Crystallization of magmas

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by

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CRYSTALLIZATION OF MAGMAS.

The object of this paper is to arrive at a better explanation of the segregation of magmatic solutions on cooling. In which magmas will be discussed from a chemical and metallurgical line of reasoning, in showing why such minerals as apatite, magnetite, etc., having a comparatively low melting point, crystallize out before feldspar and quartz, which have a comparatively high fusion point.

We will begin with the supposition that the reader is familiar with the chemical data and its diagrammatic representation of igneous rocks. These tables may be found in numerous places, as Kemp's Hand Book on Rocks, J.P. Idding's Igneous Rocks, Journal of Geology, U.S. Geological Survey Bulletins 168 and 228, and other publications. The diagrammatic representation and method of plotting may be found in Igneous Rocks by J. P. Iddings, Kemp's Hand Book on Rocks, Professional Paper no. 18 of U.S.G.S. and others.

LIQUID MAGMAS ARE SOLUTIONS. Rock making material in the liquid state is a solution, conforming to the laws of the Phase Rule. These solutions will differ from the ordinary run of Phase Rule discussions in as much as they are not aqueous, but composed of the rock-making elements, and therefore our discussion of these
elements will be at higher temperatures, and also under greater pressures.

PHASE RULE.

Gibbs adapted the laws of thermodynamics in deducing the laws of equilibrium. This system possesses only three independently variable factors, temperature, pressure, and concentration of the components of the system, and is tabulated graphically to represent the different phases a compound takes on varying the above conditions.

TYPICAL SYSTEM OF ONE COMPONENT. Tin can exist in more than one crystalline form.

We have here two breaks in the curve alpha and beta. The break alpha is the temperature at which the tin solidifies, forming white tin at the temperature beta, which is $20^0$; we find another crystalline form, gray tin, which is granular, on raising above this temperature. However, we do not have white tin formed again, but must go to the
transition point as shown in fig. 2.

In changing from a liquid to a solid state we have but one point as shown in fig. three.

![Graph](image)

we see by this temperature-time curve: at the solidification temperature the compound continues to hold the same temperature for a given length of time, altho we continue to cool, showing us the liquid is giving up heat on solidification. This is known as latent heat of fusion.

A TWO COMPONENT SYSTEM of complete solubility will give us a cooling curve similar to figure three, but the temperature, composition, diagram will be much different as we will have the solubility of one within the other. This is the case in an alloy of silver and gold; iron and manganese; or antimony and bismuth. Metal being used so, the reader unfamiliar with physical chemistry, will draw an analogy to alloys, altho the same is true of salts or minerals.
As an example of the above, if we have a liquid composed of A and B of composition x, and cool to a temperature of point a, mixed crystals will be deposited, having a composition represented by b. As the temperature continues to fall, more and more will be deposited, relatively rich in B, the liquid becoming relatively poorer in B. The composition of the liquid solution will pass along the curve a d, the composition of the solid solution at the same time passing along the curve b c; at the point c the liquid will solidify completely.

COMPLETELY INSOLUBLE. In the case of a compound where one component is not soluble, or to put it in plainer words, where we have no mixed crystals formed, we will have a eutectic, as in the case of antimony and lead, lead and tin, cadmium and zinc. We have a crystallization of the component in excess of the eutectic until this composition is reached, and then the liquid solidifies, as shown in figure five.
Then starting with a compound composed of A and B having a composition of x, on cooling when the temperature t is reached we will have crystals formed of B, and crystals of B will continue to form until the temperature t is reached, at which the solution will have reached a composition represented by x, and this being the eutectic, the whole mass will solidify, having this composition, forming crystals of each compound.

When two substances are used in place of metals, in the above, the lowest combination is known as the cryohydric point.

PARTIAL SOLUBILITY. We will now consider a case where we have a combination of the foregoing. In this case under certain conditions we will have a crystallization of both components, as shown in fig. 4, and under other conditions we will have a eutectic separating out as in the case of fig. 5. An illustration of these conditions would be given in an alloy of zinc and tin, gold and nickel, silver and copper,
as shown in fig. 6.

mixed crystals or compounds respectively, which are in equilibrium with the liquid solution at the temperature of the point $u$. These two mixed crystals represent in the one case a saturated solution of $D$ in $C$ (point $M$), and the other a saturated solution of $C$ in $D$ (point $N$).

Just as we saw the mutual solubility of two liquids varied with the temperature, so also in the case of two solids; as the temperature alters the solubility of the two solid components in one another change as indicated by the dotted line passing through $M$ and $Q$. We see that if a crystal composed of the composition $N$ is cooled down it will remain unchanged until temperature $t$ is reached; the homogeneous mixed crystals break up into a conglomerate of of the two mixed crystals, the composition of which is represented by $x'$ and $x''$ respectively.
From this then it can be seen that in the case of a substance which forms two solid solutions, the mixed crystals which are deposited from the fused liquid mass need not remain unchanged in the solid state but may at some lower temperature lose their homogeneity.

Between M and Q we have the second type of complete insolubility.

Let us now consider a specific case similar to this last. The work on melting temperatures of metasilicates of calcium and magnesium done by E. T. Allen and W. P. White at the laboratory of the Carnegie Institute is shown in fig. 7.

At 47% MgSiO₃ + 53% SiO₃ indication of the formation of the compound MgSiO₃. CaSiO₃ known as diopside, this breaks the diagram into two parts, each of partial soluble type. From left hand side we have a solid solution of CaSiO₃ and diopside will
separate out between 0 and 2%, and 46% and 76% MgSiO$_3$. From 2% to 46% structure will be a composite eutectic of CaSiO$_3$ + diopside, each saturated with a small amount of the other and an excess substance of CaSiO$_3$ or diopside, each saturated with the other, depending upon whether the composite is below or above the eutectic composition of 26% MgSiO$_3$.

The right hand side we will have an amorphous mixture of diopside and MgSiO$_3$ between 47 to 67%, and 98 to 100% MgSiO$_3$. Eutectic of diopside and MgSiO$_3$ between 75 and 96% each saturated with the other, and crystallized diopside below the eutectic composition of 68% MgSiO$_3$ and MgSiO$_3$ above this ratio. Similar to alloys of allotropy or transition below the solidification range, thus above 1100° the alpha CaSiO$_3$ or pseudo wallastonite is the stable form but unknown in nature; below this temperature the beta form, the mineral wallastonite is the the stable form known in nature. With MgSiO$_3$ the beta form is magnesium pyroxene occurring in meteorites and intergrowths with eustite. At 1365° this is transformed into orthorhombic alpha, a form distinct from eutectic and known in nature.

It will be well to consider another variable
here, pressure, which in light of the theory of Le Chatelier is as follows: If the volume of the compound is increased on cooling, an increase of pressure lowers the melting point, and if the compound contracts on solidifying, an increase in pressure tends to raise the melting point. A good example of the first case, is that of water as shown in fig. 8. The second case is illustrated by fig. 9.

D O D being the line of constant pressure.

In a system where the temperature, composition, and pressure is considered, the diagram will be as shown in fig. 10, which, with a study of the foregoing, needs no explanation.
SYSTEM OF THREE COMPONENTS.

In our first consideration of graphical representation we will work with the temperature, pressure, and concentration of two of the components fixed. In this case our graphical representation will be in the form of a triangle. The quantities of the different components are expressed as fractional parts of the whole, and the sums of their concentrations is therefore equal to unity, and can be represented by the heighth of the triangle, figure 11.
Thus the point $p$ represents a tertiary mixture of composition of $A = 0.5$, $B = 0.3$, $C = 0.2$. Now if we imagine the temperature axis drawn at right angles to the paper, shown in fig. 12 for $B$ and $C$, we will then have a special model of prismatic form as shown in figure 13.

The point $p$ being the same as in fig. 11, and point $y$ being the same as in fig. 12. The data for graphical representation is obtained as in fig. 11, and enough points found at constant temperatures to allow a plotting which is done topographically, using temperatures as elevations, as shown in fig. 14, using the lead, bismuth, tin alloy as an example.
We might readily imagine the effect of pressure on such a combination, the rules governing the previous case holding good in this one.

Systems of four components have been worked out in connection with the Zassfurt deposits. The method of graphical representation is shown in figures 15 and 16. Such a diagram represents the conditions of equilibrium only for one definite temperature, and corresponds therefore to the isothermal diagram for ternary temperature.
The given system being laid off as shown in fig. 15, and projected upon the base as in fig. 16. Here the point \( a \) represents a ternary solution saturated with respect to \( \text{B} \) and \( \text{C} \); and \( a, \ P, \) quaternary solution in equilibrium with the same two salts as solid phases. The temperature and pressure being constant a surface will represent a solution in equilibrium with only one solid phase; a line, a solution with two solid phases; and a point, one in equilibrium with three solid phases. An example of the complete isothermal diagram, as taken from Windlay's Phase Rule, page 317, is shown in Figure 17. This will also give us some idea of the complication of a molten igneous mass.
J. H. Vogt has determined the eutectic of some of the silicates as follows:

- 68% diopside with 32% olivine
- 74% melilite " 26% olivine
- 65% melilite " 35% anorthite
- 40% diopside " 60% akermanite
- 74.25% anorthite " 25.75% quartz
- 75% albite " 25% quartz

In the Journal of Geology, vol. XII, 1904, there is an article by Alfred C. Lane on The Role of Possible Eutectics in which he shows a tendency on the part of a certain group of magmas towards an alkaline-silicate ratio between .08 and .09 fixed on .083 from Idding's diagram of Professional Paper no. 18 on Chemical Composition of Igneous Rocks expressed by means of diagrams.

The eutectic ratio of alkali and SiO$_2$ is $K_2O \cdot Al_2O_3 \cdot XSiO_2 + 6SiO_2$ in which $X = 6$ or over. This eutectic harmonizes with the supposition that the combination $2KAl Si_3O_8 + 6 SiO_2$ or two atoms of orthoclase + six silica. This ratio is alkaline : silica :: 1 : 12.

We find the material in excess crystallizing out first, as it should do according to the previous dis-
cussion. If alkali is in excess of the eutectic we have nephelite, leucite, etc., crystallizing out until the eutectic is reached; then the eutectic of orthoclase and quartz forming mixed crystals. Iron and manganese combine with silica if in excess of the eutectic and insoluble in the magma, crystallizes out in a high silica ratio as augite or eutite and not olivine. In oxide of iron probably being formed, if in excess of the silica required to satisfy the alkalies and eutectics. Iron and titanium being the last to form silicates.

The general accepted theory is that the minerals apatite, magnetite, etc. are the first to crystallize; orthoclase and silica being the last. This is undoubtedly not true, but perhaps being compounds which either form high fusion eutectics or form compounds which crystallize out first when present in most magmas. In a highly alkaline magma this is not true, apatite being one of the last to crystallize, as will be shown later.

In some laccoliths, such as those of Colorado, Utah, and Arizona described by Gilbert, in the Geology of Henry Mountains by Cross, Fourteenth Annual Report U.S. Geological Survey, 1898, part III, page 437, Bull. no. 139, U.S. Geological Survey, 1896, Twentieth
Annual Report U.S. Geological Survey, 1900, part III, the page 562, in which igneous mass is uniform throughout. It is to be noted that all rocks are granite, syenite porphories and porphorite, all acid not high in alkali.

In others as Carabal Hill described by Weed and Pirsson in American Journal of Science, vol. 1, 1896, Square Butts by Weed and Pirsson in Bull. Geol. Soc. America, vol. 6, 1895, Yogo Peak by Weed and Pirsson, American Journal of Science, vol. 1, 1896, Montana, Jour. Sci., vol. 1, 1896, all in which the magma is composed of rather basic and alkaline rocks all differentiated after the commonly accepted order, the outer zone being basic and the interior more acid. The same relations are observed in many composite dykes. These cases have led us to believe the oxides of iron, magnesiuim, and calcium tend to diffuse toward the cooling surface, while aluminum, alkalies and silica tend to remain in this hotter central part.

We will now consider the case of acid and alkaline rocks. We can cite but few cases of this sort, in which the outer zone is acid and has a more basic centre. The most noteworthy case of this sort is Magnetic Cove, Arkansas, as described by W. S. Washington in the Bulletin of the Geological Society of America, vol. XI,
page 389, in which we find the reverse. The iron oxides, magnesia, lime, apatite, etc. are most abundant at the centre and aluminum, alkali and silica at the border.

**ANALYSIS OF ROCKS TAKEN AT MAGNETIC COVE.**

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The samples were taken beginning at the outer edge of laccolith and finishing at the centre.

I. Chiefly orthoclase as large tabular crystals,
with considerable nepheline, some cancrenite apparently primary, at least in part, and argrine-ausite, biotite, sodalite, titanite and magnetite are rare accessories, but amphibolite and apatite are not present.

II. Leucite porphyry composed of leucite, or rather pseudo leucite, phenocrysts often of large size lying in a dark fine grained, holocrystalline groundmass of nepheline, sharply automorphic brown garnets, diopside and argrine with very little orthoclase, titanite, magnetite, apatite and probably sodalite.

III. Fine grained nepheline-syenite (taken near western border) composed of orthoclase with nepheline, diopside with borders of argrine, some hornblende (greenish), rather abundant crystals of titanite and accessory apatite and magnetite.

IV. Is eleolite-garnet-syenite, composed of fresh nepheline in large amounts with much pale green or yellow diopside, and xenomorphic brown garnet, which is younger than pyroxene. Apatite is present in rather large crystals; while magnetite varies, being rare in some specimens and abundant in others. Hornblende, olivine, orthoclase and plagioclase are absent.

As the size of this paper does not permit of an elaborate discussion of these magmas, I shall limit
myself to the most prominent features, brought out by the foregoing discussion of the Phase Rule.

The first magma, an acid not high in alkali having a uniform composition throughout, was evidently thrown out as an eutectic, and therefore on cooling cooled uniformly throughout.

The second, a basic and alkaline rock, we have cooling and crystallizing according to the general order, apatite, magnetite, etc. being first to cool and orthoclase and silica cooling last, forming the central portion is easily explained by adhering to our hypothesis. The acid rocks forming the eutectic having the lowest fusion temperature, the small amounts of the more basic metals which are found in the centre being necessary for the eutectic.

The third, an acid and alkaline rock; here we find the outer portion more acid and our central part the basic portion, having apatite and magnetite crystals in this central portion. Again we see an excess of our eutectic crystallizing out; this time it being over on the other side of our diagram and therefore a very different order of crystals.

CONCLUSIONS.

After a thorough investigation and a reasonable
line of reasoning we find our original purpose completely upset as apatite does not always crystallize before orthoclase and silica, when present in the same magma; but we may have the reverse, depending on the composition of the magma when ejected. The explanation of this comforms with the thermo-physical-chemistry laws and is easily explained by a diagrammatic representation. We see that for compounds of one, two or three components we can tell exactly what is going to happen under certain conditions, but beyond this it gets more complicated and for a complex magma almost beyond comprehension; but from the discussion of these conditions we are able to foretell, to a great extent, the happenings of a magma on cooling.

We see that the cooling of a magma is purely a study in physical chemistry.

There is no doubt that supersaturation plays a certain part in crystallization, also that currents set up within the magmas tend to displace the crystals. But for our main solution we will have to look to the laws governing eutectic, mixed and fractured crystallization as explained in our study of these laws.

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