THE AMERICAN MINERALOGIST

JOURNAL OF THE MINERALOGICAL SOCIETY OF AMERICA

Vol. 40 SEPTEMBER-OCTOBER, 1955 Nos. 9 and 10

VARIATION OF COMPOSITION AND PHYSICAL PROPERTIES OF TOURMALINE WITH ITS POSITION IN THE PEGMATITE*

M. H. STAATZ, K. J. MURATA, AND JEWELL J. GLASS, *U. S. Geological Survey, Washington 25, D. C.*

ABSTRACT

Tourmaline crystals of the bizonal, lepidolite-bearing Brown Derby pegmatites no. 2 and no. 3 of Gunnison County, Colo., show a consistent variation in color, refractive index, and composition with position in the pegmatite. Starting with the outer wall of the pegmatite and going inward toward the core, the colors of the tourmaline crystals are black, dark green, blue, light green, and pink. The omega index decreases from 1.655 to 1.635 in the same direction.

The concentration of K, Rb, Cs, Pb, Be, and Li in tourmaline increases toward the pegmatite core. Fe, Mg, Ti, Na, Co, Ni, Cr, and V decrease in concentration toward the core; the last four are restricted to the crystals of the outermost part of the pegmatite. The main variation in tourmaline composition is a substitution of lithium for iron. Elements that remain more or less constant are Ga, Sr, Sc, Zr, Nb, Sn, Cu, Bi, and Zn. The concentrations of Mn, Y, and La show an interesting maximum at an intermediate position between the pegmatite wall and core.

Most of the spatial variations in composition of the tourmaline crystals may be explained on the basis of a gradual change in the composition of a single pegmatite fluid crystallizing in a closed system. Competition among different ions for sites in the crystal structure of tourmaline is invoked to explain the maxima in the variation trends. The variation trends of sodium and calcium, which are out of harmony with the variation trends in the composition of the pegmatite fluid, are apparently controlled by the charge requirements connected with isomorphous substitutions in the tourmaline structure.

INTRODUCTION

Tourmaline is well known for its wide variation in chemical composition and physical properties. Its atomic structure allows extensive substitution of ions of octahedral coordination such as Fe'', Mg, Li, and Al, and also those of somewhat larger coordination such as Na and Ca (Donnay and Buerger, 1950). The mineral also occurs in a wide variety

---

* Publication authorized by the Director, U. S. Geological Survey. This report concerns work done partly on behalf of the U. S. Atomic Energy Commission, and is published with the permission of the Commission.

of rocks, which shows that it can crystallize in quite different chemical environments, incorporating within itself whatever appropriate ions are available.

That the color and composition of tourmaline are grossly related to the kind of rock in which it occurs has been recognized for a long time—the common black variety, rich in iron, is found in granites, granite pegmatites, and schists; the brown magnesian variety occurs characteristically in dolomites and granular limestones; and the varicolored lithian variety is restricted to granite pegmatites. The present study deals with variation in composition and physical properties of tourmaline within zones of granite pegmatites. Our interest in this problem was first aroused by the systematic variation in the mineral's color from the outside to the center of certain pegmatites of the Quartz Creek pegmatite district, Gunnison County, Colo., during field work on behalf of the Division of Raw Materials of the U. S. Atomic Energy Commission.

Many authors, including Scharizer (1889) and Landes (1928), have emphasized the fact that in lithium pegmatites black tourmaline occurs in the outer part and the other variously colored varieties, in the inner part. Jenks (1935) studied the manner in which tourmaline varied in its optical properties with position in the lithium pegmatites of Portland, Conn. He published a very striking diagram showing progressive decrease of refractive indices from maximum values in crystals of the wall zone to minimum values in those of the pegmatite core. Unfortunately, he did not make any chemical analysis of these well-located samples. On the other hand, practically all of the chemical and spectrographic analyses of tourmaline in geologic literature are accompanied by information of only the most general kind as to the occurrence of the specimens.

We are concerned with precise locations of tourmaline crystals within the pegmatite because we wish not only to work out the spatial variation in composition of the mineral, but also to explore the thesis that this variation in part reflects changes in composition of the pegmatite mother liquor throughout the depositional history. Holland and Kulp (1949) discussed the general problem from a theoretical standpoint and have pointed out the lack of suitable data to check the theoretical conclusions. Preliminary studies of variation in composition of beryl and plagioclase with position in the pegmatite have been published by others (Page et al., 1953). Tourmaline seems to be especially suitable for such a study because it permits extensive isomorphous substitutions, involving many different elements. A list of elements compiled from analyses of tourmaline reported by Shainin,[1] de Azcona (1947), Carobbi and Pieruccini (1947), Warner (1935), and the authors includes 36 elements.

---

[1] Shainin, V. E., Unpublished analyses of tourmaline from the Newry-Rumford area, Maine.

FIELD RELATIONSHIPS

The Quartz Creek pegmatite district has an area of about 30 square miles and contains 1803 mapped pegmatites (Staatz, and Trites, 1954). Only 48 of the pegmatites contain tourmaline, and most of these show only a few crystals. The relative scarcity of the mineral in the district stands in sharp contrast to its widespread occurrence in pegmatites of other districts. Some units in the lepidolite-bearing pegmatites of the district, however, contain as much as 3 per cent tourmaline by volume.

In the field, the most striking variation of the mineral is in its color, so field relationships will be described in terms of the color of the specimens. The tourmaline is black, dark green, blue, light green, and pink. The dark-green, blue, light-green, and pink varieties are found only in the lepidolite-bearing pegmatites; the black variety occurs in both lepidolite-bearing and nonlepidolite-bearing pegmatites. Of the 48 tourmaline-bearing pegmatites, 38 contain only the black variety.

In many places in the nonlepidolite-bearing pegmatites, black tourmaline occurs in small pods of coarse-grained quartz or quartz-perthite pegmatite in an otherwise homogeneous pegmatite. Black tourmaline has been found adjacent to quartz, perthite, albite (ordinary and cleavelandite varieties), muscovite, beryl, garnet, biotite, monazite, columbite-tantalite, and gahnite, but not adjacent to lepidolite and topaz. In lepidolite-bearing pegmatites, black tourmaline is found only in the outer zones that are completely free of lepidolite, where it is commonly restricted to the extreme hanging-wall or footwall part.

Dark-green tourmaline is found usually in the zone adjacent to the lepidolite-bearing zone. Medium-green to yellowish-green tourmaline is found either in zones containing lepidolite or adjacent zones and is common in outer parts of lepidolite-bearing units and the inner parts of the adjacent unit. This variety of tourmaline is never in contact with lepidolite but occurs in the cleavelandite-quartz parts of the zone. Only pale-green and pink tourmaline crystals occur adjacent to lepidolite in lepidolite-bearing units. These two varieties frequently occur together, for example, samples 12 and 13 of Table 2; the pink variety is more abundant.

In zoned pegmatites of the Quartz Creek district having an albite-quartz wall zone and a cleavelandite-quartz-lepidolite core, the tourmaline on the hanging wall is black, becomes dark green inward and gradually lightens through shades of green to light green in the center with the lepidolite, and then darkens again as one crosses the core towards the footwall side. A dark-blue variety of tourmaline occurs as massive wavy bands in lepidolite-bearing pegmatites, where it is found in part with the medium-green and in part with the dark-green tourmaline. It was never found in close association with lepidolite. There is often a thin band of small reddish-brown garnets in the center of the blue tourmaline bands.

Collection of Samples

The relationship between color and location of tourmaline in different pegmatite units was noted along the entire length of several pegmatites. It is best seen in the back of two cuts 5 feet long (Fig. 1) in the Brown Derby no. 2 and Brown Derby no. 3 dikes. These two pegmatites are remarkably similar in composition and consist of an albite-quartz wall zone surrounding a cleavelandite-quartz-lepidolite core. The mineralogy of these two dikes, as exposed in the two cuts, with estimated volume

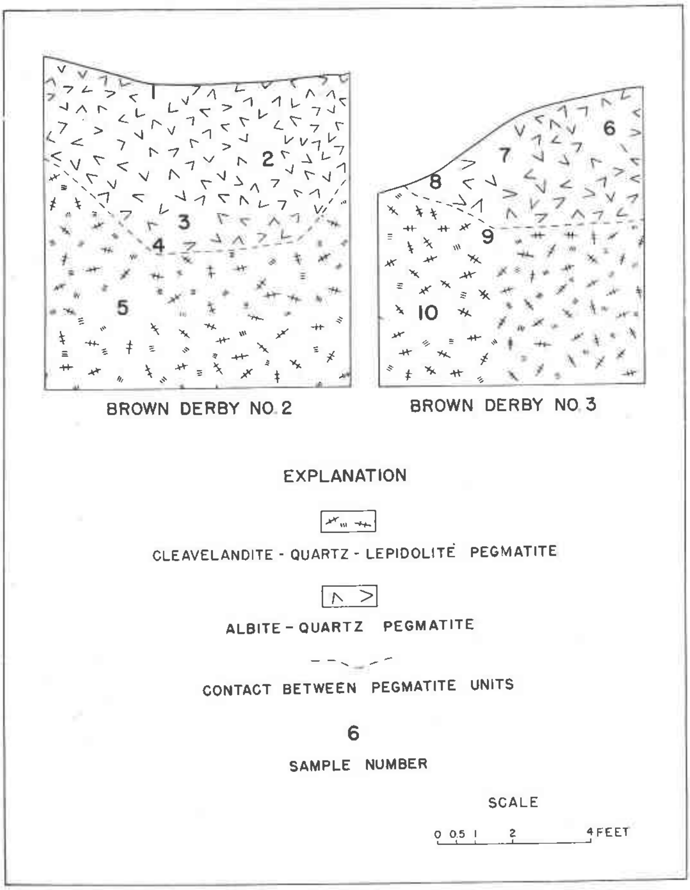

FIG. 1. Backs of vertical cuts in Brown Derby no. 2 and no. 3 pegmatites, showing location of the tourmaline samples.

percentages of the various minerals is presented in Table 1.

The mineralogy of the dikes as a whole is similar to that of the two cuts but shows some variation, chiefly in the presence of 1 to 2 per cent biotite in the wall zone of both dikes and lesser amounts of lepidolite in the core of the Brown Derby no. 2. Lepidolite is chiefly concentrated in the central part of the cores with only a rare aggregate close to the core-wall zone contact.

TABLE 1. ESTIMATED VOLUME (IN PER CENT) OF MINERALS FOUND IN PEGMATITES

Mineral	Brown Derby No. 2		Brown Derby No. 3	
	Wall zone (avg. grain size $\frac{1}{4}$ in.)	Core (avg. grain size $1\frac{1}{2}$ in.)	Wall zone (avg. grain size $\frac{1}{8}$–$\frac{1}{4}$ in.)	Core (avg. grain size 2 in.)
Cleavelandite	—	54	—	70
Albite	64	—	59	—
Quartz	30	25	35	25
Lepidolite	—	20	—	4
Muscovite	4	1	5	<1
Tourmaline	2	<1	1	<1
Columbite-tantalite	—	—	—	<1 (trace)
Beryl	—	—	—	<1 (trace)
Topaz	—	<1	—	—
Garnet	<1	—	<1	—

A suite of five tourmaline crystals was collected from the back of each of the two cuts (Fig. 1). These cuts each show a part of the hanging-wall edge of the pegmatite, the whole thickness of the wall zone on the hanging-wall side, and most of the core. The cuts are not deep enough to show the footwall side of the pegmatite and only in the cut in the Brown Derby no. 2 is any of the footwall wall zone exposed.

TECHNIQUES OF STUDY

The ten tourmaline specimens were carefully collected and separated in the field from other pegmatite minerals. Though megascopically appearing fairly clean, when examined under the microscope they were found to contain various impurities. Each sample was then carefully crushed, hand picked, and separated from as many impurities as possible with heavy solutions. Except for inclusions, such as bubbles of liquids, and microscopic crystalline intergrowths, the final samples were reasonably pure. Pure grains were selected for optical determinations. The optical data, including notations about recognizable impurities, are to be found

TABLE 2. OPTICAL PROPERTIES OF TOURMALINE CRYSTALS FROM SUCCESSIVE POSITIONS IN TWO PEGMATITES

Specimen No.	*Pegmatite*	*Color*	N_ϵ	N_ω	*Birefringence*	*Pleochroism*	*Microscopic inclusions*
1	Brown Derby No. 2	Black	1.626	1.653	.027	Gray to black	Crystals & liquid
2	Brown Derby No. 2	Dk. greenish brown	1.629	1.655	.026	Cs.* to greenish brown	Qtz. & liquid
3	Brown Derby No. 2	Dk. bluish green	1.624	1.650	.026	Cs. to bluish or greenish	Liquid & "dust"†
4	Brown Derby No. 2	Blue	1.624	1.644	.020	Cs. to blue	Qtz.
5	Brown Derby No. 2	Pink	1.618	1.635	.017	None	Cs. mica
6	Brown Derby No. 3	Dark olive	1.629	1.650	.021	Pale green to olive	Qtz.
7	Brown Derby No. 3	Yellowish green	1.623	1.644	.021	Cs. to yellowish green	Qtz. & "dust"
8	Brown Derby No. 3	Grayish blue	1.623	1.645	.022	Cs. to gray blue	Qtz. & "dust"
9	Brown Derby No. 3	Light green	1.622	1.644	.022	Cs. to gray blue	Qtz. & "dust"
10	Brown Derby No. 3	Pink	1.619	1.635	.016	None	Qtz.
Supplementary data							
11	Opportunity No. 4	Pink	—	1.637			
12	Brown Derby No. 1	Pink	—	1.643			
13	Brown Derby No. 1	Pale green	—	1.643			
14–24	Other pegmatites of district	Black	—	1.652–1.664‡			

* Cs. is symbol for colorless.

† Dust refers to minute opaque inclusions and occasionally to liquid or bubble inclusions.

‡ The two lowest values of N_ω among these black tourmaline crystals 1.652 and 1.655, were shown by specimens from lepidolite-bearing pegmatites.

in Table 2. Supplementary data based on tourmaline from other pegmatites of the district are given in the lower part of the table.

Spectrographic analyses (Table 3) were made of the purified sample by means of the *d-c* arc method (Gordon and Murata, 1952). In order to take advantage of the analytical curves already established for a large number of elements in a standard groundmass of 6 parts of quartz and 4 parts of microcline, each sample of tourmaline was mixed with an equal weight of pure quartz powder. This resulted in a mixture that corresponded approximately in composition to the standard groundmass with respect to silica, alumina, and the alkalies. All elements were determined in the range of 2230 to 4730Å excepting Li, K, Rb, and Cs, which were determined in the range of 6350 to 8850Å by means of Eastman *I-L* plates, and the samples and special alkali standards in quartz were buffered with 10 per cent Na_2CO_3.

We were fortunate in obtaining chemically analyzed tourmalines that enabled us to confirm the validity of our analytical curves for two of the most important elements, namely lithium and iron. We are indebted to W. W. Brannock and Leonard Shapiro for special chemical analyses for lithium and iron in this connection, and also to Janet Fletcher for some of the spectrographic determinations of lithium. The precision attained for the various elements was about ±5 per cent of the mean.

The results of spectrographic analysis are presented in Table 3, in which the elements are grouped according to the type of substitutional position they are believed to occupy in the tourmaline structure. All the elements found have been assigned to tourmaline because no correlation could be established between the microscopic impurities observed and the analytical results. For example, the presence or absence of "dust" impurities, reported in Table 2, could not be correlated with the fluctuations of any of the elements. Although a small amount of mica was seen intergrown with sample 5 of the Brown Derby no. 2 pegmatite, potassium in this sample is lower than in the corresponding sample 10 of the no. 3 pegmatite, which contained no mica. Furthermore, if we are satisfied that potassium is an integral part of these two tourmalines, we can then quite readily reach the same conclusion for the other large ions, Pb, Rb, Cs, and Ba, which are also enriched in these tourmalines.

VARIATION OF REFRACTIVE INDICES

The variation in the refractive indices of the tourmaline samples will be discussed only in terms of N_ω, because N_ϵ changes sympathetically with it, and the birefringence varies only moderately over the range of indices represented. The lowest value for N_ω of 1.635, for both samples 5 and 10, is among the lowest to be found in the literature for lithium

TABLE 3. SPECTROGRAPHIC ANALYSES OF TOURMALINE CRYSTALS FROM SUCCESSIVE POSITIONS IN TWO PEGMATITES

Specimen No.	*Color*	*Large ions*										*Ions of octahedral coordination*				
		Na	Ca	K	Pb	Rb	Cs	Ba	Sr	Y	La	Fe	Li	Mn	Mg	Sc
1	Black	1.1	.59	.07	.004	—	—	—	.03	—	—	6.6	.20	.29	>1.0	.001
2	Dk. greenish brown	1.1	.26	.09	.006	.002	—	.001	.004	—	—	5.3	.27	.17	.13	.0005
3	Dk. bluish green	1.4	.36	.04	.006	—	—	—	.003	—	—	4.6	.39	.60	.04	.0005
4	Blue	1.2	.31	.06	.007	.0007	—	—	.003	.08	.03	3.2	.47	.79	.02	.0008
5	Pink	.8	.64	.49	.030	.042	.005	.001	.003	—	—	.07	.61	.22	.01	—
6	Dark olive	1.4	.23	.09	.006	.006	—	—	.007	—	—	6.3	.36	.19	.15	—
7	Yellowish green	1.5	.34	.04	.004	—	—	—	.007	.02	—	4.8	.47	.62	.14	.001
8	Grayish blue	1.5	.27	.06	.005	.0008	—	—	.004	.10	—	4.8	.47	.97	.02	.0005
9	Light green	1.6	.57	.05	.010	—	—	—	.007	—	—	4.2	.60	.88	.01	—
10	Pink	0.8	.74	.70	.058	.032	.002	.002	.003	—	—	.05	.97	.14	.03	—

Specimen No.	*Color*	*Ions of octahedral coordination (continued)*												*Ion of tetrahedral coordination*
		Co	Ni	Cr	V	Ti	Ga	Zr	Nb	Sn	Cu	Bi	Zn	Be
1	Black	.003	.002	.001	.01	.24	.014	.007	—	.007	.0005	—	.09	.0006
2	Dk. greenish brown	—	—	—	—	.22	.009	.006	.022	.006	.0017	—	.10	.0006
3	Dk. bluish green	—	—	—	—	.05	.012	—	.030	.006	.0005	.004	.20	.0004
4	Blue	—	—	—	—	.01	.008	.018	.022	.005	.0005	—	.04	.0003
5	Pink	—	—	—	—	—	.011	—	—	.007	.0007	—	—	.010
6	Dark olive	—	—	—	—	.20	.010	—	.017	—	.0004	.007	.12	.0003
7	Yellowish green	—	—	—	—	.01	.011	.006	—	.02	—	.005	.10	.0006
8	Grayish blue	—	—	—	—	.02	.010	.005	—	.009	.0006	—	.06	.0003
9	Light green	—	—	—	—	.06	.015	—	—	.007	—	—	.16	.0008
10	Pink	—	—	—	—	—	.010	—	—	.005	.0007	—	—	.0063

Elements not found: Ag, Mo, W, As, Sb, Cd, In, Ge, Tl, Th, U, Au, Pt, P, Ta.

tourmaline. The highest value of 1.655 is, however, much lower than 1.682 found by Ward (1931) for a nonpegmatitic tourmaline containing 16 per cent Fe. An unanalyzed black tourmaline with N_ω of 1.698 is reported by Larsen and Berman (1934).

Many authors, including Schaller (1913), Kunitz (1926), and Winchell (1932), have discussed the relationship between refractive indices and composition of tourmaline. Maximum indices are found in iron tourmaline, and the value falls as the iron content falls and the composition approaches either that of magnesium tourmaline or that of lithium tourmaline.

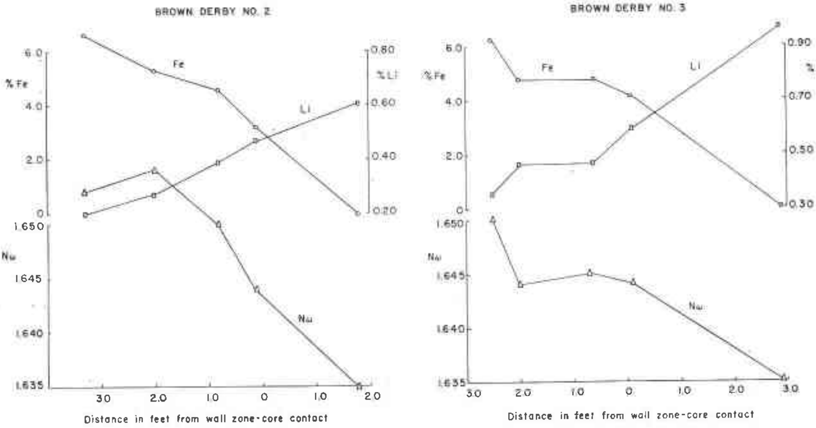

FIG. 2. Relationship between the position of a tourmaline crystal in a pegmatite dike and the crystal's iron content, lithium content, and upper index of refraction (N_ω). Center of pegmatite is to the right.

Figure 2 shows that the relative variations in N_ω of our samples is closely related to the percentage of iron. Sample 1, which is an exception, is the only one that contains appreciable magnesium, which would lower the refractive index. It is also to be noted that for any given percentage of iron the index depends on the lithium content of the samples. The iron content of tourmaline for each pegmatite ranges from 0.05 to 6 per cent, but the values of N_ω run lower in samples from Brown Derby no. 3 because of the higher lithium content.

VARIATION IN CHEMICAL COMPOSITION

Space relationships for the different tourmaline crystals within the two pegmatites are shown by plotting their actual separation in the pegmatite along the abscissa in Figs. 2 and 4. The positions of the various samples were measured in feet from the nearest point on the contact between the wall zone and the core. The outer contact of the pegmatite, which is a more prominent change, was not used because it was not exposed continuously along the back of the cuts. For both pegmatites the outermost tourmaline has been plotted to the left, and the innermost one to the right-hand side of the graph. This is desirable because we shall be constantly referring to variation in the tourmaline in the direction across the pegmatite dike from the wall zone inward.

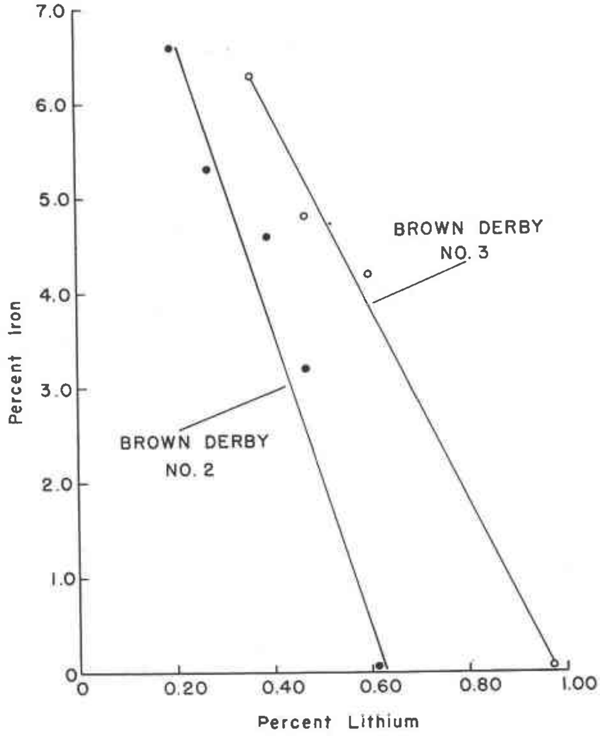

FIG. 3. Relationship between iron and lithium in tourmalines from Brown Derby no. 2 and no. 3 pegmatites.

With the single exception of sample no. 1 the tourmaline crystals contain only negligible amounts of magnesium. Therefore, the major variation in the composition of the samples is a transition from iron tourmaline to lithium tourmaline. This gives rise to the inverse relationship between Fe and Li that is plotted in Fig. 3. Although the weight percentages of Li are not high, the element looms large in terms of atomic ratios because of its low atomic weight. It must be also remembered that the substitution of Li for Fe$''$ in the octahedral positions of tourmaline involves simultaneous addition of aluminum, a major element for which we did not make an analysis. The substitution may be of the type LiAl⇌Fe″Fe″, so that a small amount of Li, with the aid of Al, will take the place of a much larger amount of Fe″. Schaller (1913) has shown that the maximum concentrations of aluminum are found in lithium tourmalines low in iron and magnesium.

The several types of variation shown by different ions of tourmaline are presented in Fig. 4, in which points along the abscissa are plotted in the same way as in Fig. 2. Eleven of the 28 elements found in the spectrographic analyses have been plotted; those omitted were either found in only a few specimens or showed little variation. A number of the ions show similar trends, so these will be discussed together.

Four general types of variations are noted: (1) an increase in the percentage of the element in the tourmaline toward the center of the pegmatite, (2) a decrease in the percentage, (3) little variation in the percentage, and (4) a sharp increase and then a decrease in the percentage of the element.

The amounts of lithium, potassium, calcium, lead, and beryllium in the tourmaline increase toward the center of the pegmatite. In addition, rubidium and cesium, which were found in only a few specimens, showed their greatest concentration in the pink tourmaline from the central part of the core. The beryllium, lead and potassium curves are fairly level until the tourmaline in the central part of the core is reached; then they rise abruptly. The most gradual rise occurs with the element lithium. The increase of lithium, potassium, rubidium, and cesium of the tourmaline in the central part of the pegmatite seems to be a direct result of the higher concentration of these elements found there, as indicated by the associated minerals (Table 1). Beryl, the only mineral that contains major amounts of beryllium, is restricted to the core. Lepidolite, which is concentrated in the central part of the core, contains approximately 8 per cent potassium, 2 per cent lithium, 1 per cent rubidium, and 0.1 per cent cesium (Stevens, 1938). The increase in calcium toward the center of the pegmatite, however, is in opposition to the decrease in calcium shown by the albite of these pegmatites. One sample of albite and one sample of cleavelandite were taken from the wall zone and core, repectively, from the Brown Derby no. 2 and no. 3 pegmatites. The composition of each sample with respect to alkalies and alkaline earths is given in Table 4.

Because albite is the only major mineral capable of accommodating calcium in each unit of the two pegmatites, a general decrease in the total calcium content is indicated towards the center of the pegmatite. Among the other minerals present in the core, lepidolite is known to contain only traces of calcium (Stevens, 1938) and hence does not act as a significant repository for this element. The depletion of strontium that

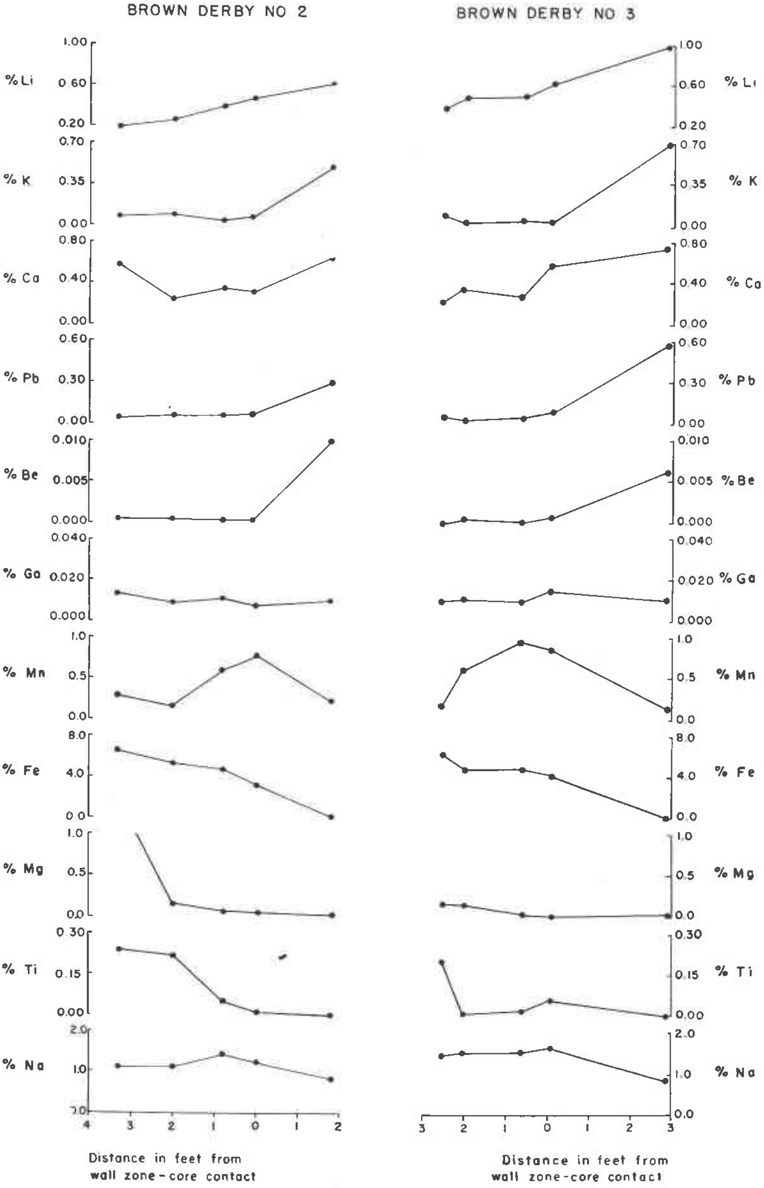

FIG. 4. Relationship between the position of a tourmaline crystal in a pegmatite dike and the crystal's content of various metallic elements. Center of pegmatite is to the right.

is indicated in Table 4 also supports the idea of a decrease in calcium towards the core. The contrary trend of enrichment of calcium in tourmaline crystals in the direction of the core must therefore be due to some peculiar requirement of the tourmaline structure, such as the use of calcium in place of sodium to balance charges arising from substitutions in the structure.

Lead seems to be found chiefly in the tourmaline. Lead was looked for but not found in either the equigranular and platy (cleavelandite) forms of albite or in the lepidolite from both pegmatites.

A general decrease in the amount of iron, titanium, magnesium, and sodium occurs toward the center with the elements cobalt, nickel, chromium, and vanadium occurring in only one specimen adjacent to the outer wall of the pegmatite. The sodium content of the tourmaline is fairly constant but is lower in the pink tourmaline of the core. This relationship is the opposite of the calcium in the tourmaline, which increased in the core. It is also the opposite of the sodium content in the albite, which increases with a decrease in calcium, indicating a general increase of sodium in the central part of the pegmatite. The decrease of sodium in tourmaline is due to the incorporation of substantial amounts of potassium and calcium, the entry of potassium being governed by its abundance and of calcium by probable charge requirements as previously discussed. Titanium in amounts of 0.20 per cent or greater was found in three specimens, which ranged from black to dark greenish brown, and which contained the highest amounts of iron. In specimens closer to the center of the pegmatite, the titanium content dropped rapidly to less than a fourth of this value and then its concentration toward the center was low and erratic.

Table 4. Partial Analyses of Albite in Brown Derby No. 2 and No. 3 Pegmatites

	Brown Derby No. 2		Brown Derby No. 3	
	Wall zone	Core	Wall zone	Core
Na[1]	7.84	8.34	7.98	8.50
Ca[2]	.15	.10	.21	.13
Sr[2]	.005	0	.003	0
K[1]	.10	.13	.11	.11
Li[2]	.001	.002	.001	.003

[1] Flame photometer determinations by S. M. Berthold.

[2] Spectrographic determinations by K. J. Murata. Zero in unit column means that the concentration of the element was below the limit of spectrographic sensitivity. Barium, rubidium, and cesium were also undetected.

Several elements, found in small amounts, occur with minor and apparently no consistent variation. A good example is gallium, which is illustrated in Fig. 4. The variation of this element is small and does not appear related to the type of tourmaline or to the surrounding minerals. Elements with similar behavior include strontium, scandium, zirconium, niobium, tin, copper, bismuth, and zinc. Only minor amounts of these elements appear to be retained in the tourmaline structure; thus, though their presence in the pegmatite fluid may be noted by their presence in tourmaline, a large increase in the amount of these elements would probably not bring a corresponding increase of these elements in the tourmaline. These elements, with the exception of niobium, are not the chief constituents of any mineral in these two pegmatites. The minor amounts of these elements present in the pegmatite fluid substitute into whatever mineral that will accommodate them.

Three elements, manganese, yttrium, and lanthanum increase and then decrease in the tourmaline on going from the outside toward the center of the pegmatites. Maximum concentration is found in the blue tourmaline of both pegmatites. The blue tourmaline commonly surrounds small brown spessartite-almandite crystals. Garnet, the chief manganese mineral, is found in the wall zone and outer part of the core. No garnet occurs in the central part of the pegmatite adjacent to the pink tourmaline with the low manganese content. The reason for the probable increase in manganese content of the tourmaline in the inner part of the wall zone, which is not paralleled by the manganese content of the pegmatite as a whole, as indicated by the garnet, will be discussed later.

Three major factors control the amount of an ion that is incorporated into tourmaline or any other mineral: (1) the structure of the mineral, which determines the ease of incorporation of an ion of a certain size; (2) the presence or absence of other ions which would compete with that ion for a position in the mineral's structure; and (3) the concentration of the ion in the pegmatitic fluid. If an ion fits into a particular position in the tourmaline structure and the pegmatitic fluid contains no other ions that fit better in the same position, then an increase or decrease of this original ion in the pegmatitic fluid will be reflected by an increase or decrease in its content in the tourmaline. An ion, whose concentration does not increase in the pegmatitic fluid, may actually show a higher concentration in the tourmaline, if some other ion which fits better in the same position in the tourmaline decreases in concentration. An example may be manganese, whose concentration rises in tourmaline from the outside toward the inner part of the wall zone as the concentration of iron decreases. The concentration of manganese in the outer part of the wall zone, however, is as high as that in the inner part, as indicated by numerous garnet crystals. The decrease of manganese in the tourmaline at the inner edge of the wall zone and core probably represents an actual decrease in manganese concentration in the pegmatite, as is suggested by the less common occurrence of garnet crystals, the central part of the core being entirely free of them.

The major transition from the outside to the center of the pegmatite is from iron to lithium, which occurs gradually with the lessening of iron. Iron appears to fit better into the tourmaline structure than does lithium, and iron-rich tourmaline crystals are common in pegmatites or parts of pegmatites containing biotite and magnetite. Light-pink and light-green tourmaline crystals are found only where iron-rich minerals are absent. Iron is responsible for the density of color; the lightest tourmaline, irrespective of the color, carries the smallest amount of iron. After the iron content has increased to approximately 6.5 per cent the tourmaline becomes black in hand specimen and greater amounts of iron or varying amounts of other elements do not visibly affect its color. Thus, among the lighter shades of tourmaline in pegmatite, the color density may be used for approximating the iron content, or inversely the lithium content.

Chromium, vanadium, and titanium have ionic radii of 0.64 Å, 0.65 Å, and 0.69 Å, respectively, and thus can easily substitute for ferric iron (ionic radius of 0.67 Å) in the tourmaline structure. Nickel has the same ionic radius as magnesium (0.78 Å) and may enter into the tourmaline structure with equal ease. Cobalt with an ionic radius of 0.82 Å may substitute for ferrous iron (0.83 Å), as can both nickel and magnesium. Some of these elements (Cr, V, Ni, and Co) occurred in only the black tourmaline that was collected adjacent to the outside wall of the pegmatite (specimen no. 1). The small amount of these elements present may well be used up by the first tourmaline formed. Goldschmidt (1937) formulated a rule on the crystal chemistry of ionic crystals which states, "If two ions have almost the same radius the smaller one has the tighter bond." In the case of crystallization from a melt the smaller ion will be concentrated in early crystals of an isomorphous series. Thus, as Cr^3 and V^3 have slightly smaller ionic radii than Fe^3, and as Ni^2 and Co^2 have a slightly smaller ionic radii than Fe^2, chromium, nickel, cobalt, and vanadium will be favored to substitute in the early crystals in place of iron.

The abrupt rise in the lead, rubidium, and cesium content in the pink tourmaline crystals from the central part of the pegmatites may be due to two causes: (1) increase in concentration of the elements in the fluid, and (2) decrease in the fluid of ions that fitted into the tourmaline structure more easily.

The tourmaline from the outside of the pegmatite to the core shows a gradual change in composition of such major components as iron and lithium. Some of the minor elements also parallel the change of these elements. The increase of some elements in tourmaline is commonly the same as occurs in other minerals that surround the tourmaline. The change noted in the Brown Derby no. 2 and no. 3 pegmatites is a gradual one that is most simply explained by means of a single process in which the pegmatite fluid changes in composition during crystallization. In other words the tourmaline was formed from one fluid whose chief method of change was of decreasing some elements by crystallizing out minerals rich in these elements and increasing the elements left in solution. Hydrothermal replacement, with its influx of new fluids, would produce erratic variations in the concentration of such elements as lithium and iron from the outside wall to the core. This is not what is found, and it is believed that the two pegmatites were formed in a closed system by gradual crystallization from the wall inward.

REFERENCES

AZCONA, J. M. L., DE (1947), Is there lead of radioactive origin in tourmaline?: *Rept. Comm. Measurement of Geol. Time,* Washington, 1943–1946, p. 61.

CAROBBI, GUIDO, AND PIERUCCINI, RENZO (1947), Spectrographic analysis of tourmalines from the Island of Elba with correlation of color and composition: *Am. Mineral.,* **32,** 121–130.

DONNAY, GABRIELLE, AND BUERGER, M. J. (1950), Determination of the crystal structure of tourmaline: *Acta Crystallographica,* **3,** 379–388.

GOLDSCHMIDT, V. M. (1937), Principles of distribution of chemical elements in minerals and rocks: *Chem. Soc. London Jour.,* pt. **1,** 655–673.

GORDON, MACKENZIE, AND MURATA, K. J. (1952), Minor elements in Arkansas bauxite: *Econ. Geol.,* **47,** 169–179.

HOLLAND, H. D., AND KULP, J. L. (1949), Distribution of accessory elements in pegmatites: *Am. Mineral.,* **34,** 35–60.

JENKS, W. F. (1935), Pegmatites at Collins Hill, Portland, Connecticut: *Am. Jour. Sci.,* 5th ser., **30,** 177–197.

KUNITZ, W. (1926), Chemisch-optische Untersuchungen an der Turmalin- und Glimmergruppe: *Zeits. Krist,* **64,** 521–523.

LANDES, K. K. (1928), Sequence of mineralization in the Keystone, South Dakota, pegmatites: *Am. Mineral.,* **13,** 510–530 and 537–558.

LARSEN, E. S., AND BERMAN, HARRY (1934), Microscopic determinations of the non-opaque minerals: *U. S. Geol. Survey, Bull.* **848,** 247.

PAGE, L. R., AND OTHERS (1953), Pegmatite investigations 1942–1945 Black Hills, South Dakota: *U. S. Geol. Survey Prof. Paper* **247.**

SCHALLER, W. T. (1913), Beitrag zur Kenntniss der Turmalingruppe: *Zeits. Krist.,* **51,** 321–343.

SCHARIZER, RUDOLPH (1889), Ueber die chemische Constitution und ueber die Farbe der Turmalin von Schuttenhofen: *Zeit. Krist.,* **15,** 337–365.

STAATZ, M. H., AND TRITES, A. F. (1954), Geology of the Quartz Creek pegmatite district, Gunnison County, Colorado: *U. S. Geol. Survey, Prof. Paper* **265.**

STEVENS, R. E. (1938), New analyses of lepidolites and their interpretation: *Am. Mineral.,* **23,** 607–627.

WARD, G. W. (1931), Chemical and optical study of the black tourmalines: *Am. Mineral.,* **16,** 145–190.

WARNER, T. W., JR. (1935), Spectrographic analyses of tourmalines with correlation of color and composition: *Am. Mineral.,* **20,** 531–536.

WINCHELL, A. N. (1932), Ferrotremolite, oxyhornblende, and tourmaline: *Am. Mineral.,* **17,** 472–477.

Manuscript received Aug. 4, 1954.