Some Aspects of the Role of Water in Rock Melts

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ABSTRACT

Water will diffuse and distribute itself in a magma so that the chemical potential of the water is the same throughout the magma chamber. By this mechanism water tends to be concentrated in the magma chamber in the regions of lowest pressures and temperatures. Alkalis and certain metals will co-ordinate with the water and, similarly, be concentrated in the regions of lowest pressure and temperature.

Thus certain magmas with appropriate distribution of water may well crystallize from the bottom upward or from the core outward, the reverse of which is generally assumed.

The equipotential distribution of water in a melt may well explain certain volcanic phenomena such as apparent changes of volatile content of lava as an eruption proceeds and recurrent eruptions of crude periodicity at a given site.

Some extensions of the main thesis are presented with the hope of partially explaining the origin of some ultramafic rock bodies, certain alkaline rocks, and the reasons why ore deposits tend to be concentrated in and around the apices of stocks.

Basalts with high ratio of FeO/Fe_2O_3 will differentiate toward a ferrogabbro as iron is concentrated in the residual liquid, thus following Fenner's trend of differentiation. Basalts with low FeO/Fe_2O_3 will differentiate toward a diorite and granite with silica and alkalis concentrated in the residual liquid, thus following Bowen's trend. The role of water in determining the ratio of the iron oxides and the trend of differentiation is discussed.

INTRODUCTION

For almost a century the importance of water in the origin of certain igneous rocks has been recognized. But, as is to be expected where precise measurements are lacking, geologists do not agree as to the effect of water, either quantitative or qualitative. The first quantitative information concerning the solubility of water in igneous rocks came from the work of Roy Goranson at the Geophysical Laboratory, Carnegie Institution of Washington, more than 20 years ago. In a series of papers Goranson (1931; 1932; 1936; 1937; 1938) reported measurements of the solubility of water in granitic melts, as well as the solubility in albite and orthoclase melts. Practically no new experimental contributions to the problem of the solubility of water in rock melts have been recorded since the publication of Goranson's results, though work is again in progress on this exciting topic.

The aim in this paper is to present what is known or can be reasonably well surmised about the quantity and distribution of water in a magma chamber. Some of the *possible* consequences will then be considered insofar as the quantity and distribution of water in a melt affects the processes of magmatic differentiation, ore genesis, and volcanic activity.

The writer stresses that it is *possible* consequences and not *proven* consequences that are being considered in this paper. In particular certain petrogenetic concepts,

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[*] Publication No. 38, Institute of Geophysics, University of California, Los Angeles 24, California.

advanced many years ago but abandoned on what seems to be insufficient grounds in recent years, are revived in this paper.

ACKNOWLEDGMENTS

DISTRIBUTION OF WATER IN A MAGMA

Much interesting petrologic information results from considering the distribution of water in a magma body at rest in the earth's crust. Let us assume a stock or batholith of reasonably uniform chemical composition (exclusive of water content) and several miles in vertical extent emplaced in the earth's crust. Water present in solution in such a melt will migrate by diffusion and distribute itself so that its free energy will have the same ultimate value at every point in the melt, and its partial pressure will be approximately uniform throughout. This by no means indicates that the quantity of water will be the same in every part of the melt. In a batholith, the quantity of water may be sharply different from place to place, for the requirement of equilibrium is solely that the free energy of water, and thus approximately its partial pressure, will be the same throughout the melt.

This distinction between quantity and partial pressure may not be clear to all geologists. The partial pressure of water is that pressure which could be read if we were able to introduce into the melt at various points a magic gage which would read only water-vapor pressure. It is possible indeed and is probably the normal case that the confining pressure, the weight of the column of melt and rock above the point under investigation, greatly exceeds the partial pressure of water in the melt. As the confining pressure is increased at any one point, if the quantity of water in solution is held constant, the partial pressure of water vapor at that point increases also, though not at the same rate as the confining pressure. In effect, higher confining pressure increases the partial pressure of the water by trying to squeeze it out of the melt, a consequence of the large partial molar volume of water in the melt. Furthermore, with the same quantity of water throughout, partial pressures will be higher in the hotter portions of the magma than in cooler marginal portions. Thus there are two effects, one owing to temperature differences and the other owing to confining pressure differences, which produce variations in the quantity of water from place to place in an igneous melt.

If the magma has been in place in the earth's crust long enough to reach diffusion equilibrium, the partial pressure of water in the melt will be substantially the same throughout. This can be so only if the actual quantity of water present is higher in the cooler portions of the melt and in the portions under the lowest confining pressure —i.e., the upper portions, the cupolas, and other upward-extending apophyses.

We may thus consider variations of water content at a given level in a magma chamber and with depth in the chamber.

VARIATIONS OF WATER CONTENT AT AN ISOPIESTIC LEVEL

At a given level in a magma chamber we may assume that pressure is constant and that probably marginal portions of the magma chamber are cooler than the central portions. At constant pressure a gas is more soluble in a cooler liquid than in a hotter one, hence we may as a first approximation deduce that the marginal portions of the melt are more water-rich than the central portions. However, this is very much a simplification. Equilibrium conditions cannot be present owing to the temperature gradient across the contact. Only steady-state conditions can hold. The solution of the problem of water distribution under these conditions is essentially a problem in thermodynamics of irreversible processes and involves data which are not now at hand.

However, this writer adopts the time-honored technique of ignoring aspects of the problem which he cannot treat. Approximate values of the quantitative variation of water in an igneous melt owing to temperature differences can be obtained from Goranson's data if certain other assumptions are made. The most nearly complete set of data currently available is that of solubility of water in an albite melt. These values are similar to the less complete data for granite, and it is assumed that they also apply to our hypothetical magma.

The variation in water content with temperature is numerically rather small but important. The increase in solubility of water at constant pressure amounts to roughly 0.5 per cent by weight for each 100°C decline in temperature. Water thus may tend to diffuse toward the cooler marginal portions of the melt and toward the presumably cooler upper portions of the melt. The effect of this outward and upward migration of water will be twofold. The wetter marginal portions of the melt will tend to have a freezing temperature somewhat lower than that of the dryer central portion of the melt, and the normal tendency of the melt to freeze from the periphery inward will be somewhat offset. The outward-migrating water, diffusing from the hotter core, will also be accompanied by other volatile materials. Metal sulfides closely associated and concentrated with the volatile components of a melt may well join in the outward migration. They may migrate as volatile metal sulfide complexes or, more likely, they may co-ordinate with water and move with the diffusing water. The marginward concentration of metal sulfides with indications of hydrothermal activity is a commonly observed phenomenon, associated with mafic plutons. This mechanism may well explain the hydrothermal mask usually superimposed on nickel sulfide deposits in the marginal portions of noritic masses, although possibly immiscible settling plays the dominant role in the origin of these deposits.

Magmas may develop high marginal-water concentrations in other ways. Assume, for example, that a relatively dry hot magma is intruded into cool wet sediments. The temperature of the sediments close to the magma will rise very rapidly, and in consequence the partial pressure of water in the sediments may increase at a rapid rate, provided the water is in pore spaces which do not communicate readily with the surface of the earth. Suppose the sediments are initially at 200°C and have interstitial water at a partial pressure of 100 atmospheres. If the sediments are heated to 400°C by the magma, and the water cannot escape, the partial pressure of the water

will increase from 100 atmospheres to more than 3400 atmospheres. The water may then escape by diffusing *into* the magma. The marginal portions of the melt may thus become greatly enriched in water and in components from the surrounding country rock which the dense hot water fluid can readily dissolve and transport.

The role of water in lowering the melting point of a magma is well known. For instance, a partial pressure of water of 2000 atmospheres, when total pressure approximately equals water pressure, will lower the melting point of albite approximately 300°C (Goranson, 1938, p. 84). Recent work at the Carnegie Institution by Bowen and Tuttle, not yet published, indicates that similar orders of magnitude apply to the water-granite system.

Under such conditions, where marginal portions of a magma become saturated with water and the central portion is relatively much dryer, it would seem to be quite possible for crystallization of the melt to begin in the central portions first, though they are at a higher temperature, for the liquidus is reached at much higher temperatures in the dryer part of the melt than in the wetter. Ultramafic rocks at Kane Peak, the Blashke Islands, and Mt. Burnette, on the coast of southeastern Alaska, seem to be instances of crystallization from the center outward (Kennedy and Walton, 1946; Walton, 1951). The country rock for several hundred feet around these bodies has been converted to a granulitic hornfels, and much interchange of material took place along the margins of the bodies between the intrusive mass and the country rock. Further, crystallization at the present level of exposure almost certainly began in the central portions of the melt and proceeded toward the margins. The olivine in the core of the mass is Fa_{10}. It steadily increases in iron content and decreases in magnesium until at the margins the olivine is Fa_{50}. Plagioclase changes regularly in composition from An_{96} near the center to An_{30} near the margins. Similarly, the iron-magnesium ratio in olivines and pyroxenes steadily increases from the central to the marginal portions of the body. The various rock types, mapped on the basis of mineral compositions and ratios, form a set of vertical cylinders. Other examples of crystallization which may have proceeded from the center of a mass toward its margins are not rare and may perhaps be explained by postulating some such marginal enrichment in water as is here advocated.

VARIATION OF WATER WITH DEPTH IN A MAGMA COLUMN

The discussion thus far has dealt largely with water variations in a magma, as a result of temperature gradients along a horizontal plane. Probably of more significance are variations of water content with depth in a magma. The situation of most interest is one in which the partial pressure of water is the same throughout the magma but where the confining pressure, as it must of necessity, increases with depth in the magma. This is the normal equilibrium case where the partial pressure of water becomes approximately uniform owing to diffusion of water in the melt,[1] and the

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[1] Actually the partial pressure of water in the melt will not be uniform throughout the melt with equilibrium conditions. A correction must be made for the weight of the water-vapor column. If the melt is at approximately 800°C and contains water vapor at a partial pressure of 500 atmospheres, at equilibrium the increase in partial pressure with depth amounts to approximately 1 atmosphere for each 300 feet. Compared to the rate of increase of confining pressure, this is trivial and may be neglected.

confining pressure increases at the rate of approximately 1 atmosphere for each 12 feet of depth in the melt.

The important case, and indeed the usual case, of a magma in which confining pressure is greater than the partial pressure of water was first considered by Goranson (1937) in a paper which has been much neglected by petrologists. Verhoogen (1949) extended Goranson's treatment to include the effects of the gravitational field on water vapor in a magma. Goranson's values, only slightly modified, are plotted and shown in Figure 1, which shows the equilibrium distribution of water in a melt of albite composition in the gravitational field. The diagram presented is for the 1000° C isotherm. A bar, the unit of pressure used, is approximately equal to an atmosphere, which in turn is equal to about 12 feet of rock load.
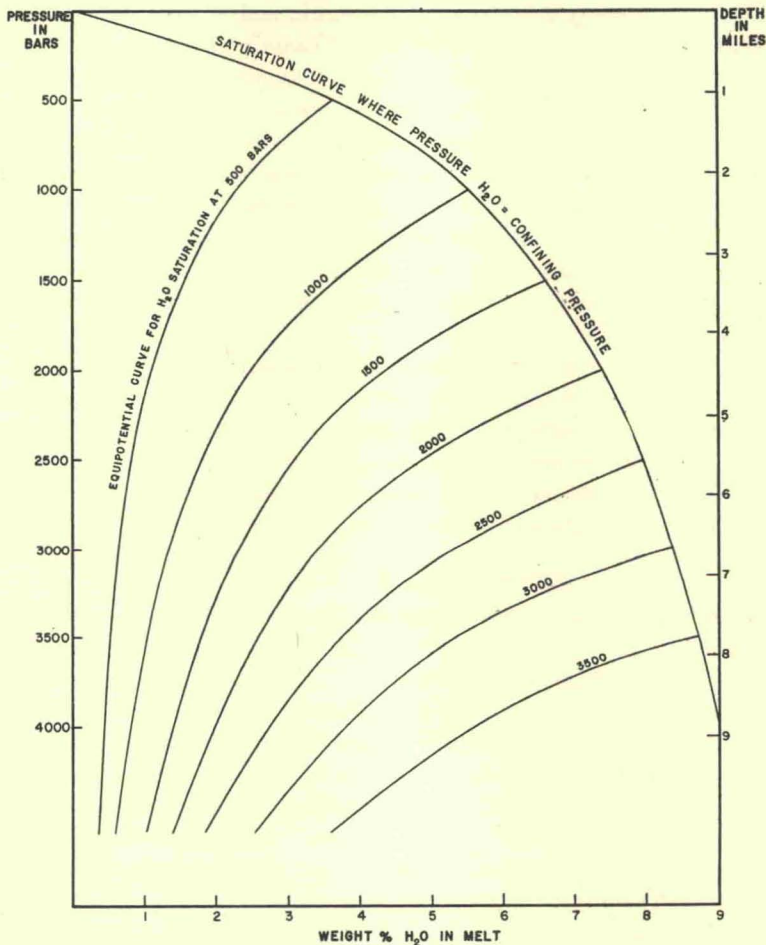

FIGURE 1.—*Equilibrium distribution of water in a melt of albite composition in the gravitational field of the earth*

The parabolic curve of negative slope represents the saturation curve for water in the albite melt. This curve shows the maximum amount of water than can be retained by a melt at any depth where the confining pressure on the melt exactly equals the vapor pressure of water in the melt. No such water distribution is possible in a melt, of course, for in such a system the partial pressure of water increases rapidly with depth, and there would be a strong tendency for water to diffuse upward. With the slightest upward diffusion of water, the vapor pressure would exceed the confining pressure, and violent explosion would ensue. The curves of equilibrium distribution of water with depth in a melt are also shown in Figure 1. These curves, of positive slope, are shown for various saturation pressures.

As an example, let us assume that the top of a magma column extends to within 4½ miles of the surface of the earth. The confining pressure due to the weight of the rock load is approximately 2000 bars at this depth, and, if the magma is saturated with water, the top of the magma column will contain about 7.4 weight per cent water. The equilibrium water content of the melt diminishes very rapidly with increasing depth. At a depth where the confining pressure has increased to 3000 bars, the water content of the melt will have diminished to less than 3.5 per cent, and the melt will be far from saturated. At a depth where the confining pressure is approximately 4000 bars, the water content will have decreased to about 2 per cent. It appears, from examination of this diagram, that the deeper the burial of the magma chamber, the stronger the tendency for most of the water to be concentrated in the uppermost portion. Further, a magma chamber can be saturated with water vapor only at its very top.

It has been assumed that the magma chamber is at constant temperature. Most magma chambers probably show increasing temperature with increasing depth as a result of the geothermal gradient. The general tendency for water to be concentrated in the upper portion of the magma chamber as a result of the effect of confining pressure would thus be reinforced by the temperature gradient, for, as discussed previously, water is more soluble in the cooler parts of the chamber.

GEOLOGICAL IMPLICATIONS

Many igneous phenomena can be understood, at least in part, by assuming that the water in a magma chamber diffuses and approaches equilibrium distribution of the sort indicated in Figure 1.

Most volcanic eruptions exclusive of plateau basalts show somewhat the same sequence of events. Many of them, like the recent eruptions of Paricutin and San Benedicto, start with abundant ash outpourings. It is during this period that a cinder cone is constructed. The first lavas that appear after the construction of a volcanic cone are generally relatively fluid, highly vesicular, and rich in water. Later lavas that may appear during an eruption are marked by higher viscosity and contain less and less volatiles. This is precisely the sequence of events to be expected if we assume that water is distributed in the melt in a volcanic conduit more or less as indicated in Figure 1. The magma at the top of the conduit is highly charged with volatiles and erupts explosively to form ash clouds and pumice and cinder cones. This is followed by magma of lower water content which flows out relatively quietly, vesiculating and

intumescing, but with insufficient volatiles to explode. The last lava to emerge is poor in volatiles and hence is of higher viscosity. It seems to this writer that it is predominantly the decline in volatiles in the magma that brings an eruption to an end. If the water distribution with depth is along the saturation curve, or is even uniform with depth, it seems likely that a volcanic eruption might be much more catastrophic, coming to an end only when the magma chamber was drained or nearly drained, somewhat analogous to the emptying of a geyser tube. However, with water concentrated in the uppermost portion of a volcanic conduit, the "punch" of the magma has disappeared as soon as the wet top has been discharged and dryer, deeper, melt moves up to take its place.

An excellent example of a sequence of events where eruption apparently proceeded with decreasing volatile content is seen in the rhyolite flows and associated rocks of Yellowstone Park and vicinity[2]. Crystal tuffs and poorly consolidated ash make up the lowermost beds, and are the products of the opening stages of an eruption. The ash beds are overlain by collapsed froth flows, the so-called "welded tuffs"[3]. These are almost certainly the products of eruptions less rich in volatiles. The tuffs are in turn overlain by obsidians which here represent the outpouring of magma essentially free of volatiles.

An interesting corollary results from the hypothesis that, as a volcanic eruption proceeds, volatile content decreases. Most lavas that emerge from a vent are at their liquidus—*i.e.*, they contain some phenocrysts. The liquidus temperature of a dryer magma must be higher than that of a wetter magma. Therefore we can postulate that the later lavas which emerge should be hotter than the earlier ones. This remains to be checked by careful temperature measurements at the site of an eruption.

Recurrent, somewhat rhythmic eruptions at a given volcanic structure can be readily explained. Eruption will cease when the wet cap of the volcanic conduit has been discharged and dryer magma moves into place. However, the equilibrium relations among partial pressure of water, depth, and total water content will have been disturbed. Diffusion of water will again take place into the magma at the lower confining pressure of the top of the magma column. Thus the partial pressure of water in the top of the column will build up steadily until it is again high enough to blast aside the restraining rock and permit renewed eruption. If the magma column connects to a relatively large body of melt at depth, it seems perfectly possible to have recurrent volcanism over a long time span at a single site. One of the major controls on frequency of eruption would be the diffusion rate of water in the magma.

The part of the magma chamber in which freezing takes place may well be controlled by the distribution of water in the magma chamber. The large mafic laccoliths may give some evidence for this. If the magma is dry or relatively dry, the lowermost portion of the body will have a higher temperature but only slightly higher freezing point than that of the upper portion of the chamber. As a consequence the

[2] The writer is indebted to Mr. F. R. Boyd for information concerning the sequence of events in the eruptions of Yellowstone Park.

[3] The writer prefers to call the "welded tuffs" of Yellowstone Park collapsed froth flows. The term "welded tuff" seems to imply aerial deposition and origin from nuées ardentes. The great areal extent of the deposits in Yellowstone Park make it seem most unlikely that they could have been deposited from a hot cloud. It is interesting to note in this connection that none of the *observed* nuées ardentes have ever produced rocks of "welded-tuff" texture, though all "welded tuffs" are commonly attributed to nuées ardentes.

freezing will take place dominantly in the upper portion of the body. The crystals may settle through the melt and accumulate on the floor of the magma chamber, producing the sharp layers and extreme magma fractionation noted at the Skaergaard and Stillwater complexes. The high FeO/Fe_2O_3 ratio[4] in the rocks of the Skaergaard and the Stillwater, as well as the absence of hydrated phases, are further confirmatory evidence that water content of the bodies was low.

In contrast with laccoliths like the Stillwater and Skaergaard are the layered but essentially undifferentiated mafic bodies of Mt. Crillon, Alaska,[5] and Tow Lake, Manitoba (Hunter, 1954). In these bodies the composition of the feldspars, olivines, and pyroxenes remains practically the same from the bottom to the top, though many thousands of feet of layered rocks are exposed. The ferrous/ferric ratio and the local presence of amphiboles indicate that these magmas were relatively rich in water. A floored water-rich magma body, with water distributed along an equal chemical potential curve as indicated in Figure 1, might well freeze from the bottom upward. The uppermost portions of the magma chamber, though cooler, would have their liquidus temperature greatly reduced owing to the volatile content. The hotter but dryer lower portions of the melt would, under appropriate circumstances, crystallize first. Mafic magmas crystallizing from the bottom upward would probably undergo much less crystal settling, and thus chemical fractionation, than would similar magmas crystallizing from the top downward, where separation from the magma of early-formed crystals by settling could be extreme. The temperature gradient through the magma would have to be such that the latent heat of crystallization of the solid phases could escape without bringing to a halt freezing on the floor of the magma chamber.

Some granitic stocks and upward-extending apophyses may, by a similar mechanism, freeze at some depth and trap a low-melting, volatile-rich "wet top" above them. Such a mechanism may perhaps account for the pegmatitic facies apparently developed *in situ* in some igneous rocks.

The mechanisms just considered may offer partial solution to one of the major problems associated with the origin of ore deposits—that of a mechanism for concentrating the volatiles and metals in a large batholith into a small segment of the batholith, where they may form an ore deposit *in situ* or from whence they may escape into fracture systems to form veins. We need only assume a large batholith at depth with a modest content of volatiles and metals. If the shape of the batholithic body

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[4] In an earlier paper, the writer (Kennedy, 1948) had deduced an intimate relationship between the partial pressure of water in a melt and the ratio of ferric to ferrous iron. This relationship was based on the assumption that the O_2 partial pressure in the melt produced by the dissociation of water must equal the O_2 pressure produced by the dissociation of the iron oxides and that total water pressure controlled the reaction. Dr. L. H. Adams has kindly considered this problem and pointed out that the assumed relations hold only when partial pressure of hydrogen present is that produced by dissociation of water. Inasmuch as some hydrogen is present, though necessarily in small amounts, beyond that produced by water dissociation, the writer's computation of the water content of the Southern California gabbro, previously reported, is invalid. Thus no direct value of water content from iron-oxide ratio can be calculated unless hydrogen pressure is also specified. Nevertheless, relationship does appear to hold. In general, magmas which for other reasons are deduced to be dry have a high FeO/Fe_2O_3 ratio, and magmas which are deduced to be wet have a low FeO/Fe_2O_3. Is it possible that the primitive magma is both relatively free of volatiles and contains essentially only ferrous iron? Oxidation of the iron and development of free hydrogen would result if water distilled into the magma during its upward journey. This does not seem unreasonable if we assume that primitive magmas form by partial fusion of a peridotitic substratum.

[5] The writer is indebted to Mr. Darwin L. Rossman, U. S. Geological Survey, for much information on the detailed petrology of the Mt. Crillon mafic body. A thickness of approximately 32,000 feet of layered rocks is exposed in the Mt. Crillon area.

changes, solely by the intrusion of a stock or other apophysis, upward into a lower-pressure environment, volatiles will immediately begin to diffuse upward and concentrate in the stock. Concentrations of volatiles many-fold that of the parent batholith are readily possible. The close spatial relationship between ore deposits and the apices of batholiths is well known and was pointed out many years ago by B. S. Butler (1915).

It is not enough to show that the distribution of water in a magma is such that it will tend to concentrate in the apices of stocks. What of the metals? High mobility of copper and silver in superheated water at high pressures may be readily shown in the laboratory. It is necessary to extrapolate somewhat and assume that in the magma chamber the metals, exclusive of iron and aluminum, tend to co-ordinate with the volatile materials, sulfur and water, and are transported with volatiles as they diffuse into portions of the magma with lowest confining pressure. It seems unlikely, of course, that these substances can move as a separate gas phase, in the sense of bubbles forming and rising through the melt. If the batholith is large, migration by diffusion of volatiles into the apical portions may take a very long time. Upward escape of volatiles from the site of accumulation may take place almost throughout the life of the magma chamber, and resultant long periods of hydrothermal activity are possible. It is not necessary to postulate that the period of hydrothermal activity associated with the freezing of a magma takes place only at a late stage in the history of the magma when the volatiles have been concentrated by separation of anhydrous phases.

Several other suggestions in regard to ore genesis result from this postulated mechanism for the concentration of the hydrothermal constituents in the cupolas of magma chambers. Rates of upward diffusion of metal-volatile complexes depend both on the strength of co-ordination between the metal and its carrier and on the partial molar volume of the complex formed. It is, of course, extremely unlikely that all metals would complex and diffuse upward at the same rate. If ebullition of a hydrothermal fluid from its zone of concentration into a fracture system took place and continued over any long time span, it seems likely that the metal species being fed to the vein system would change with time. Further, these changes with time should be reasonably consistent from magma to magma and from ore deposit to ore deposit. This might, in part, account for the commonly observed "standard sequence" of sulfide minerals crystallizing at a given point in a vein. It is certain, of course, that, in addition, changing temperature of the vein and changing chemistry of the hydrothermal solution due to reaction with wall rock will also play major roles in determining the species of minerals deposited.

Much accumulated evidence suggests that the sulfur-vapor pressure in a hydrothermal solution at a given point in a vein decreases in a fairly regular fashion from early to late during a period of mineral introduction. The earliest-deposited constituents have a higher sulfur-metal ratio than do the late-deposited constituents. This can be explained, on the basis of the thesis presented here, by the reasonable assumption that the volatile sulfur-rich complexes diffusing in the magma have a higher partial molar volume than do the metal-rich complexes. Sulfur would thus be fed preferentially from the magma into a fracture system during the earlier stages of a cycle of hydrothermal activity.

It is by no means necessary for the water and associated metal and sulfur complexes to escape from the magma into the surrounding rock in order to make an ore deposit. If we assume a starting magma with relatively low water content and relatively high metal and sulfur content, it seems quite possible to build up high concentrations of metal-rich and sulfur-rich complexes in the apices of stocks. Separation of anhydrous phases by continued cooling would increase the vapor pressure of volatiles in the stock until at some late stage, after the stock had largely solidified, explosive rupture and brecciation of the stock could occur. Release of pressure on the contained volatiles would cause deposition of the less-volatile constituents in the fractured, brecciated rock. This general genetic picture is advanced as a possible explanation for the porphyry copper deposits, though considerable extensions of this hypothesis are necessary to explain many of the details of these deposits.

The problems of the origin of alkaline rocks and of extensive introduction of alkalis into metamorphic rocks have received much careful consideration by geologists for many years, and many competing ideas are current. This writer would like to present a hypothesis of the origin of certain types of alkaline rocks, more by way of setting up a straw man for a target rather than with any deep conviction.

Few geological generalizations can be made about alkaline rocks. The most striking ones are that plutons of alkaline rocks are almost always post-tectonic or present in unfolded terranes. Alkaline lavas are present in many volcanic provinces, where they are usually the last lavas to emerge and are in many places present as late outpourings on earlier "normal" calc-alkaline rocks. There seems to be little doubt that they can form by differentiation of more normal rock types. The more widely current theses of origin, involving assimilation of limestone beds or some combination of crystal fractionation and crystal separation, may explain the origin of certain bodies, but for many examples these mechanisms appear to fall short.

The exciting work of George Morey[6] offers a possible clue. Morey has shown in a series of papers that the alkali silicates are extremely soluble in superheated water vapor at high pressure. The alkali silicates seem to have this property uniquely among the rock-forming mineral components. Solubility in dense water vapor appears to be trivial or essentially nil for most of the other rock-forming oxides. Morey has been able to dissolve in water vapor, at 400° C and at a pressure of 2200 bars, over 40 weight per cent of alkali silicate. Once the alkalis in a system are fixed as solid alkali-alumino-silicates, their solubility in water vapor diminishes to essentially nil. The high solubility of alkali silicates in gaseous water seems to this writer the best of evidence that they tend strongly to associate or co-ordinate with water molecules. There seems no reason to believe that this would not be equally true if both constituents, alkali and water, were dissolved in a magma rather than as separate gas phases. Migration of water into the upper part of a stock, to reach equilibrium distribution, should also concentrate the alkalis in the upper portions of the stock. They may be fixed there by the crystallization of orthoclase and other alkali-rich minerals. Morey has shown that the solubility of alkalis in water is very much a function of the pressure on the system. As pressure decreases the solubility also decreases sharply. Consequently, escape of volatiles from the magma chamber, following any pressure

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[6] *See* most recent paper by Morey and Hesselgesser (1952). Many of Morey's earlier papers are in point.

release on the system resultant from fracturing, etc., may well occur with much of the alkalis left behind. By this mechanism successive waves of alkalis may be introduced and high concentrations built up.

Solutions escaping from the melt under high pressures, however, will contain abundant alkalis. The common alkaline wall-rock alteration associated with many ore deposits is well known. Fewer instances are well documented in which alkalis have been introduced into metamorphic terranes. A particularly good example, where the extent and degree of chemical change is unequivocal, has been described by Billings (1941). Several per cent of potash has been introduced into the Littleton schist, dominantly along the noses of folds. The older minerals are extensively replaced by muscovite. The total quantity of potash introduced and the volumes of rock involved are extremely large. The structural control of potash enrichment in the Littleton schist, along the noses of plunging anticlines, strongly suggests the role of ascending solutions as carriers for the potash.

Late-stage introduction of orthoclase and replacement of earlier-formed minerals has been described by many petrologists. Rather striking examples of late enrichment of igneous rocks in orthoclase are seen at Jumbo Basin, Alaska (Kennedy 1953, p. 9). Terzaghi (1935) had presented evidence and emphasized the fact that many potash-rich rocks may acquire their potash by hydrothermal alteration.

Volatiles escaping from intrusive alkaline rocks may be extremely rich in alkalis. Larsen and Buie (1941, p. 1833) describe contact relations between a headed dike in the Highwood Mountains and sandstone into which the dike is intruded. The dike is shonkinite rich in pseudoleucite. For several mm beyond the contact the sandstone contains more than 50 per cent introduced orthoclase, and, locally, crystals of pseudoleucite, 5 mm in diameter and otherwise similar to those found in the dike itself, have grown in the sandstone, as much as 10 cm from the igneous rock.

The foregoing considerations lead to some extremely tentative explanations for the distribution of alkaline rocks in space and time. As noted earlier, they are characteristically late in an igneous cycle and are either post-tectonic or in tectonically undisturbed terrane. This is precisely the position where they might be found if long periods for diffusion were required to produce high-alkaline concentrations in the cupolas of bodies of batholithic proportions. Diffusion upward into a low-pressure environment takes place in response to a change of shape in the magma chamber. A syntectonic magma chamber might well undergo so many changes of shape and consequent changes of sites of accumulation of alkalis that no sufficiently long period could elapse to allow diffusion to produce an alkali-rich derivative. The rate of diffusion in a gravitational field is a function of the partial molar volume of the complex formed in the melt, and the upward migration of the alkalis might well be extremely slow.

Similar arguments can be used to explain the time relations of alkaline rocks. By this hypothesis they would be expected to appear late in the cycle of igneous activity. It is necessary to assume the alkaline rocks were generated in an isolated cupola that establishes surface connections only in the waning stages of magmatism. It is difficult, of course, to explain how they can emerge, as they occasionally do, from a vent that has earlier erupted normal rocks. Complex mechanics are required, but this remains a difficulty with any thesis of origin.

The idea that alkaline rocks may be generated by migration of volatiles in a magma chamber of "normal" composition is not a new one. The work of Morey and Goranson, however, makes it possible to suggest a plausible mechanism. This hypothesis was succinctly stated by Lindgren (1933, p. 161) more than 20 years ago. ". . . . differentiation . . . . largely through gas transfer, resulted in trachytes, phonolites, basanite and many other types of alkaline flow rocks." The fundamental similarity of the role of gases in producing alkaline rocks as well as ore deposits was noted by Lindgren and is emphasized here.

ROLE OF WATER IN THE CRYSTAL DIFFERENTIATION OF BASALTIC MAGMAS

The course of crystallization of basaltic magmas has been of interest since the first speculations that basalts—world-wide, plentiful, and compositionally uniform —might represent parent magmas from which most other magmas spring. Daly's demonstration that basaltic rocks are members of almost every post-Cambrian igneous province and compositional series did much to further the acceptance among petrologists of the concept that basalts are parental to other rocks. Bowen (1928, p. 4) in his genetic story of igneous rocks states "In the present discussion the parental nature of basaltic magma is taken as a fundamental thesis. . . ." Many petrologists have found the view unacceptable, however, and the advocates of granitization and spokesmen for primary dioritic or monzonitic magmas appear to be growing in numbers.

There has been no general agreement among those who have enthusiastically welcomed parental basalts as to the mechanism by which this parenthood is achieved. Crystal differentiation, whether by settling, armoring, or filter pressing, has probably enjoyed the widest advocacy and most general acceptance. Proponents of liquid immiscibility, gas transfer, and the Soret effect have more or less successfully pleaded their case for specific instances.

Knowledge of the crystallization process of basalt will at once permit the test of the compatibility of the two dominant ideas in modern-day petrology: (1) crystal differentiation as the major mechanism of igneous differentiation, and (2) parental basalts. Acceptance of these hypotheses implies that continued subtraction of material from a basalt by effective removal of the early-formed crystals will cause the residue to follow the typical calc-alkalic differentiation trend with successively formed residues of diorite, granodiorite or monzonite, and granite.

Bowen has been perhaps the strongest of the advocates of fractional differentiation with early silica and alkali enrichment. He brings to the support of his thesis an abundance of very pertinent laboratory information, largely derived from the studies of the two-, three-, and four-component systems carried out by the Carnegie Institution, and a wide knowledge of geological literature. The salient features of his arguments may be summarized: In the three-component system albite-anorthite-diopside, labradorite and diopside will begin to separate almost simultaneously if present in about equal amounts. It seems likely that the same would be true in the four-component system where $FeSiO_3$ is the additional component. This seems to check well with some natural basalts where the evidence indicates that feldspar and

pyroxene either crystallize simultaneously or overlap widely in crystallization periods. Bowen's second major point is that the early separation of olivine in stoichiometric excess necessitates the late formation of free silica, should complete reaction between olivine and liquid be prevented.

Fenner (1929; 1931; 1938) has presented convincing arguments and evidence that certainly in many cases crystallization of basaltic magmas does not proceed in a direction toward dioritic and granitic residues, but that differentiation proceeds toward a ferrogabbro, owing to iron enrichment by fractionation of the crystallizing basalt. Wager and Deer (1939) confirmed Fenner's views in a quantitative manner by showing that in the Skaergaard magma absolute enrichment in iron continued until about 95 per cent of the magma had crystallized. They assumed that the enrichment of alkalis and silica which took place during the crystallization of the remaining 5 per cent of the magma was also due to fractional crystallization, though the possibility of contamination was not excluded.

With the hope of resolving the conflicting views of Bowen and Fenner, the present writer undertook to remelt and crystallize some natural basalts in laboratory crucibles. These experiments have been in part reported (Kennedy, 1948). It became immediately apparent that the same basalt could be made to follow a Bowen trend of differentiation, enrichment of residual liquids in alkalis and silica, or could be made to follow a Fenner trend, with enrichment in iron, depending on the partial pressure of oxygen under which the melt is crystallized.

If the basalt is crystallized under modest pressures of oxygen much of the iron in the melt will be converted from ferrous to ferric iron, and the first phase to appear, at approximately 1280°C, is a spinel, a solid solution of magnetite and magnesioferrite (FeO, MgO)Fe_2O_3. This spinel comes out early and in great abundance, impoverishing the liquid in both iron and magnesium. Calcium-rich plagioclase next appears, at approximately 1200°C, and the melt is changing in composition directly toward a diorite. The early precipitation of spinel enriches the melt in silica even more than does the precipitation of olivine. The general trends of such a differentiation are sharply in the direction Bowen advocates.

If, on the other hand, the crystallization is carried out in a near vacuum or in a slightly reducing environment where the partial pressure of oxygen is kept extremely low, no Fe_2O_3 and thus no early spinel is formed. Olivine very rich in magnesium appears at about 1240°C. At slightly lower temperatures anorthite appears, and only very slight amounts of iron are extracted from the melt by the early-formed phases. Thus the trend is strongly in the direction advocated by Fenner, toward the production of an iron-rich residue. This is the general trend observed in the Skaergaard.

As with many geological arguments, there are thus circumstances under which both protagonists are correct. The significance of the ferrous-ferric ratio in the control of the trend of differentiation has also been deduced from field evidence. Walker and Poldervaart (1949, p. 662) state ". . . . . alkali enrichment throughout the crystallization period is more characteristic of differentiation in calc-alkaline provinces or in basic volcanic associations with high Fe_2O_3:FeO ratios." It is interesting to note in this connection that the Skaergaard magma, which shows extremely strong iron en-

richment by differentiation, also has one of the lowest reported ratios of Fe_2O_3:FeO. Hisashi Kuno has also deduced a similar control as being of importance in the differentiation trend of some Japanese lavas[7].

Had the Skaergaard magma acquired water free of gaseous hydrogen at any time during its history, some of the ferrous iron would have oxidized to ferric iron by dissociation of the water, and the course of crystallization of the melt would have changed in proportion to the degree of oxidation. Though we can make no direct computation of the water content of a melt from knowledge of the ratio of the iron oxides, the strong correlation between state of oxidation of the iron and water content is apparent from field observations. The writer would like to suggest that in this manner the role of water in determining the differentiation trend of basaltic magmas is a major one.

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[7] The writer would like to acknowledge stimulating discussions with Professor Kuno on this matter.

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