts of undercooling observed in the present experiments and this is borne out by the apparent ease with which plagioclase crystallizes below the lower dashed line (fig. 3). The cooling rate may control the crystallization of plagioclase in some other way although it is difficult to envisage the precise mechanism that could give rise to such an effect, and in any case the total variation in the cooling rates is small as all experiments were lowered to run temperature as quickly as possible.

In most of the cooling experiments the individual samples were quenched after different periods at the run temperature but in a few cases two or more samples were quenched at the same time or very close together. Two particularly important instances of this were the experiment in which two samples were quenched together after 2.3 hours at 1168 °C and that in which another two were quenched after 23 hours at (coincidentally) 1168 °C. In both these experiments one of the samples contained plagioclase whereas the other did not. Since in each experiment both samples were held for the same time above the liquidus and were subjected to the same cooling rates and approximately the same amount of mechanical disturbance, none of these factors can be responsible for the sporadic nature of plagioclase crystallization in the field of unpredictability. As variations in the smoothness of the container walls are an unlikely explanation, the factor or factors influencing the nucleation of plagioclase in this field remain uncertain but at least some of the more obvious possibilities have been discounted.

Effect of excessive heating

As suggested above, relics of plagioclase structure might persist in the liquid after melting and influence the nucleation of plagioclase on subsequent cooling. The further above its liquidus temperature a sample is heated the more likely these relic structures are to be destroyed. There is evidence supporting both the contention that the structure

of the liquid exerts some control over crystallization and the possibility that the structure of a silicate liquid varies with the amount of heating in excess of that required for melting. The former has been implied by Biggar *et al.* (1971) who suggested that when glass is used as a starting material in experiments the crystallization of plagioclase is inhibited possibly in favour of 'simpler structures'. It has been demonstrated that for certain non-silicate melts, e.g. molten sulphur (Gingrich, 1965), the structure changes with temperature and it is probable (Morey, 1954) that the same is true of silicate liquids since glasses quenched from different temperatures usually show variations in physical properties such as density and refractive index (Lillie and Ritland, 1954).

Another possibility is that after the plagioclase has melted local concentrations of the elements derived from the feldspar are preserved in the melt because of its relatively high viscosity and these may facilitate plagioclase nucleation if the melt is cooled before they can disperse. Again, the higher the temperature to which the liquid is heated the more likely any such residual concentrations are to equilibrate with the surrounding liquid.

The consequence of either relic structures or local chemical concentrations (or both) persisting in the liquid is that the further above its liquidus a sample has been the more likely supercooling is to occur and the greater its probable extent. There is some support for the existence of such a relationship. Schairer (1959) has observed 'that when melts have been *severely* overheated . . . crystallization may be inhibited' and the extreme supercooling reported by Brown and Schairer (1968) could be due, at least in part, to overheating—in this case by about 100 °C.

In the cooling experiments described above (fig. 3) care was taken to ensure that the sample was never more than 12 °C, and rarely more than 10 °C, above the liquidus temperature. To test the possibility that excessive heating increases the extent of supercooling a series of experiments was conducted on FG 10104 as follows: The sample of powdered rock was raised to a temperature in excess of its liquidus and held for 15 to 20 hours to equilibrate with the furnace atmosphere before cooling to run temperature. In each case the duration and run temperature were chosen to fall just below the lower dashed line in fig. 3. During cooling the temperature fell from the maximum to below the liquidus in less than 10 minutes. Despite overheating FG 10104 by amounts ranging from 50 °C to more than 100 °C for periods of up to 20 hours, it proved impossible to supercool any of the experiments into the field below the lower line (fig. 3) without plagioclase crystallizing. It can only be concluded therefore, at least for this particular basaltic composition, that excessive heating of the liquid has no observable effect on the extent to which the crystallization of plagioclase is inhibited.

Effect of other crystalline phases

Any variation in the bulk composition of a basaltic melt will affect the extent to which it can be supercooled. This could be due largely to changes in the viscosity of the melt since it is known that the higher the viscosity the more likely supercooling is to occur. Brown and Schairer (1968) considered that the large amount of supercooling observed in their experiments could have been due to 'the combination of high SiO₂

and Al_2O_3 and low $\text{Na}_2\text{O} + \text{K}_2\text{O}$ in the rocks'; Si being an element that raises the viscosity of the liquid while the alkalis have the opposite effect (Bottinga and Weill, 1972). The effect of varying the water content of the melt is difficult to evaluate, since on the one hand it will lower the viscosity (Shaw, 1963) but on the other, may lead to less favourable conditions for plagioclase growth (Lofgren, 1973).

However, another way in which variation in bulk composition could affect the supercooling and crystallization of plagioclase from a basaltic magma such as FG 10104 is through the introduction of another crystalline phase above the temperature at which the supercooled liquid would otherwise precipitate plagioclase.

It is well known that a crystalline phase does not require a nucleus of itself on which to grow but can grow on nuclei of other materials, for example diopside crystals can be grown on nuclei of spinel (Rogers, 1970). This raises the possibility that the crystallization of another phase, say olivine or pyroxene, from a liquid that was already super-saturated with respect to plagioclase would promote the crystallization of feldspar.

In the heating experiments on basalt FG 10104 the penultimate phase to melt is the clinopyroxene, which does so between 1178 and 1182 °C. Because of the difficulties in picking out and positively identifying the last few small grains of olivine in the presence of abundant augite the temperature at which the olivine melts is more difficult to determine and the only certain observation is that the olivine peaks disappear from the X-ray powder diffraction patterns of samples heated above 1130 °C, implying that the temperature at which the last of the olivine melts is unlikely to be much higher. In most basalts with plagioclase as the liquidus phase olivine, when present, melts at a higher temperature than the clinopyroxene. As well as being unusual in this respect, the relatively low melting temperature of the olivine in FG 10104 seems anomalous in view of the fact that the rock, which is quite fine-grained, contains numerous small phenocrysts of olivine as well as plagioclase and pyroxene (Waters, 1961). Preliminary studies of the effect of supercooling on the pyroxene indicate that, like the plagioclase, its nucleation and crystallization can be suppressed at temperatures below 1140 °C (at least for short times) and certainly pyroxene crystals have not been observed in any of the cooling experiments shown in fig. 3.

From the point of view of studying the effect of the crystallization of another phase on the supercooling and non-nucleation of plagioclase, it is unfortunate that the pyroxene crystallization can also be suppressed by relatively rapid undercooling and that the melting temperature of the olivine is too low. To study this effect a 9:1 mixture of FG 10104 and an analysed olivine was made up (Table I). This new starting material (FG 10104-OL) has olivine as its liquidus phase and a melting temperature of 1275 ° (± 3 °)C. No plagioclase could be found in heating experiments at temperatures above 1181 ° (± 3 °)C. This suggests that the change in composition from FG 10104 lowers the plagioclase melting temperature by some 17 °C but it should be pointed out that 10 to 20 ° below the liquidus of FG 10104 plagioclase crystals are small and scarce and the last few crystals would be extremely difficult to spot in experiments on FG 10104-OL, where olivine is abundant. Consequently, 1181 °C can only be regarded as a minimum value for the melting temperature of plagioclase in FG 10104-OL.

A number of cooling experiments were made on FG 10104-OL. The method was identical to that used for the pure basalt except that the initial heating was only to temperatures between 1200 and 1210 °C (to melt the plagioclase) and not above the liquidus: after cooling, all the samples were held at run temperature for 4 hours before quenching. Samples of FG 10104-OL cooled to 1157 °C contain only olivine and liquid. Below this temperature plagioclase begins to crystallize in the 4-hour experiments and by 1147 °C relatively large, well twinned laths are abundant. These laths, like those formed in many of the cooling experiments on the pure basalt, are often zoned suggesting that once nucleation occurred they grew rapidly and diffusion rates in the adjacent melt became an important factor. The crystallization of plagioclase from FG 10104-OL can therefore be delayed until the same sort of temperature as from the pure basalt and this, together with the total absence of plagioclase overgrowths on olivine, invalidates the hypothesis that a basaltic melt could not be supercooled below the temperature at which the first crystals appear because the presence of crystals would result in precipitation of the phase (or phases) in which the liquid was supersaturated.

Discussion

The facts that a basaltic liquid can be supercooled and the crystallization of plagioclase (and pyroxene) inhibited are significant both in the interpretation of experimental data and with regard to the cooling and crystallization of natural magmas.

The projections of the upper and lower dashed lines in fig. 3 intersect the liquidus temperature at approximately 300 and 10^5 hours respectively. Thus, for this particular composition, experiments of less than 300 hours' duration just below the liquidus will fail to crystallize plagioclase while 10^5 hours would be necessary to *guarantee* feldspar nucleation. Because the projections are linear (see below) these times can be regarded only as minimum values. In the majority of experimental studies on basaltic systems run times are of the order of 1 to 24 hours and the significance of the above observations for such studies is self-evident. It is not intended to imply that all data derived from short experiments on basaltic compositions are in error: indeed there is no reason to question the results of experiments where the sample has never been above run temperature. However, in the light of the above evidence considerable caution should be exercised in interpreting the results of experiments of short duration that involve a nucleation process as representing an equilibrium relationship.

In determining fig. 3 the samples were cooled as rapidly as possible from above the liquidus and held for a predetermined time at a constant temperature before quenching. This is markedly different from the way in which natural magmas cool and the relationships so determined may not be strictly applicable to a realistic cooling situation, but, assuming that they are approximately so, it is interesting to consider the effects of gradual cooling.

The dashed lines in fig. 3 are shown as straight lines and projected as such to times beyond the available data. Actually they are curves with the general form:

$$T = 1198 - a(\log t^* - \log t)^n,$$

where T is the temperature, t^* is the time required for feldspar to nucleate at the

liquidus temperature (1198 °C) and t is the time required at temperature T . Such curves are tangential to the liquidus temperature at $t = t^*$, and become asymptotic to the temperature axis at very small values of t ; the latter indicating that if the sample is held at any sub-liquidus temperature for a short enough time (i.e. very fast cooling) nucleation never occurs—i.e. the liquid is quenched to a glass. It is evident from fig. 3 that both curves are nearly linear over the range of times for which they have been determined experimentally (with time on a log scale) indicating that in both cases n is near unity. To a first approximation the upper and lower lines can be respectively represented by the two linear equations:

$$T = 10.5 \log t + 1172 \quad \text{and} \quad T = 9.25 \log t + 1148.$$

Only cooling at a constant rate will be considered. Such cooling is unlikely in nature but the cooling of a body of magma over a restricted range of temperature

TABLE II. *Nucleation temperatures and cooling times for a range of constant cooling rates for basalt FG 10104*

Cooling rate °C/hour	Nucleation temperature °C		Total cooling time (hours)		Time at or below nucleation temperature	
	lower line	upper line	lower line	upper line	lower line	upper line
	10	1144.3	1168.4	5.8	3.4	0.4
5	1147.1	1171.6	11.0	6.2	0.8	0.9
2.5	1149.9	1174.7	20.8	11.1	1.6	1.8
2	1150.8	1175.8	25.6	13.4	2.0	2.3
1	1153.6	1178.9	48.4	23.6	4.0	4.6
0.5	1156.4	1182.1	91.3	41.0	8.0	9.1
0.25	1159.2	1185.2	171.4	69.3	16.1	18.2
0.1	1162.8	1189.4	391.8	131.4	40.2	45.6
0.05	1165.6	1192.6	727.9	199.6	80.3	91.2

below its liquidus can be regarded as linear to a degree of approximation that improves inversely with the rate of cooling. For cooling at a constant rate (R °C per hour) from the liquidus temperature (1198 °C) an infinite series of lines can be constructed according to the equation: $t = H - (1198 - T)/R$ or $T = 1198 + Rt - RH$, where t is the time at or below temperature T and H is the time elapsed since cooling commenced. This series of parallel lines has a slope of R .

The crystallization of plagioclase will only be a possibility or certainty when the line of cooling intersects the upper or lower curve respectively. For any cooling rate this will first occur when the cooling line is tangential to the appropriate curve. For the upper curve this condition is satisfied for a cooling rate of 1 °C per hour at $T = 1178.92$ °C (attained after 19.08 hours cooling); after a further 4.56 hours at or below 1178.92 °C plagioclase nucleation is possible. Similar solutions for both upper and lower curves for a range of cooling rates are given in Table II (rounded off to one place of decimals). For cooling rates outside the range given in Table II the linear approximations are inadequate for meaningful solutions. The validity of the theoretical

nucleation temperatures and cooling times in Table II can be checked by cooling FG 10104 at constant rates from above its liquidus temperature and such experiments are in hand.

A petrologically significant consequence of such supercooling relationships is that the temperature at which plagioclase will nucleate from the liquid varies with the rate of cooling. The rates at which basic magmas cool in nature vary considerably. Hess (1960) calculated that it required 5×10^4 years for the temperature of the Still-water magma to fall from 1225 to 1100 °C, i.e. a rate of less than 3×10^{-7} °C per hour. On the other hand, the upper surfaces of lava flows are known to cool several hundred degrees in the 24 hours following eruption. Under very slow cooling conditions in plutonic bodies, plagioclase will crystallize from a basic liquid such as FG 10104 at the liquidus temperature, i.e. equilibrium crystallization. Cooling rates of the order of those in Table II are, however, probable in lava flows and possibly some of the smaller minor intrusions and could result in differences in the temperatures at which feldspar and other phases crystallize and even in the order in which they appear. If the cooling rate is fast enough to lower the crystallization temperature of plagioclase below that at which equilibrium crystallization occurs and other phases that are not susceptible to supercooling (e.g. olivine), or less so than the plagioclase (? pyroxene), crystallize in this interval then the sequence in which the phases appear would be quite different from that in a slowly cooled magma of the same bulk composition. Such a mechanism could conceivably produce a porphyritic rock (e.g. with olivine phenocrysts) from a basaltic composition that was a low-pressure equilibrium cotectic liquid from which all three major phases (olivine, plagioclase, and augite) would normally be expected to begin crystallizing simultaneously (or nearly so).

It is therefore interesting to consider basalt FG 10104 itself. Under equilibrium conditions at 1 atmosphere, plagioclase will begin to crystallize from the liquid at 1198 °C. This will be joined by augite at 1180 (± 2) °C and eventually by olivine (probably below 1150 °C). Under such conditions the only likely phenocrysts are plagioclase; pyroxene phenocrysts being less likely and olivine phenocrysts being highly unlikely. However, the actual rock contains about equal amounts of olivine, plagioclase, and pyroxene phenocrysts which, conventionally, would be interpreted as indicating that all three minerals began to crystallize at about the same temperature (possibly prior to eruption so that the phenocrysts could have grown under conditions of slower cooling). Although the possibility of pre-eruptive crystallization at great depth (and hence high pressure) cannot be ruled out, the 1 atmosphere equilibrium phase relations seem to eliminate the possibilities of post-eruption phenocryst formation or pre-eruption crystallization at shallow depths. An alternative interpretation might be that some or all of the phenocrysts are cumulus, i.e. have been added to the liquid from higher levels of the flow or in the magma chamber prior to eruption. Again, however, the phase relations render this improbable.

On the other hand, if the basaltic magma that formed the flow from which FG 10104 was collected was erupted as a liquid free from phenocrysts and cooled relatively quickly, at least over the first 50 °C or so, then another interpretation becomes possible in the light of the above experiments. The rapid cooling could have produced a super-

cooled liquid by depressing the temperatures at which plagioclase and pyroxene begin to crystallize to around that at which the precipitation of olivine commences, resulting in the near simultaneous appearance of all three minerals. Once nucleation of plagioclase and pyroxene began the supersaturated state of the liquid might well result in the initial nuclei growing to phenocryst proportions. The phenocrysts of olivine could have formed in the normal way, i.e. as the first phase to crystallize, or simply because of the propensity of olivine for fast growth and the formation of large crystals. It can be seen from Table II that temperature depressions of the order required by such a hypothesis are not only possible but indeed are probable for the sort of cooling rates likely to follow the eruption of a lava flow.

Fractionation trends followed by volcanic rocks differ from their plutonic counterparts largely because the relatively rapid cooling produces zoned crystals and prohibits re-equilibration of earlier formed crystals with the liquid. The fact that under certain conditions, such as those described above, the sequence in which the major crystalline phases appear can change must extend the range of possible deviations from equilibrium crystallization or equilibrium fractional crystallization. Yet a further complication ensues from the observation of Lofgren (1973) that plagioclase crystals grown from a supercooled liquid are reversely zoned, so that the compositions of co-existing minerals formed during rapid cooling might differ markedly from those formed under equilibrium conditions. To appreciate the significance of this it is only necessary to consider the number of attempts in the literature to deduce meaningful information from the compositions of co-existing phases (or parts of zoned phases that are thought to have crystallized simultaneously) in volcanic and other rapidly cooled rocks.

There is obviously considerable scope for further speculation on the petrological significance of supercooling in basaltic magmas but it would be desirable to await the results of further work, particularly with regard to the supercooling of pyroxene.

Acknowledgements. The writer is greatly indebted to W. S. MacKenzie, G. M. Anderson, C. M. B. Henderson, and D. L. Hamilton for helpful discussion and to Prof. MacKenzie for his constructive comments on the manuscript. W. S. MacKenzie and W. J. Wadsworth very kindly supplied the sample of basalt and the analysed olivine respectively. The work is part of the N.E.R.C. supported experimental petrology research project at Manchester University, and this financial support is gratefully acknowledged.

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[*Manuscript received 8 November 1973*]