

Differentiation and diffusion in laboratory charges of basaltic composition during melting experiments

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Abstract

Uncrushed or coarsely powdered diabase differentiates during rapid melting at 1250° and over, by the sinking of pyroxene and floating of plagioclase. Similar processes may occur during partial melting in nature. Diffusion coefficients for the elements Na, Fe(2+), Mg, Al, and Ti at 1300° C were estimated from the time required to eliminate the gravitationally stable composition gradients set up in the charges during differentiation. All the elements have the same diffusivity, $10^{-6.6}$ cm² sec⁻¹, within the experimental precision of about 0.4 log units. Diffusion of most of the elements is probably interdependent because of charge-balance requirements. The estimated rate of redox equilibration seems to imply diffusion of an oxygen species at about the same rate as the cations.

Introduction

In this paper we report details of crystal-liquid differentiation observed during rapid melting of natural basaltic rock and rock powder. The gravitationally stable composition gradients set up in the charges by differentiation allowed estimation of the rates of chemical diffusion of the major elements.

Differentiation during melting

In order to investigate nucleation mechanisms (Berkebille and Dowty, 1982), samples of Rocky Hill diabase, a tholeiitic basalt (analyses in Table 1) were melted in furnace atmospheres of Argon or a 10/1 mixture of CO₂/CO. Samples were held in either 20 ml nickel crucibles or platinum wire loops.

The first runs consisted of large chunks (about 1 cm) of basalt in Ni crucibles. Three initial runs were melted by insertion of the charge into the furnace at 1250° C, and annealed at that temperature for 16–24 hours before cooling at 50°, 10° and 2° per hour. Resulting textures were similar except for the size of the crystals (Fig. 1a, b). In the lower two-thirds of the charges, large dendritic olivine blades grew inward from the walls, with feathery pyroxene and

Fe–Ti oxides in the interstices; no plagioclase was present. In the upper third, hollow prisms of plagioclase grew inward from the walls and perhaps downward from the surface, with some interstitial feathery pyroxene; no olivine was present. Crystallization of plagioclase from the top and olivine from the bottom sometimes resulted in a void in between, into which the longer olivine blades protrude (Fig. 1a).

Differentiation was verified by quenching a run from 1250° C after holding it at this temperature for 16 hours. About a dozen irregular remnant crystals of plagioclase were found floating on the upper surface, and a few clumps of tiny (0.1 mm diameter) euhedral olivine crystals were found on the bottom. These olivine crystals had obviously crystallized from the liquid, as judged by their morphology and the fact that there is no olivine in the original rock. Electron microprobe analyses showed that the liquid itself varied widely in composition; for example (in weight percent); Al₂O₃ 16.0 top, 10.1 bottom; FeO 7.9 top, 13.0 bottom; TiO₂ 0.6 top, 2.4 bottom. Microprobe analyses also showed NiO contents of up to 3% at less than 1 mm from the crucible, but

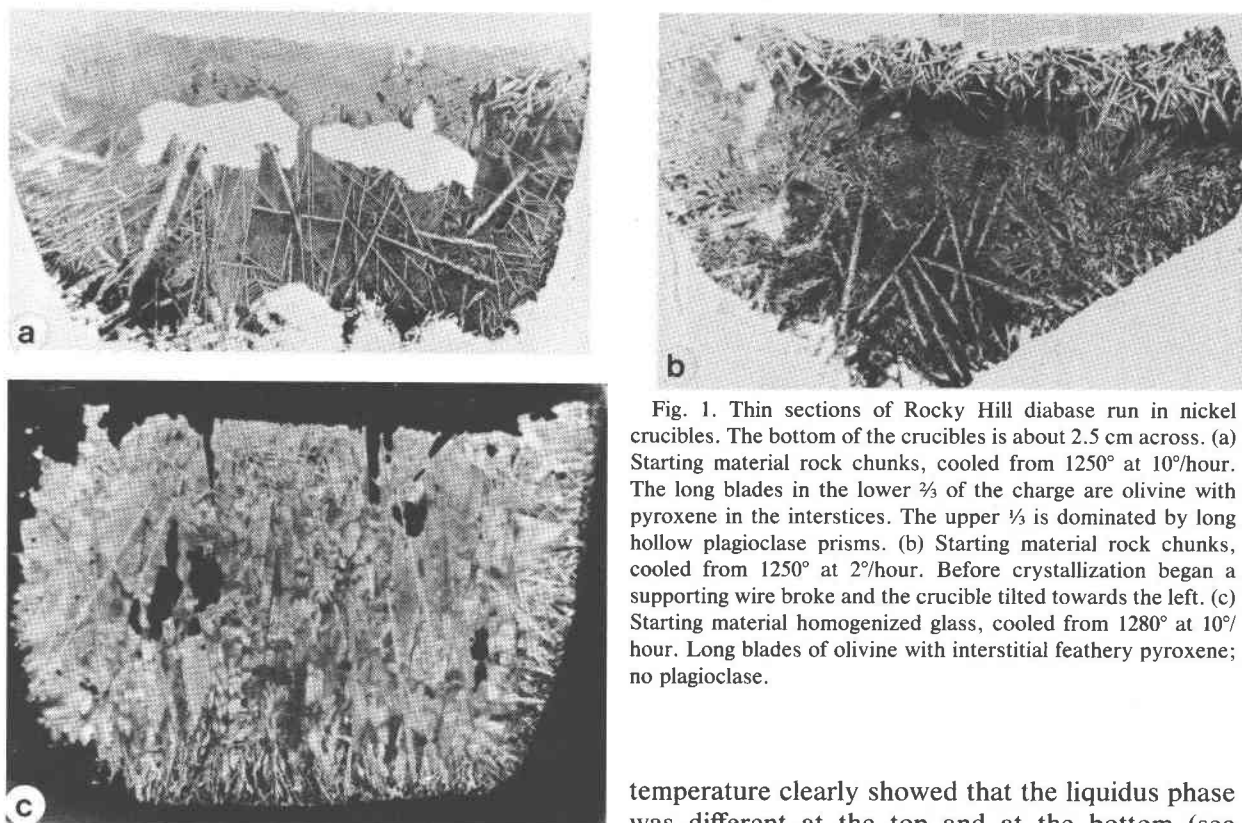


Fig. 1. Thin sections of Rocky Hill diabase run in nickel crucibles. The bottom of the crucibles is about 2.5 cm across. (a) Starting material rock chunks, cooled from 1250° at 10°/hour. The long blades in the lower $\frac{2}{3}$ of the charge are olivine with pyroxene in the interstices. The upper $\frac{1}{3}$ is dominated by long hollow plagioclase prisms. (b) Starting material rock chunks, cooled from 1250° at 2°/hour. Before crystallization began a supporting wire broke and the crucible tilted towards the left. (c) Starting material homogenized glass, cooled from 1280° at 10°/hour. Long blades of olivine with interstitial feathery pyroxene; no plagioclase.

NiO contents were negligible at greater than about 3 mm from the crucible. Microprobe analyses of the crystallized runs also showed up to 8% NiO in olivine very near the crucible, but again concentrations dropped off drastically away from the wall and no significant nickel was found in pyroxene or plagioclase.

Dynamic crystallization runs made from pre-homogenized glass did not show differentiation (Fig. 1c).

The initial runs on Rocky Hill material in Pt-wire loops were done with sintered pellets made from a "powder" containing some grains up to 1 mm in diameter. These runs were all made in a 10/1 mixture of CO₂/CO. Differentiation was apparent through a distinctly darker color (greenish brown) in the lower part of the bead. Runs annealed for up to 16 hours at 1250° C contained residual plagioclase crystals near the top, and residual pyroxene and new olivine crystals near the bottom. Runs annealed at 1300° and 1350° C showed persistence of crystals for shorter times. Even when the original crystals had been melted by annealing at 1350° C, the new crystals which formed on reduction of the

temperature clearly showed that the liquidus phase was different at the top and at the bottom (see Berkebile and Dowty, 1982, Fig. 4c, d). Plagioclase crystallized on the wire at the top, and olivine on the wire at the bottom, at temperatures as high as 1250° C, or 50° higher than the liquidus determined for the homogeneous material.

The only reasonable mechanism for most of this differentiation is crystal sinking and flotation. This must occur in a very short time interval; were differentiation not to occur, total melting would presumably take only a few minutes at 1350°, although no direct determination has been made. The observed compositional variation (Table 1; Fig. 6) shows that most of the differentiation is caused by separation of plagioclase and pyroxene, although some sinking of ilmenite probably also occurs. Remnant plagioclase crystals were always found at the very top of the runs, indicating that they floated; it is probable, though less certain, that pyroxene sank. Olivine must originate in the formal sense by incongruent melting of pyroxene, but it is clear that the olivine crystals are all newly grown from the liquid and not a product of solid-state transformation of pyroxene. It is quite possible that olivine crystals may nucleate on the dissolving pyroxenes, but no direct evidence for this has been observed. The essential constancy of SiO₂ and CaO shows

Table 1. Electron microprobe analyses (wt.%) of glass beads of Rocky Hill basalt annealed at 1300°C.

	3 hrs top	3 hrs bottom	200 hrs top	200 hrs bottom
SiO ₂	56.0	54.1	54.4	54.5
TiO ₂	0.8	1.0	0.8	0.5
Al ₂ O ₃	15.8	9.7	12.6	13.1
CaO	11.5	12.1	11.7	11.6
MnO	0.2	0.2	0.4	0.0
FeO	6.2	10.0	7.4	7.4
MgO	6.4	10.8	8.8	8.7
K ₂ O	0.6	0.6	0.6	0.6
Na ₂ O	2.5	1.6	3.4	3.5

Analyses normalized to 100%.

that sinking of olivine does not play a major role in differentiation. Some separation of early Si-rich partial melt may have occurred, as suggested by slightly higher Si content at the top (Table 1), but such a process was clearly much less important than crystal movement.

Implications for laboratory crystallization experiments

Clearly, whenever a charge is melted from rock powder or rock itself, there exists the possibility of differentiation. The experiments described in this paper probably represent an extreme, since the material was very coarse. There are, however, grounds for suspecting that some differentiation has occurred in a few previous experiments. For example, Lofgren (1977) showed swirling patterns in beads of a synthetic feldspar-rich composition which had been partially crystallized at 1150° and then remelted at 1280° C. Lofgren *et al.* (1978) assumed that these patterns were due to convection, but thermal convection is impossible in a charge this small in a large furnace.

If charges are ground to a uniformly fine powder, differentiation of this sort may be negligible. Nevertheless, it should be the responsibility of every investigator to show, by microprobe analysis if possible, that his charges actually melt to a homogeneous liquid.

Chemical diffusion in natural basalt liquid

The differentiated charges show large, easily measurable composition gradients, which are gravi-

tationally stable. The chemical differences are those which are likely to arise from several types of geological differentiation, as well as crystal growth. A good opportunity was therefore presented for measuring realistic multicomponent or chemical diffusion of major elements in basalt liquid.

Charges of Rocky Hill diabase, sintered from coarse powder, were melted in Pt wire loops in the CO₂/CO gas mixture and annealed from 1 to 200 hours at 1300°. The beads were sectioned vertically and analyzed with the electron microprobe, using wavelength dispersive methods for Si, Ti and Na, and energy dispersive methods for Al, Mg, Fe and Ca. Some representative scans are shown in Figure 2, and complete analyses of the extreme compositions are given in Table 1. As might be expected, the compositional gradients are not perfectly uniform from one bead to another. There are sometimes significant differences in the absolute levels of

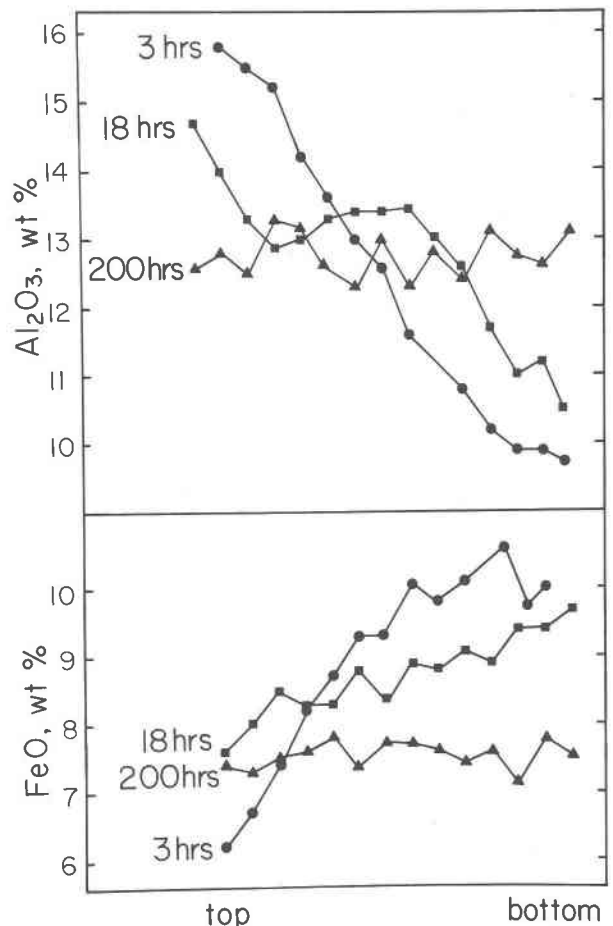


Fig. 2. Electron microprobe analyses on vertical sections of 5 mm beads of Rocky Hill diabase, run for the indicated times at 1300°. Starting material was crushed rock.

major components, presumably due to variations in the number of large grains of the different minerals included in each charge. With this sort of rather haphazard starting conditions, accurate numerical analysis of the actual measured concentration gradients does not seem justified. Instead, the data were fitted by linear least-squares to give, for each element and annealing time, a sort of average gradient. The initial time for the diffusion experiment was taken to be 3 hours annealing, because all the crystals have normally melted by this time at 1300°. Figure 3 shows the gradients for each element and annealing time, divided by the gradient measured in the 3 hour run.

A solution to the diffusion equations for the case of eradication of a compositional gradient in a spherical drop does not seem to have been found. It will therefore be assumed that the situation can be adequately represented by the well-known results for a uniform sheet, with compositional gradient perpendicular to the surface (Crank, 1975). If the initial gradient is linear, the concentration C at any point x as a fraction of the difference between initial maximum and minimum concentrations is given by

$$C = 0.5 - 2 \sum_{n=1}^{\infty} \exp \frac{-Dn^2\pi^2t}{s^2} \cos \frac{n\pi x}{s} \frac{1}{n^2\pi^2} \quad (1)$$

where D is diffusivity, s is the thickness of the sheet, and t is time. Some calculated profiles for the measured annealing times, minus three hours, are shown in Figure 4.

Comparison of the measured and calculated profiles gives an estimate of $D = 10^{-6.6} \text{ cm}^2 \text{ sec}^{-1}$ for all the elements measured, namely Fe, Al, Na and Ti. Silicon and calcium did not show a gradient large enough for measurement. Magnesium was not measured because of poor precision but apparently parallels iron rather closely. Diffusivity for Na could be slightly larger than that for the other ions, but the difference is probably within the total error of the analysis. The measured and calculated profiles certainly do not match perfectly; in particular, the measured gradients for 30, 60 and 112 hours seem to be too close together. The fact that this is seen for all the elements shows that it is a result of slightly different initial gradients. Despite such problems, the calculated profiles suggest that the true diffusivities are not likely to be higher than $10^{-6.2}$, which would give essentially flat profiles for times greater than 30 hours, or lower than $10^{-7.0} \text{ cm}^2 \text{ sec}^{-1}$, which would give little change for 18–19 hours. This assumes that equation (1) for flat sheets

is applicable, and that the diffusivities are not a function of composition over the relatively small range encountered in the beads.

These results are roughly compatible with previous studies on isotope or tracer diffusion in basalt at 1300°, as reviewed by Hofmann (1980). However, the value for self-diffusion of sodium measured previously by Hofmann and Brown (1976), $D =$

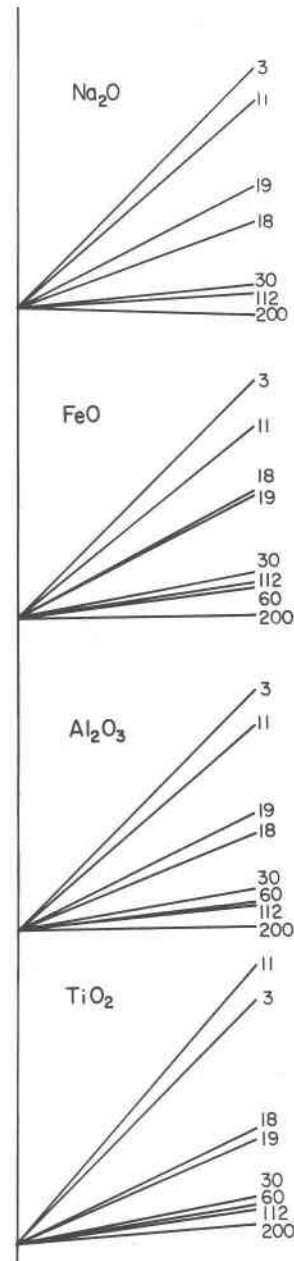


Fig. 3. Least-squares compositional gradients, as fractions of the gradients for the 3 hour run, in beads of Rocky Hill diabase run for the indicated times at 1300°.

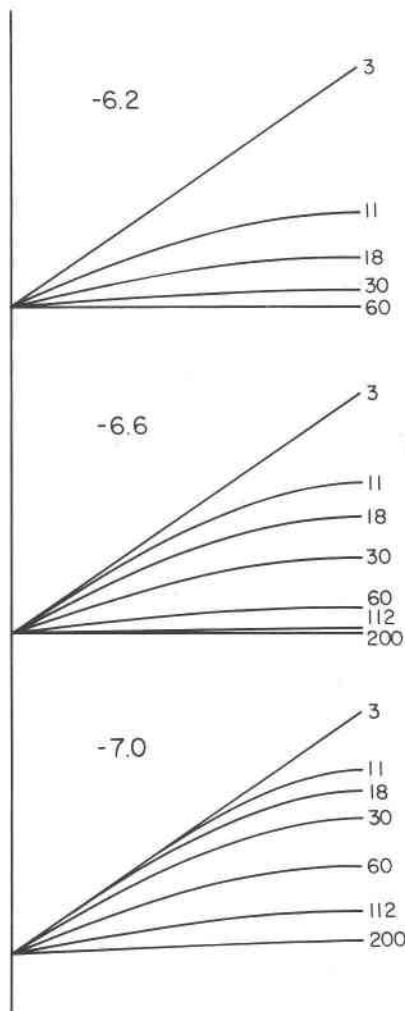


Fig. 4. Compositional gradients computed with equation (1) for 5 mm beads. Starting time was taken to be 3 hours.

$10^{-5.6} \text{ cm}^2 \text{ sec}^{-1}$, is significantly higher than the estimate made in this study. Also, the value for titanium of $D = 10^{-7.1}$ which is calculated from Hofmann's empirical equation (the diffusivity of Ti has not been measured) is lower than the present estimate. Certainly, the very different charges of the sodium and titanium ions would suggest a difference in self-diffusion coefficients larger than the total error of the present study. It is quite likely, therefore, that there is strong coupling of diffusion of ions in the basalt because of charge-balance requirements. The differentiation involves primarily movement of $\text{Al} + \text{Na}$ vs. $\text{Fe}^{2+} + \text{Mg}$, and homogenization would essentially be a process of interdiffusion of these pairs. The observed diffusion rates may be an average of the self-diffusion rates of all

these ions, probably weighted toward the slowest-moving ion, presumed to be Al. Settling of ilmenite would introduce the additional pair $\text{Ti} + \text{Fe}$, but the diffusivity of Ti may have a relatively small effect on the more abundant ions.

Powell *et al.* (1980) recently reported diffusivities of several ions in basalt, derived from the composition gradients adjacent to growing crystals, and also concluded that there is strong coupling among certain elements. They found generally smaller diffusivities and much larger differences between elements than in the present study, but both of these are expected in view of the lower temperatures they used (1050–1100°).

Some information on rate of reduction of the glass was also obtained. Beads of Rocky Hill composition have a brown color in section when run for only a few hours in the 10/1 gas mixture, and become paler brownish green when held for longer times. A brown color is usually associated with the presence of appreciable Fe^{3+} , which absorbs light through various types of charge transfer with Fe^{2+} and oxygen. The color change suggests that the original oxygen fugacity of the rock was higher than that of the gas mixture, although some oxidation could have occurred during preparation.

To estimate the approximate rate of redox equilibration, a group of beads was held at 1375° in air for 30 hours, then individual beads were run for 3.5, 7, 12.5 and 28 hours at 1300° in the 10/1 gas mixture. As before, color became paler with longer times. The color difference between the first three runs was pronounced, and still distinct, though not very great between the 12.5 and 28 hour runs.

We cannot derive quantitative diffusion coefficients from this type of experiment, but we can certainly say that at least 15 hours, probably more than 30 hours, are required to attain redox equilibrium in 5 mm beads in this gas mixture (assuming that the rate of oxidation is the same as that of reduction). Naney and Swanson (1981) have recently obtained similar results for an andesite composition. The diffusion coefficient of the species responsible for the redox change could be as low as those of the ions Fe^{2+} , Al^{3+} , *etc.*, and could certainly be no larger than $10^{-6} \text{ cm}^2 \text{ sec}^{-1}$. This suggests that in this furnace atmosphere the redox mechanism requires diffusion of an oxygen-bearing species. In an anhydrous environment O^{2-} diffusion rates tend to be roughly similar to those of divalent cations (Dowty, 1980). Some of the many possibilities are diffusion of O_2 , or interdiffusion of O^{2-} plus Fe^{3+}

with Fe^{2+} . In some crystals, redox equilibration can take place by diffusion of vacancies and electron transfer among Fe ions. The rate in the present case appears to be too slow for this, but another possibility is O^{2-} diffusion combined with charge transfer between Fe^{2+} and Fe^{3+} . Hydrogen diffusion likewise should be much faster than the observed rate and is evidently not effective in the CO_2/CO atmosphere, but could be important in H_2 -bearing gas mixtures.

Differentiation during melting of natural rocks

In the past, petrologists dealing with problems of differentiation usually assumed implicitly that magmatic liquids are essentially homogeneous. This approach may have been fostered in part by calculations which show that basalt magma bodies of any reasonable size are subject to thermal convection. However, such calculations are often made on the assumption that the liquid is homogeneous, an assumption which is hardly justified if the process of partial melting induces density stratification. With the recent verification of strong zonation in silicic magma chambers (*e.g.*, Hildreth, 1979; Smith, 1979), more attention has been paid to magma inhomogeneities, but the possibilities for production of such inhomogeneities during partial melting have not been fully investigated. A consideration of the process of partial melting, in light of the experimental results presented in this paper, suggests that production of density stratification in magmas during partial melting may be the rule rather than the exception. There appear to be basically two ways in which stratification could be established: (1) Through actual flotation of low-density crystals, presumably feldspar in most instances, as in the present study, although quartz might also be involved in melting of crustal rocks; and (2) through progressive increase in the density of the partial melt being generated from a given body of source material.

The first process requires a fairly mafic magma composition, probably basaltic, since feldspar does not float in silicic liquids. One case in which this process could be important is in the generation of anorthosite. Suppose that a body of rock of intermediate to basic composition in the lower crust or upper mantle begins to melt. If plagioclase is to be present in a basaltic source, the depth would have to be less than that of the eclogite transition. Our experiments show that the result would not necessarily be separation and ascent of a granitic or

andesitic partial melt, but perhaps more likely, generation of an upper portion of liquid rich in floated feldspar, and a lower portion containing sunken mafic crystals. The upper portion would certainly be lighter than the surrounding solid material and would tend to rise, perhaps undergoing further melting on quasi-adiabatic decompression, while the lower portion could remain in place or actually sink. A liquid or feldspar-liquid mix generated in this way could have many of the characteristics of the anorthositic gabbro which is assumed by some investigators to be the parent magma of anorthosites. A somewhat analogous situation is that of the differentiation of the early lunar crust. A popular hypothesis is that the outer part of the moon was totally molten soon after its accretion and that the crust was formed by crystallization and flotation of feldspar (Smith *et al.*, 1970). However, there is no obvious reason why formation of a feldspar-rich layer could not have occurred during melting.

It seems unlikely that the process of feldspar flotation is involved in the generation of typical basaltic or granitic magmas. The mantle source region of most basalts probably contains few if any minerals lighter than the liquid generated by partial melting, and granitic and even granodioritic liquids are lighter than feldspar. The striking cyclic zonation of the Bishop Tuff magma chamber (Hildreth, 1979) clearly could not have been generated by flotation of feldspar because the presumed upper parts of each zone are strongly depleted in Sr^{2+} , Ba^{2+} and Eu^{2+} , ions which are strongly partitioned into potassium feldspar.

On the other hand it is difficult to imagine the generation of basaltic or granitic magma in substantial quantities with absolutely no variation in composition over time, and since the lightest liquids in both systems are the earliest, the possibility of density stratification cannot be lightly dismissed. Many aspects of both types of process could be elucidated by suitably designed experiments.

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