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The residual liquids of crystallizing magmas.

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I N the Mineralogical Magazine for September, 1930, Dr. Frederick Walker describes 'A tholeiitic phase of the quartz-dolerite magma of central Scotland'. Several pages of the article are devoted to a consideration of the phenomena he has observed in these rocks in their bearing upon certain views which I have expressed. In most respects Dr. Walker has clearly grasped the essential features of my thesis, and his efforts to obtain further information on the various points have been well directed. I am glad to welcome such a discussion as he has given, even though his conclusions are somewhat opposed to mine. In one respect, however, he has apparently overlooked an essential feature of my argument. On this matter, and on some points of evidence given, I should like to present some discussion. I desire also to examine certain other recent papers by Daly and Barth and by Bowen, Schairer, and Willems, in which the views expressed in my article have met with some criticism.

In the article¹ to which Dr. Walker refers I have examined the course of crystallization of basalts with reference to the theory that all other igneous rocks have been derived from basaltic magmas

¹ C. N. Fenner, The crystallization of basalts. Amer. Journ. Sci., 1929, ser. 5, vol. 18, pp. 225-253 [Min. Abstr., vol. 4, p. 507].

by processes which involve a separation, at different stages, of crystalline minerals from residual liquids, and that the differences in chemical composition exhibited depend solely upon the differences between crystalline aggregates and the liquids in which they are formed. This is a view which is now accepted by probably a majority of petrologists, and is of fundamental importance in petrogenic theory. While I have recognized that such a process should be of great importance, and I should consider it a major factor in many occurrences where basic intrusives have separated into a highly olivinic lower portion and a relatively olivine-free upper portion, I have observed many phenomena, especially in field work but also in laboratory investigations, which seem inconsistent with the view that this process alone is able to meet, or, in nature, has met all the requirements of the phenomena of differentiation.

In the article on the crystallization of basalts the argument is that in order to determine if crystallization is the all-important factor in petrogenesis that it is assumed to be, it would be helpful to direct our attention to natural phenomena occurring under such conditions that nothing but crystallization could have been effective, and examine the results. It is doubtful whether, in the absolute sense, rocks which meet this requirement can be found, but many surface basalts approximate to the requirements sufficiently closely for the purpose. They have probably received little or no contaminating material; a large part of their easily volatile ingredients has escaped before crystallization has proceeded far; convection currents have not obscured the results; and later hydrothermal action has not greatly affected them. It is, then, to such surface basalts that we should look for information.

In carrying out this idea a great number of thin sections of plateau basalts from different parts of the world were examined. It was found that in the great majority of instances, when crystallization was almost complete, the last little residue of magma in the interstices among larger crystals deposited feldspar, pyroxene, and large amounts of magnetite. It was pointed out that the composition of the residue thus indicated was hardly compatible with the theoretical view that it should be of granitic or rhyolitic composition, as has been maintained in the theory of crystallization-differentiation.

In my argument the fact was not overlooked that plutonic bodies of apparently cognate origins vary in composition among themselves in such a manner as to indicate differentiation along lines quite different from that indicated by the study of basalts, but doubt was expressed

whether these differences could be attributed solely to the effect of crystallization.

For most igneous magmas the site of differentiation is necessarily placed in the deeper regions of the lithosphere, as they arrive at or near the surface in an already differentiated condition. However, although most plutonic bodies show little or no differentiation after emplacement, yet a considerable number do exhibit differences of composition of one kind or another within their mass, and all these have been claimed to be examples of crystallization-differentiation by those who recognize no other process of differentiation. For some of these bodies I would readily grant that crystallization has been an important factor, but for others I would feel much doubt, and in some instances there seems reason to question whether some of the results attributed to crystallization-differentiation have been effected within a liquid magma at all, but rather to suppose that they are post-consolidation effects or results of intense alteration of wall rock. In general, I suspect that many phenomena which have been cited as evidences of crystallization-differentiation need further consideration to make sure that they are not due in part to other processes.

Some explanation and amplification of these statements may be desirable in order to present a more concrete picture. We know that in some manner a separation of magmatic ingredients has been effected, but the question here raised is whether we are yet in a position to assume that crystallization has been the sole agent in bringing this about. We may not be able to point with confidence to any other process to meet the demands, but this is not a prerequisite for a consideration of the evidence.

Among processes for effecting separation we may regard crystallization as a factor of large possibilities, and sublimation of volatile compounds also must be an effective agent, but it is not plain that, alone or in combination, they are able to meet all the requirements of all cases. Liquid immiscibility, formerly much favoured by some geologists, is apparently of very limited application in dry melts, but may be of more importance in natural magmas, though the evidence so far brought forward does not appear convincing. Diffusion is not a well known quantity. It has been shown to be exceedingly slow in its operation under certain conditions of experimentation, but the possibility has been suggested that various combinations of the lighter elements with bases may be more mobile, and when dissolved in a melt consisting chiefly of silicates may diffuse more rapidly than

the silicates themselves. The suggested process has some resemblance to Soret's principle, but differs in certain important respects; for example, that it is not an effect of differences of temperature but of the tendency of volatile material to escape from the system, and that chemical reactions between the magma and the escaping volatiles are involved in an important manner. It is not advocated here as a definitely known process, but is suggested as an example of unexplored possibilities.

With respect to crystallization-differentiation specifically, there seems reason to doubt whether the scope of the theory itself and the field relations have yet been examined with sufficient critical care, and assumptions seem to be involved which pass over wide gaps in both theoretical and field information. Moreover, some of its fundamental principles appear to be irreconcilable with what we find in the rocks themselves. Rhyolites and granites are looked upon as the last liquid residues from the cooling and crystallization of basaltic magma, and, *ipso facto*, direct solution and assimilation of basic rocks by rhyolites and granites, except in small amounts, are held to be impossible; but I have observed phenomena in the Katmai region and in Yellowstone Park which, I believe, cannot be explained otherwise than by solution, on a large scale, of basic andesites and basalts by rhyolitic extrusives, without loss of fluidity.¹

In the face of such evidence I cannot believe that rhyolites represent simply the last remaining and coldest liquid derived from the crystallization of basalt. Some large source of energy is required which is not provided in the theory. In fact, assimilation on such a scale is expressly rejected by the theory and is contrary to the postulates on which the reasoning is based.

In another class of processes the effects produced may simulate those of crystallization-differentiation, while actually of quite different origin. Such effects may be brought about by the mingling of unlike magmas, successive injections of magma, assimilation of foreign material, post-consolidation endomorphism and substitutions in igneous masses, especially their upper portions, by gases and hydrothermal solutions; and the metasomatism of roof and wall rocks by emanations to such a degree that a wholly igneous aspect is brought about. In these suggestions there is little that is novel except, perhaps, the view that such features have led to confusion in inter-

¹ Detailed descriptions will be published later, after the necessary laboratory work has been done.

preting phenomena of differentiation. They represent essentially processes which have been advocated by geologists irrespective of theories of differentiation.

Singly or in co-operation all these may have played a part in one or another instance. There are still numerous processes indicated as probable or possible which require much further consideration. The nature of the magma itself as it exists in the depths of the earth, the quantity and composition of the dissolved gases, the energy content, how magmas originate and what causes them to move upward toward the surface, the effects of relief of pressure in releasing gases and changing equilibrium relations, in what manner the magma becomes emplaced among the surrounding rocks, are matters about which there have been many speculations but few fundamental conclusions so firmly established as to be generally agreed upon. The great simplicity of the theory of crystallization-differentiation has been a strong recommendation in its favour, but it may be a case of applying too simple a conception to an extremely complex set of phenomena.

It is not intended to imply that there is anything mysterious about magmas or that they transcend known physical or chemical principles or that they are not amenable to laboratory investigation, but at the best our knowledge of the fundamental causes of volcanism and of certain phases of its development is meagre. It is important to maintain a proper perspective in these matters, and to realize that experimental investigation in certain fields of volcanism has hardly been begun; in fact, in some respects our knowledge is so slight that it would be difficult to decide to what degree the conditions that might be chosen for experimentation corresponded to those of natural systems.

In addition to the large-scale phenomena of differentiation certain smaller features require consideration, such as felsic veins or dikes in basic rocks, and microgranitic and myrmekitic aggregates in similar bodies. These also have been included among the evidences or proofs of the nature of the residue left by crystallization. In my paper I recognized, and, in fact, emphasized the existence of such features, and propounded to those who attribute their formation to crystallization alone the problem of explaining the reason for such a difference in composition of residues in abyssal or hypabyssal rocks from those found in surface basalts in which crystallization was the only important factor.

Recognition of the fact that in surface basalts crystallization has caused variation in a certain direction, while in deep-seated rocks the residue may show variation in a quite different direction, was fundamental to my argument, but it seems to have escaped Dr. Walker's attention, for it is hypabyssal rocks that he has here studied. I do not find it surprising or inconsistent with my views that the residue left from the crystallization of tholeiitic dolerites should be somewhat at variance with what I found for surface basalts. In effect, what might appear, from a reading of Dr. Walker's paper, to be a problem for me to solve is essentially the problem that I had put before others. My own answer is simple: that in deep-seated rocks other factors than primary crystallization have participated. I shall enlarge upon this in discussing other features of his paper.

Before doing so, however, I will pass to a consideration of certain other articles which are closely related to the matters already touched upon. Attention may be called to what seems a similar misunderstanding at one point of Daly and Barth's discussion of certain features of my paper, in their article on the Karroo dolerites, which appeared in the *Geological Magazine* for March, 1930.¹ They state that the picritic basalt of Hawaii is richer in total iron than the dominant Hawaiian basalt from which they believe the picritic basalt to have been derived by enrichment in olivine, and they believe that this does not support my contention that the early crystal fractionation of basaltic magma should enrich the residual liquid with iron.

This view, however, represents only a part of my argument. I did not suppose that differentiation should always give a liquid portion enriched in iron and a crystalline or partly crystalline portion impoverished in iron. That was the normal result observed in those cases where we could be sure that crystal separation had been the dominant factor, but it would only be generally true if crystal separation were generally the dominant factor—the very point against which the argument was directed. When results of another sort are observed, as is frequently the case, this fact itself suggests that somewhere along the line of differentiation some other process than crystal separation has intervened.

The relations that Daly and Barth supposed to be in opposition to my views are actually those cited by me in support of the argument. On this matter there is a great difference between the deductions that

¹ R. A. Daly and T. F. W. Barth, *Geol. Mag.* London, 1930, vol. 67, p. 109, footnote 2.

I sought to make and those ascribed to me by these authors. To put the thesis in the simplest terms, crystal separation alone, acting upon a basaltic magma, is observed to lead to a residual liquid rich in iron. In the differentiation of plutonic bodies this result is sometimes apparent, and in some of these instances we may confidently ascribe a leading role to crystal separation. Often, however, the derived liquid is poorer in iron than the original basaltic magma, and the participation of other processes is thus indicated.

In a later explanatory note on Karroo dolerites, contributed by Daly and Barth to the *Geological Magazine* for November, 1930,¹ it is shown that the FeO : MgO ratios for many derived basalts is lower than for the world plateau basalts. They contend that if these derived basalts have originated from the plateau basalts by the dropping out of olivine crystals, a higher FeO : MgO ratio should have been the result. I believe that this is a reasonable deduction, and that the lower ratio actually present is in accord with the argument I made, namely, that other processes than crystal separation have participated.

Of considerable interest in connexion with the subjects with which we are dealing is a recently published article by Bowen, Schairer, and Willems on the system $\text{Na}_2\text{SiO}_3\text{-Fe}_2\text{O}_3\text{-SiO}_2$.² In their article the various reactions that may take place under different conditions are brought out, but it is only with a part of the results that we are concerned here. It is shown, as one of the characteristics of the system, that several compounds which crystallize from the cooling melt may later be wholly or partly resorbed, and may or may not again appear. From this it follows that very different final results may be obtained according to whether or not a reactive mineral of this kind remains in contact with the melt or is removed or in any manner protected from reaction. They show that in this system the final product may be in one case an aggregate in which haematite is present and in another case may be of very different composition, without haematite but with quartz as one of the constituents. A petrologic application is made in the suggestion that in a similar manner the iron-bearing silicates of a basalt may exhibit discontinuous reaction relations with the liquid and thus present the possibility of obtaining, through alternative courses of crystallization, an iron-rich residue containing magne-

¹ R. A. Daly and T. F. W. Barth, *Geol. Mag. London*, 1930, vol. 67, p. 481.

² N. L. Bowen, J. F. Schairer, and H. W. V. Willems, *The ternary system : $\text{Na}_2\text{SiO}_3\text{-Fe}_2\text{O}_3\text{-SiO}_2$* . *Amer. Journ. Sci.*, 1930, ser. 5, vol. 20, pp. 405-455.

tite or a residue of granitic or syenitic composition. This is indicated as an answer to the problem propounded in my article. The idea is expressed in the following terms:

'Alternative courses of a quite parallel character are demonstrated . . . in the present system. The parallel is even greater than it may seem because in the present system low fractionation gives the iron-rich final liquid and high fractionation the siliceous liquid, and it is in the quickly cooled (and therefore ordinarily little fractionated) basalts that the late crystallization of iron-rich liquid has been urged, and in the more slowly cooled dolerites (and in sub-alkaline series of rocks formed *ex-hypothesi* by crystallization-differentiation) that the late crystallization of siliceous liquid has frequently been well demonstrated' (Bowen Schairer, and Willems, *op. cit.*, p. 451).

According to this explanation, it is necessary, in the crystallization of a basaltic liquid, to separate crystals from liquid at a certain stage in order to obtain a siliceous final liquid, otherwise later reaction between solid and liquid phases will lead to an iron-rich residue. This represents some modification of previous views of Dr. Bowen regarding the course of crystallization in a basaltic magma. There seems to be recognition that the theory in its earlier form was not sufficient to account for the iron-rich residue found in basalts. I doubt if the new suggestion offers a solution of the problem.

It is a far extrapolation from a system of the composition with which these authors here deal to that of a basaltic magma. The resorption of a constituent by the liquid, and the results attendant upon it, are of the sort that occurs in any crystallizing system in which an incongruently melting constituent appears, and such constituents are of common occurrence in systems experimentally investigated. It would be more convincing to give some evidence that in actual basaltic magmas the iron minerals break up in similar fashion at the right stage or are separated from contact with liquid in the right way to produce the required effects.

In the system experimentally investigated by these authors it was ascertained that no compound was formed between Fe_2O_3 and SiO_2 alone, but that the presence of considerable Na_2O is essential, and this fact may have much to do with the characteristic properties of the system. In natural magmas of basaltic composition the relations between iron oxides and silica appear to be quite different. A large amount of the FeO present (together with MgO and CaO) enters into firm combination with silica, as metasilicates, and the resulting crystalline minerals take up Fe_2O_3 , either in solid solution or in some

other form of combination, and hold it tightly bound. Very different results may therefore be expected in the different cases.

The authors seem to imply that it is only in the quickly cooling surface basalts that iron-rich residues are obtained. It is, in fact, in such rocks that the evidence is most plain, for in these the complications from other possibilities are least, and therefore it was on these that I laid most emphasis, but I pointed out evidence of the not unusual presence of considerable amounts of magnetite and biotite of late crystallization in diabases (dolerites) also, as illustrating the occasional occurrence of a similar course of crystallization under hypabyssal conditions, although believing that in these rocks other processes frequently introduce complications due to entirely different factors.

In the system $\text{Na}_2\text{SiO}_3\text{-Fe}_2\text{O}_3\text{-SiO}_2$ the diagrams show that under certain assumptions almost as much iron may be present in the final residue as in the original melt, and the authors regard this as an important matter, but in basalts the iron minerals in the last residues are often obviously greatly in excess of the amount in the original magma, and not only is magnetite prominent, but pyroxene as well.

The previously quoted article and supplementary note by Daly and Barth lead to inferences that have a further bearing on the article now under consideration. As already mentioned, the work of Daly and Barth indicated that certain basaltic magmas derived at an early stage from a general parent magma show a lower FeO : MgO ratio than the original magma, and it is difficult to explain such a result by any principle brought out in connexion with this experimental investigation, for the authors recognize without question that the separation of FeO-MgO minerals tends to increase the FeO : MgO ratio in the liquid.

In this experimental system, as in many other silicate systems which have been investigated, the breaking down of reactive minerals in the process of cooling throws SiO_2 into the liquid, and this is deemed of great theoretical importance in arriving at a final liquid with excess quartz. The prevalence of this phenomenon is curious, and it may have significance as a co-operative factor in petrogenic processes. Let us not forget, however, that among the actual magmatic minerals of common occurrence it is not obvious that this tendency is of great importance except for the appearance of olivine in basalts in regions of composition where the normative mineral is pyroxene. Moreover, in accomplishing such reactions pneumatolytic processes seem actually

to be more effective than processes occurring in melts. In acid andesites and even in rhyolites, gas bubbles and other cavities or porosities of the rock frequently contain olivine or haematite, together with one or more of the silica minerals. We should remember, too, such phenomena as those described by Dr. Zies for the Valley of Ten Thousand Smokes, where, in a single small area of fumarolic activity, gases rising from a rhyolite had deposited several thousand pounds of nearly pure magnetite.¹ Also 'during one of the eruptions of Vesuvius a fissure 3 feet wide was thus filled with hematite in a few days.'²

Not only orthomagmatic processes but thermal waters also have the effect of separating quartz even from very basic rocks, and some of the quartz of late crystallization in basic rocks attributed to orthomagmatic processes may in fact be a hydrothermal product. In the well-known deposits of zeolites and associated minerals in the Watchung basalts of New Jersey probably the most abundant single mineral is quartz, of which rather large masses occur. This and albite were among the earliest minerals of secondary origin deposited.³ Babingtonite and an acicular green mineral which is probably aegirine also appeared at an early stage of postmagmatic alteration. Progressive changes ensued as the solutions cooled, and the final result of these secondary processes was to remove nearly all the iron, magnesia, and titania from certain parts of the original rock, and leave little but silica, alumina, lime, and the alkalis (together with some B_2O_3 , fluorine, CO_2 , and SO_3) in various mineral combinations. One may ask whether similar aqueous solutions, at a somewhat higher temperature, circulating in zones of fracture and crushing, would not form dike-like bodies of quartzo-felspathic character distinguishable with difficulty from true dikes of orthomagmatic derivation, and whether certain bodies of this sort which have been interpreted as of orthomagmatic origin are not due to hydrothermal action.

¹ E. G. Zies, The fumarolic incrustations in the Valley of Ten Thousand Smokes. National Geogr. Soc. Washington, Contrib. Tech. Papers, 1924, Katmai ser., vol. 1, no. 3, p. 166 [Min. Abstr., vol. 2, p. 439].

² L. V. Pirsson and C. Schuchert, A textbook of geology. 3rd edition, 1929, part I, p. 267.

³ The secondary minerals occur chiefly in the interstices among the boulder-like masses of an extrusive pillow-lava. The conditions of occurrence show that the minerals are due to the action of thermal waters of ultimately meteoric derivation. The possibility that they represent in any sense residues from orthomagmatic crystallization is eliminated.

As bearing upon the general relations of iron compounds to other components of magmas, and the possibility of their removal by crystallization to give residues poor in iron, the authors argue that in the competition in a crystallizing magma between the two principal solid solution series—plagioclase feldspars and iron-bearing metasilicates (e.g. pyroxenes)—it is not possible to tell with our present knowledge which side will prevail in the diminishing residual liquid. Strictly, this is true, but there are certain general principles which control the result and give a suggestion of what is likely to occur.

The competition is chiefly between the lowest melting plagioclase feldspar—albite—and the lowest melting pyroxene, which may be either ferrous metasilicate, ferrous calcium metasilicate, or some still more complex mineral compound. The final result, with respect to the relative amounts of plagioclase and iron-pyroxene left in the liquid, is dependent upon two physical properties of the two competing minerals—the temperature of melting and the molar heat of melting (or solution). For albite these properties are almost exactly known from Dr. Bowen's determinations; for the iron-pyroxenes experimental investigations encounter the difficulty that is always present in dealing with iron minerals—the difficulty of preserving the state of oxidation unaltered; therefore, our knowledge of these properties is not at all exact. What little evidence we have hardly indicates that the physical properties of the iron-bearing pyroxene are so different in these respects from those of albite that we should expect to obtain as a result of crystallization the overwhelmingly large amounts of albite and the vanishingly small amounts of iron-pyroxene (or its equivalent) that we find in many rhyolites and granites.

This has a bearing of some importance upon the theory of crystallization-differentiation. The view adopted in the theory is that iron metasilicates are almost completely eliminated by crystallization, as this assumption is necessary to obtain a magma of rhyolitic composition, but this can hardly be said to rest upon either experimental or theoretical evidence except of the vague sort explained above, which, as far as it goes, seems to point in the contrary direction. It is likewise opposed by the continuance of pyroxene in the last residues of basalts, as explained in my previous paper. There is here an important gap in the theory, and the bridge across it rests upon an assumption for which evidence is lacking.

In the theory of crystallization-differentiation an outstanding feature is its elasticity. In systems containing reactive constituents

so many possibilities of alternative courses of crystallization are open and so little is known about directive or restraining influences, that a great variety of results may be obtained by supposing certain reactions to have occurred or to have been prevented, or by supposing that separation of crystals and liquid has or has not been brought about at the proper moment. A theory of so many inherent possibilities lends itself to the ready explanation of what has been found to occur, but is not of great assistance in predicting what is likely to occur. This characteristic is apparent throughout the literature of the subject. The great desideratum at present seems to be more concrete evidence from the rocks themselves that processes occur in the manner and of the sort postulated. In the basalts that I have studied there seems to be nothing in the present relations of the constituents that indicates the processes suggested by Dr. Bowen and his collaborators to explain the formation of iron-rich residues. So far as may be deduced from thin sections the course of crystallization brought about the precipitation of plagioclase, pyroxene, and magnetite almost from the beginning, and an uncomplicated continuance of deposition of these three minerals to the end, with magnetite in large amount in the final residue.

In considering petrogenic processes one may doubt also whether 'filter-pressing' and 'armouring of crystals'—processes of undoubted reality in a limited sense—are really so widely prevalent or effective in differentiation as is often assumed, or whether invoking them when required to assist in explanation does not give to the process a somewhat artificial aspect; also whether the fact that such widely different processes as magmatic crystallization on the one hand and hydrothermal metamorphism (accompanied by metasomatism) on the other frequently give the same or closely similar mineral assemblages has not led to confusion and misinterpretation of evidence.

Let us return now to Dr. Walker's paper and consider certain other matters contained in it, on which differences of interpretation from those given by him may be allowable. On page 376 Dr. Walker states:

'Both tholeiites support Dr. Fenner's contention that iron is concentrated in the residuum of basaltic rocks; for the chlorophaeite—a mineral rich in iron—is of late formation in both rocks and so is the ilmenite in the northern exposures of Kinkell quarry. The author believes, however, that this late crystallization of minerals rich in iron left a still later residue much poorer in that constituent—a constituent whose presence in any abundance would raise the refractive index of the glass far above the recorded values.'

I had suggested in the article referred to that in the crystallization of basalts (and, *a fortiori*, of dolerites or diabases) there should be a tendency for certain minor elements to be concentrated in the last residue, and possibly a sufficient amount of borates, phosphates, and silicofluorides might sometimes be retained to lower the refractive index of the glass, especially if at the same time iron were carried away as a volatile halide. This idea was tested to some degree by Dr. Walker by having a spectrographic examination and a quantitative estimation made of boron in the Dalmeny rock. It was 'proved conclusively that boron was present. . . . Phosphate cannot be present in the glass, for the normative and modal apatite agree closely in both rocks. It is, however, extremely doubtful if the presence of B_2O_3 in the glass (in this case under 1%) would lower the refractive index, for the three best-known boro-silicates, tourmaline, axinite, and dumortierite, all have high refractive indices'.

In Dr. Walker's specimens the amount of glass in the rock was relatively large, while my suggestion referred to rocks in which crystallization had proceeded so far that only small amounts of glass were left in which these minor constituents may have become concentrated. With the increased concentration of B_2O_3 thus affected, Dr. Walker's finding of boron seems to give some support to my suggestion rather than the contrary. As for lack of phosphates the validity of the evidence cited by Dr. Walker appears doubtful. In the description of one of the rocks he says that 'numerous needles of apatite may be detected in the mesostasis'. This indicates, at least, that phosphates had been thrown into the residue during the later stages of crystallization of the main constituents, and I doubt if it is possible to estimate the quantity of such acicular apatite crystals in the mode exactly enough to be certain that some quite significant percentage of occult phosphate may not be contained in the glass.

The difficulty of exact determination of modal quantities in these rocks is shown by certain other figures given by Dr. Walker. For the southern Kinkell rock, iron-ore in the mode is given as 17.6%. From the accompanying analytical figures it appears that this would use up all the FeO , Fe_2O_3 , and TiO_2 present, leaving none for the chlorophaeite, enstatite-augite, or glass, which is obviously impossible.

On the suggestion that iron may be volatilized as a halide from the last residues, no evidence is contributed by Dr. Walker other than

the expression of belief that it was eliminated by crystallization, as quoted above. On the other hand, the view that the removal of iron in volatile combination is a factor during the magmatic history, and especially near the end of crystallization, is supported by considerable evidence. An instructive experiment which illustrates the process may be easily performed by mixing a little sodium chloride with powdered basalt, and heating the mixture in a covered platinum crucible. Iron is volatilized as chloride and then, in contact with air, is deposited as haematite. The small haematite scales often observable in porous andesitic and rhyolitic lavas appear to be of analogous origin; likewise the fumarolic magnetite deposits in the Valley of Ten Thousand Smokes, and deposits of magnetite and haematite elsewhere.

In connexion with some intrusive bodies, removal of great quantities of iron at a late stage of magmatic history is exemplified in pyrometamorphic ore-deposits of magnetite and associated minerals. Whether, in such instances, one attributes the removal of iron from the parent body to gaseous emanations or to aqueous solutions, it seems that the intrusives from which they have been derived have been deprived of a portion of their iron by processes not closely correlated with crystallization-differentiation.

The economic importance of ore-bodies of this category has directed much study to their relations, but chiefly to the exomorphic phenomena of which they are a part. There must, however, be equivalent endomorphic changes. In fact, they illustrate a set of processes of general character, by which a crystallizing and cooling mass of rock is penetrated and searched out by migrating gases and hydrothermal solutions. Some of the results of this action have been determined, but it is doubtful if all the effects have yet been recognized. It seems to have been satisfactorily demonstrated by various workers that micropegmatites, myrmekites, and similar aggregates have often been formed by such post-magmatic processes, and, in the face of this, it is hardly safe to assume, without more evidence than has been contributed, that the presence of aggregates of this character in the interstices of dolerites (diabases) is to be attributed to the final stage of magmatic consolidation. In relation to this Dr. Walker makes statements with which I can hardly agree. He says (p. 735):

‘ Had the glass been permitted to crystallize it would, doubtless, have formed the interstitial micropegmatite so characteristic of the British Permo-Carboniferous quartz-dolerites. It may be added at this point that there is no evidence

that this micropegmatite is of deuteric formation, for it may be found in absolutely fresh rocks (e.g. that of Auchterarder station). Hydrothermal alteration has certainly taken place in some examples, and it may be detected by the albitization or analciticization of the plagioclase which it causes. The light quartzofelspathic veins which so commonly represent the last magmatic residue often contain twinned albite-oligoclase and acicular hornblende or augite, which cannot be regarded as other than normal products of crystallization.¹

In this statement Dr. Walker apparently makes his chief criteria of lack of hydrothermal alteration the fresh appearance of the rocks and the fact that oligoclase-albite has not been albitized or analciticized. If this were accepted as a standard of general applicability it would seem to bar any fresh rock in which oligoclase or oligoclase-albite is present from being regarded as a product of hydrothermal metamorphism. Many petrologists hold different views. In a late issue of the *Mineralogical Magazine* Dr. F. C. Phillips¹ expresses a principle of probably general applicability in metamorphism as follows: 'In low-grade dynamic metamorphism the reconstituted feldspar is a pure albite, but as the metamorphic grade increases a more calcic member of the series becomes stable.'

Professor Sederholm, who has made very thorough studies of myrmekitic structures, states that the feldspar is commonly an oligoclase-albite, and concludes that, in most cases at least, these structures have been formed by circulating solutions and gases after the primary consolidation of the rock.² We may quote also from a recent publication of Knopf and Anderson:³

'The resultant ores and rocks seem unaltered to the unaided eye and have therefore that appearance of "lack of hydrothermal alteration" so commonly cited in support of the orthomagmatic origin of certain ore deposits. Rocks in which actinolite, biotite, and plagioclase have formed metasomatically are bound to look fresh and unaltered; in fact, it is characteristic of pneumatolytically altered rocks to have that appearance.'

Likewise many of the phenomena of granitization described in the classic works of Adams and Barlow on the Haliburton-Bancroft region, of Sederholm on certain areas in Finland, and of Lacroix on the Pyrenees, give contributory information. Thus we have excellent authority for believing that pneumatolysis or a high grade of hydro-

¹ F. C. Phillips, Some mineralogical and chemical changes induced by progressive metamorphism in the Green Bed group of the Scottish Dalradian. *Min. Mag.*, 1930, vol. 22, p. 247.

² J. J. Sederholm, On synantetic minerals and related phenomena. *Bull. Comm. Géol. Finlande*, 1916, no. 48.

³ A. Knopf and C. A. Anderson, The Engels copper deposits, California. *Econ. Geol.*, 1930, vol. 25, p. 33.

thermal metamorphism frequently produces the same or very similar assemblages of minerals as orthomagmatic crystallization, and this is a source of very real difficulty in petrogenic interpretations.

There is a large group of phenomena of this sort to which much more investigation should be devoted before satisfactory criteria can be established for determining in what manner various examples have originated, and a first requirement in such researches seems to be recognition of the fact that certain phenomena of alteration brought about by hydrothermal processes at low or moderate temperatures should not be expected to result when the conditions are those of high-temperature metamorphism or pneumatolysis, nor is lack of fresh appearance to be looked for under these conditions. Dr. Lindgren has stated: 'Complete recrystallization, development of silicate minerals with little or no water, and coarse texture are typical of deposits formed by replacement at high temperatures, probably above 400°.'¹

It should also be recognized that in replacement processes minerals of secondary formation frequently crystallize with idiomorphic boundaries (metacrysts). So many examples of this have been described and they are of such common occurrence that it would hardly be necessary to call attention to the fact were it not that it seems to be frequently overlooked, and assignment of a mineral to a primary origin made on the basis of its idiomorphic outlines.

In not a few descriptions, alteration effects which have been pointed to as illustrating the reaction principle in magmas, seem equally explicable as results of hydrothermal metasomatism. Processes so fundamentally unlike may lead to almost identical results, and the implications and conclusions to be drawn are entirely at variance.

Acceptance of the essentially magmatic origin of great bodies of plutonic rocks should not cause us to attribute everything found in them to primary magmatic processes. Probably all such bodies have been subjected after consolidation to the action of autogenous (and perhaps xenogenous) vapours and solutions, and it remains to be determined to what degree such phenomena as myrmekites and micropegmatites, and even larger features such as certain dike-like sheets of felsic minerals and variations of composition in different portions of a mass, are due to primary crystallization from a magma and to what degree they are the result of later pneumatolytic and

¹ W. Lindgren, *Mineral Deposits*, 3rd edition, 1928, p. 204.

hydrothermal replacement phenomena in an already consolidated mass.

In connexion with the tholeiites that Dr. Walker studied attention may be called to a series of tholeiite dikes examined by Holmes and Harwood,¹ which are regarded by them as outlying extensions of the Mull swarm. Some of these show an iron-rich mesostasis and some a quartz-alkali-felspar mesostasis, and they possess other puzzling characteristics. The authors point to the 'remarkable feature that wherever Tertiary tholeiites occur several different types are to be found in proximity' (p. 41). In endeavouring to find an explanation evidence of various kinds is discussed at considerable length. They find that 'differentiation by crystallization and separation of the residual liquid was not the process involved in the production of the different types of tholeiites', and conclude (p. 49):

'Our study, however, finally leads to the belief that there is no satisfactory alternative to the assumption of mixing by one process or another. Similar arguments apply to many of the puzzling rocks of Mull, such as inninmorite and the rocks of the "differentiation column"; to the common association of rocks of strongly contrasted composition in composite dikes and sills in Mull and other Tertiary centres; and indeed, to all provinces in which gabbros, dolerites, and basalts, on the one hand, occur dominantly with granites, granophyres, quartz-porphyrries, and rhyolites, on the other, without any noteworthy development of intermediate types.'

The evidence that Holmes and Harwood have brought forward (presented in detail in their discussions) raises a justifiable doubt as to the validity of the crystal differentiation explanation of these occurrences, and their alternative explanation is supported in principle by many occurrences of strongly contrasted types of rock in other regions, but it is not certain that it offers the only explanation in all the cases to which they apply it. In regard to the composition of basaltic or tholeiitic glasses specifically, a subsequent change of composition may, in some instances, be of importance. The minerals deposited in the last stages of magmatic crystallization should be a good index of the composition of the magma (or glass) at that time, but after this period has come to an end it is questionable whether the composition of the glass that is finally left remains the same, even though the glassy aspect may be retained. This has been brought forcibly to my attention by some analyses I have recently made.

In the pillow-lavas found in certain areas of the Triassic Wat-

¹ A. Holmes and H. F. Harwood, *The tholeiite dikes of the north of England*. *Min. Mag.*, 1929, vol. 22, pp. 1-52.

chung basalts in New Jersey each pillow is covered with a dark green to nearly black, shining to dull-shining crust of what appears to be nearly unaltered glass and has generally been so regarded. There is no doubt that it was originally a glassy phase of the basalt, but it has undergone a remarkable change in composition. Two specimens of material which were obtained several hundred feet apart in separate quarries at Paterson were analysed. Specimen W 401 A is the glassy looking crust, and W 401 B is the finely crystalline basalt immediately adjacent; W 402 A and W 402 B have similar relations. The analyses are not yet quite complete as regards certain minor constituents, but are sufficiently so for this purpose.

| | W 401 A. | W 401 B. | W 402 A. | W 402 B. |
|--|----------|----------|----------|----------|
| SiO ₂ ... | 43.39 | 52.43 | 46.88 | 52.33 |
| TiO ₂ ... | 1.43 | 1.13 | 1.20 | 1.09 |
| Al ₂ O ₃ + P ₂ O ₅ ... | 15.25 | 14.36 | 15.75 | 14.29 |
| Fe ₂ O ₃ ... | 2.75 | 1.86 | 3.13 | 2.40 |
| FeO ... | 9.86 | 8.10 | 6.42 | 7.90 |
| MnO ... | 0.13 | 0.14 | 0.09 | n.d. |
| MgO ... | 10.70 | 7.22 | 9.31 | 7.20 |
| CaO ... | 4.66 | 9.82 | 2.64 | 10.43 |
| Na ₂ O ... | 2.21 | 3.44 | 0.57 | 2.40 |
| K ₂ O ... | 2.10 | 0.42 | 5.42 | 0.36 |
| H ₂ O ... | 7.59 | 1.18 | 8.53 | 1.62 |
| CO ₂ ... | 0.06 | n.d. | n.d. | n.d. |
| | 100.13 | 100.10 | 99.94 | 100.02 |

It is readily seen that while the two crystalline specimens (W 401 B and W 402 B) agree closely in composition, and are similar to other Watchung basalts, each differs remarkably from its contiguous glass. These results make one dubious whether any basaltic or doleritic glass, if not of absolutely fresh appearance, can be assumed to have the composition it had in the beginning. The striking fact is not that circulating waters, especially those of thermal character, should act upon this unstable material, but that they should effect such changes of composition without altering very conspicuously the physical appearance.

In these Watchung rocks the hand-specimens give little hint that the glass has been altered to any such degree as is shown by the analyses. In the thin section W 401 A gives likewise little indication of alteration; W 402 A shows more effect, but of a kind which, under less favourable conditions of observation and with less data, might lead to incorrect conclusions. Certain bands and irregular

areas are seen to have been bleached to a nearly colourless material of low refraction and very low birefringence. The relation of this bleached material to the adjacent glass, and the analytical figures, show that it is a result of alteration, which has changed the composition greatly; but if similar material, with its vague optical properties, were observed under ordinary circumstances among the crystalline areas of a basalt, it would probably be regarded as representing a glass little modified from its original character. Its low refraction and lack of colour would then suggest a residue of quartzo-felspathic composition.

These results may have an application to Dr. Walker's specimens and to others which have been described. In many such cases there seems to be no means of determining to what extent the isotropic or nearly isotropic material that is found should be considered to represent the composition of the original glassy residue. In any event, Dr. Walker's conclusion regarding the results of crystallization in the tholeiites is not, after all, so very different from what I found for basalts, and, on the other hand, it does not conform to the standard set by the crystallization theory. Dr. Walker believes that iron was concentrated in the residuum up to a late stage, but was removed before the final product was reached. According to this interpretation, the composition of the residuum during the intermediate and penultimate stages of crystallization was enriched in iron, and was therefore quite different from the composition of what should be the corresponding rocks of the crystal differentiation series—siliceous andesites or trachytes.

In examining the articles of Walker, of Daly and Barth, of Bowen, Schairer, and Willems, and of Holmes and Harwood, one is impressed with the different view-points regarding the phenomena in basaltic rocks that are the subject of discussion. It seems evident that more investigation of some fundamental problems is called for.

I am happy to observe that in another recent article Dr. Walker recognizes that other processes than crystallization have been factors in differentiation. He states :

'An examination of the literature of natural occurrences indicates that even the best-known type-examples possess some features which prevent them from being entirely convincing. Other processes of differentiation, or subsequent intrusions, may, for instance, conspire to confuse the issue.'¹

¹ F. Walker, *The geology of the Shiant Isles*. *Quart. Journ. Geol. Soc. London*, 1930, vol. 86, p. 374.

I should be inclined to add to this that often post-magmatic processes, of the sort we have discussed, similarly confuse the evidence, but, on the whole, the attitude expressed by Dr. Walker, and the consequent desirability of refraining from attributing all phenomena of differentiation immediately to crystallization but attempting to discriminate among the various processes, represent essentially what I have urged for several years. It is only by examination and discussion of the evidence that agreement may finally be reached.

The principal subject of the present article has been the discussion of the character of the residues left by the crystallization of magmas, especially in their relation to certain features which have been held to support the view that crystallization has been the only effective agent in differentiation. It has been pointed out here that in many instances a reasonable doubt may be held as to whether these features have originated in the manner assumed, and whether the conclusions to which they are supposed to point are justified.

It hardly comes within the scope of the article to discuss in detail the broader problems of differentiation, but as this is the subject toward which all the discussion tends, I wish to add a short summary of some of the outstanding points of evidence that, I believe, should be taken into consideration in forming an opinion on the matter. These may be listed as follows:

Features which appear to be inconsistent with the present theory of crystallization-differentiation are:

1. The observed ability of rhyolites, and probably granites, to dissolve large quantities of basic rocks. This evidence is a matter of field observation, and is directly opposed to the fundamental conceptions of the theory in its present form.

2. The nearly linear variation of composition often shown in rock series. This feature is well illustrated in the rocks of the Katmai region.

3. The difficulty of explaining by this theory the origin of many monomineralic and bimineralic ultrabasic bodies—*anorthosites*, *pyroxenites*, *dunites*, bodies of *magnetite* or *chromite*, &c.—without resort to auxiliary hypotheses which appear artificial and speculative. This is exemplified in the remarkable banded rocks of the Bushveld complex, where the presence of sharply defined layers of *anorthosite*, *magnetite*, *chromite*, *bronzitite*, &c., and their repetition in the sequence at widely separated levels are characteristic features. In other regions monomineralic and bimineralic basic rocks appear to

occur as true intrusive dikes, some of which likewise are very difficult to explain.

4. The occurrence, in some regions, of alternate outpourings of typical basalt and typical rhyolite, with little or no lava of intermediate composition, throughout a volcanic period. There is difficulty in bringing this phenomenon into accord with any idea of differentiation, and especially with the theory of crystal fractionation. It has the appearance of discontinuous variation, and, if it stood by itself, one would suppose that the sharp contrast of products, without intermediate gradations, would indicate independent genesis of the two types of lava. The floods of Pliocene basalts and rhyolites of the northern part of Yellowstone Park (probably fissure eruptions) illustrate this alternation. It is among them that the previously mentioned examples of assimilation of basalt by rhyolite have been found.

5. The lack of agreement in the composition of the residue left by the crystallization of surface basalts with the requirements of the theory. Closely related to this is the decrease in the $\text{FeO} : \text{MgO}$ ratio in certain plutonic magmas under conditions where the theory indicates an increase; also the gap in evidence to support the view that crystallization would be more effective in eliminating iron-pyroxene (or its equivalent) than in eliminating albite from the magma.

Considerations which should be kept in mind in applying any theory of differentiation are :

6. The doubtful and ambiguous character of some of the evidence, as emphasized in the present paper. In many plutonic masses and occasionally in surface lavas differences of composition among the various parts may have been brought about, not by true differentiation, but by post-consolidation processes, of which the effects simulate closely those of differentiation in the liquid magma, and are likely to cause confusion and misinterpretation.

7. Confusion may similarly be caused by such processes as mixing of magmas before injection, or by successive injections, or by solution and assimilation of foreign material.

8. It should be recognized that any process tending to bring about a separation of a magma into relatively light and heavy portions will result eventually in density stratification. Separation of crystalline phases of greater or less specific gravity is not the only means by which density stratification may be brought about, and evidence of density stratification is not necessarily evidence of crystal fractionation.

For the eventual development of a satisfactory conception of the processes by which differentiation has been effected we may recognize at present :

9. The indubitable efficacy of crystal separation in some instances, and the theoretical necessity that such a process should effect changes of composition. The objections to considering it the sole process have been discussed in this and other papers.

10. The proven occurrence of mineral-bodies formed by sublimation, and the theoretical necessity that mineral matter should be removed from the magma in this manner. The chief uncertainty in determining the quantitative magnitude of operation lies in the fact that in many instances bodies of this origin have probably been modified by later hydrothermal action and their characteristics obscured, or the sublimates may have escaped into regions beyond observation. The process can hardly be the chief factor in differentiation, but may be important in modifying the effects of other processes.

11. Finally, we should have proper appreciation of our lack of knowledge of some of the fundamental properties of magmas, and recognize the possibility that some process not yet manifest to us may have participated in a fairly simple but effective manner.
