

SPECTROGRAPHIC ANALYSIS OF TOURMALINES FROM THE ISLAND OF ELBA WITH CORRELATION OF COLOR AND COMPOSITION

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INTRODUCTION

The colors of the beautiful crystals of tourmaline from the Island of Elba and their zonal coloration have always attracted the attention of naturalists. Dolomieu (1) in 1798 examined the tourmalines of Elba described as "half white and half dark"; Ottaviano Targioni Tozzetti (2) (the son of Giovanni Targioni Tozzetti, the great Tuscan naturalist of 1700) described for the first time the tourmalines of different colors that Lieutenant Ammannati collected when he was garrisoned on the Island of Elba.

Antonio D'Archiardi (3), in his "Mineralogia della Toscana," recorded some interesting data on the succession of colors on the crystals and on the variation of density with color; Giovanni D'Achiardi (4) wrote his doctor's thesis on the tourmalines from Elba, after examining about 6000 crystals or fragments of crystals.

More recently, E. Grill (5) found some new forms on the tourmalines from the Island of Elba. From the crystallographic studies of G. D'Archiardi, we note a regular variation of the axial ratio with the color; we have, for example, the lowest value of the axial ratio for the yellow-green tourmalines ($a:c=0.441154$), then follow in order the dark, the colorless, the pale pink, the dark yellow, the greenish yellow, and, lastly, the yellow tourmalines with $a:c=0.454079$. Consequently, the color varies with the chemical composition of the crystals, as is also shown by the specific gravity and by the refractive indices. The black crystals have the maximum density (3.167–3.174), then come the greenish yellow, the pale pink, the colorless (3.017), and the yellow, which are the lightest of all (2.950–3.014).

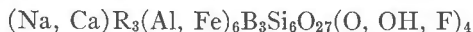
It thus appears that the succession of colors is very similar to that obtained by arranging the crystals according to the increasing value of the ratio $a:c$.

When we consider the double refraction, we can show that the colorless crystals must be classified with the slightly pink and the greenish crystals. We obtain the following succession: pink ($\omega-\epsilon=0.0200$ for yellow light), colorless (0.0204), greenish yellow (0.0220).

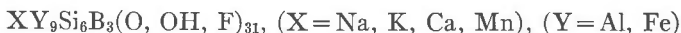
We may conclude that the color, or at least some colors, are influenced by the chromophores which enter in solid solution to a considerable ex-

tent. For some colors (black, green, greenish yellow, and red), the color cannot be attributed to minor constituents present in such small quantities that they could have no influence on the axial ratio and other physical characters.

The structure of the solid solution forming the tourmalines has been determined by M. J. Buerger and W. Parrish (6) on crystals from the Etta Mine, South Dakota, to which they have assigned the space group C_{3v}^5 . Miss Kulazzewski (7) and Machatschki (8) had previously reported on the structure of tourmaline. The formula of the solid solution may be written, according to Buerger and Parrish, as:



and in a general way, according to Machatschki:



The elements must be grouped together, as in all minerals, on the basis of ionic radii. Sodium may be replaced by calcium and manganese; 9Y is never represented in nature by 9Al, but instead by Al_3Li or $\text{Al}_5(\text{Mg}, \text{Fe})_4$. The lithium is almost always present, and from the point of view of isomorphism there is equality in the group of the two atoms LiAl with 2 Mg.

For the Elba tourmalines, there was lacking a spectrographic research of the minor constituents, which was necessary for a study of the relationship of composition and color.

SPECTROGRAPHIC ANALYSIS

We have prepared spectrograms of twenty differently colored samples from the black, green and red, to the greenish yellow, all coming from the Museum of this Institute. Every one had been separated from a clear and transparent crystal and carefully examined under the microscope; the very fine powder was crushed in clean mortars, dried in an oven, and then vaporized in the arc of very pure carbon electrodes 0.6 centimeters in diameter of the Ruhstradt firm. The substance (40 mg.) was placed in a cavity .2 cm. in diameter and 1.2 cm. deep, and volatilized in the arc with 190V and 8A for 6'45".

We have used a Zeiss Qu 24 spectrograph; the field of observation was between 5000 and 2300 Å. The focusing adjustment of the slit was for 2800 Å. We used Hartmann's diaphragm T 10 with nine windows and as intermediate screen the D5. The breadth of the slit was 0.006 mm. We used Ferrania Cappelli ultracontrast orthoplates and developed for five minutes with methyl hydroquinone in the developer.

After measuring the wave-lengths corresponding to all lines made on the positive of the spectrogram obtained by enlarging the photographic plates twenty times with the projection comparator, we ascertained for every identified element the presence of the complex or series of lines which characterize it. We have verified this complex not only by various tests, but also by direct experiment on plates especially prepared.

The identified elements (including the normal constituents of the tourmalines) are the following:*

B, Si, Ti, Al, Fe, Ni, Mg, Cu, Mn, Ca, Ba, K, Na, Li, Cs, Be, V, Ta, Sc, Sn, Ce.

In the course of the qualitative analysis, we have also made estimates of the relative abundance of the various constituents in each sample.

In Table 1 we give our results.

We reserve for a later research an exact quantitative spectrographic analysis; in the meantime, we can report the following conclusions drawn from the accompanying table:

Lithium is present in all samples studied, even in the intensely green or black varieties, where it had not been previously identified by the usual chemical methods; the spectrographic analysis has shown that it is present in larger amounts in the pink, yellow, or colorless crystals, while it is present only in minimum amounts in crystals rich in iron.

Copper is always present; it was found in greater quantity in the blue crystals. Iron is present in greater quantity in the green or black tourmalines, as we already know; nickel is present in very small quantities only in the tourmalines very rich in iron. Barium is always present, but in largest quantities in tourmalines rich in iron. The quantity of manganese is greater in the yellow and yellow-green crystals and least in those which are black; this is in accord with results obtained by the usual chemical methods.

Calcium is present in larger quantities in the yellow than in the others; it is absent in the red tourmalines. Beryllium was present in all samples, because it is an isomorphous substituent of silicon. Scandium is present in larger quantities in the green and red tourmalines, and tin is present in larger amounts in the black. Tantalum is present only in the pink, yellow, or colorless crystals, while titanium was found in larger amounts in the crystals containing high iron content.

* We have looked with particular care for the complex of the last lines of the following elements: Rb, Sr, Cr, Zn, Co, Ga, In, P, As, La, Nd, Eu, Nb, Ge, Zr but with negative results.

TABLE 1

Specimen No.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	18a	18b	19	20
Color	black	black	black	green black	dark green	yel- low green	light green	yel- low	yellow green pink	light pink	wine red	wine red	light red	light pink	pink	pink	yel- low	yel- low	blue	pink yel- low	color- less	color- less
B	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
Si	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
Ti	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M
Al	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
Fe	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
Ni	G	G	G	G	G	G	G	G	G	G	G	G	G	G	G	G	G	G	G	G	G	G
Mg	Trtr	Trtr	Trtr	Trtr	Trtr	Trtr	Trtr	Trtr	Trtr	Trtr	Trtr	Trtr	Trtr	Trtr	Trtr	Trtr	Trtr	Trtr	Trtr	Trtr	Trtr	Trtr
Cu	G	G	G	G	G	G	G	G	G	G	G	G	G	G	G	G	G	G	G	G	G	G
Mn	Tr	Tr	Tr	Tr	Tr	Tr	Tr	Tr	Tr	Tr	Tr	Tr	Tr	Tr	Tr	Tr	Tr	Tr	Tr	Tr	Tr	Tr
Ca	Trtr	Trtr	Trtr	Trtr	Trtr	Trtr	Trtr	Trtr	Trtr	Trtr	Trtr	Trtr	Trtr	Trtr	Trtr	Trtr	Trtr	Trtr	Trtr	Trtr	Trtr	Trtr
Ba	Tr	Tr	Tr	Tr	Tr	Tr	Tr	Tr	Tr	Tr	Tr	Tr	Tr	Tr	Tr	Tr	Tr	Tr	Tr	Tr	Tr	Tr
K	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S
Na	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
Li	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
Cs	Vs	Vs	Vs	Vs	Vs	Vs	Vs	Vs	Vs	Vs	Vs	Vs	Vs	Vs	Vs	Vs	Vs	Vs	Vs	Vs	Vs	Vs
Be	Tr	Tr	Tr	Tr	Tr	Tr	Tr	Tr	Tr	Tr	Tr	Tr	Tr	Tr	Tr	Tr	Tr	Tr	Tr	Tr	Tr	Tr
V	Vs	Vs	Vs	Vs	Vs	Vs	Vs	Vs	Vs	Vs	Vs	Vs	Vs	Vs	Vs	Vs	Vs	Vs	Vs	Vs	Vs	Vs
Ta	Vs	Vs	Vs	Vs	Vs	Vs	Vs	Vs	Vs	Vs	Vs	Vs	Vs	Vs	Vs	Vs	Vs	Vs	Vs	Vs	Vs	Vs
Sc	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S
Sn	Vs	Vs	Vs	Vs	Vs	Vs	Vs	Vs	Vs	Vs	Vs	Vs	Vs	Vs	Vs	Vs	Vs	Vs	Vs	Vs	Vs	Vs
Ce	Trtr	Trtr	Trtr	Trtr	Trtr	Trtr	Trtr	Trtr	Trtr	Trtr	Trtr	Trtr	Trtr	Trtr	Trtr	Trtr	Trtr	Trtr	Trtr	Trtr	Trtr	Trtr

Key to chart symbols: X = normal constituent, G = great, M = medium, S = small, Vs = very small, Tr = trace, Trtr = very minute trace.

GEOCHEMICAL CONSIDERATIONS

All the minor constituents determined by spectrographic means may be considered as isomorphous substituents of the major constituents of the tourmalines. Their presence is thoroughly justified by the following geochemical considerations.

It is very well known that lithium, owing to its too small radius (0.78), does not replace the sodium or potassium in minerals, but substitutes for magnesium (0.78). It is found, therefore, in small quantities in diorites, gabbros, and in more basic rocks (9); in the acid rocks it forms its own minerals, such as spodumene or amblygonite, and it partly substitutes for magnesium as in tourmalines ($Al\ Li = 2Mg$).

While rubidium substitutes for potassium and is enriched in the feldspars, particularly in amazonite (up to 2.74%), caesium yields its own minerals in the residuum of the crystallization of the acid rocks, or is present in traces in the potassium minerals, for it has a radius very different from potassium ($K = 1.33$, $Cs = 1.65$). Rubidium is present in the micas to a larger extent than is the caesium (muscovite 0.40% Rb_2O ; 0.015% Cs_2O) (10). Therefore, caesium concentrates itself more than the rubidium in the residuum of the crystallization of the granite of the Island of Elba, and we find it in the tourmalines, while rubidium is absent.

Barium found by us in every sample is a replacement of potassium ($Ba\ 1.43$, $K\ 1.33$); it is known that it is contained in orthoclase (up to 1.5%). The maximum quantity of barium is therefore in the syenites and trachytes (0.18%) (11); the nepheline syenites and the phonolites have only 0.058%, the granites and the liparites 0.048%, the diorites and andesites 0.026%, and the gabbros and the basalts 0.007%. The basic rocks deprived of potassium are also deprived of barium. In the diorites, barium is contained in the biotite (up to 3%); the calcareous rocks have barium only in small quantities.

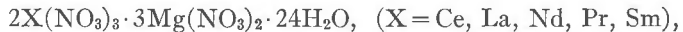
Beryllium, owing to its small radius (0.34), is a minor constituent of acid rocks where it substitutes for silicon (0.39); the quantity of beryllium is greatest in the pegmatites (12), where it forms its own minerals; its isomorphism with magnesium is limited, and so in the basic rocks, it is absent or present in quantities smaller than 0.001%. In the crystals of tourmaline that we have studied, beryllium substitutes for silicon and is always present.

As in the first two groups of the periodic system, a geochemical analogy does not exist between sodium and potassium, and between magnesium and calcium, so there is no analogy in the third groups between aluminum and scandium. Scandium is a substitute for magnesium, and it is hidden in the iron and magnesium minerals (13); all the magmatic

olivines contain scandium, as do augite, diallage, and other pyroxenes and amphiboles (Mg 0.78 Å, Sc 0.89, Zr 0.87).^{*} Therefore, in the tourmalines, the quantity of scandium present is larger in the green iron and magnesium-rich crystals. Titanium is present in all analyzed samples, and it is a substitute for iron and silicon. The geochemistry of niobium and tantalum is not very well known, but tantalum should have a behaviour like phosphorus and in the tourmalines substitute for silicon. Copper is present in the tourmalines as an isomorphous substitute for magnesium.

In the first group of the periodic system, Cu, Ag, and Au are clearly chalcophil; likewise in the second group, Zn, Cd, and Hg; and in the third, Ga, In, Tl; but the first element of the three series is often hidden in the minerals of the rocks. Copper in very minute traces is very common as a substitute for the isomorphous group Mg-Fe²⁺ in the silicates of the rocks. This substitution has not been studied sufficiently, and cases of isomorphous substitution of magnesium by copper in simple compounds are not known in chemistry.

Many years ago, one of us (14) demonstrated that in the very well known double nitrate of the series:



magnesium can be partially or entirely replaced by copper and also by cadmium.

MINOR CONSTITUENTS AND COLOR

In the solid solution which constitutes the crystals of tourmaline that we have studied, the presence of the minor constituents that we have found is explained by their isomorphism with some major constituents; there remains to be determined the relationship between minor constituents and color.

The question of the color of allochromatic minerals is one of the partially solved mineralogical problems. Formerly, we always attributed the color to the presence in the crystals of elements which usually gave colored compounds; only recently have we noticed in colored allochromatic minerals the absence of colored compounds, and the color was then attributed to a physical phenomenon, as ionic deformation in the crystal.

Kraatz, Koschlov, and Wöhler (15) thought color was due to inorganic pigments. Weinschenk (16) found titanium in the smoky quartz, and he prepared some colored corundum with inorganic pigments.

^{*} Newhouse has also reported that magnetite of granitic pegmatites contains scandium and not the others. (*Carnegie Inst. Wash. Publications*, Year Book, No. 40 for the year 1940-41, pages 142 to 144. Issued December 12, 1941.)

Brauns (17) was the first to use the absorption spectrum for the identification of the chromophores. Then followed Weigel and Habich (18), and especially Kolbe (19), who compared the absorption curve of a number of chemical compounds in pure crystals and in solutions with those of various allochromatic minerals.

In particular, he studied the absorption of the compounds of Mn, Cr, Fe, and Ti. From such comparisons, it appears probable that titanium would produce part of the color of amethyst; ferrous iron, of the green tourmalines, of clinocllore and of xanthophyllite; ferrous and ferric iron, of blue sapphire, spinel, and of green corundum; chromium, of the red and green spinel, of alexandrite, blue disthene and of the emerald; trivalent manganese, of the pink tourmalines and of red almandine. The absorption curve of the pink tourmalines presents also a certain affinity with that of potassium permanganate.

But the question of the color of allochromatic minerals is certainly not concluded with the investigations by means of the absorption curve of the constituent which has produced the color. In many cases, the color is determined by substances which isolated are colorless or have a different color from that which they bestow on the mineral in which they are found.

K. Chudoba (20) has shown that green zircons have a specific weight less than $ZrSiO_4$ and reveal some differences in the structure; they contain amorphous SiO_2 and ZrO_2 . On heating to 1450° , the specific weight increases, and the color changes from blue to yellow.

Perhaps the presence of amorphous material might be due to radioactive substances. Machawsky (21) has drawn attention to other variations of color due to the heating; morion becomes yellow at 500° ; amethyst becomes colorless at $300-400^\circ$, then opalescent and then yellow at $575-750^\circ$; some amethysts from Paraguay become yellow at $390-450^\circ$, but return to the amethyst color upon exposure to radium. Analogously, as Chudoba has pointed out, green beryl becomes blue if it is heated at 400° ; yellow or brown topaz becomes pink upon heating, and with ultra-violet rays changes to yellow again.

These changes of color are in part due to chemical reactions, and specifically to a change resulting from the oxidation of the chromophore. The change of color of green tourmalines and of beryl when heated would be due to the oxidation of iron, that of topaz to the oxidation of vanadium. However, in many cases, it is not a chemical but a physical phenomenon; it is a question of the deforming influence of ions on the orbits of other ions which are easily deformed, as for example in PbI_2 , which is yellow on account of the deforming influence of Pb'' , while NaI is colorless because Na' is only slightly deformed.

In fact, it is not possible to explain as a chemical phenomenon the pink color of beryl as due to the presence of caesium [Klemm and Wild (22)] or the green color of the microcline as due to the presence of rubidium and caesium (Goldschmidt) (23). Likewise, according to its dispersion, the same pigment can give different colors to fluorite (Chudoba, Kleber, and Siebel) (24); so, at times, the color does not depend on the chemical nature of the chromophore.

In the particular case of tourmaline, Scharizer (25) in 1889 stated for the crystals from Schuttenhofen that the deep green color was due to iron and that the crystals became pink when manganese is present; that is, when the ratio MnO/FeO increases. When the content of iron equals manganese, the color deepens with the increase of the content of titanium. The deep green or black tourmalines are associated (in Schuttenhofen) with rutile and ilmenite, while the blue tourmalines often contain tin and are associated with cassiterite.

Scharizer (25) stated that lithium would be absent in the deeply colored tourmalines. Rammelsberg (26) and Sommerland (27) drew attention to the fact that red and pink tourmalines from Scheitauks contain manganese but no iron. Riggs (28) found that the red and pink lithium tourmalines contain manganese. Kuntz (29) believes that the red and pink colors depend on trivalent manganese and that scandium and cerium also contribute to the coloring.

MacCarthy (30) attributes yellow and green colors to iron in various stages of oxidation. It seems that we should pay but slight attention to the ideas of Vernadsky (31) on the presence in the tourmaline of a kaolinic nucleus that, added to other groups, would give colors, as is the case in sodalite, haüynite, and cancrinite. The presence of this nucleus does not appear to be in accord with the composition of tourmaline.

In the opinion of Wild (32), the chromophores in tourmaline are Fe, Mg, Mn, and Co (magnesium would not cause color, but would have some influence on the others). Secondary agencies of color would be Ga and Sn; casual chromophores include Ni, Pb, Bi, and Sn. Wild assigns the responsibility of every color to a combination of elements. In the opinion of Holden (33), the color of rubellite is due to trivalent manganese (while the divalent and the tetravalent manganese would not affect the color), and colorization by heating would be a process involving reduction.

Recently, T. W. Warner (34) made a spectrographic analysis of the tourmalines from San Diego,* and he has found the following elements present in every sample: Li, Na, Mg, Ca, Al, B, Mn, Si, V; and in some of

* One sample is indicated as coming from Brazil.

them K, Cu, Fe, Pb, Sn, Ti, and Be. In the opinion of Warner, Li, Na, Mg, Ca, Al, and B have no influence on color; copper is more frequent in the green tourmalines than in those which are pink; instead, tin is more marked in the pink.

Concluding our researches from the point of view of color, we may affirm that:

The green color, as previously noted, is due to the presence of divalent iron.

The pink color is due to the presence of manganese with lithium and caesium.

The blue color is caused by the presence of copper, and particularly if strengthened by the strongly deforming action of Cu^{II} in the same way as in the copper ammonium complex, where the deep blue color is due, according to Fajans, to the deforming action of Cu^{II} on the electronic orbits of the molecule of ammonium.

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