

FLUID INCLUSIONS IN MINERALS FROM ZONED  
PEGMATITES OF THE BLACK HILLS,  
SOUTH DAKOTA

PAUL L. WEIS, *U. S. Geological Survey, Washington 25, D. C.*

ABSTRACT

A study of fluid inclusions in minerals from zoned pegmatites was undertaken in an effort to check the hypothesis that zoned pegmatites formed through fractional crystallization in a restricted system. Beryl, spodumene, tourmaline, garnet and quartz containing fluid inclusions were heated, and temperatures of cavity filling were determined by the visual method.

Twelve pegmatites were sampled, but extensive results were obtained from only three pegmatites. Beryl from inner zones of the Bob Ingersoll No. 1 and Highland Lode pegmatites gave lower temperatures than beryl from outer zones. The Peerless pegmatite gave results that showed a reverse trend.

Temperatures observed in beryl ranged from 216 to 515° C. Results from individual crystals showed a range of 9 to 200° C., and individual zones showed ranges of 65 to 230° C.

Sources of error in interpretation are discussed, and an effort is made to calculate true temperatures of crystallization, insofar as available information permits.

Data were too meager to provide an adequate check on the hypothesis of fractional crystallization, although tentative support is given by results from two pegmatites. Estimates of pressures prevalent at the time of crystallization, together with inferred pressure-volume-temperature data, imply that some early-formed beryl crystallized at temperatures in excess of 500° C.

CONTENTS

Abstract.....	671
Introduction.....	672
Description of inclusions.....	673
Behavior during heating.....	676
Composition of fluids in inclusions.....	677
Results.....	679
Highland Lode (John Ross Mine).....	679
Bob Ingersoll No. 1 pegmatite.....	681
Bob Ingersoll No. 2 pegmatite.....	681
Peerless pegmatite.....	681
Hugo pegmatite.....	684
Tourmaline.....	684
Quartz.....	684
Spodumene.....	685
Garnet.....	685
Discussion.....	686
Interpretation.....	693
Temperature zoning.....	693
Temperatures of crystallization.....	694
Summary and conclusions.....	695
Acknowledgments.....	696
References.....	697

## INTRODUCTION

The existence of primary zonal structures in certain pegmatites has been recognized for many years. A paper by Cameron, Jahns, McNair and Page (1949) has offered the most recent evidence suggesting that zones develop through fractional crystallization of material in a restricted system. This paper gives the results of an attempt to check that hypothesis. If zoned pegmatites have crystallized from a restricted system, a systematic variation in temperature during crystallization may be expected. If this variation exists, it should be demonstrable by an examination of fluid inclusions. If the hypothesis is correct, fluid inclusions in minerals from outer zones might be expected to show disappearance of their vapor phases at higher temperatures than similar inclusions in minerals found in inner zones. It was hoped that a study of fluid inclusions would show whether such differences existed.

The pegmatites of the Black Hills, South Dakota, were selected as being best suited for the purposes outlined above. The pegmatites are well exposed, unaltered, and many consist of three to eight mineral assemblages in well defined zones (Page et al., 1952). More than 50 have been mapped in considerable detail. Fluid inclusions are known to exist in many of the pegmatite minerals. Beryl, which was found to be most satisfactory in earlier studies of this type (Cameron, Rowe and Weis, 1953) is known to occur in comparative abundance.

Twelve pegmatites, the New York, John Ross (Highland), Triangle A, High Climb, and Helen Beryl pegmatites in the Custer district, and the Bob Ingersoll No. 1 and No. 2, the Etta, Hugo, Peerless, Dan Patch No. 2, and Hesnard pegmatites in the Keystone district were sampled. Selection was based on the exposures available, number of zones, mineralogy, and detailed knowledge of their internal structure. Beryl, garnet, tourmaline, spodumene, amblygonite, apatite, microcline and quartz were collected. An effort was made to collect as many different minerals from as many different zones as possible. Euhedral crystals were collected wherever possible, to facilitate preparation of oriented sections.

After the specimens were sawed and polished, they were examined under the microscope. Those that were found to contain fluid inclusions were retained for further study in the heating stage. No fluid inclusions were found in microcline, apatite, or amblygonite. Beryl, spodumene (hiddenite), garnet, tourmaline and quartz were found to contain fluid inclusions in at least a few specimens.

More than 300 polished sections were prepared and examined; some 5,000 fluid inclusions were studied, and temperatures of disappearance were determined for approximately 1,100, including about 850 thought to be primary, and 250 of other types. Approximately 200 polished sec-

tions of beryl were made, including samples from all 12 pegmatites, but only 53 sections, from five pegmatites, were found to contain primary type inclusions in sufficient numbers to provide adequate temperature data. All temperature measurements on inclusions were made at least twice before they were considered valid. Those that could not be duplicated within 2° C. were discarded. It was found that temperatures obtained from a particular inclusion could ordinarily be duplicated many times, over periods of two to six months.

#### DESCRIPTION OF INCLUSIONS

It is essential in the use and interpretation of data from fluid inclusions that a distinction be made between primary and secondary inclusions. Unfortunately, some students of fluid inclusions in the past have made little or no effort to do this. No temperature data should be considered acceptable unless each inclusion studied is classified with respect to occurrence, behavior, distribution, shape, contents and relationship to crystallographic directions and secondary features of the host mineral. Proper interpretation can be made only after a thorough and careful examination of each and every polished section used. The indiscriminate use of data derived from fluid inclusions without proper attention to the recognition of criteria that may assist in distinguishing between primary, secondary, and doubtful inclusions must lead eventually to the accumulation of information that is largely meaningless.

Polished sections of Black Hills minerals were found to contain five types of inclusions, distinguishable by shape, distribution and contents. They may be divided into two groups: solid inclusions and fluid inclusions.

There are two kinds of solid inclusions present. One consists of euhedral to subhedral crystals of single minerals such as feldspars, tourmaline, quartz and mica (Fig. 1). The other consists of irregular shaped aggregates of fine-grained material, which appears to be made up of more than one mineral. Solid inclusions of both kinds were noted in beryl, quartz and tourmaline, but were not studied in detail.

The fluid inclusions can be divided into three general categories, distinguished on the basis of shape, distribution and relationship to crystallographic directions in the host mineral. Type I inclusions, consisting of a liquid and a gas, have shapes ranging from long, slender rods with rounded ends (Fig. 2) or irregular ends (Fig. 3) to shorter, broader shapes, showing negative crystal faces (Fig. 2). They all showed direct relationships to crystallographic elements in the host minerals. Elongate inclusions are invariably arranged with their long axes parallel to the *c*-axes of the beryl, spodumene, or tourmaline crystals in which they were found.

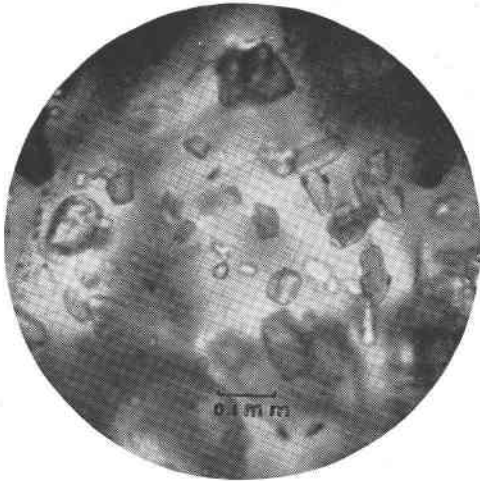


FIG. 1. Inclusions of individual mineral grains in tourmaline.

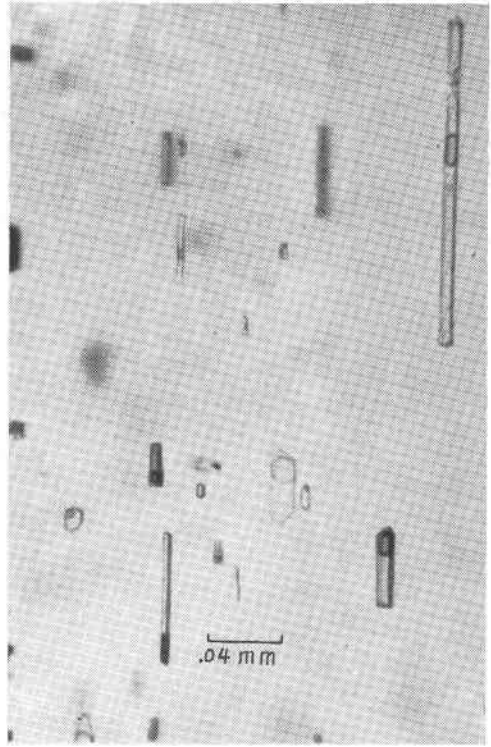


FIG. 2. Elongate fluid inclusions (Type I) in beryl. Uniform distribution and alignment parallel to crystallographic axes of the host mineral suggest that the inclusions are primary.

Negative crystal cavities are arranged so that their faces are parallel to corresponding crystal faces in the host. Inclusions of this type are commonly found more or less evenly distributed throughout the crystals, or throughout considerable portions of the crystals, and are apparently unrelated to fractures or other secondary features. They are believed to have formed at the same time as the host minerals, and therefore are considered to be primary.

*Type I.* Elongate Type I inclusions with rounded ends were found in beryl and tourmaline. Spodumene characteristically contains cavities with irregular ends (Fig. 3). Beryl and garnet contain negative crystal cavities of various shapes. A few inclusions in spodumene contain in addition to the usual liquid and vapor phases, a solid, homogeneous material of unknown composition (Fig. 4). These inclusions give results in the same temperature range as those that had no included solids, and an

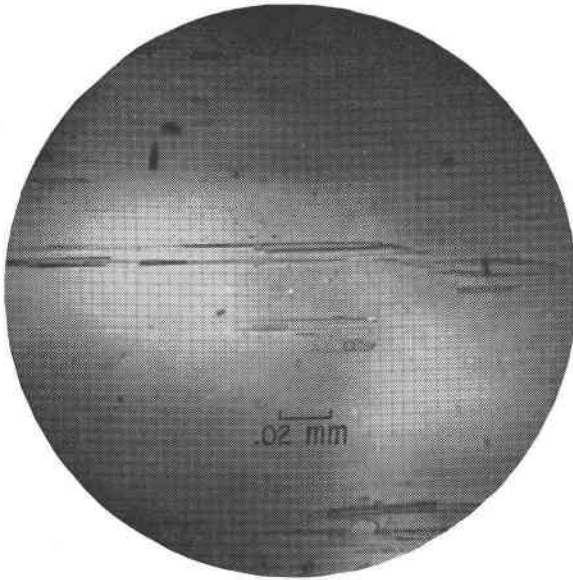


FIG. 3. Type I fluid inclusions in spodumene.

effort to dissolve the material by heating specimens to 600° C. was unsuccessful. The solid material is therefore interpreted as representing an accidental inclusion, rather than material that was precipitated out of solution from the liquid in the cavity.

*Type II.* Fluid inclusions of Type II were found in beryl, quartz and tourmaline. They consist of a liquid and a vapor phase, in irregular or rounded cavities that show no systematic relationship to either crystallographic elements or to recognizably secondary features. Some crystals contain hundreds of thousands of these inclusions, and nearly all speci-

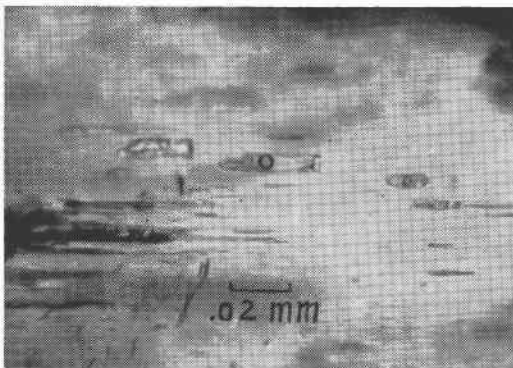


FIG. 4. Fluid inclusions containing mineral grains. Spodumene.

mens contained at least a few. They are almost invariably more numerous than Type I inclusions. They may be of primary origin, but since some doubt exists, they were not used in the interpretation of results.

*Type III.* Inclusions of Type III may be of any shape or orientation. They are found along curving or intersecting planes that are generally unrelated to crystallographic elements of the host. In many specimens they were more abundant than inclusions of Type I. The planes in which they occur appear to be healed fractures, hence the inclusions are probably secondary. They were not considered in this study.

#### BEHAVIOR DURING HEATING

The behavior of the fluid inclusions was similar to that noted in other studies of this sort. In general, one of three things happened when the inclusions were heated—the vapor bubble either shrank and disappeared, expanded to fill the cavity, or faded without appreciable expansion or contraction. Shrinkage and eventual disappearance of the vapor phase was by far the most common type of behavior noted in the inclusions used in this study. More than a thousand inclusions in beryl, garnet, spodumene, quartz and tourmaline showed this “normal” behavior. Nineteen inclusions in beryl showed expansion of the vapor phase when heated, and five inclusions in beryl showed a fading phase boundary. As compared with previous studies (Cameron, Rowe and Weis, 1953), the “abnormal” behavior exhibited by expanding or fading vapor bubbles was much less common in minerals from the Black Hills pegmatites than in those from pegmatites of Connecticut.

One of the most striking features of the results was the wide range of temperatures obtained from some of the crystals. One crystal from the Peerless mine, for example, showed temperatures of cavity filling over a range of nearly 200° C.—this in inclusions identical in appearance and apparent degree of filling at room temperature. At the other extreme, a crystal from the Bob Ingersoll No. 2 pegmatite had a difference of only 9° C. between the highest and the lowest of more than 30 temperature determinations made on different inclusions. No reason for these differences in results could be found.

The minerals examined in the heating stage showed marked differences in their physical properties. Difference in brittleness was the most outstanding characteristic noted, with the more brittle minerals exhibiting a much greater susceptibility to fracturing at all temperatures, particularly below the temperatures at which the cavities were filled by the liquid phase. Quartz was the mineral that gave the most trouble; great difficulty was experienced in finding inclusions that would remain unfractured at sufficiently high temperatures to permit the filling temperatures to be

reached. This was true even with slices 3 to 5 mm. thick. Consequently no significant data were obtained from quartz. Tourmaline and garnet are also very brittle and had to be heated very slowly. Much of the tourmaline was dark colored and had to be cut into very thin slices to allow sufficient light transmission for observation, and the thinness of the sections was undoubtedly a factor in its behavior. Most inclusions in tourmaline showed temperatures of filling below  $300^{\circ}$  C.; fracturing would undoubtedly have been a greater problem if it had been necessary to go to higher temperatures. Garnet was difficult to polish, because of incipient fractures, but comparatively little difficulty was experienced during heating. Spodumene fractured only rarely, in spite of its good cleavage. Beryl gave the least trouble of all. Cavities fractured and leaked very rarely. It was often necessary to heat an inclusion well above its filling temperature, in order to measure other inclusions in the same section, but if the sections were heated at rates of 2 to  $4^{\circ}$  C. per minute, few inclusions fractured until they were heated  $50^{\circ}$  C. or more above their filling temperatures, and many were heated  $100^{\circ}$  above this temperature without fracturing. Beryl, therefore, appeared to be the least brittle of any of the minerals studied.

#### COMPOSITION OF FLUIDS IN INCLUSIONS

Attempts to determine the composition of the fluids in Type I inclusions were largely unsuccessful, although indirect evidence was obtained that has a bearing on the problem. The behavior of the fluids throughout a wide temperature range suggests that the liquid in the cavities is aqueous. It has a very low viscosity at all temperatures above its freezing point, as shown by the mobility of the vapor bubbles. Freezing points measured for a few inclusions were found to range from  $-19^{\circ}$  C. to  $-3^{\circ}$  C. It was noted that inclusions with the highest temperatures of vapor phase disappearance also had the lowest freezing points. For example, an inclusion in beryl whose vapor phase disappeared at  $465^{\circ}$  C. was found to freeze at  $-19^{\circ}$  C., whereas an inclusion in spodumene showed a temperature of disappearance of  $260^{\circ}$  C. and a freezing temperature of  $-4^{\circ}$  C.

A spectrographic analysis of the fluids was attempted by Prof. V. W. Meloche of the Chemistry Department of the University of Wisconsin, but he was unable to provide a positive identification of any ions in the solutions.

Calculations of hypothetical expansion curves that could be expected from inclusions containing pure water were compared with expansion curves actually measured in some of the long, slender inclusions found in beryl and spodumene. The calculated curves were found to be similar to,

but not identical with the measured curves (Cameron, Rowe and Weis, 1953). None of the cavities appear to contain saturated solutions, and none of the inclusions examined showed evidence suggesting that they contained fluids having a critical temperature below that of pure water (374° C.).

All of the above features could be explained if it is assumed that the inclusions contain solutions of water and moderate amounts of soluble salts. The few available analyses of fluid inclusions list NaCl, KCl, and other simple salts, in concentrations as high as 12 per cent (Ingerson, 1947, p. 378), but no analyses of fluids in pegmatite minerals have been made. It is reasonable to suppose that fluids containing simple salts could occur in inclusions in pegmatite minerals, but concentrations of 20 to 40 per cent would probably be required to raise the critical temperatures of the solutions high enough to account for the presence of liquids at 515° C., the highest temperature at which they were observed. Further

TABLE 1.<sup>1</sup> SEQUENCE OF MINERAL ASSEMBLAGES IN ZONED PEGMATITES, BLACK HILLS, SOUTH DAKOTA

	Peerless	Highland Lode	Helen Beryl	Bob Ingersoll #1	Hugo
1. Plagioclase-quartz-muscovite	X	X	X	X	X
1a. *	X				
2. Plagioclase-quartz					X
3. Quartz-perthite-plagioclase, with or without muscovite	X	X	X		X
4. Perthite-quartz		X	X	X	
5. Perthite- (or microcline-) quartz-plagioclase-amblygonite-spodumene			X	X	X
6a. †Plagioclase-quartz	X	X		X	X
6. Plagioclase-quartz-spodumene					
7. Quartz-spodumene			X		X
8. Lepidolite-plagioclase-quartz				X	
9. Quartz-microcline					X
10. Microcline-plagioclase-lithiamicas-quartz	X				X
11. Quartz					

<sup>1</sup> From Internal Structure of Granitic Pegmatites. Cameron, Jahns, McNair and Page: *Econ. Geology, Monograph 2*, (1949).

\* 1a—A variant of assemblage 1 is distinguished in the Peerless on the basis of a change in proportions of the essential minerals.

† 6a—In which spodumene is not an essential mineral, is considered as a variant of assemblage 6.

X—indicates mineral assemblage recognized in zones.



consideration is given to the question of composition in the section on discussion of results.

## RESULTS

The most striking feature of zoned pegmatites is the consistency of arrangement of mineral assemblages from pegmatite to pegmatite and from district to district (Cameron, Jahns, McNair and Page, 1949). Table 1 shows the sequence of mineral assemblages described in the Black Hills pegmatites included in this study and the zones in which they occur. In all cases zone numbers and the mineral assemblages to which they refer correspond to the zone numbers shown on the graphs of temperature determinations.

Results of temperature studies on beryl crystals from three of the twelve pegmatites studied were extensive enough to show trends when plotted in graphical form. In these graphs (Figs. 5, 6, and 7), the zones from which the samples were taken are indicated at the bottom (abscissa), and the temperatures are given on the vertical scale (ordinate). Each dot represents the temperature of disappearance of the vapor phase of one inclusion. All inclusions in beryl that were plotted were of fluid Type I.

### *Highland Lode (John Ross Mine)*

The Highland Lode pegmatite (Fig. 5) contains four zones. Beryl occurs in the three inner zones, and primary type inclusions were found in all of the beryl studied. Seven crystals were collected: three from Assemblage 3 (First intermediate), one from Assemblage 4 (Second intermediate), and three from Assemblage 6a (Core). One of the crystals in Assemblage 6a was very near the center of the core; the other two were near the outside of the core. In the graph they are shown separately as subdivisions of the zone.

Temperature values ranged from 216° to 404° C. Temperatures for the first intermediate zone (Assemblage 3) ranged from 264° to 357° C. The mean temperature for all inclusions in this zone was 313° C. In the second intermediate zone (Assemblage 4) temperatures ranged from 216° to 361° C. However, a group of fifteen inclusions gave values ranging from 216° to 234° C.; although they appeared of primary type, they gave values much different from other inclusions and may represent a special group. The other inclusions from this zone ranged from 276° to 361° C., with a mean of 314° C. Inclusions from the two crystals in the outer part of the core gave temperatures ranging from 254° to 316° C. Their mean temperature was 290° C. Inclusions from the crystal nearest the center of the core ranged from 217° to 402° C., with a mean temperature of 257° C.

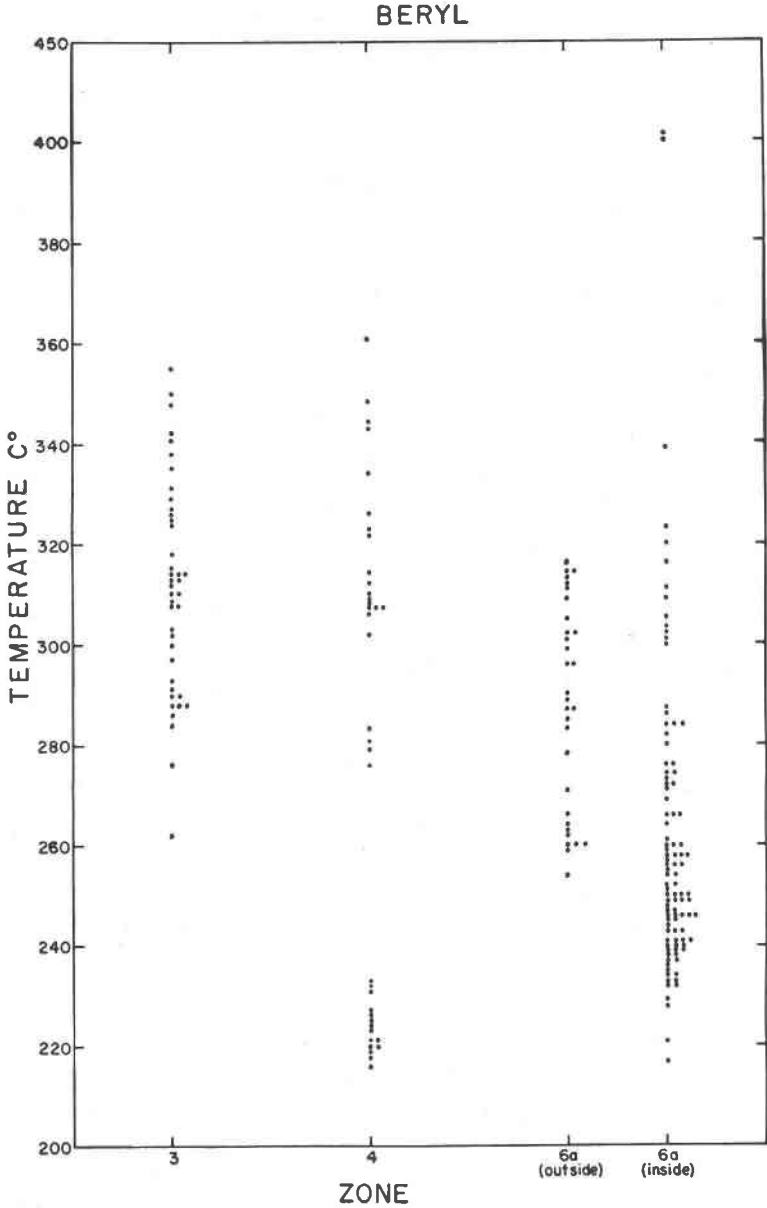


FIG. 5. Temperatures of disappearance of vapor phases in fluid inclusions in beryl. Highland Lode (John Ross) pegmatite, Custer, South Dakota. Each dot represents the temperature of disappearance measured in one inclusion.

*Bob Ingersoll No. 1 Pegmatite*

The Bob Ingersoll No. 1 pegmatite contains five zones (Fig. 6). Beryl is present in three of these zones, but only samples from the wall and the core contained primary type inclusions. Two crystals from the wall zone (Assemblage 1) gave temperatures ranging from 317° to 515° C., with a mean temperature of 395° C. Two crystals from the core (Assemblage 8) gave temperatures ranging from 308° to 489° C., with a mean temperature of 355° C. Another crystal from the wall zone contained many secondary type inclusions with temperatures ranging from 140° to 200° C. A rounded crystal of beryl from the contact between the third and fourth intermediate zone (Assemblages 3 and 6a) contained thousands of negative crystals that give temperatures ranging from 120° to 170° C. Negative crystals from this specimen were somewhat different in appearance from those usually found in beryl. Their corners were commonly slightly rounded, rather than sharp, and the inclusions appeared flattened parallel to one prism face. They appear to be of Type I, but are sufficiently different in appearance to make their classification uncertain, and are therefore not shown on Fig. 6. A crystal from the wall zone contained several negative crystal cavities that appeared to contain the customary two phases, but no change was apparent when heated to 560° C. Observation became difficult at this temperature, and heating was discontinued. No definite behavior pattern was established in this last group of inclusions.

*Bob Ingersoll No. 2 Pegmatite*

Inclusions of primary type were found in three beryl crystals from the Bob Ingersoll No. 2 pegmatite. One crystal from the wall zone contained four inclusions ranging from 302° C. to 365° C. Two crystals from Assemblage 7 (core) gave temperatures ranging from 290° to 349° C. In one of these specimens, thirty-three inclusions gave temperatures ranging from 341° to 349° C.; the mean of all temperature values from this zone was 335° C.

*Peerless Pegmatite*

The Peerless pegmatite contains five zones (Fig. 7). Beryl occurs in the outer three; however, the outer two are distinguished only on the basis of variations in the proportions of their mineral constituents, and are in reality subdivisions of Assemblage 1. One crystal from the outer sub-zone gave temperatures ranging from 257° to 405° C. with a mean temperature of 317° C. Four crystals from the inner sub-zone gave temperatures ranging from 232° to 450° C. The mean temperature from this zone was 359° C. Two crystals from Assemblage 3 gave temperatures ranging



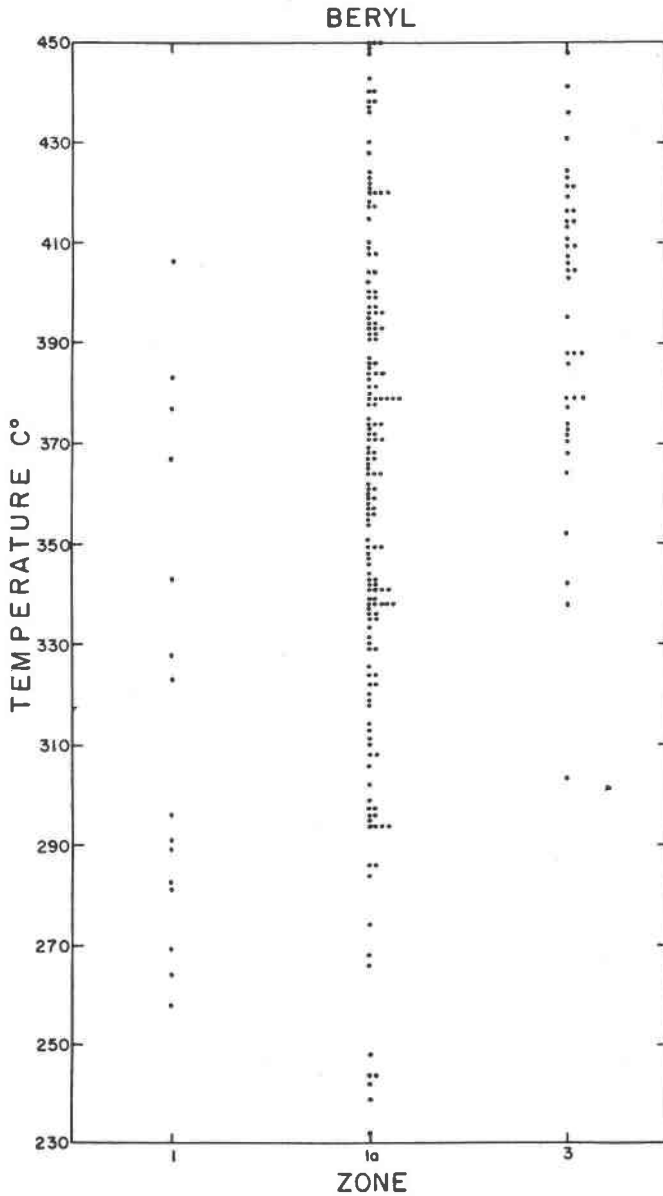


FIG. 7. Temperatures of disappearance of vapor phases in fluid inclusions in beryl. Peerless pegmatite, Keystone, South Dakota. Each dot represents one inclusion.

from 304° to 447° C. The mean temperature was 405° C. A single tapering crystal from the inner sub-zone of Assemblage 1 was 22 inches long and had a maximum diameter of 8 inches. Samples were collected from three points along the outside of the crystal and three points along its core. Temperatures obtained from the outer part of the crystal had a mean of approximately 380° C. and from the inner part, 343° C. No variation from end to end was apparent. Similar measurements on smaller crystals showed no systematic differences.

#### *Hugo Pegmatite*

The Hugo pegmatite contains beryl in at least five of its eight zones; however, only one crystal from Assemblage 2 contained inclusions of primary type (Type I). Nineteen negative crystals gave a mean temperature of 328°, with a range of 309° to 353° C.

#### *Tourmaline*

Primary type inclusions (Type I) were found in seventeen tourmaline crystals from five pegmatites. They showed no consistent trends from zone to zone. It was noted that the temperature values were always considerably lower than those obtained from beryl from the same pegmatite or from corresponding zones from other pegmatites. Temperatures above 300° C. were found in only three inclusions, from two different pegmatites. The mean temperature for all inclusions in tourmaline was approximately 250° C.

No differences in the appearance of fluid inclusions in tourmaline and beryl were noted. An appreciable difference in the compositions of solutions in the inclusions from the two minerals might account for the contrasting results, but the existence and importance of such a difference cannot be evaluated without accurate chemical analyses of the fluids. Beryl, spodumene and garnet give results that cross-check rather well, suggesting that there may be some characteristic peculiar to tourmaline which accounts for the difference.

#### *Quartz*

Two specimens of quartz from the Hugo pegmatite were heated. One of these showed poorly developed negative crystals along a plane that may have been a healed fracture. Fourteen inclusions gave values ranging from 376° to 411° C., with a mean of about 398° C. A second quartz specimen from the Hugo contained disseminated, poorly developed negative crystals. Twenty-four inclusions from that specimen gave temperatures ranging from 383° to 422° C., with a mean temperature of about 400° C.

*Spodumene*

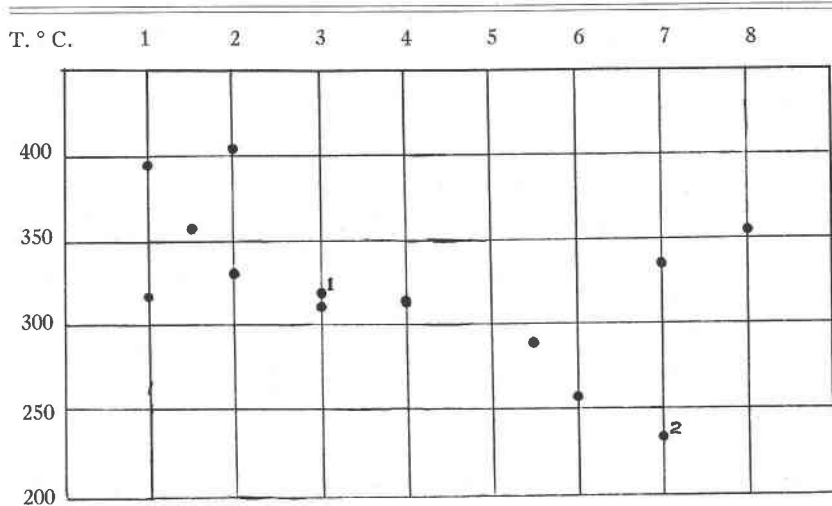
Several fragments of semi-transparent green spodumene were collected from the core of the Helen Beryl pegmatite (Assemblage 7). Rod-shaped inclusions of Type I were very abundant in these specimens. They gave temperatures ranging from 179° to 282° C., with a mean of about 235° C.

*Garnet*

Two garnet crystals from the second intermediate zone (Assemblage 3) of the Highland Lode gave temperatures ranging from 301° to 342° C. The mean temperature was 318° C. The inclusions were negative crystals in planes parallel to octahedral faces.

The most notable feature of the foregoing results is the broad range of temperatures obtained from individual pegmatites, individual zones, and even from individual crystals. Certain trends are suggested, as in the Peerless, which shows an apparent increase from a mean of 317° C. in the wall to 395° C. in zone 3. The Bob Ingersoll No. 1 gave the opposite trend, with a decrease from 395° in the wall to 355° in the core. The Highland Lode also suggests a downward trend, from 314° in zone 3 to 257° in the center of zone 6a. Table 2 summarizes the results in graphic

TABLE 2. PEGMATITE ZONE



- 1. Garnet, Highland Lode pegmatite.
- 2. Spodumene, Helen Beryl pegmatite.

Composite results of temperature studies on all pegmatites. Each dot represents the mean of all temperatures in one zone of one pegmatite. Pegmatites include the Peerless, Highland Lode, Helen Beryl, Hugo, Bob Ingersoll No. 1, and Bob Ingersoll No. 2.

form, and shows both the somewhat ill-defined tendency toward decreasing temperatures in inner zones, and the very considerable difference in temperatures from equivalent or adjacent zones of various pegmatites. This great difference in temperatures certainly emphasizes the need for further work and adequate interpretation, if nothing else. Presentation of conclusions based on such variable results is obviously not justified, particularly since there is at present no sure basis for accounting for the wide range of temperatures of the results. However, although no conclusions are justified, certain possible interpretations are implied. To evaluate these, it is necessary to consider the many factors which may influence the results obtained from any one inclusion or group of inclusions.

#### DISCUSSION

The pegmatites of the southern Black Hills have been intruded into a pre-Cambrian series of complex structure and uncertain age. The pegmatites themselves have been dated by Goodman and Evans (1933). Using the uranium-lead ratio method, they determined that the Bob Ingersoll No. 1 pegmatite was 1,500 million years old.

The country rocks of the area are schists, amphibolites and quartzites. Garnet, staurolite and sillimanite schists predominate. Sillimanite has been recognized in rocks adjacent to most of the pegmatites.

Structural features near the pegmatite contacts indicate that the pegmatitic material behaved as a viscous or plastic mass as it was intruded, and that it was forcibly injected into the country rock under considerable pressure. The schist within several feet of the pegmatites is crumpled and distorted. Induced foliation, rolls and sharp contacts are common. There has been little chemical alteration of the country rock; the only visible change that has taken place is the formation of a tourmalinized zone one to six inches thick in the schist at the contacts of almost all of the pegmatites.

The structural and mineralogic features associated with their contacts suggest that the pegmatites were intruded under considerable pressure but no quantitative data are available. Unfortunately, much of the discussion to follow requires some knowledge of the pressures prevailing at the time of pegmatite intrusion and crystallization, if all of the observations are to be interpreted fully. An attempt is made to interpret the observations in terms of the pressures most probably present, and where possible, maximum and minimum pressures and their effects are indicated.

The primary purpose in most studies of fluid inclusions is to learn the temperature of crystallization of the minerals in which they occur. Sorby, in his original work, dealt principally with minerals presumed to



have crystallized from aqueous solutions at relatively low pressures and temperatures, and in his study he made certain basic assumptions that he used to interpret what he saw. It has since been pointed out (Bailey and Cameron, 1951) that in each new study of fluid inclusions, it is necessary to reconsider the seven assumptions that are basic to the method. Each assumption must be evaluated anew, in terms of evidence obtained in that particular study, and an attempt must be made to relate them to each other and to the problem as a whole. The seven basic assumptions are as follows:

1. The fluid exactly filled the cavity at the time of formation.
2. Primary and secondary types of inclusions can be distinguished.
3. The solutions were aqueous; no gases such as  $\text{CO}_2$  or  $\text{H}_2\text{S}$  were present.
4. Pressure at time of inclusion was low or can be estimated.
5. No change in ratio of cavity volume to liquid volume has taken place since the inclusions were formed.
6. No gain or loss of material has occurred in the cavity.
7. The sample is representative.

Assumption 1, that the cavity was exactly filled by fluid, is probably correct for all of the inclusions considered in this study. If temperatures were much above  $500^\circ\text{C}$ . at the time of crystallization, the inclusions may have been filled by a gas, rather than by a liquid. Whether this is true or not will depend upon the composition of the fluids and the pressure on the system, as well as the temperature of formation, since the presence of dissolved salts will lower the vapor pressure and raise the critical temperature of water. The state of the fluid is unimportant to the method, however; true temperatures of crystallization can be calculated in either case as long as pressure-volume-temperature relationships of the solution, and the pressure at the time of crystallization are known.

If the fluid was included as a gas, it must necessarily have filled the cavity at the time of inclusion. If it was included as a liquid, it would fill the cavity or that part of it which was unoccupied at that time. If a gas was also present, simultaneous inclusion of both phases might take place, but that appears extremely improbable. A solid is present in some of the cavities in spodumene, but it may actually be just an inclusion of spodumene itself; in any event, since the solid particles do not appear to go into solution at elevated temperatures, their presence serves only to decrease the volume of the cavity.

The inclusion of a gas phase and a liquid phase simultaneously would have a much more serious effect, as has been pointed out elsewhere (Cameron, Rowe and Weis, 1953). In some studies of fluid inclusions, such a situation seems possible, but inclusion of a vapor and a liquid phase at the same time in inclusions in Black Hills beryl does not appear likely. The peculiarities in behavior expected if two phase inclu-

sions had formed were not observed. Cavities in beryl from several Connecticut pegmatites have been found to contain  $\text{CO}_2$ . The presence of at least minor amounts of  $\text{CO}_2$  should therefore probably be suspected in all the pegmatites of that district. Visual evidence suggests that neither  $\text{CO}_2$  nor any other gases are present in the inclusions in Black Hills pegmatite minerals. It has been found by measurement and calculation that expansion curves of salt solutions lie on one side of the calculated curve for pure water and the expansion curves for water plus  $\text{CO}_2$  lie on the other side of the calculated curve. All expansion curves measured in elongate inclusion in Black Hills pegmatite minerals lie on the salt solution side of the calculated curves. The addition of  $\text{CO}_2$  or other gases should lower the critical temperature of water; the presence of liquid phases at temperatures as high as  $515^\circ\text{C}$ . in inclusions in beryl shows that critical temperatures have been raised. The only set of conditions possible that may have resulted in the inclusion of two phases would be those under which combinations of liquid water and water vapor are present in the system. This appears extremely unlikely. Even moderate pressures would serve to keep concentrated salt solutions in a liquid state. Keevil (1942) has given the vapor pressure of a saturated solution of NaCl in water at  $500^\circ\text{C}$ . as 318 atmospheres; saturated KCl and water at  $500^\circ\text{C}$ . has a vapor pressure of only 204 atmospheres. Pure water at  $500^\circ\text{C}$ . requires a pressure of about 690 atmospheres to maintain its critical density (the density of liquid water at its critical temperature,  $374^\circ\text{C}$ .). The minimum and maximum pressures are therefore 204 and 690 atmospheres, and the solutions in the inclusions, if the compositions are inferred correctly, must have vapor pressures somewhat between these limits. In the absence of more precise data, a pressure about halfway between the two extremes (450–500 atmospheres) should give at least an approximation of the proper magnitude. One mile of rock cover (specific gravity 2.7) can exert a lithostatic pressure of 420 atmospheres; it would appear probable that pressures in excess of that equal to two miles of rock cover would be ample to account for the observed behaviors of all of the inclusions. Such pressures are quite in keeping with the geologic occurrence of the pegmatites, and they might conceivably have been two or three times higher. As temperatures dropped during the crystallization of the pegmatite, pressures could be expected to remain fairly constant, thereby maintaining the fluids in a liquid state throughout the range of crystallization. Even if pressures were not constant, a lowering of pressure to the point where it would equal the vapor pressures of the fluids would result in the instantaneous formation of a vapor phase, and the inclusions would again consist of only one phase. Features within the pegmatites do not appear

to favor the assumption that pressure changes of considerable magnitude took place during crystallization. Although crystallization might be expected to reduce the volume of the pegmatitic material somewhat, any significant thickness of rock cover would probably exert enough pressure to take up all of the "slack" formed in this way, maintaining original pressures with little change. If the rocks surrounding the pegmatites had sufficient rigidity to resist external pressures, the pressures inside the pegmatites might be greatly reduced, but the extent and the plastic nature of wall rock deformation indicate that wall rocks were not at all rigid.

Fluctuations in pressure due to external forces appear equally improbable. No evidence of post-intrusive deformation has been seen in the pegmatites; furthermore, large unfractured crystals are not likely to grow in an environment characterized by fluctuating pressures and the structural disturbances that would probably accompany them. The laws of probability appear to favor the interpretation that the fluids were in a liquid state when they were included in the cavities, unless both pressures and temperatures were substantially below the minimum figures listed above, as they might have been if they were the result of hydrostatic, rather than lithostatic load. The possibility of higher pressures and temperatures is discussed in a section below.

Assumption 2, that the inclusions are primary, is considered above. All visible criteria indicate that Type I fluid inclusions are related to primary crystallographic features, and that they bear no relationship to recognizable secondary features. On the basis of visual criteria, Type I inclusions represent the only group likely to be primary.

The third assumption, that the solutions are aqueous, has been answered in part. Behavior of the fluids at various temperatures, measurements of freezing temperatures, the presence of a liquid phase at temperatures up to 515° C., limited information on analyses (Ingerson, 1947, p. 378), the low viscosity of the solutions, and the expansion curves actually measured, can all be best explained by the known properties of dilute solutions of simple salts in water. No other liquids that are likely to occur in pegmatites are known to have this combination of physical and chemical properties. Concentration of some of the solutions, at least, must be fairly high, since the critical temperature of a 10% KCl solution is 435° C. and 81 inclusions in beryl were observed to contain a liquid phase at temperatures between 450 and 500° C. It is hardly possible that the fluids are saturated at 500° C.; this would result in such a marked degree of supersaturation at room temperatures that crystallization of salts would be almost certain to occur. (Water at 25° C. is saturated by 26.5% KCl.) The presence of CO<sub>2</sub> is not indicated by the

behavior or the expansion curves of the liquids. More soluble gasses might be present in the cavities, provided they do not constitute a sufficiently large proportion to cause a significant variation in the expansion curve of the solution, but the presence of soluble gas in the inclusions has not been detected.

Sorby's original paper on fluid inclusions assumed that they represented samples of the mother liquor from which the mineral crystallized. The apparent composition of the fluid inclusions in beryl are quite different from the composition of the mother liquor which many geologists visualize as having produced pegmatites. It may be possible that small quantities of water, containing various concentrations of the more soluble salts, were present in the original parent material as immiscible droplets.

Another possibility is suggested in a paper by Raistrick (1949, p. 360), who describes a melt of sodium trimetaphosphate from which crystals were being grown. He states that bubbles of what was believed to be moisture were formed at the surface of the growing crystals. An analogous process is plausible; crystallization of anhydrous pegmatite minerals might cause water droplets to form as local concentrations at the growing crystal face, and some of them might become trapped in cavities as the crystal continues to grow. The concentration of water in solution might be variable over short distances; this, together with local variations in rates of crystallization might in turn cause variations in the amount of water formed locally, and thereby account for the erratic distribution of the fluid inclusions. Their abundance, and the availability of highly soluble salts such as KCl and NaCl for solutions, might also vary locally as a result of factors only indirectly related to the crystallizing mineral and its composition. These ideas belong to the realm of speculation at present, but they appear to be possible, and further work may add information as to their validity.

Inclusions formed in this way would be perfectly valid indicators of crystallization temperatures, even though they did not represent a sample of the parent fluid from which the crystals formed. Sorby's original idea is none the less sound, however. In many minerals one would expect that a sample of the parent fluid could be entrapped and preserved. If pegmatites crystallize from true igneous melts, such a sample should now consist of either a glass with a composition near the average composition of the pegmatite, or a heterogeneous mixture of small crystals, including at least the commoner and more abundant minerals found in the pegmatite. It may be that inclusions of this type actually exist; many pegmatite minerals contain fine-grained inclusions of unknown composition that may be true samples of the fluid from which the pegmatites grew. Certainly they justify further investigation as a check on that possibility.

Assumption 4, that pressure at the time of crystallization was small (that is, not far above the vapor pressure of the solution) or can be estimated, has been considered in part in a preceding section. It is undoubtedly one of the most difficult, as well as one of the most important assumptions to answer. It has been shown that pressures in excess of 400 atmospheres were almost a certainty if a liquid state is to be maintained at 500° C., as it was in a few of the inclusions; thus we have a fairly reliable lower limit for pressures during crystallization. The establishment of an upper limit for pressures is a much more difficult matter. There is no evidence of any kind that provides conclusive information, although all of the geologic features associated with the pegmatites are compatible with the idea that pegmatites formed at a considerable depth. Deformation of wall rock by intrusion, formation of thin tourmalinized zones in the wall rocks at the pegmatite contacts, association of the pegmatites with rocks of medium to high metamorphic grade, the size of the pegmatite crystals, suggesting a stable, deep-seated environment during cooling, all could be explained by crystallization at depths up to 10 miles or more, but none of these features necessarily requires such depths. It has long been postulated that volatile constituents concentrated in the rest magma are responsible for the giant crystals in pegmatites. Presumably these volatiles are held within the pegmatitic fluid until crystallization is complete, and this might require considerable pressure—but how much pressure? Unfortunately, neither geologic history nor visible features provide a useful answer. The fact that deformation of the wall rocks as a result of intrusion was by folding and recrystallization, rather than by fracturing, appears to favor a substantial depth, but the rest of the features could have formed over a wide range of pressures. The only upper limit for pressure is that point at which metamorphism of the pegmatites themselves would begin, and that point has never been satisfactorily established.

Assumptions 5 and 6 can be considered together. The possibility of change in cavity volume has been discussed by others, and is not important in the temperature range that we are concerned with. No evidence of deposition on the insides of the cavities was seen, but if additional beryl was deposited, it probably could not be detected. The amount of beryl likely to have been deposited from an aqueous solution, even at high temperatures, is not likely to have much effect on the magnitude of the results. The change in cavity volume—liquid-volume ratio through the gain or loss of material from the cavity is a different matter. Kennedy (*Econ. Geol.*, 1950, p. 543) cites work by Grunig which shows that water under pressures of 1500 atmospheres and at a temperature of 150° C. can be forced into inclusions in fluorite. The probability of diffusion of material in or out of inclusions in beryl appears to be much

less, however. Liquid  $\text{CO}_2$ , which would exert a pressure of nearly 70 atmospheres at room temperatures, has been described in beryl from Connecticut (Cameron, Rowe and Weis, 1953) and pressures of that magnitude, applied over a long period of time, should cause some migration of material out of the cavities if migration of ions or molecules was possible. Apparently the space lattice of beryl is not sufficiently "porous" to permit such change to take place.

Leakage was noted in a number of specimens as they were being heated. Quartz gave the greatest difficulty in this respect, but even beryl was seen to fracture in a number of specimens. Fracturing and leakage at some time during the geologic past also remains a possibility. The behavior of the fluids in the inclusions does not favor this possibility. Leakage would be expected to reduce the density of the fluids in the inclusion, and this, in turn, would result in a larger vapor bubble and higher temperatures of disappearance, up to a certain point, but if more liquid was lost, the vapor-liquid ratio would alter enough to cause the liquid phase to shrink and disappear or to fade and disappear as it is heated. Behavior of these types was extremely rare; only 24 of more than 1100 inclusions showed shrinking or fading liquid phases. It is very unlikely that many of the cavities leaked just enough to cause high disappearance temperatures, yet so few leaked enough to cause the unusual behaviors. Similarly, the addition of material to the cavities is not indicated. Additional material might be expected to give low temperatures, whereas temperatures tended to be high.

Assumption 7, that the sample is representative, must be answered from each crystal, zone and pegmatite studied. The results shown in Fig. 7 for Zone 1 in the Peerless pegmatite, for example, are probably not significant. Fifteen inclusions, that gave results covering a range of 150 degrees, are of questionable significance indeed, although comparison of the results with those from the adjacent Zone 1a, in which 174 inclusions were measured, shows fairly good agreement in range, at least. However, the necessity of compiling a large volume of data cannot be overemphasized. Of the pegmatites described in this study, the writer feels confident that only one, the Highland Lode pegmatite, has been adequately sampled and studied. The others have trends that are suggestive, but subsequent work might modify those trends considerably, and more data are definitely needed. Unfortunately, a study of this type is tedious and time-consuming, and not all pegmatites, nor all crystals, contain visible primary type inclusions. In addition, the complexities of behavior and interpretation demand the most careful observation; the problems are numerous enough even when all possible data has been gathered.

## INTERPRETATION

*Temperature zoning*

In view of the many uncertainties involved in the evaluation of the assumptions, it is obvious that no definite interpretations of the results are possible. Despite the difficulties, however, certain aspects of the results require some comment. It must be kept in mind that the objective of this section is not to present conclusions; many of the ideas presented are highly speculative, and are intended only to provide suggestions that may serve as useful guides in the course of further work of this type.

The original objective of the study was to determine whether temperature zoning existed in correspondence with mineral zoning. Only one pegmatite yielded abundant data for more than two zones. This pegmatite, the Highland Lode mine, contained four zones, and inclusions were measured in three zones (Fig. 5).

Interpretation appears simple if the mean temperature of each zone is considered. The outermost zone for which data was obtained had a mean temperature of  $313^{\circ}$  C., the next zone  $314^{\circ}$ , the outer part of the core  $290^{\circ}$  and the inner core gave a mean temperature of  $257^{\circ}$  C. Results from the outer zone may be incomplete. However, the difference between the highest and lowest mean, even considering the inner part of the core as a separate unit, is only  $107^{\circ}$  C., whereas the differences between the highest and the lowest temperatures measured in each zone are  $93^{\circ}$ ,  $85^{\circ}$  (for the upper group),  $62^{\circ}$  and  $185^{\circ}$ , for zones 3, 4, 6a (outside), and 6a (inside), respectively. Thus the range of temperatures measured in individual zones has a magnitude comparable to the difference between the highest and lowest mean.

Although no explanation can be offered to account for this wide range of temperatures formed in individual zones or in individual crystals, the writer feels that the existence of a trend toward lower mean temperatures nearer the core may be significant, and that it may be explained by decreasing temperatures during crystallization. However, this apparent trend was found in only one pegmatite, and is hardly sufficient to prove the original hypothesis. It appears to support the hypothesis, *in this particular pegmatite*.

The Peerless pegmatite near Keystone, yielded extensive data from only one zone, but the mean temperatures from the three zones studied suggest an increase in temperature from the walls inward (Fig. 7). This may be due in part to insufficient data, but the geologic history of the pegmatite also undoubtedly plays an important role. The Peerless pegmatite is a complex body, consisting of at least two, and possibly three limbs. Detailed study by the U. S. Geological Survey has shown that it was very probably formed as a result of two or more separate intrusions,

and this complex history may account for the trends that appear to contradict the results found in the Highland Lode.

Table 2 summarizes in composite form the results from all of the pegmatites. Each dot on the table represents the mean of all temperature determinations from one zone in one pegmatite. It will be noted that no clear-cut trend toward decreasing temperatures in the interior of the pegmatites has been established. Obviously, much more data, from many more pegmatites, is desirable.

#### *Temperatures of crystallization*

The determination of true temperatures of crystallization is not a necessary prerequisite in the recognition of temperature zoning, as long as the relative differences in temperature are known. It is of interest, however, to see how far the interpretation of results can be carried, and how much information they can provide in determining the true tem-

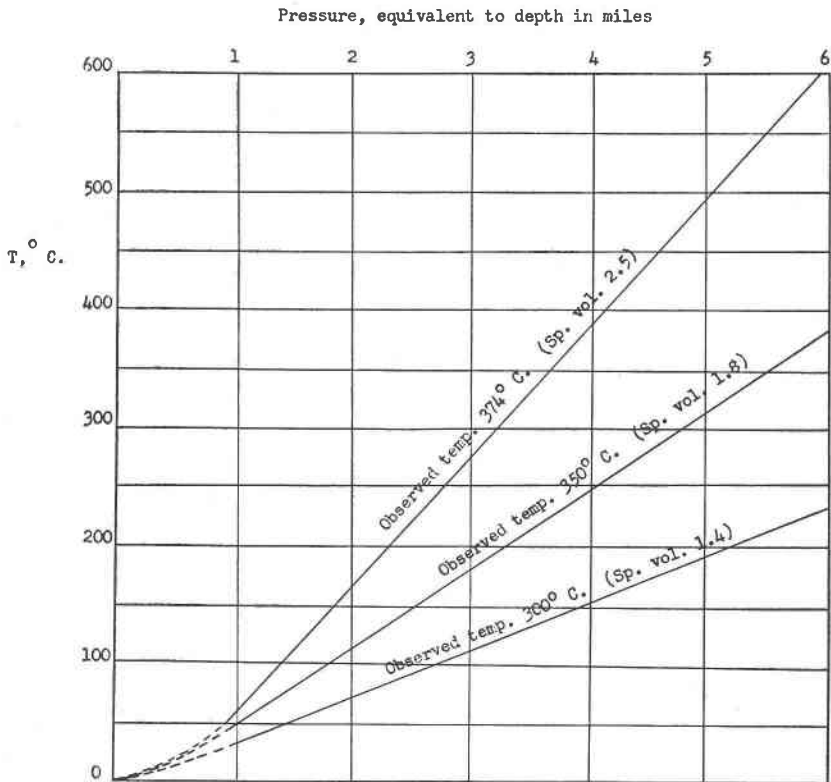


FIG. 8. Curves showing temperature to be added to observed temperature of disappearance of vapor phase. Corrections are for inclusions containing pure water.



peratures of pegmatite crystallization. To do this requires an estimate of the pressures that existed at the time of crystallization, and a knowledge of the pressure-volume-temperature relationships of the fluids in the cavities.

It appears likely that pressures were equivalent to the weight of a column of rocks between 1 and 10 miles thick (420 to 4200 atmospheres). The compositions of the fluids in the inclusions are imperfectly known, and practically no pressure-volume-temperature information is available for salt solutions. The only accurate pressure-volume-temperature data available are for pure water, and that, therefore, constitutes the only source of information useful for predicting behavior.

Figure 8 gives pressure corrections required for inclusions containing pure water. Similar correction curves for salt solutions cannot be calculated from data now available, but since their vapor pressures are lower, the corrections for pressure will almost certainly be greater for salt solutions than for pure water. The significance of the curves in Fig. 8 lies in the fact that a moderate increase in observed temperatures of disappearance results in a marked increase in the size of the correction required, making the relative differences between high and low observed temperatures much greater. Perhaps if the pressure corrections could be applied with assurance to the results presented in this paper, the differences between temperatures observed in the various zones would be more clear-cut, and the evidence for temperature zoning might be somewhat stronger. Although none of the evidence is conclusive, the writer feels that pressures at the time of formation were at least the equivalent of two miles of rock cover. Inclusions giving observed temperatures in the 400–500° C. range would therefore probably require corrections of at least 200 to 300°C. Evidence from fluid inclusions thus appears to indicate that pegmatites may have begun to crystallize at temperatures as high as 600 to 800° C. These figures are put forth purely as a tentative hypothesis, subject to revision in the light of further investigations, and they should not be accepted until abundant supporting evidence of a more precise nature is available.

#### SUMMARY AND CONCLUSIONS

The original objective of the study was to determine whether temperature zoning existed in correspondence with mineralogical zoning in pegmatites. This objective was not achieved. Only one pegmatite, the Highland Lode, provided adequate data, and while a trend toward decreasing temperature in interior zones is suggested, the wide range of temperatures measured in each of the four zones makes the validity of the interpretation questionable.

The results have also shed some light on the possible range of temperatures at which pegmatite crystallization took place. Actual measurements ranged from 216° to 515° C. Although pressure corrections cannot be accurately estimated, a pressure correction of only 400 to 800 atmospheres might add as much as 200 to 400° to these values, and place them in the same range as might be expected in crystallizing granites. Even though temperature estimates are necessarily more qualitative than quantitative, the results appear to indicate that temperatures were high—higher, at least, than earlier fluid inclusion studies have indicated.

The need for much more information has been demonstrated throughout the course of the investigation. It is necessary to have a more accurate basis for evaluating the many possible sources of error, particularly those related to pressures at the time of crystallization, composition of the fluids, and the pressure-volume-temperature relationships of the fluids. The possibility that material has been added or subtracted from the cavities needs further study. The significance of the wide range of temperatures measured in individual crystals and individual zones must also be determined.

Several lines of investigation have been brought to light that may yield important dividends to future investigators. If they are carried out, their results may be expected to add considerably to our knowledge of the history of pegmatite crystallization. Fine-grained, heterogeneous solid inclusions merit attention as possible samples of the original pegmatitic parent material. Accurate quantitative chemical analyses of the fluid inclusions are badly needed. When they have been made, a study of the pressure-volume-temperature relationships of the fluids should be undertaken. Such studies would be of tremendous assistance in the interpretation of existing data and any additional data made available in the future. Studies of fluid inclusions should be continued, in as many pegmatites and as many localities as possible, to accumulate more information of the type presented here. Such studies may unearth valuable information bearing on interpretation, as well as providing more data on the temperatures themselves.

The fact that dissolved salts have the effect of lowering vapor pressure and raising the critical temperature suggests the possibility that many deposits now believed to be pneumatolytic may actually be hydrothermal. This concept appears to be worthy of investigation.

#### ACKNOWLEDGMENTS

Much of the work described in this paper was carried out in 1950 and 1951 in the Department of Geology at the University of Wisconsin, where it was submitted as a thesis for the Ph.D. degree. Subsequent work was done at the University of Virginia in 1951 and 1952.

The writer wishes to acknowledge the assistance of Dr. E. N. Cameron of the Department of Geology, University of Wisconsin, who supervised the original work. Dr. V. W. Meloche and Dr. Harvey Sorum, of the University of Wisconsin Department of Chemistry were also extremely helpful. Dr. R. B. Rowe, of the Canadian Geological Survey, assisted considerably in his many discussions with the writer while the laboratory work was in progress.

The writer also wishes to express his thanks to Earl Ingerson, Michael Fleischer and J. K. Grunig, all of the U. S. Geological Survey, for their critical review of the manuscript.

## REFERENCES

- BAILEY, S. W., AND CAMERON, E. N. (1951), Temperatures of mineral formation in bottom-run lead-zinc deposits of the upper Mississippi Valley, as indicated by liquid inclusions: *Econ. Geology*, **46**, 626-651.
- BENEDICT, MANSON (1939), Properties of saturated aqueous solutions of potassium chloride at temperatures above 250° C.: *Jour. Geology*, **67**, 252-276.
- CAMERON, E. N., JAHNS, R. H., MCNAIR, A. H., AND PAGE, L. R. (1949), Internal structure of granite pegmatites: *Econ. Geology, Monograph 2*.
- , ROWE, R. B., AND WEIS, P. L. (1953), Fluid inclusions in beryl and quartz in pegmatites of the Middletown district, Connecticut: *Am. Mineral.*, **38**, 218-262.
- DREYER, R. M., GARRELS, R. M., AND HOWLAND, A. L. (1949), Liquid inclusions in halite as a guide to geologic thermometry: *Am. Mineral.*, **34**, 26-34.
- GOODMAN, C., AND EVANS, R. D. (1941), Age measurements by radioactivity: *Geol. Soc. Am., Bull.* **52**, No. 2, p. 534.
- HARNED, H. S., AND OWEN, B. B. (1943), The physical chemistry of electrolytic solutions. Reinhold Pub. Co., New York, N. Y., p. 272.
- INGERSON, EARL (1947), Liquid inclusions in geologic thermometry: *Am. Mineral.*, **32**, 375-388.
- KEEVIL, N. B. (1942), Vapor pressure of aqueous solutions at high temperatures: *Jour. Am. Chem. Soc.*, **64**, 841-850.
- KENNEDY, GEORGE (1950), Pressure-volume-temperature relations in water at elevated pressures and temperatures: *Am. Jour. Sci.*, **248**, No. 8, 550-564.
- PAGE, L. R., ET AL. (In preparation), Pegmatite investigation 1942-1945, Black Hills, South Dakota: *U. S. Geol. Survey, Prof. Paper 247*.
- RAISTRICK, B. (1949), Crystal growth. Discussions of the Faraday Society, No. 5, p. 360.
- SORBY, H. C. (1858), The microscopical structure of crystals: *Quart. Jour. Geol. Soc. London*, **14**, 453-500.

*Manuscript received Sept. 12, 1952.*