

## PEGMATITE CRYSTALLIZATION

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### ABSTRACT

The authors try to analyze the geological, physical, and chemical conditions which control precipitation and growth of pegmatite minerals. The growth and persistence of large crystals is attributed as follows: (1) The great chemical complexity of the solutions, which reaches its climax in the last stages of magmatic differentiation; (2) establishment of temperature gradients along the pegmatite thorofores, both from place to place in the thorofores, and from them into the wall rock. The variation in these temperature gradients and in the speed of flow of solutions provides optimum conditions for replacement and crystal growth processes; (3) the tendency of certain crystals in suitable solutions to gain increased stability with increase in size.

### INTRODUCTION

In a study of pegmatite crystallization the most important aspects deal with the nature of the fluids which build the pegmatite, temperature considerations, replacement, and conditions favoring the formation of large crystals which are uniquely characteristic of pegmatites. Following the reasoning of Fersmann<sup>1</sup> and others, the pegmatite-forming process will be considered for the majority of cases as a one-stage affair.

Systems of various rock components have been prepared synthetically and studied by others, and the results of such studies furnish indisputable data as to the behavior of hypothetical magmas not complicated by the presence of the minor constituents characteristic of actual magmas. However, as a magma crystallizes, the constituents present in minor amount, being far from saturation, tend to accumulate in the mother liquor, unless they are coerced into precipitation with the great mass of essential rock minerals (such as the association of some titanium, zirconium, and hafnium with silicon in silicates). The mother liquor is thus changing gradually in character with respect to the minor constituents, and by the time pegmatite formation has become well established, the mother liquor is quite different from the original mass; consequently, the "mass production" methods of common igneous rock formation may not apply closely in most cases to pegmatites.

### NATURE OF PEGMATITE FORMING SOLUTIONS

Pegmatites differ from igneous rocks in several respects, the most important being the accumulation of certain rare elements in the peg-

<sup>1</sup> Fersmann, A., Über die geochemisch-genetische Klassifikation der Granitpegmatite: *Mineral und Petrog. Mitteilungen*, **41**, 64 (1931).

matite. These rare elements, in general, are not widely diffused and never characteristic of the so-called parent rock. This difference in composition between pegmatite and parent rock must be the result of a process of rare element concentration whereby, in general, the rare elements are not precipitated with the bulk of the rock-forming material, but are reserved in the mother liquor. During the formation of the parent rock, the rare elements represent minor constituents of the magma, with reference to which it is unsaturated. Consequently they are not precipitated. On the other hand, the magma is saturated with respect to the rock-forming components. As a result of the crystallization of the parent rock, the mother liquor changes progressively. It begins as a solution dominantly rich in the essential rock-forming components, and of an apparently simple composition. This apparent simplicity is due to the very small proportion of accessory constituents. The mother liquor finally becomes highly complex, containing as essentials many constituents which ordinarily are merely accessory, including certain very scarce elements, which usually are not recognized at all in igneous rocks.<sup>2</sup> Finally, then, enrichment with respect to the rare elements and the minor rock-forming components is accomplished and their precipitation becomes possible.

Thus we have a solution whose solvent power depends upon nearly every one of the components originally present in the parent magma. During the formation of the parent rock, the solvent power had been determined overwhelmingly by a limited group of rock-forming constituents; in the pegmatite stage, however, the solvent power increased in versatility as a result of the complexity of the resultant mother liquor. This complexity probably contributes to the formation of large crystals, and may be an important factor in replacement.

Other materials besides the rare elements accumulate in the mother liquor. These are the most volatile and the most soluble components of the magma, and they are important in determining the physical character and the chemical properties of the mother liquor. Water, and compounds of fluorine are most prominent in this connection. Such compounds as the fluosilicates and fluosilicic acid, and fluorides such as fluorite, are excellent fluxes and cause the mother liquor to become more fluid.

Minerals will be formed from such solutions by one or more of several changes, all of which must result in saturation of the solution with respect to the mineral components before precipitation can occur. These are as follows:

<sup>2</sup> Fersmann (*ibid.*, p. 205) points out that most pegmatites carry about twenty-five different minerals; the Norwegian pegmatites are exceptional with about seventy-five. Most igneous rocks contain less than ten different minerals; of course the number of different minerals indicates the relative complexity of the parent solutions.

- (1) Lowering of temperature. This is the most important change leading to mineral formation.
- (2) Escape of part or all of the volatile solvents or precipitation of a mineral involving the solvent.
- (3) Saturation of the mother liquor with a particular component due to solution of country rock, or of previously formed pegmatite material. In these cases, ordinary pegmatite minerals would be formed nearer the source of mother liquor than normally; new minerals may be formed by the reaction of pegmatite fluids with the wall rock, as in the formation of andalusite in contact rocks.

For minerals to precipitate, it is immaterial whether the solution be "dilute" or "concentrated," but in any case, the solution must be saturated. The terms "dilute" and "concentrated" have no meaning in this connection because they are purely relative—a solution can be dilute and still be saturated.

Re-solution of previously formed minerals can take place whenever the mother liquor is unsaturated toward them. Nevertheless, a substance which precipitates may thereafter be prevailingly insoluble in the same solvent, even though the solvent later becomes unsaturated with reference to it; this insolubility probably accounts for many mineralogical phenomena, as will be pointed out later.

#### TEMPERATURE CONSIDERATIONS

We must assume that the major part of pegmatite formation immediately follows the solidification of the parent rock,<sup>3</sup> and that cracks or openings suitable for pegmatite development form in the parent rock and in the country rock. Certain residual liquors result from the formation of the parent rock. The mouths of the cracks will necessarily be at the temperature of the original mother liquor, and as this residual liquor is forced into the cracks, temperature gradients will be established both along the stream of pegmatite flow and transverse to it into the country rock. Cooling will necessarily be slow because the cracks pass through hot country rock previously heated by conduction, diffusion, etc., from the parent magma. The rate of cooling of the pegmatite-forming fluids depends for one thing upon the cooling rate of the country rock traversed by the cracks. Since the country rock cools slowly, the cracks maintain a low temperature gradient, and the passing fluids must also cool slowly. The moving pegmatite fluids normally will be at a higher temperature than the crack walls, provided the flow of fluid is essentially uniform; if the flow is not uniform, for a time there may be regions where the fluid

<sup>3</sup> Frank L. Hess has interpreted the introduction of spodumene into North Carolina pegmatites as being considerably later than the formation of earlier pegmatite material, partly dependent upon and localized by diastrophic movements. Cf. Spodumene pegmatites of North Carolina, *Econ. Geol.*, 35, 950 (1940).

temperature drops to the wall rock temperature. Necessarily, the general direction of pegmatite flow will be the direction of lowering temperature. The temperature gradient, in association with other factors, will then determine the distribution of the pegmatite minerals.

The slow rate of cooling of the pegmatite zone will favor the growth of large crystals, but it is evident that the large crystals characteristic of pegmatites cannot be accounted for entirely by this slow rate of cooling. Certainly a much slower and more uniform cooling rate existed in the central regions of the parent rock during its formation, but extremely large crystals are not found there.

#### THE PEGMATITE THOROFARE

We suggest that the space of pegmatite formation be called a "pegmatite thorofare." The pegmatite process may be considered as a one-stage affair; that is, *ideally there is a single major injection of magmatic mother liquor into the pegmatite thorofare which continues until the supply of mother liquor is exhausted.* Naturally, the ideal case is rare. In many cases, what may be considered the normal course of procedure is interrupted by diastrophism or other geological events which have no necessary connection with the pegmatite process. In such cases, there may be either an interrupted and later renewed injection of pegmatite fluids or the whole process may be permanently cut short along any one thorofare under consideration, and the end stages of injection may be bypassed through entirely different thorofares. Consequently any particular pegmatite vein may represent any or all parts of the pegmatite sequence. Perhaps a pegmatite which represents within itself all significant changes in the mother liquors in chronological relations is as rare as an outcrop which shows a continuous stratigraphic sequence from Cambrian to late Permian.

Considering the high temperatures and pressures in operation, and the very high mobility of the pegmatite solutions (especially those termed "pneumatolytic"), the thorofares may range in size from skeins of sub-microscopic spaces to open cracks yards wide.

As the mother liquor travels through the pegmatite thorofare, the pegmatite minerals are precipitated individually, as saturation is reached at definite temperatures. At the same time, solution of pegmatite minerals or country rock may take place at any point followed by precipitation of these dissolved materials at some point of lower temperature—that is, generally at a place farther from the source of mother liquor (provided the flow is essentially uniform); this is replacement. Thus there is a process of precipitation which may be accompanied by solution while the pegmatite fluids are flowing essentially in a one-way direction

through the pegmatite thorofare. This may be likened to a process of unloading and loading at various stations along a transportation system or thorofare, for actually, the pegmatite fluid is the medium of transport of pegmatite constituents.

The speed of flow will vary from place to place along the thorofare, being slow at places of easy or wide passage, and rapid in constrictions or in places of reduced permeability. Supposing the wall rock to have the same temperature at two places, one of narrow passage, and the other of large cross section, then the fluid will pass swiftly through the narrow places and slowly in the large openings. The swift flow will carry high temperatures farther down the thorofare than the slow stream can. Consequently, the temperature gradient between fluid and wall rock along the thorofare increases in places of fast flow and drops definitely at places of slow movement. At the down-stream part of a constricted passage, there should be an unusually high temperature gradient between fluid and wall rock. We might expect free precipitation and selective solution, or abundant replacement, at the upstream side of the wide spaces in pegmatite thorofares, where there would naturally be a sharp drop in the temperature gradient between the pegmatite fluid and the wall rock.

Inasmuch as narrow passageways increase the relative area of heat conduction from passing solutions into the walls of country rock, there must be limiting conditions under which very fast small streams of fluid would cool so rapidly that the temperature gradient down stream would fall more rapidly than in places where the channels are large in cross sectional area and the fluids move slowly. A balance tends to be established, of course, between the temperature of the passing fluids, the surface of the thorofare, and the temperature gradient from the surface into the country rock. Consequently, suggestions as to places of steep temperature gradient must be very general in application.

In cases such that the parent magma supplies pegmatite fluids under varying pressures, then the speed of flow at any one place will vary from time to time. Such variation in the speed of flow again causes a change in the physical chemical regime of the whole pegmatite thorofare. When the speed of supply increases, the temperature of the fluid at any given point must rise, and the temperature gradient between fluid and wall rock or early pegmatite crystals must increase, and *vice versa*. For these and probably other reasons, there can hardly be much uniformity in physical chemical conditions at any point along a pegmatite thorofare for very long. Whenever there is a rapid temperature change, it causes alternation between solution and precipitation at crystalline surfaces, thus promoting the process of replacement.

Supposing the country rock to be affected by diastrophism, then the existent pegmatites may be either crushed into increased compactness, or shattered into open cracks. In either case the speed of flow of pegmatite liquors will change, thereby tending to increase or reverse the existing processes of deposition or replacement. In certain areas, fracturing is known to have been of primary importance in pegmatite mineralization.<sup>4</sup>

Variation in the speed of flow of pegmatite fluids may result in replacement. When temperatures become higher at the surface of a crystal (or at the wall rock), the mother liquor may become unsaturated toward the material, depending on its composition and the period of its formation in the pegmatite process. This unsaturation will result in solution of the material provided the latter is not passive towards the solvent. As solution proceeds, the material will be replaced by higher temperature minerals which ordinarily would precipitate at a place nearer the source of mother liquor. In other words, where the speed of flow increases the temperature difference between fluid and wall rock, or earlier pegmatite crystals, increases. Then materials, with reference to which the solvent is far from saturation, may dissolve freely; but at the same time the fluid, constantly cooling as it flows to regions of lower temperature, is precipitating the common rock-forming minerals (at least) with reference to which the fluid is saturated. Such a condition of selective solution and compulsory precipitation is favorable to replacement.

Where the speed of flow decreases, the temperature difference between wall rock and solvent is low, and solution of solids is at a minimum. However, as in all other cases, the fluids are actually cooling as they flow and therefore are constantly renewing the tendency to precipitate. The result is that where fluids flow slowly there is a general tendency for precipitation without solution, effecting ordinary crystallization without replacement. When the fluids maintain a constant speed of movement, a general balance between supply and precipitation becomes established, and proceeds so long as this flow continues and space for crystal growth remains. This is represented in nature by the common high-temperature granite pegmatites.

Figure 1 is designed to illustrate in a general way the distribution of solution, precipitation, and replacement along a thoroughfare as a result of differences in cross-sectional area of the space available for the flow of fluids, and corresponding variations in the speed of flow of the passing solutions.

<sup>4</sup> Hess, Frank L., The spodumene pegmatites of North Carolina: *Econ. Geol.*, **35**, 942-966 (1940); Hess, Frank L., Whitney, R. S., Trelithen, J., and Slavin, M., The rare alkalis in New England: *U. S. Bur. Mines, I. C. 7232*, 8-10 (Jan., 1943).

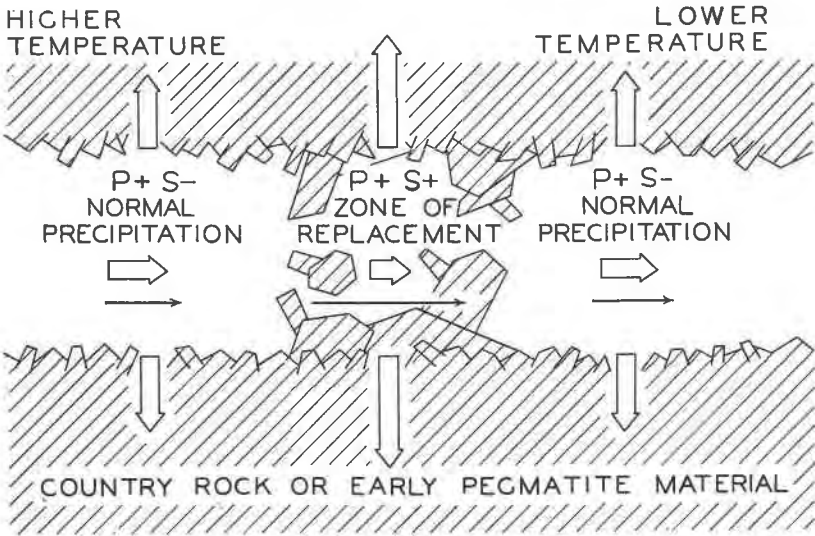


FIG. 1. Diagram to illustrate relations of precipitation, solution and replacement with the temperature gradients along a pegmatite thorofare.

Solid arrows indicate direction and relative speed of flow. Length of hollow arrows indicates relative intensity of temperature gradients. P+ stands for precipitation. S, + or -, stands for important or negligible solution, respectively.

FORMATION OF LARGE CRYSTALS

The very coarse crystallization of pegmatites is unique in that it is found in no other naturally occurring aggregate of minerals. One of the most important factors which is necessary for large crystal formation is a steady, uniform supply, or else a repeatedly renewed supply, of material to the growing crystal. This may be accomplished by lowering the temperature of a system of solvent and solute, wherein the solvent is saturated and the solubility of the solute decreases with lowering temperature. Another process would involve a decrease in the amount of solvent, such as one of the common rock-forming minerals in the case of a magma. Precipitation may be increased also by an actual mechanical removal of the solvent, due to diastrophic or irruptive processes. Such processes must account in part for large crystals in pegmatites, but there must be other factors operative. Certainly a steady, uniform supply of material is not all that is necessary for large crystal development. This must be so because we do not find very large crystals in the centers of igneous intrusions wherein the conditions of crystallization (slow cooling particularly) were certainly more uniform than in a pegmatite, and where

there was an abundance of material available from solution. This at once indicates that pegmatites are formed under conditions materially different from those controlling igneous rock formation.

From the data based on more than three hundred pegmatites, given by Fersmann,<sup>5</sup> several important points may be presented:

- (1) In the epimagmatic zone (800°–700°), the structure is generally aplitic or graphic. Very large crystals are not characteristic. The rarer minerals found here, such as monazite, garnet, zircon, titanite, etc., may be considered to have precipitated by virtue of their limited solubility in the cooling mother liquors. Quartz is often abundant. In the epimagmatic stage of pegmatite formation, the mother liquor may be considered still to be essentially simple in composition, and the common rock-forming components<sup>6</sup> are still crystallizing in much the same manner as in the parent rock.
- (2) The pneumatolytic-pegmatoidal zone (600°–400°) is characterized by the large crystals of pegmatites, and in its later stages by a variety of complex minerals. The complexity of the pegmatite minerals found here indicates that the parent mother liquor itself had been complex, most of the abundant igneous rock-forming components having crystallized during the epimagmatic and early pneumatolytic stages. It is important to recognize also that the pneumatolytic zone is the characteristic place in the pegmatite where the very large crystals are found. These facts immediately suggest that the formation of large pegmatite crystals is intimately connected with the complex nature of the solvent.
- (3) A characteristic feature of the hydrothermal zone (400°–50°) is the precipitation of fluorine compounds such as apatite, cryolite, and fluorite from the remaining complex solvent. The precipitation of silica is more pronounced in the hydrothermal zone than in the late pneumatolytic-pegmatoidal zone.
- (4) An inescapable observation regarding large pegmatite crystals is the fact that they are all silicates. The preponderance of silicates indicates something as to the nature of the solvent. We may conclude at least that the pegmatite mother liquor which eventually leads to minerals characteristic of the hydrothermal zone not only must be an excellent solvent for silicates, but must be high in fluorine compounds. This is supported by the fact that the precipitation of silica is negligible in the late pneumatolytic stage where fluorine compounds constitute an effective proportion of the mother liquor; following the precipitation of fluorine compounds, however, in the hydrothermal zone, the silica is also precipitated. Apparently the silica is held in solution by fluorine compounds. In the pneumatolytic stage, these fluorine compounds, such as fluosilicic acid, in addition to acting as solvents for silicates, must have promoted the fluidity<sup>7</sup> of the mother liquor. Apparently this combination of fluidity and high solvent power promotes the growth of large silicate crystals.

It is a well known fact that large crystals of a mineral are less susceptible to chemical treatment and to solution, in general, than are small

<sup>5</sup> *Loc. cit.*, pp. 64–83.

<sup>6</sup> The writers do not recognize the euhedral habit of zircon, titanite, and monazite necessarily to indicate early crystallization in an igneous rock any more than in the case of garnet, which is universally recognized as metacrystic.

<sup>7</sup> By promoting fluidity, the writers mean that the solution becomes more mobile, and the movement of ions, atoms, and molecules is promoted.



crystals or amorphous forms of the same mineral. *The mere size of pegmatite crystals encourages their persistence at least, and probably promotes their growth.* It was pointed out earlier that a substance once precipitated may thereafter be insoluble in its solvent even though the solvent later becomes unsaturated with respect to it. It is probable that large pegmatite crystals represent such a case. Once such a crystal has formed, it will be more or less passive toward resolution as a result of changing conditions in the pegmatite thorofores, but in later periods of precipitation it may resume its crystallization. This would permit the crystal periodically to increase in size, without suffering corresponding periods of wastage. The zoning often observed in large pegmatite crystals probably is due to such a process—the material crystallizing after a discontinuance of precipitation in some cases being of a slightly different, but analogous composition.

In order to promote large crystal growth in a simple solvent it is possible that a condition of infinitesimal alternation between wastage and crystallization must be provided. H. C. Kremers<sup>8</sup> has postulated the same sort of theory to explain the growth of synthetic single optical crystals from the fused state. There is probably a region, perhaps scarcely more than a surface, of alternation in which impurities remain in solution and the pure material deposits in its proper place in the crystal lattice.

Such crystal growth must not be confused with that of large crystals growing at the expense of small ones, which is a matter of low ratio of surface to mass. This may also be pertinent to the problem of large crystals in pegmatites. It is a fact that renewed precipitation in pegmatites commonly takes place on crystals already well grown, and rarely in the form of a new generation of microlites. Consequently large crystals maintain their identity and increase in size, whereas microlites cannot persist.

No one of these conditions alone is responsible for large crystal growth in pegmatites. It seems to require a combination of special processes and conditions. These special features appear to be in the main:

- (1) A constantly and/or repeatedly renewed stream of magmatic mother liquors.
- (2) A persistently dropping temperature.
- (3) Restriction of flow of the mother liquors into definite thorofores which in the generalized case are operative for a long time.
- (4) A progressive complexity and chemical versatility of solutions.
- (5) The presence of active solvents and fluxes for silicates.
- (6) Conditions causing variations in the speed of flow along the thorofores, both from place to place and from time to time.
- (7) Other conditions promoting selective solution and precipitation, regrowth, and replacement.

<sup>8</sup> Personal communication from H. C. Kremers of the Harshaw Chemical Company, Cleveland, Ohio.

- (8) The persistence of certain minerals beyond their expected conditions of stability.
- (9) The increase in stability of certain crystals with the attainment of great size.

#### CONCLUSION

It is probably impossible to find any pegmatite or group of pegmatites in the same igneous suite which illustrates clearly all phases and all varieties of the better known mineralogical, textural, and structural features characteristic of pegmatites. Nevertheless, there appears clearly to be a gradational relationship between various types of pegmatites. It does not seem reasonable to expect to find all mineralogical variations in the same igneous suite, because each magma has its own assortment of constituent elements peculiar to itself. The resultant pegmatite of course cannot provide minerals composed of elements which are not represented adequately in the parent magma. There will always be differences in members of the same class of pegmatites derived from different magmas. Uniformity is not to be expected.<sup>9</sup> General accordance to type, however, seems to persist. The types represented in all parts of the world appear to show a coherent, progressive relationship, type to type, in spite of irregularities and hiati in any local aggregate of pegmatites. The process of pegmatite crystallization, like the cycle of erosion has its interruptions and its rejuvenations.

The conditions which compel the formation of large crystals in pegmatites are complex and probably are mutually coordinating in their effects. They appear to be most effective at temperatures definitely lower than those of igneous rock formation. The pegmatite solutions are extremely complex in composition, and correspondingly versatile in their activities. They are relatively enriched in silicate fluxes and in pneumatolytic components. The crystals once formed tend to persist in spite of potential solution, and to gain stability with increase in size. Variations in the flow of solutions affect the temperature gradients and thus promote selective replacement and enlargement of certain crystals.

Among all pegmatites of the pneumatolytic-pegmatoidal zone, no other feature displays such persistence as coarse crystallization, and perhaps the development of very large crystals requires a group of mutually augmenting conditions which constitutes the most nearly universal characteristic of pegmatites.

#### ACKNOWLEDGMENTS

The authors express appreciation of those who have kindly checked parts of this paper. Thanks are due Drs. L. F. Audrieth, H. F. Johnstone, and T. Moeller of the University of Illinois, and Dr. H. C. Kremers of the Harshaw Chemical Company, Cleveland, Ohio.

<sup>9</sup> Cf. Hess, *et. al.*, *loc. cit.*, p. 10.