THE DISTRIBUTION OF ACCESSORY ELEMENTS IN PEGMATITES. I. THEORY

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CONTENTS

ABSTRACT

A mathematical theory for the distribution of accessory elements in pegmatites is derived. The admittance of accessory elements by crystal lattices, the distribution of accessory elements as a function of the distance from the wallrock-pegmatite contact, and the effect of disturbing factors on the cooling history of a pegmatite are discussed. The theory is illustrated with an artificial example and suggestions are made relative to its testing by experimental data. It is proposed that such testing will elucidate the mechanism of pegmatite formation.

INTRODUCTION

Theoretically the distribution of elements accessory to the mineral types of pegmatites is dependent on the mode of formation of the pegmatite. The problem of the origin of pegmatites can therefore be approached through a study of the distribution of these elements. In this paper a theory has been formulated for this distribution. Since quantitative field and laboratory tests of the theory developed are possible, this theory should serve to clarify and improve the existing concepts of the origin of pegmatites.

Theories for the origin of pegmatites have been numerous and divergent. In the first quarter of the nineteenth century Charpentier (1823) proposed magmatic injection and crystallization. Later Credner (1875) suggested "lateral secretion." In the 1920–1930 period students of complex pegmatites such as F. L. Hess (1925), Schaller (1925), and Landes (1925) favored replacement of an earlier simple "magmatic" pegmatite by hydrothermal solutions. The detailed mapping of a great number of pegmatites by the Federal Survey in the period 1939–1945 has resulted in the best documented picture of lithologic units in pegmatites. In their paper, Cameron, Jahns, McNair, and Page (to be published) note the existence of units called replacement bodies and fracture fillings, but find that in most areas these are quantitatively insignificant compared to zones ("successive shells, complete or incomplete, that reflect to varying degrees the shape or structure of the pegmatite body. Where ideally developed they are concentric about an innermost core"). These authors "adopt the theory that the zones have developed from the walls inwards, essentially by fractional crystallization and incomplete reaction in a restricted system."

If such an origin is assumed for the pegmatites, the distribution of accessory elements can be more easily explained than if one assumes the replacement mechanism. In the physical chemical derivation to follow, it is assumed that zoned pegmatites are formed by magmatic injection and fractional crystallization, but the effect of other mechanisms is also considered. If suitable experimental data fit the distribution of accessory elements as predicted for the Cameron, Jahns, McNair, Page concept of origin, it will be a strong support for their theory.

Previous experimental work on the distribution of trace elements in pegmatites has been very limited. Ahrens (1947; to be published), Hahn and Walling (1938), Mattauch (1937), have determined the content of strontium and rubidium in specimens of lepidolite, muscovite, phlogopite, pollucite, and feldspar. Bray (1942) has completed a regional study of trace element distribution. However, quantitative studies of the variation of the content of accessory elements in the same pegmatite, not only from one mineral to another but also in any given mineral at different points in the pegmatite, are few in number.

The theoretical treatment of the distribution of accessory elements in minerals of pegmatites will be divided into three parts.

(1) The distribution of accessory elements as a function of the ease of entrance, or admittance, of the element into growing crystal lattices.

(2) The distribution of accessory elements in a particular lattice type as a function of the distance from the wallrock pegmatite contact.

(3) The effect of loss or addition of material, convection, shattering, veining, and replacement in the cooling history of pegmatites.

ADMITTANCE OF ACCESSORY ELEMENTS BY CRYSTAL LATTICES AND CRYSTAL AGGREGATES

On the surface of any ionic crystal there are sites at which cations and anions can be added. In a suitable medium ions will be constantly arriving at and leaving from these points. When the number of ions arriving is greater than the number leaving, the crystal is growing. Incorporation of foreign ions into a crystal possessing an ionic lattice will occur when foreign ions arrive and stay at sites on the crystal surface. There are two possible interpretations for the incorporation of foreign ions: (1) the foreign ion can be considered as replacing an ion of the main lattice constituent already lodged on the surface of the crystal, and (2) the foreign ion can be thought of as capturing an empty site which would normally be occupied by an ion of the main lattice constituent.

The mechanism of foreign-ion incorporation has been variously interpreted by authors on the basis of either of these mechanisms in treating such widely differing phenomena as foreign-ion incorporation in aqueous solutions and in crystallizing melts.

However, these two processes are essentially the same since incorporation of foreign ions is a dynamic process and depends only on the relative ease with which the two ions can attach themselves to the available sites, and on the geometric difficulties of closing the next layer above the foreign ion in the growth of the crystal. It is not surprising, therefore, that the equations relating the concentration of the foreign ion in the lattice as a function of the amount of material crystallized are the same whichever interpretation is used as the point of departure.

Two excellent examples of the applicability of this type of reasoning are to be found in the incorporation of radium ions in a $BaSO_4$ precipitate and in the incorporation of potassium and copper ions in crystals of NaCl grown from a melt.

Similar lines of reasoning lead to analogous conclusions for the case of non-ionic lattices. In that case the unit cell containing the foreign element acts in the same fashion as the foreign ion, and surface energy as well as geometric considerations will be related to this unit cell rather than to the foreign ion alone.

Incorporation During Precipitation from Dilute Aqueous Solutions

The mechanism for foreign element incorporation is clearly illustrated by the system $BaSO_4$—$RaSO_4$, investigated by Hoskins and Doerner (1928). In the experiments of these authors H_2SO_4 was added so that the solubility product, K, of $BaSO_4$, but not that of $RaSO_4$, was exceeded. It was found that the $RaCl_2$ remaining in solution after precipitation of the $BaSO_4$ was less than the original amount. Some radium ions must therefore have been included in the $BaSO_4$ precipitate. According to Hoskins and Doerner (1928) the following reaction had taken place.

$$BaSO_4 + RaCl_2 \rightleftarrows RaSO_4 + BaCl_2.$$

This means that at equilibrium there is exchange of radium ions in solution with barium ions in the precipitate and vice versa; i.e., one particle is removed from the crystal surface for each one added. The relation between the concentration of the four components of the system at equilibrium can be expressed by the equation

$$\frac{A_{(\mathrm{Ra}^{++})\text{ on surface}}}{A_{(\mathrm{Ba}^{++})\text{ on surface}}} = K\frac{A_{(\mathrm{Ra}^{++})\text{ in solution}}}{A_{(\mathrm{Ba}^{++})\text{ in solution}}}$$

where A stands for the activity of the components (see Taylor, 1942, p. 374 ff.). In the following derivations it will be assumed that the activities can be replaced by the concentration of the specific components. The above expression therefore becomes

$$\frac{\text{No. of Ra}^{++}\text{ on surface}}{\text{No. of Ba}^{++}\text{ on surface}} = K\frac{[\mathrm{Ra}^{++}]\text{ in solution}}{[\mathrm{Ba}^{++}]\text{ in solution}}. \tag{1}$$

The magnitude of K is a measure of the ease of replacement of barium ions in the crystalline phase by radium ions. K will therefore be called the "admittance factor," for the admittance of radium ions to the $BaSO_4$ lattice.

Hoskins and Doerner (1928) found K to be constant over a wide range of concentration of the components of the system. Therefore the ratio of the number of radium ions to the number of barium ions in the crystal is directly proportional to the ratio of the concentration of radium to barium ions in solution over this range of concentrations.

If, in the general case, a_c is the ratio of the ions on the crystal surfaces and a_s the ratio of the ions in solution, then equation (1) can be simplified and rewritten in the form

$$a_c = Ka_s. \tag{2}$$

The magnitude of K for any such exchange reaction depends on several factors.

(1) The ionic radii and valence similarity of the ions taking part in the reaction. In the $RaSO_4-BaSO_4$ reaction K would be expected to be greater than in the reactions $BeSO_4-BaSO_4$ or $K_2SO_4-BaSO_4$, because the ionic radius of barium, 1.37Å, is more nearly equal to that of radium, 1.52 Å, than that of beryllium, 0.34 Å, and also because the charge on the potassium ion is only one whereas that on the barium ion is two. It is, however, a well known phenomenon of natural silicates that the ionic radius is more critical in determining the possibility of substitution than is valence.

(2) The deformability of the incorporated ions and the ease with which the precipitate is ionized.

(3) The presence in the solution of foreign substances affecting the solubility of the precipitate. Normally this is of minor importance.

(4) The solubility of the accessory element in the liquid phase. This

principle is formulated in the Paneth-Fajans-Hahn adsorption rule: (Kolthoff and Sandell, 1943)

> Those ions whose compounds with the oppositely charged constituent of the lattice are slightly soluble in the solution in question are well adsorbed by the ionic lattice.

Thus, if a compound CA is only slightly soluble, C is more easily adsorbed by the lattice of compound BA than if CA were readily soluble. In the first instance K is larger than in the second.

(5) The temperature at which precipitation occurs. Kolthoff and Noponen (1938) write:

> The heterogeneous mixed crystals of barium and lead sulfate formed on precipitation from acetate medium age very slowly in the supernatant liquid at room temperature but very markedly on digestion at 95° C.

Also, Kolthoff and Eggertsen (1939) write:

> The coprecipitation of chloride with AgBr decreases with increasing temperature during precipitation.

In both of these cases, therefore, an increase of temperature during precipitation caused a decrease in the constant K. It is therefore possible that a similar relation will hold in other cases under similar circumstances.

(6) The pressure in the reacting system. It is to be expected that in most cases the influence of pressure will be slight since the volume changes involved in most liquid-solid exchange reactions are small.

Other factors possibly affect K, but those enumerated above probably represent the most significant ones.

When precipitation is rapid the system may not attain equilibrium during the growth of the crystalline phase. In that case, the amount of foreign material incorporated by the crystalline mass is determined not only by K but also by the rate of crystallization. Kolthoff and Noponen (1938) write:

> The amount of coprecipitation of lead with $BaSO_4$ when the latter is precipitated from acetate solution depends greatly on the speed of addition of precipitant. With very fast addition of the latter the amount of coprecipitation is practically independent of the order of mixing the reagents.

The reverse of this process occurs during rapid crystallization of the precipitates already formed. Kolthoff and Eggertsen (1939) write, when considering the type reaction

$$\underset{\text{(solid)}}{BC} + \underset{\text{(solution)}}{A} \rightleftarrows \underset{\text{(solid)}}{AC} + \underset{\text{(solution)}}{B}$$

> When the reagent C is added slowly to a well-stirred mixture of A and B, the distribution of A (in BC) usually will occur according to the logarithmic expression. (See equation

(10)). However, when the primary precipitate formed is subject to rapid crystallization, the initial distribution of A (and B) will change very rapidly. The primary precipitate, which consists of heterogeneous mixed crystals of BC and AC, will tend to become homogeneous.

As the concentration of the foreign element in a crystalline aggregate is increased, strain is increased in the lattice due to the presence of the foreign element. It is therefore to be expected that, beyond a certain value of the concentration of the foreign ion in the crystal aggregate, the ratio of a_c/a_s will decrease appreciably with the increasing concentration of the foreign element in the liquid phase as this strain effect becomes significant. This is shown graphically in Fig. 1. A point is reached beyond which the amount of foreign element incorporated in the lattice is nearly independent of the concentration of the foreign element in the liquid phase. The maximum concentration of the foreign element in the crystal aggregate will be called A_c.

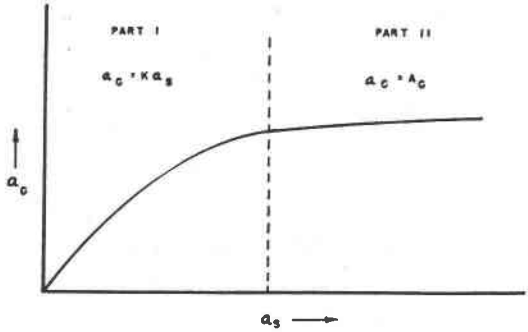

FIG. 1. a_c as a function of a_s.

Incorporation During Crystallization from a Melt

Relations similar to those obtained in aqueous solutions can be observed under quite different conditions. This is illustrated by experiments conducted by McFee (1947) on the incorporation of foreign elements in NaCl crystals during crystallization from a melt. The crystals were grown upward from the base of a cylindrical platinum crucible by lowering the crucible containing the melt of NaCl and the chloride of the foreign element from a hotter to a cooler region of a furnace. The single crystal formed during each run was removed from the crucible and cut into 2 mm. cylinders at right angles to the axis of growth. These cylinders were subsequently analyzed for potassium and copper. The original concentration of potassium was 0.104 atomic per cent, that of copper 0.100 atomic per cent. McFee found that, within experimental error, at these concentrations K was constant at all points in the crystals formed under similar conditions of growth. The curve of Fig. 2 shows that K increased sharply with the rate of growth of the crystal along its long axis. For potassium it was found that K is relatively independent of the rate of growth for rates of growth less than 5 mm. per hour. Above 10 mm. per hour K was found to increase rapidly. If the same is also true for other lattice types and conditions of growth, it can be concluded that in pegmatites K is essentially independent of the rate of crystallization, because the rate of crystallization in pegmatites is probably much slower than 5 mm. per hour.

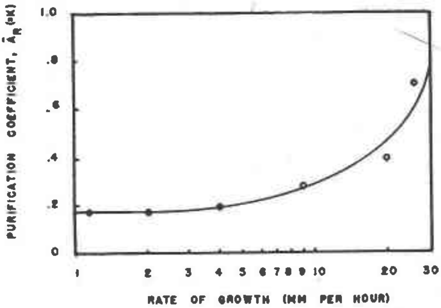

FIG. 2. Taken from R. H. McFee, 1947.

It was stated that in the course of McFee's experiment K was found to be essentially constant under equilibrium conditions. This was only because the amount of the foreign element in the NaCl melt was relatively small. For larger concentrations of foreign elements in the crystallizing melt K deviates from its value for low concentrations. To calculate this deviation the variation in the melting point of the mixture must be determined. A quantitative mathematical and experimental determination of the relative concentration in the melt and in the solid phase of the two constituents of an isomorphous substitution series (complete solid solution) was carried out by Bowen (1913) in his paper on the melting phenomena of the plagioclase feldspars. Bowen's assumptions are contained in the following paragraph:

> For the case of complete solid solution of the type exhibited by the feldspars, we may derive equations expressing the relation between the composition of the liquid and solid in equilibrium at any temperature in the following manner. If both the liquid solutions and the solid solutions are *perfect physical solutions*, i.e., if there is no heat effect or volume change on mixing, then Raoult's law of vapor pressure lowering, and the Clausius equation for the change of vapor pressure with temperature should apply to both components in both phases.

By means of the equations developed by Bowen the concentrations of albite and anorthite in the melt and in the solid phase at temperatures between the melting points of the two components of the plagioclase system were calculated. The liquidus and solidus curves thus obtained closely approximated the values experimentally obtained by Bowen.

From these equations it is possible to derive the following expression for the factor K for the reaction

$$\underset{\text{solid phase}}{\text{(Albite)}} + \underset{\text{melt}}{\text{(Anorthite)}} \rightleftarrows \underset{\text{melt}}{\text{(Albite)}} + \underset{\text{solid phase}}{\text{(Anorthite)}}$$

$$K = e^{L_{Ab}/R(1/T_{Ab}-1/T)-L_{An}/R(1/T_{An}-1/T)} \tag{3}$$

where

T = temperature (in degrees Kelvin) at which K is being determined
T_{Ab} = melting point of albite (1373°K)
T_{An} = melting point of anorthite (1823°K)
L_{Ab} = latent heat of melting (molal) of albite
L_{An} = latent heat of melting (molal) of anorthite
R = universal gas constant.

Or

$$K = e^{(C/T+D} \tag{4}$$

where

$$C = \frac{L_{An} - L_{Ab}}{R} \tag{5}$$

and

$$D = \frac{1}{R}\left(\frac{L_{Ab}}{T_{Ab}} - \frac{L_{An}}{T_{An}}\right). \tag{6}$$

This means that, if both C and D are positive, K will be largest at the melting point of albite and smallest at the melting point of anorthite. Figure 3 is a plot of K versus T for the plagioclase system, as derived

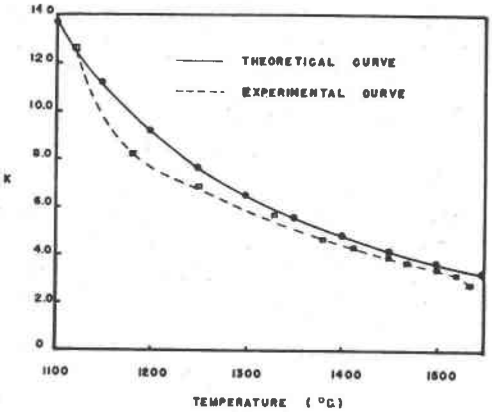

FIG. 3. "K" as a function of the temperature in the plagioclase system, derived from Data of N. L. Bowen, 1913.

from Bowen's diagram, together with the theoretical curve derived from equation (4).

When the percentage of one of the components in a solid-solution pair is small, K will vary but slightly from its value at the freezing point of the major constituent. If, for instance, the percentage of anorthite in an albite-anorthite system is less than one per cent, K for the system of equation (3) would be approximately

$$K \cong e^{L_{Ab}/R(1/T_{Ab}-1/T_{Ab})-L_{An}/R(1/T_{An}-1/T_{Ab})} \tag{7}$$

or

$$K \cong e^{L_{An}/R(1/T_{Ab}-1/T_{An})}. \tag{8}$$

By analogy it should be possible to calculate K for any such isomorphous substitution series provided that the melting points of the components and the latent heat of melting of the minor constituent are known.

It is of interest to note that, when the melting point of the minor constituent is higher than that of the major constituent, K will be greater than 1; if the two constituents melt at the same temperature, K equals 1; and if the melting point of the minor constituent is less than that of the major constituent, K will be less than 1. The heat of melting is always positive.

Values of K larger than the experimentally determined values of McFee were found when equation (8) was used to determine K for the systems $KCl-NaCl$, and $CuCl_2-NaCl$. This indicates that the systems $NaCl-KCl$ and $NaCl-CuCl_2$ do not form ideal isomorphous substitution series.

From McFee's experimental results and the theoretical derivation of K for ideal isomorphous series, it can be stated that the following factors directly affect the magnitude of K for pairs of substances crystallizing from a melt. K is affected by

(1) the melting points of the major and minor constituents,
(2) the latent heat of melting of the major and minor constituents,
(3) the temperature of solidification,
(4) the deviation of the system from that of an ideal isomorphous substitution series,
(5) the deviation from equilibrium during crystallization.

Each of these factors has its counterpart in the factors listed above as affecting K during reactions in aqueous solutions.

From the foregoing discussion it can be concluded that incorporation of foreign elements, even in such widely different processes as the $BaSO_4$-$RaSO_4$ "exchange" in aqueous solution and the incorporation of foreign elements in crystals forming from a melt obey the same general relationships.

Application to Pegmatites

These theoretical considerations are applicable to the study of pegmatites because field investigation by Schaller (1925), Page (personal communication), Jahns (1946), and others indicate that in the cooling history of many pegmatites the pegmatite liquid passed through a stage corresponding to a crystallizing melt (magmatic stage) and also through a stage corresponding to an aqueous solution (hydrothermal stage). It has been shown above that incorporation of accessory elements into crystal lattices obeys similar laws under both magmatic and hydrothermal conditions. Consequently it can be assumed that under conditions intermediate between these two extremes the incorporation of foreign elements will obey the same laws.

THE DISTRIBUTION OF ACCESSORY ELEMENTS IN PEGMATITES AS A FUNCTION OF THE DISTANCE FROM THE WALL ROCK-PEGMATITE CONTACT

A. Only One Lattice Type Present in the Pegmatite

Mathematical expressions will be derived to express the concentration of accessory elements in a pegmatite as a function of the distance from the wall rock contact. Two cases can be distinguished. The first corresponds to the concentration relation expressed by Part I of Fig. 1 (linear conditions); the second case corresponds to the concentration relation expressed by Part II of Fig. 1 (saturation conditions).

Linear Conditions. If linear conditions prevail, the incorporation of the accessory element is controlled by the equation

$$a_c = Ka_s.$$

Let us consider again the reaction

$$BaSO_4 + RaCl_2 \rightleftarrows RaSO_4 + BaCl_2$$

in which the concentration of the products and reactants is controlled by equation (1).

$$\frac{\text{no. of } Ra^{++} \text{ on surface}}{\text{no. of } Ba^{++} \text{ on surface}} = K \frac{[Ra^{++}] \text{ in solution}}{[Ba^{++}] \text{ in solution}}.$$

It was noted that when H_2SO_4 is added to a solution of $BaCl_2$ and $RaCl_2$, the concentrations of $BaCl_2$, $RaCl_2$, $BaSO_4$, and $RaSO_4$ are controlled by the equations

$$BaCl_2 + H_2SO_4 \rightleftarrows BaSO_4 + 2HCl$$

and

$$BaSO_4 + RaCl_2 \rightleftarrows BaCl_2 + RaSO_4$$

provided that the solubility product constant of $RaSO_4$ is not exceeded.

In Table 1 the concentrations of reactants and products at different stages of precipitation are defined.

TABLE 1

CONCENTRATION OF COMPONENTS IN $RaSO_4$-$BaSO_4$ SYSTEM

Component	Concentration before addition of H_2SO_4	Concentration after a small volume of H_2SO_4 has been added	Final Concentration
$BaSO_4$	0	$*\Delta[BaSO_4]$	$[BaSO_4]_F$
$RaSO_4$	0	$\Delta[RaSO_4]$	$[RaSO_4]_F$
$BaCl_2$	$[BaCl_2]_0$	$([BaCl_2]_0-\Delta[BaSO_4])$	$[BaCl_2]_F$
$RaCl_2$	$[RaCl_2]_0$	$([RaCl_2]_0-\Delta[RaSO_4])$	$[RaCl_2]_F$

* The symbol Δ represents a small increment.

The change in the $BaCl_2$ concentration, $\Delta[BaCl_2]$, is equal in magnitude to the change in concentration of $BaSO_4$, $\Delta[BaSO_4]$. Similarly, the change in the $RaCl_2$ concentration, $\Delta[RaCl_2]$, is equal in magnitude to the change in concentration of $RaSO_4$, $\Delta[RaSO_4]$. Mathematically expressed, these relations are

$$|\Delta[BaCl_2]| = |\Delta[BaSO_4]|$$

$$|\Delta[RaCl_2]| = |\Delta[RaSO_4]|.$$

When these relations are substituted into equation (1), that equation becomes

$$\frac{\Delta[RaCl_2]}{[RaCl_2]_0-\Delta\,|[RaCl_2]} = K\frac{\Delta[BaCl_2]}{[BaCl_2]_0-\Delta[BaCl_2]}. \tag{9}$$

From this expression the concentration of $RaSO_4$ can be calculated in terms of the concentration of the other components after a volume of H_2SO_4 has been added such that the concentration of $BaCl_2$ is $[BaCl_2]_F$. The effect of adding H_2SO_4 on the components in expression (3) must then be summed. This can be done by integrating expression (3) from the initial to the final state of the system. Expression (3) then becomes

$$\log\frac{[RaCl_2]_F}{[RaCl_2]_0} = K\log\frac{[BaCl_2]_F}{[BaCl_2]_0}. \tag{10}$$

Equation (10) can be rearranged to the form

$$[RaCl_2]_F = [RaCl_2]_0\left(\frac{[BaCl_2]_F}{[BaCl_2]_0}\right)^K. \tag{11}$$

At equilibrium in the final state equation (1) is valid. Therefore

$$\frac{[RaSO_4]_F}{[RaCl_2]_F} = K\frac{[BaSO_4]_F}{[BaCl_2]_F}. \tag{12}$$

Thus the final concentration of $RaSO_4$ will be

$$[RaSO_4]_F = [RaCl_2]_F \cdot K \cdot \frac{[BaSO_4]_F}{[BaCl_2]_F}. \qquad (13)$$

The substitution of expression (11) for $[RaCl_2]_F$ in this equation yields

$$[RaSO_4]_F = K[RaCl_2]_0 \frac{[BaSO_4]_F}{[BaCl_2]_F} \left(\frac{[BaCl_2]_F}{[BaCl_2]_0} \right)^K. \qquad (14)$$

When this expression is rearranged, it becomes

$$[RaSO_4]_F = K[RaCl_2]_0 \frac{[BaSO_4]_F}{[BaCl_2]_0} \left(1 - \frac{[BaSO_4]_F}{[BaCl_2]_0} \right)^{K-1}.$$

If both sides are divided by $[BaSO_4]_F$, then

$$\frac{[RaSO_4]_F}{[BaSO_4]_F} = K \frac{[RaCl_2]_0}{[BaCl_2]_0} \left(1 - \frac{[BaSO_4]_F}{[BaCl_2]_0} \right)^{K-1}. \qquad (15$$

By definition,

$$\frac{[RaSO_4]}{[BaSO_4]} = a$$

and

$$\frac{[RaCl_2]}{[BaCl_2]} = a_s.$$

Therefore equation (15) can be rewritten in the form

$$a_{c_F} = K \cdot a_{s_{0,1}} \left(1 - \frac{[BaSO_4]_F}{[BaCl_2]_0} \right)^{K-1*}. \qquad (16)$$

This means that the concentration of Ra in the precipitate is:

(1) linearly related to the original concentration of $RaCl_2$ in solution;
(2) linearly related to the admittance factor, K;
(3) related to the fraction of barium sulfate precipitated by the expression

$$\left(1 - \frac{[BaSO_4]_F}{[BaCl_2]_0} \right)^{K-1}.$$

Let the molar volume of $BaSO_4$ be defined as F_{BaSO_4} and the molar volume of $BaCl_2$ as F_{BaCl_2}. Also, let

v = final volume of $BaSO_4$
V = original volume of $BaCl_2$.

It follows that

$$\frac{[BaSO_4]_F}{[BaCl_2]_0} = \frac{v/F_{BaSO_4}}{V/F_{BaCl_2}}. \qquad (17)$$

In a pegmatite of one lattice type the solid phase will correspond to the precipitate of $BaSO_4$ and the liquid phase to $BaCl_2$. Let the molar volume

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* The subscript 0,1 is used for the sake of consistency with equations 24 ff.

of the solid phase be F_c and the molar volume of the liquid phase be F_s; then equation (16) can be written in the form

$$a_{c_F} = Ka_{s_{0,1}}\left(1 - \frac{vF_s}{VF_c}\right)^{K-1}. \tag{18}$$

In most cases the difference between F_s and F_c is negligible. Then equation (18) reduces to the form

$$a_{c_F} = Ka_{s_{0,1}}\left(1 - \frac{v}{V}\right)^{K-1}. \tag{19}$$

McFee (1947) has derived expression (19) from the relationship

$$a_c = Ka_s$$

in a somewhat different manner in his work on the distribution of accessory elements in NaCl crystals.

In Fig. 4, a_c is plotted as a function of v/V for various values of K at $a_{s_{0,1}} = 1$, and $F_s = F_c$. Three general cases can be distinguished.

(1) K less than 1. In this case, a_c increases with v/V; i.e., the concentration of the foreign element increases with continued crystallization.

(2) K equals 1. In this case a_c is independent of the state of crystallization; i.e., the foreign material will be uniformly distributed throughout the crystallized mass.

(3) K is greater than 1. In this case the concentration of the foreign element decreases with progressing crystallization.

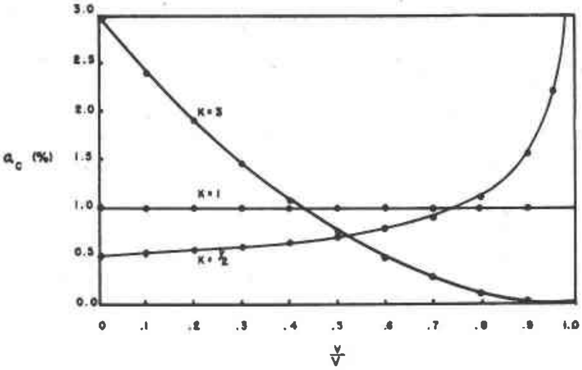

FIG. 4. a_c as a function of v/V for values of "K" greater than, equal to, and less than one.

In nature it is to be expected that cases (1) and (3) would be most widely represented since case (2) merely represents a boundary condition between them. According to Page (personal communication) the "mineralizers" in South Dakota pegmatites would fall into class (1) because many "mineralizers," such as lithium salts, appear to be successively enriched in the rest-liquid of pegmatites. That the alkalies in general tend to be concentrated in the rest-liquids is indicated in the report on the Strickland-Cramer deposit of Connecticut by Jenks (1935). In listing the optical data gathered for six specimens of beryl from different zones of the pegmatite, Jenks finds that the index of refraction of beryl is higher at low temperatures than at high temperatures of deposition. A definite relation between refractive index and the percentage of alkalies has been established by Winchell (1933). On this basis Jenks concludes that the percentage of alkalies in the beryl formed during the late stages of crystallization is greater than that formed during the initial stages of cooling of the pegmatite.

An example of the third case ($K > 1$) has already been cited in the case of the plagioclase system. Since anorthite melts at a higher temperature than albite,

$$\left(\frac{1}{T_{Ab}} - \frac{1}{T_{An}}\right)$$

will be positive. Therefore K will be greater than unity. Page (personal communication) has found that in the pegmatites of the Keystone District of South Dakota the indices of refraction of plagioclase feldspars in numerous pegmatites show that the contained plagioclase is either uniform in composition from wall to wall or its anorthite content decreases from the wall to the core, and that these changes in the anorthite content of plagioclase in the pegmatite are analogous to the normal variation of plagioclase composition in igneous rocks.

Saturation Conditions. Under saturation conditions Part II of the curve in Fig. 1 is applicable to the problem. In this part of Fig. 1, a_c is independent of a_s. Therefore, if the saturation concentration of the foreign material is A_c, it follows that after a volume "v" has crystallized from the melt or solution a quantity $A_c v$ of the foreign constituent has been incorporated in the crystalline mass, and the concentration of the foreign material in the solution or magma at this point will be

$$\frac{a_{s_{0,1}}V - A_c v}{V - v}. \tag{20}$$

The concentration of the foreign constituent in the crystalline mass will be independent of the volume, v, which has crystallized out; i.e., no variation in the percentage of the foreign element from wall to wall will be noticed. In this sense, therefore, the distribution of the foreign constituent will be the same as in the case in which $K = 1$ and in which a_c and a_s are linearly related. It may therefore be difficult to determine which of the two situations was responsible for the distribution. A laboratory determination of K for such an incorporation reaction may be necessary to solve the problem.

If we consider an incorporation reaction in which the complete curve of Fig. 1 graphically depicts the relationship between a_c and a_s, it is possible to determine the distribution of the accessory element, and the effect of K and A_c on its distribution. When K is greater than or equal to unity the saturation region will not be reached and the distribution of the accessory element will follow the appropriate curve in Fig. 4. When K is less than unity, the distribution of the accessory element will follow the curve for $K<1$ in Fig. 4, until a_s reaches the value A_c/K. At that point the saturation region of the main constituent with respect to the accessory element is reached. For material crystallizing out at a later stage, a_c will be equal to the saturation concentration, A_c, as indicated in Fig. 5. The larger A_c is for the substitution reaction, the greater will be the volume of the pegmatite for which the distribution of the accessory is controlled by equation (2).

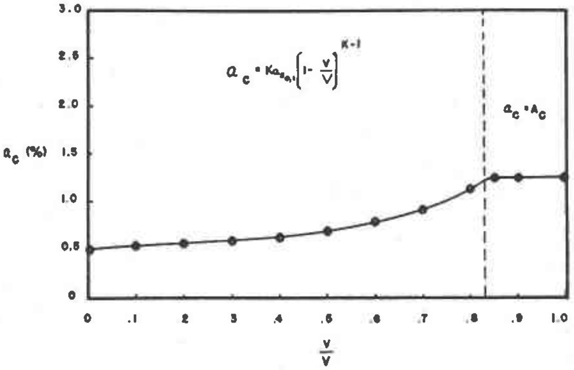

FIG. 5. a_c as a function of v/V before and after entering the saturation region. $K=0.5$; $a_{s_{0,1}}=1.0$; $a_c=1.25$.

B. *More Than One Lattice Type Present*

In the past paragraphs expressions for the distribution of an accessory element as a function of the amount of material crystallized were developed for the case in which only one lattice type is present in the pegmatite. It is now of interest to investigate the distribution of accessory elements when more than one lattice type is present, as is usually the case in pegmatites. Two situations are possible: either the zones of the pegmatite are monomineralic, or they contain more than one lattice type. Both possibilities are to be discussed.

Monomineralic Zones. It will first be assumed (1) that the cooling body solidifies from the wall-zone inward, the core being the last portion of the body to solidify, and (2) that no disturbing factors such as addition or escape of material, convection, shattering, veining, or replacement affect the cooling history of the pegmatite, and that the pegmatite cools slowly enough so that diffusion gradients do not affect the nature of the solutions at the boundary of the crystalline phase. With these assumptions, the theoretical distribution of accessory elements can be calculated for the following cases:

(1) The relation

$$a_c = Ka_s$$

is true throughout the crystallization history of the pegmatite.

(2) The relation

$$a_c = A_c$$

is true throughout the crystallization history of the pegmatite.

(3) The above relations apply to the crystallization process at different stages during the solidification of the pegmatite liquid.

(1) The distribution equation for an accessory element for which the equation

$$a_c = Ka_s$$

describes the distribution of the element in the solid and liquid phase is to be derived.

Let v_1 be the total volume of the constituents of lattice type 1 in the melt. Let a_{c_1} be a_c for the foreign element in lattice type 1. Furthermore, let $a_{s_{1,2}}$ be the ratio of the quantity of the foreign element in the melt to the concentration of the main constituent of lattice type 2 in the melt after type 1 has just finished crystallizing out and type 2 is just beginning to solidify.

$$a_{s_{1,2}} = \frac{\text{[foreign element] in melt}}{\text{[main constituent of lattice type 2] in melt}}. \tag{21}$$

Further, let C_f be the original concentration of the foreign element in the melt. Therefore, since the original volume of the melt was V, the total number of moles of the foreign element in the pegmatite is $C_f \cdot V$. The volume of the foreign element incorporated by a small volume, Δv, of lattice type 1 will be

$$\frac{\text{[foreign element] in solid phase}_1}{\text{([foreign element] + [main constituent]) in solid phase}_1} \cdot \Delta v.$$

When the percentage of the foreign element is small, this expression is approximately equal to

$$\frac{\text{[foreign element] in solid phase}_1}{\text{[main constituent] in solid phase}_1} \cdot \Delta v.$$

But this by definition is $a_{c_1} \cdot \Delta v$.

The total quantity in moles of the foreign element incorporated in lattice type 1 will be the sum of $a_{c_1} \cdot \Delta v$ over the volume of lattice type 1 which will have crystallized out before lattice type 2 starts to solidify. This volume will not be exactly equal to v_1, the total volume of the constituents of lattice type 1 in the melt, since the solubility of the solid phase in the liquid phase is never zero. The volume of lattice type 1 which has crystallized out when lattice type 2 begins to solidify will be called v_1'.* The total quantity in moles of the foreign element incorporated in lattice type 1 will therefore be

$$\frac{1}{F_f}\int_0^{v_1'} a_{c_1} dv$$

where F_f is the molar volume of the foreign element.

The quantity of the foreign element remaining in the melt after the crystallization of lattice type 1 will be the original quantity minus the amount removed by incorporation into lattice type 1. Therefore the number of moles of the foreign element remaining in the melt will be

$$C_f V - \frac{1}{F_f}\int_0^{v_1'} a_{c_1} dv. \tag{22}$$

Let C_2 be the original molar concentration of the major component of lattice type 2 in the melt. The number of moles of the component of lattice type 2 present in the melt before the commencement of crystallization of lattice type 2 is therefore

$$C_2 \cdot V. \tag{23}$$

Substituting expressions (22) and (23) into expression (21), $a_{s_{1,2}}$ becomes

$$a_{s_{1,2}} = \frac{C_f}{C_2} - \frac{1}{F_f C_2 V}\int_0^{v_1'} a_{c_1} dv. \tag{24}$$

In this expression

$$a_{c_1} = a_{s_{0,1}} \cdot K_1 \left(1 - \frac{v}{v_1}\right)^{K_1 - 1} \tag{25}$$

where

$a_{s_{0,1}}$ = ratio of moles of foreign element to moles of main constituent of lattice type 1 at start of crystallization.

K_1 = admittance factor of the foreign element in question to lattice type 1

$F_{c_1} \cong F_{s_1}$.

By analogy, $a_{s_{2,3}}$, defined as the ratio of the quantity of the foreign material to that of the main constituent of lattice type 3 in the melt at the start of the solidification of lattice type 3, can be written in the form

---

* It follows from equation (19) that if v_1' were equal to v_1, all of the foreign element would be incorporated into lattice type 1 irrespective of the value of K for the element in lattice type 1. This can be shown by integrating the expression a_{c_1} dv between the limits 0 and v_1.

$$a_{s_{2,3}} = \frac{C_f}{C_3} - \frac{1}{F_f C_3 V}\left[\int_0^{v_1'} a_{c_1} dv + \int_0^{v_2'} a_{c_2} dv\right] \tag{26}$$

v_2' is defined as the volume of lattice type 2 which has crystallized out before lattice type 3 has started to solidify. The quantity a_{c_2} is defined by the expression

$$a_{c_2} = a_{s_{1,2}} \cdot K_2 \left[1 - \frac{v}{v_2}\right]^{K_2-1} \tag{27}$$

where

K_2 = admittance factor of the foreign element in question to lattice type 2

and

$$F_{c_2} \cong F_{s_2}.$$

By analogy to expressions (24) and (26), $a_{s_{(n),(n+1)}}$ will be

$$a_{s_{(n),(n+1)}} = \frac{C_f}{C_{(n+1)}} - \frac{1}{F_f C_{(n+1)}} \sum_{i=0}^{i=n} \int_0^{v_1'} a_{c_i} dv. \tag{28}$$

In this expression

$C_{(n+1)}$ = concentration of lattice type (n+1) in the original pegmatite melt (or solution)

a_{c_i} = ratio of the concentration of the foreign element to the concentration of the main constituent in the crystalline phase of lattice type

$$a_{c_i} = a_{s_{(i-1),(i)}} K_i \left[1 - \frac{v}{v_i}\right]^{K_i-1} \tag{29}$$

and

$$F_{c_i} \cong F_{s_i}.$$

In a similar manner the concentration of a foreign element at the interface of any two lattice types of the pegmatite can be calculated.

To determine the concentration of a foreign element in a lattice type after a certain portion of that lattice type has crystallized, equation (29) must be modified. For instance, if this concentration is to be determined after one half of lattice type (n+1) has crystallized out, then a_c at that point will be

$$a_c = a_{s_{(n),(n+1)}} \cdot K_{(n+1)} (\tfrac{1}{2})^{K_{(n+1)}-1}. \tag{30}$$

Since $a_s = a_c/K$, the ratio of the concentration of the foreign element to that of the main constituent in the melt at this point in the process of crystallization will be

$$a_s = a_{s_{(n),(n+1)}} (\tfrac{1}{2})^{K_{(n+1)}-1}. \tag{31}$$

A similar procedure can be applied to find a_c and a_s at other points not at the interface between lattice types.

(2) It is possible to calculate also a_c and a_s at the same point, e.g., after one half of lattice type (n+1) has crystallized out, for the case in which the saturation region of all the lattice types 1 to (n+1) with respect to the foreign material in question is maintained. When half of lattice type

(n+1) has crystallized out,

$$a_c = A_c \tag{32}$$

and

$$a_s = \frac{C_f V - \dfrac{1}{F_f}\sum\limits_{i=0}^{i=n} A_i v_i' - \dfrac{A_{c(n+1)} V_{(n+1)}}{2F_f}}{\dfrac{C_{(n+1)} V}{2}}. \tag{33}$$

Under these conditions, the residual solutions will be enriched in the foreign constituent.

(3) A third case is possible. The distribution of lattice types may be such that at one point in the crystallization process the concentration of the foreign material is such that a_c and a_s are proportional, while at another stage of crystallization the saturation region of a lattice with respect to the foreign constituent is maintained. Under such conditions the equations derived above no longer apply for the whole crystallizing body. It will then be necessary to investigate the distribution of foreign elements in each pegmatite zone separately.

More Than One Lattice Type Per Zone. In many pegmatites more than one mineral type is present in each zone. Intimate mixtures of lepidolite and cleavelandite, or spodumene and quartz, and of many other constituents have been described. Such mixtures require that the equations developed above be modified somewhat. Let there be two lattice types, 1 and 2, intimately associated at a certain point in the pegmatite. Then

$$a_{c_1} = a_s K_1 \tag{34}$$

and

$$a_{c_2} = a_s K_2 \tag{35}$$

provided that the concentrations are such that a_s and a_c are linearly related in both lattice types. The amount of foreign material removed from the solution or magma during the crystallization of a volume v in this area will be

$$\int_0^v (p_1 a_{c_1} + p_2 a_{c_2}) dv$$

where p_1 and p_2 are the fractions of lattice types 1 and 2 respectively. If, therefore, $C_f/(C_1+C_2)$ is substituted for $a_{s_0 1}$, the expression $(p_1 a_{c_1} + p_2 a_{c_2})$ is substituted for a_c in the original derivation, and $(p_1 K_1 + p_2 K_2)$ is substituted for K, a_c can be determined as a function of v/V. Thus

$$p_1 a_{c_1} + p_2 a_{c_2} = \frac{C_f}{C_1 + C_2}(p_1 K_1 + p_2 K_2)\left(1 - \frac{v}{V}\right)^{(p_1 K_1 + p_2 K_2 - 1)}. \tag{36}$$

when $F_c \cong F_s$. Analogous expressions can be derived for the case in which a larger number of lattice types are present in a given zone of the cooling pegmatite.

When the saturation conditions are maintained throughout the crystallization of lattice types 1 and 2 under the same conditions as above, the equations for a_{c_1} and a_{c_2} will be

$$a_{c_1} = A_c$$

and

$$a_{c_2} = A_c$$

respectively.

It is of interest to apply the above formulae to a specific case. Let the pegmatite under consideration consist of two lattice types, 1 and 2, which crystallize out simultaneously but are crystallographically incompatible. Let one accessory element be present in the original melt, in a concentration of one per cent, and let the admittance factor of this accessory element be 0.5 for lattice type 1 and 2.0 for lattice type 2. Let the ratio of the concentration of lattice type 1 to lattice type 2 be one to three. In that case

$$p_1 = 0.25$$
$$p_2 = 0.75.$$

Also, let $F_c \cong F_s$ for both lattice types. When the above values are substituted in equation (36) the following expression is obtained.

$$0.25a_{c_1} + 0.75a_{c_2} = 0.01(1.625)\left(1 - \frac{v}{V}\right)^{(0.625)} \tag{37}$$

or

$$0.25a_{c_1} + 0.75a_{c_2} = 0.01625\left(1 - \frac{v}{V}\right)^{(0.625)}. \tag{38}$$

From equations (34) and (35) it is known that

$$a_{c_2} = a_{c_1} \cdot \frac{K_2}{K_1}.$$

Therefore

$$a_{c_2} = a_{c_1} \cdot 4.0.$$

When this value for a_{c_2} is substituted into equation (38), the following value of a_{c_1} is obtained:

$$a_{c_1} = \frac{0.01625}{3.25}\left(1 - \frac{v}{V}\right)^{(0.625)}$$

or

$$a_{c_1} = 0.0050\left(1 - \frac{v}{V}\right)^{(0.625)}. \tag{39}$$

Also

$$a_{c_2} = 0.020\left(1 - \frac{v}{V}\right)^{(0.625)}. \tag{40}$$

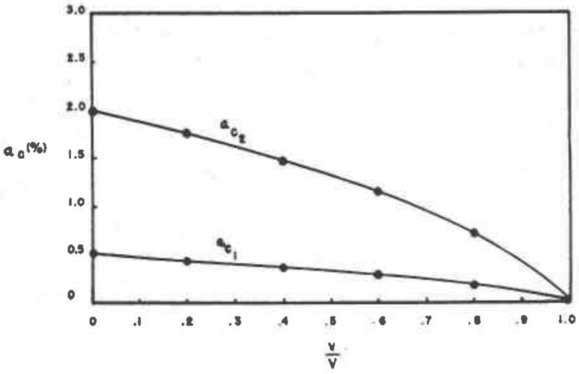

FIG. 6. a_{c_1} and a_{c_2} as functions of v/V.

TABLE 2. CALCULATION OF a_{c_1} AND a_{c_2} AS FUNCTIONS OF v/V

(v/V)	(1−v/V)	$(1-v/V)^{(0.625)}$	a_{c_1}	a_{c_2}
0	1.0	1.00	0.500%	2.00%
0.20	0.8	0.870	0.435	1.74
0.40	0.6	0.725	0.362	1.45
0.60	0.4	0.565	0.287	1.13
0.80	0.2	0.366	0.183	0.73
1.00	0	0	0	0

In Table 2 a_{c_1} and a_{c_2} are recorded as functions of v/V. In Fig. 6 the data of Table 2 is graphically presented.

It is of interest to note that, whereas $K<1$ for the lattice type 1, the concentration of the accessory in this lattice type decreases rather than increases with increasing v/V. This is due to the presence of lattice type 2 in such quantities that for the combination of lattice types 1 and 2 K is greater than 1.

If the concentration of lattice type 1 in the crystalline mass were such that for the combination of 1 and 2 $K<1$, then the concentration of the foreign constituent would increase in both lattice types as the processes of crystallization proceeded.

The assumption made at the beginning of this section about the direction of crystallization in pegmatites is not always warranted. Not in all cases does crystallization start at the wall of the pegmatite and proceed toward the center of the body. Page (personal communication) states that "many of the larger pegmatites of New England contain pods of coarse quartz, perthite, plagioclase, muscovite, beryl, and other minerals in various combinations and proportions. The sequence of lithologic units outward from any given pod is commonly consistent for a particular pegmatite." In such a case the volume of pegmatite crystallized out, v, must be calculated from the center of the pod outward rather than from the wall of the body inward as in pegmatites where zones are concentrically arranged around the core.

By means of the expressions developed in the foregoing sections it should be possible to calculate the distribution of elements foreign to the lattice types of pegmatites for a great variety of these bodies, provided the following data are available.

(1) The total volume and shape of the pegmatite.
(2) The concentration of the foreign element and of the constituents of the various lattice types in the original melt.
(3) The volume of each lattice type which crystallizes out before the next lattice type begins to solidify.
(4) The value of the admittance factor, K, for the foreign element for each lattice type as a function of a_c.
(5) The molar volume of the foreign element and of the lattice types of the pegmatite both in the liquid and solid state.
(6) The fraction of each lattice type in the various zones of the pegmatite.
(7) The disturbing factors in the cooling history of the pegmatite.

THE EFFECT OF DISTURBING FACTORS IN THE COOLING HISTORY OF A PEGMATITE ON THE DISTRIBUTION OF ACCESSORY ELEMENTS

In the above distribution treatment several assumptions were made about the absence of disturbing factors in the process of crystallization in pegmatites. Some of these assumptions may not be valid in specific cases of pegmatite crystallization, and therefore should be discussed in their bearing on the foregoing derivations.

(1) One of these assumptions was that the material present in the pegmatite at the beginning of crystallization is retained by the pegmatite during solidification, and is finally incorporated in the material crystallizing in the last stages of cooling. This is not the case when, as has been shown in some instances, some of the original constitutents escape from the solidifying mass, and enter the surrounding rock. This tendency to escape from the rest liquid is especially true of the volatile constituents of the pegmatite mass. For these constituents either $K<1$ in most of the lattice types of the cooling mass, or their concentration is such that the saturation region of the $a_c=a_s$ curve is occupied during the cooling process.

In either case, the effect of the escape of the volatile constituents on their concentration in lattice types crystallizing after their escape, depends on the equations controlling the concentration of the volatile constituents in these lattice types. If the concentration is controlled by the equation

$$a_{c_n} = K_n a_{s_n}$$

then the escape of a volume of the volatile constituents, such that a_{c_n} is decreased by Δa_{s_n}, will decrease the concentration of the constituent in lattice type n by the amount $K_n \cdot \Delta a_{s_n}$; i.e.,

$$\Delta a_{c_n} = K \Delta a_{s_n}. \tag{41}$$

On the other hand, if the concentration of the volatile constituents in the melt, after the escape of some of the volatile constituents, is such that $a_{c_n} = A_{c_n}$, then the escape of volatile constituents will inappreciably alter their concentration in lattice type n, unless by this escape the region in which a_{c_n} is proportional to a_{s_n} is entered.

(2) Convection currents might be set up in pegmatites by uneven cooling. This would result in non-uniform crystallization and composition at different parts of the pegmatite body.

(3) Shattering and veining of pegmatites have been reported from a number of districts (Cameron, Jahns, McNair, Page—to be published). In many instances cracks appear in the pegmatite before final consolidation. In that case the residual liquids fill the gaps created in the wall. Subsequent cooling may then lead to deposition of either mono- or polymineralic veinfilling. Zoning parallel to the walls of the cracks has been reported. Such zones correspond to those developed in the main body of the pegmatite after the formation of the veins. It is to be expected that the distribution of accessory elements in the vein-filling material will be similar to the distribution in the corresponding zones of the main body.

When the vein-filling material reacts with crystalline pegmatite, replacement phenomena appear. This is a special case of the general problem of replacement treated below.

(4) Another assumption made in the derivation of the distribution equations was that interaction of the residual liquid with the crystal mass already formed is negligible. This situation might not prevail when:

(a) the increase of pressure due to the concentration of volatile constituents in the residual liquids causes corrosion of the crystalline phase by the residual liquids; or
(b) additional material added in some way to the rest liquids endows the rest liquids with such corrosive properties. Additional material of this nature might be added from the source of the original pegmatite melt through fissures in the pegmatite and country rock developed subsequent to partial solidification of the pegmatite

The effect of interaction of the rest liquids with the crystallized portion of the pegmatite on the distribution equations developed in earlier sections of this paper may be considerable. It is to be expected that interaction would take place between the material crystallizing in newly formed fissures and the earlier minerals surrounding these fissures. The formation of pseudomorphs of earlier minerals by the corrosive action of the rest liquids indicates that the changes due to such interaction may be profound. It is therefore to be expected that in a pegmatite in which there has been considerable interaction of the rest liquids and the crystalline phase, the plot of concentration of foreign elements versus distance from the wall-rock pegmatite contact would not follow the equations previously developed. It is also to be expected that the degree of deviation from these relations will be proportional to the amount of interaction between the rest liquids and the crystalline phase.

(5) Finally, crystallization may at times be so rapid that the rate of diffusion of materials from the central part of the pegmatite affects the composition of the pegmatite liquids at the liquid-solid boundary. Since the cooling time of pegmatites must have been considerable, it is probable that the effect of the diffusion gradient on the distribution of accessory elements in the solid phase was in most cases negligible. However, this can only be proved when data on the rate of cooling, viscosity, and composition of the pegmatitic liquids is more complete.

General Summary and Application

The means of incorporating an accessory element in a crystal mass have been discussed and theoretical relations between a_s and a_c (the ratio of the concentration of the accessory to the main constituent in the liquid and in the solid phase), have been formulated. These theoretical relationships were first applied to the case of a crystallizing pegmatite containing only one type of lattice, then to one containing more than one type of lattice in zonal arrangement, and subsequently to a mass containing several lattice types somewhat more randomly arranged within the crystallizing mass. For each of these cases, the distribution of accessories was discussed. Two conditions were discerned: (1) a_c proportional to a_s ("linear" conditions), and (2) a_c independent of a_s ("saturation" conditions). Finally, some of the assumptions made in the derivation of these relationships were investigated and an attempt was made to ascertain the effect of relaxing some of the conditions imposed by these assumptions.

These theoretical relationships must now be tested by evidence gathered in the field and by suitable supporting laboratory experiments. The field evidence needed can be obtained by cross-sectional sampling of pegmatites, the cooling history of which can be at least partially ascertained from field relationships. A clearly zoned pegmatite in which replacement phenomena are relatively unimportant would be the most desirable object of study. Adequate laboratory analyses of rock specimens should then yield data to support or invalidate the expressions derived above for a_c as a function of v/V.

Laboratory experiments on the incorporation of accessories in crystal masses, similar to the experiments carried out by McFee (1947), will serve to determine the necessary data on the admittance of various lattices for accessory elements under different conditions of crystallization.

Work is in progress in this laboratory in order to obtain necessary data for the evaluation of the theory. Preliminary results are encouraging.

ACKNOWLEDGMENTS

The authors wish to acknowledge their indebtedness to Professors P. F. Kerr, C. H. Behre, W. H. Bucher, and R. J. Holmes of the Geology Department of Columbia University and to Dr. T. S. Lovering for critically reading and constructively commenting on this paper. Our thanks are especially extended to Dr. L. R. Page of the United States Geological Survey, who checked and revised the reported field evidence, and to Dr. T. I. Taylor, Professor of Analytical Chemistry at Columbia University for his comments on the chemical aspects of this paper.

The writers assume all responsibility for the views expressed in this study.

Since this paper was written, the article by H. Neumann (1948) has come to the authors' attention. The problem treated by Neumann involves the distribution of the original constituents of the magma between the molten and the fluid phases developed during the process of solidification. This problem is similar to the main question treated above, i.e., the distribution of the constituents of the pegmatitic fluids between the solid and liquid state after emplacement. It is of note that the fundamental equations are the same in both cases.

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