

NOTES AND NEWS

SPECTROGRAPHIC ANALYSIS OF TOURMALINES WITH CORRELATION OF COLOR AND COMPOSITION

T. W. WARNER, JR., *Pomona College, Claremont, California.*

Previous work on the subject of tourmaline analysis in an endeavor to associate chemical composition with color has been reported by Wild,¹ Riggs,² Bastin,³ and discussed by Doelter.⁴ A number of non-spectrographic chemical analyses are tabulated by Doelter⁴ and Dana.⁵ In an article by Holden,⁶ the color of rubellite is attributed to a manganese content of 0. X-2% Mn_2O_3 .

The spectrographic examinations were made by means of a large Gaertner quartz spectrograph,⁷ using a slit width of 0.035 mm. W. and W. panchromatic plates were used to photograph the visible spectra and Eastman D. C. ortho plates for the ultra-violet. By this means the spectral range was covered from 7000 Å to 2400 Å. A 100 volt direct current arc which drew 18 amp. on a closed circuit was used to excite the spectra. Acheson purified graphite electrodes, 3/8" in diameter, were used.

The samples of tourmaline were very carefully chosen from flawless material, the color ranging from very dark green to red. In some cases where flawless material was unobtainable in the rough crystals, cut stones were used. In so far as was possible careful attention was given to avoid using zoned crystals. In the case of bi-colored samples, however, it was found that in every case the material was zoned to some slight extent along the *c*-axis. In these cases the sample was selected from the core of the crystal avoiding contamination as much as possible.

Each sample was prepared by the following procedure: First, the crystal was inspected for general suitability, such as clarity,

¹ Wild, *Centr. Mineral. Geol.*, Abt. A, 1931, pp. 327-33.

² Riggs, The Analysis and Composition of Tourmaline; *Am. Jour. Sci.*, (3) vol. 35, pp. 35-51, 1888.

³ Bastin, Geology of the pegmatites and associated rocks of Maine: *U. S. Geol. Survey*, Bull. 445, 1911.

⁴ Doelter, *Handb. Mineralchemie*, 11, 2, pp. 749-788.

⁵ Dana, *System of Mineralogy*, 6th Ed., p. 642.

⁶ Holden, *Am. Mineral.*, vol. 9, pp. 101-8, 1924.

⁷ Spectrographic examinations were made in one of the Pomona College Laboratories using apparatus and technique customarily employed by Dr. Theodore Kenard.

TABLE 1

Spec. No.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
ELEMENTS															
Li	Vs	Vs	S	S	S	Vs	Vs	Vs	Vs	tr	tr	S	tr	tr	tr
Na	Vs	Vs	Vs	Vs	Vs	Vs	Vs	Vs	Vs	tr	tr	tr	tr	tr	tr
Mg	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
Al	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M
B	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M
Cu	tr	Vs	tr	tr	tr	tr	tr	tr	tr	tr	tr	tr	tr	tr	tr
Fe	trtr-	M	trtr-	S	S	S	-	trtr-	trtr	M	S+	S-	Vs	trtr	trtr
Ga	tr	trtr	tr	tr	tr	trtr	tr	trtr	tr	tr	tr	tr	tr	tr	tr
Mn	tr	Vs+	Vs-	Vs	S	Vs	tr+	Vs	tr	tr	Vs-	tr	Vs	S	Vs
Pb	tr	tr	-	tr	trtr	-	tr+	tr	tr	tr	tr	tr	tr	tr	tr
Si	M+	M+	M+	M+	M+	M+	Vs	M+	tr	M+	M+	Vs-	tr	Vs-	tr
Sa	Vs	trtr	-	trtr	tr	tr	S	tr	tr	trtr	tr	M+	M+	M+	M+
Ti	trtr	trtr	-	-	-	trtr	trtr	tr	tr	trtr	tr	trtr	trtr	trtr	trtr
V	trtr--	trtr--	trtr--	trtr--	trtr--	trtr--	trtr--	trtr--	trtr--	trtr--	trtr--	trtr--	trtr--	trtr--	trtr--
Be	-	-	-	-	-	S	-	-	-	-	-	-	-	-	-
Locality	S.D.	Brazil	S.D.	S.D.	S.D.	S.D.	S.D.	S.D.	S.D.	S.D.	S.D.	S.D.	S.D.	S.D.	S.D.

KEY TO CHART SYMBOLS: trtr—very minute trace tr—trace Vs—very small S—Small M—Medium S.D.—San Diego

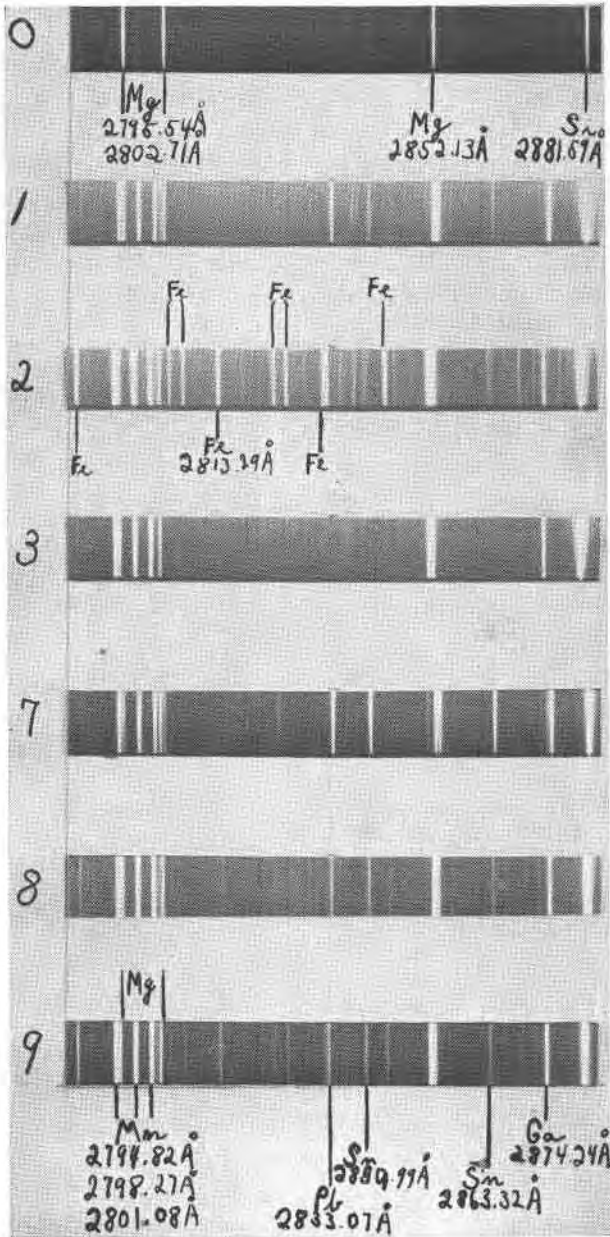


FIG. 1

zoning, and surface deposit. It was then crushed by wrapping carefully in paper and striking it with a hammer. This precaution was a vital necessity to avoid any iron contamination which might in any way develop. The pieces thus obtained were selected individually using a 10 power binocular microscope. The particles were handled by tweezers which had been dipped in "air-plane dope," the substance which was found to be the safest in avoiding contamination. The selected particles were then ground in a thoroughly cleaned new agate mortar. Paraffin shields were made which fitted snugly to the sides of the mortar, preventing the material from being scattered or contaminated. The crushing process was continued until the tourmaline was reduced to a coarse powder. The powder thus obtained was again examined under the microscope and any suspicious particles were removed. The sample was then carefully measured and loaded on the electrode by means of a paper chute, the electrode having been previously hollowed at the tip so as to collect the material and prevent dispersion on arcing.

In photographing the visible spectra, an exposure of 30 seconds was given. A 40 second exposure was used in the ultra-violet. Three consecutive exposures were made of each sample in each case. Before volatilizing any sample, the spectrum of the electrodes was taken so as to avoid any confusion in the interpretation of the plates. Fifteen samples were studied and fifty-two elements were tested for. A large piece of the original crystal, or in the case of the cut stones an exact duplicate of the specimen used, was retained for color comparison. The plates thus obtained were interpreted by means of dilution standards.⁸ Traces as slight as .0005% were noted.

The object of this investigation was to discover, if possible, what elements were responsible for the various colors in tourmaline. (See table 1.) Figure 1 shows an enlargement of the spectra, 0 being the blank arc while Nos. 1, 2, 3, 7, 8, and 9 correspond to the respective samples.

One fact definitely established is that the iron content varies directly and proportionately with the depth of color in the greens, and inversely in the pinks and reds, being totally absent, or, if present, only in extremely minute traces in the reds. The darker

⁸ Spectrograms were interpreted by comparing with standard plates showing the dilution spectra of the various elements. These plates were loaned and the interpretations of the spectrograms checked by Dr. Theodore Kennard.

greens had the most iron, the content becoming less in the lighter shades, but never becoming as slight as the content of even the lightest pink.

Pink tourmaline, when heated in a crucible to about 550°C. was found to turn colorless. This change appears to be fairly rapid and in all cases where crystals were heated the color was constant throughout, no zoning becoming apparent. When powdered portions were given the same treatment the change was not so rapid or complete, some of the pink coloring remaining even after longer periods of heating. This result might be explained on the following basis. Holden⁶ considers that certain pink minerals, including quartz and rubellite, are colored by trivalent manganese. Divalent and tetravalent manganese were not believed to be significant in this respect. Assuming this to be the case and if the decoloration is a reducing process, then upon heating in air a powder would be less likely to change than a solid crystal.

Using samples of rose quartz which had been heated until they were colorless, Holden⁶ subjected the specimens to radium radiation. On such exposure the quartz regained some of its pink coloration. Doelter⁴ found that white tourmaline exposed to radium radiation also assumed a faint pink. In this work, the pink tourmaline changed to colorless at about 560°C. In view of the similarity between these experiments, it might be safe to assume that manganese is partly responsible for the color of pink and red tourmaline. This assumption that manganese is responsible for the pink coloration has not yet been definitely established, but as manganese was present in every sample tested, it is certainly a possibility. Further investigation in the field of absorption spectroscopy will be necessary to verify this potential possibility.

Li, Na, Mg, Ca, Al, B, and Ga were found to remain nearly constant in all the samples tested. In the cases where the amounts varied, the variation did not coincide with differences of color. Therefore, it would seem apparent that these elements are not responsible in themselves for color variation. Tin was slightly more pronounced in pink than in green, and copper was more common in green than in pink. The following elements were found to be present in every case when tested for: Li, Na, Mg, Ca, Al, B, Mn, Si, and V. K, Cu, Fe, Pb, Sn, Ti, and Be were found in some samples, but not in all. Ag, Ge, Re, As, Hf, Rh, Sb, Ru, Bi, Hg, Sc, Au, In, Ta, Ir, Te, Cb, La, Th, Cd, Mo, U, Ce, Ni, W, Co, P, Yt, Pd, Zn, and Pt were tested for and not found.

In view of the facts obtained, let us assume that the natural color of tourmaline is either pink or red. Pink and red crystals, when subjected to heat, become colorless. Iron in tourmaline changes the natural pinks to greens. Scharizer⁹ definitely states that with increasing manganese content color shifts from blue through green to red. There appeared to be a tendency towards this relationship in the samples tested with the spectrograph. Riggs² found that, while the lithia tourmalines contain more or less manganese and give red, green, blue and colorless crystals, the shades of color were not dependent on the absolute amount of manganese present but rather on the ratios existing between that element and iron. When the ratio Mn:Fe was approximately 1:1, pink, colorless, or very pale green resulted. An excess of Mn produced red variation, and where iron was the predominating element of the two, various shades of green resulted. In the author's work, this ratio relationship was found to exist in practically every case and appears to have an extremely important bearing on color change. The depth of green is due to the intensity of iron concentration, while variation in the blue and bluish greens may be due to changes of copper content, the blues having lower concentration than the yellow greens, which are the highest. Purple and lavender tourmaline may be the result of valence changes in iron. It is known that ferrous or ferric iron may be responsible for either green or reddish colorations. Holden⁶ found the amethyst color in purple quartz due to iron. The correlation between composition and color in the cases of different colored portions of bi-colored crystals was identical with that of single crystals of the corresponding colors.

Due to the accuracy of spectrographic investigation, it is felt that the results obtained have disproved statements to the effect that magnesium is responsible for color changes. In an examination of red tourmaline Wild¹ considered Ga to be a possible pigment, but failed to find any trace of Mg. In the material which was examined spectrographically, however, the Mg remained constant in both red and green experiments. Contradictory data on heat discoloration is discussed by Doelter.⁴ From the recorded observations there is an indication that iron is one, and possibly the most important, factor in gem coloration. In this connection, it is interesting to note that Papish¹⁰ found iron to be the significant pigment in rubies.

⁹ Scharizer, *Z. Kryst.*, vol. 15, p. 355, 1889.

¹⁰ O'Leary, Roger, and Papish, *Science*, vol. 80, pp. 412-414, 1934.