# Observations on the colouring of pink and green zoned tourmaline.

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THIS investigation was concerned with two aspects of the colour-zoning in tourmaline: firstly, the origin of the green and pink colours; secondly, the reason for the apparent incompatibility of these two forms. Much of the previous work on the colour of tourmaline has involved the use of emission spectra.[1,2,3] This method provides information as to which elements are present; it does not, of course, indicate which of the twenty or so elements identified is responsible for the colour, although it may be possible to infer this. Absorption spectra, on the other hand, are directly concerned with colour. They have been employed quite extensively in Germany,[4,5] and more recently in Russia,[6,7] but the earlier data and instruments were often inadequate. The last decade has seen marked improvements in the technique of absorption spectroscopy, particularly in the development of photoelectric methods for the quantitative recording of spectra, and the method is likely to prove one of increasing value.

The tourmalines studied form part of the collection of the late Prof. W. T. Gordon, and are from San Diego County, California. The pink-green colour zoning is most generally parallel to the basal pedion,

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[1] G. Carobbi and R. Pieruccini, Spectrographic analyses of tourmalines from the island of Elba with correlation of color and composition. Amer. Min., 1947, vol. 32, pp. 121–130. [M.A. 10–317.]

[2] J. P. Mateos, El color en la tourmalina. Notas y Comunic. Inst. Geol. y Minero de España, 1944, no. 13, pp. 217–289. [M.A. 9–198.]

[3] T. W. Warner, Spectrographic analysis of tourmaline with correlation of color and composition. Amer. Min., 1935, vol. 20, pp. 531–536. [M.A. 6–266.]

[4] E. Kolbe, Über die Färbung von Mineralien durch Mangan, Chrome und Eisen. Neues Jahrb. Min., Abt. A, 1935, Beil.-Bd. 69, pp. 183–254. [M.A. 7–135.]

[5] B. Lange and W. Eitel, Über eine Methode zur Untersuchung der Absorption. . . . Tschermaks Min. Petr. Mitt., 1931, vol. 41, pp. 435–452. [M.A. 5–122.]

[6] N. M. Melankholin, On the colouring of magnesial-ferruginous mica. Trav. Lab. Crist. Acad. Sci. URSS, 1940, no. 2, pp. 61–72. [M.A. 9–197.]

[7] S. V. Grum-Grzhimailo, On the colouring of minerals caused by chrome. Trav. Lab. Crist. Acad. Sci. URSS, 1940, no. 2, pp. 73–86. [M.A. 9–190.]

although it may be parallel to the prism faces. This latter zoning is less common, but is often shown by the larger crystals, characteristically with a less strongly marked colour change. Irregular patchy pink-green colouring, unrelated to the crystal form, is most uncommon. Where the colour changes from a strong pink to a strong green there is usually a sharp contact between the two zones. Where a pink crystal grades into green, it often does so by means of an intermediate colourless zone. The colouring of both pink and green forms can be markedly inhomogeneous, although this is not often the case. A common feature of this Californian tourmaline is the occurrence of long cylindrical cavities which run parallel to the c-axis of the crystal.[1] These are possibly 'negative' crystals, since they may be striated internally in the same way as the prism face is striated. It is this material that is used for cutting 'cat's-eye' cabochons. It seems likely that the cavities are formed under conditions of rapid growth and it would be satisfactory to be able to correlate the different coloured forms with different conditions of growth. However, the cavities occur equally in the pink and green forms; they may stop sharply at the boundary between the two, or they may pass from one to the other without interruption. It appears likely that the change from pink to green or vice versa, with the boundary parallel to a crystal face, marks a change in the composition of the parent solution during growth. The existence of the cavities is controlled by the rate of formation of the crystals; a change in the rate of formation may or may not coincide with the change in composition.

The instrument used to measure the absorption was a Hilger medium quartz-spectrograph. This has been fitted with a photo-electric attachment which moves a vacuum photocell slowly across the emergent light beam. The changes in the intensity of the light are recorded by the photocell and are used to produce corresponding changes in the position of a small light beam. The movements of this beam are recorded on photographic paper on a revolving drum, thus providing automatically an accurate and detailed record of the absorption. The wave-length region studied was from 350 to 600 m$\mu$. The tourmaline crystals were sectioned parallel to the c-axis, $\frac{1}{8}$–$\frac{1}{4}$ inch thick, and both sides of the slice were polished carefully. A polaroid plate placed between the light source (an over-run thin-envelope car-headlamp bulb) and the crystal section made it possible to measure the absorption of both ordinary and extra-

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[1] R. Johns and L. A. Wright, Gem and lithium-bearing pegmatites of the Pala district, San Diego County, California. Special Rep. Division Mines, California, 1951, no. 7-A, 72 pp. [M.A. **11**–487.]

ordinary rays. Both the pink and green crystals, when free from inclusions and internal cracks, gave well-defined and reproducible curves. Crystals with a brownish tinge were unsatisfactory and could not be used for absorption measurements; it appears that the brown colour is due to finely divided included material.

The absorption curves of a number of solutions coloured by metallic ions were measured by the same method for the purposes of comparison.
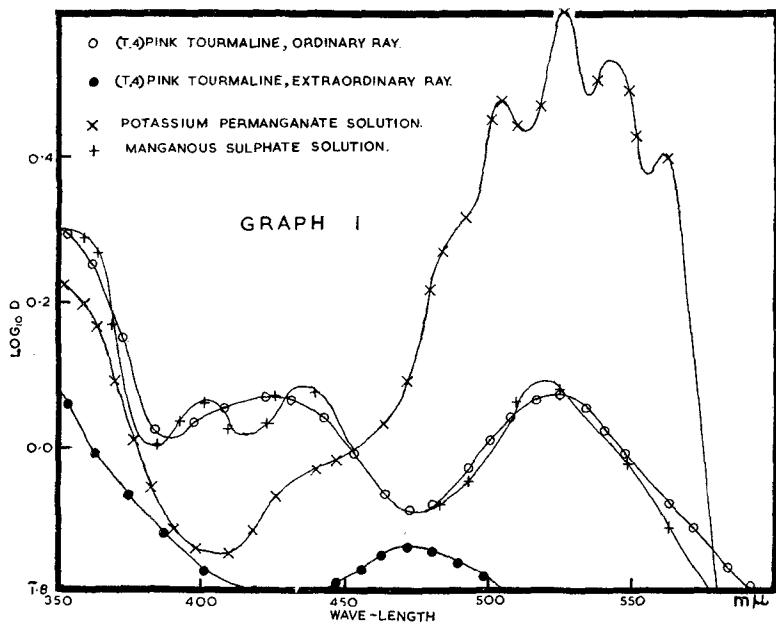


FIG. 1. Absorption curves of pink tourmaline.

*Absorption curves (graphs 1-4).*[1]

*Graph 1.*—It can be seen that the absorption of the ordinary ray of pink tourmaline corresponds very closely to that given by manganous sulphate solution, although some of the fine structure is lacking. The absorption maxima are in the yellow-green and blue-violet, so that light emerging from the crystal is enriched in red and blue-green. The absorption curve of pink tourmaline has been compared to that of potassium permanganate (Kolbe, 1935, loc. cit.). There is clearly no justification for such a comparison in the case of the Californian crystals.

[1] D = optical density = $\log_{10}$ (incident intensity/(transmitted intensity).

A solution containing the trivalent manganese ion (manganic alum gives an absorption curve somewhat resembling that of the permanganate ion $MnO_4'$, but without the fine structure and with much less contrast (ratio of maximum to minimum). It also has a subsidiary peak in the blue region so that the light transmitted is mainly red and violet. The $Mn^{+++}$ ion is unstable, except in the presence of excess acid, so it is unlikely to be the cause of the colour of tourmaline.
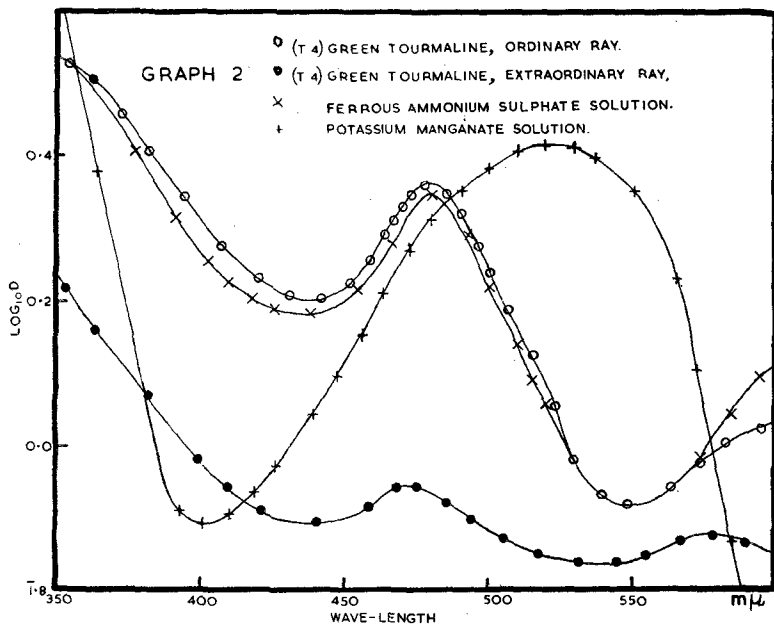


FIG. 2. Absorption curves of green tourmaline.

*Graph 2.*—The absorption curve of the ordinary ray of green tourmaline is very similar to that given by ferrous ammonium sulphate solution: the maximum absorption for both is in the blue-green and red regions and there are minima in the blue and yellow-green. This is unlike the curve given by the rather unstable brownish-green solution of potassium manganate ($K_2MnO_4$).

*Graph 3.*—In the green part of the crystal (T. 4) the absorption of the ordinary and extraordinary rays are similar in form; they differ in intensity and in the position of the absorption maxima. There is only a small shift in the position of the latter, but it is in the sensitive blue-green region of the spectrum and results in the clearly marked

pleochroism seen in the hand-specimen. The absorption of the extra-
ordinary ray of the pink crystal, while almost negligibly small, shows the
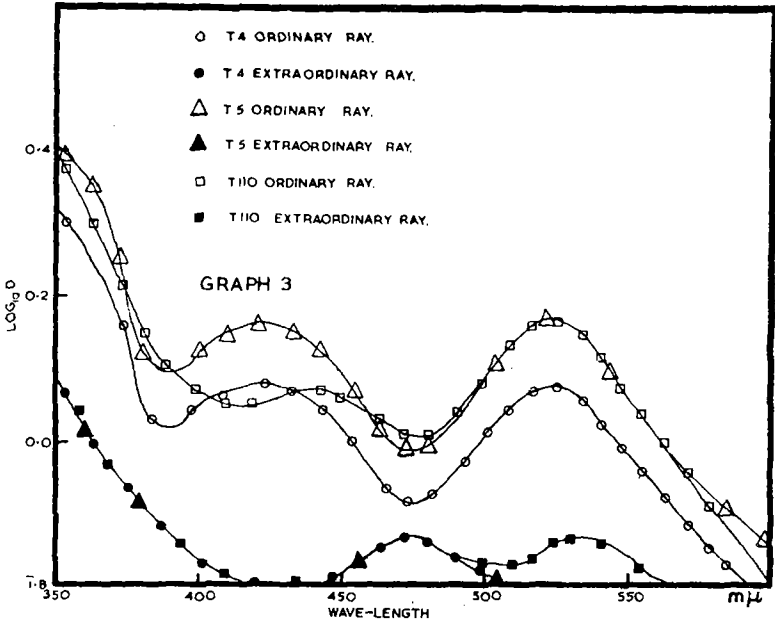general form of the green absorption curve.



Fig. 3. Comparison of absorption curves of pink and green tourmaline.

*Graph 4.* —This graph compares the absorption of the pink sections of
three crystals. Two of the crystals (T. 4 and T. 5) agree closely although
with some difference in the depth of colour. It is considered that the
general form of these curves is typical of the absorption of this group
of crystals. T. 110 diverges from the normal; the pink colour is stronger
than usual and is also more complex. In addition, this crystal reacts
differently on heating and may be from another locality— possibly
Brazil.

A comparison of the green portions of the same three crystals gives
a graph similar to graph 4.

Thus from the absorption curves it may be concluded that the pink
colour is due mainly to divalent manganese; the green colour to divalent
iron. It is important to see how far these conclusions are endorsed by
chemical analyses and by the behaviour of the mineral on heating: also

to suggest if possible why crystals are either pink or green, but never pink plus green (the brownish tinge of some large crystals is due to included solid material).
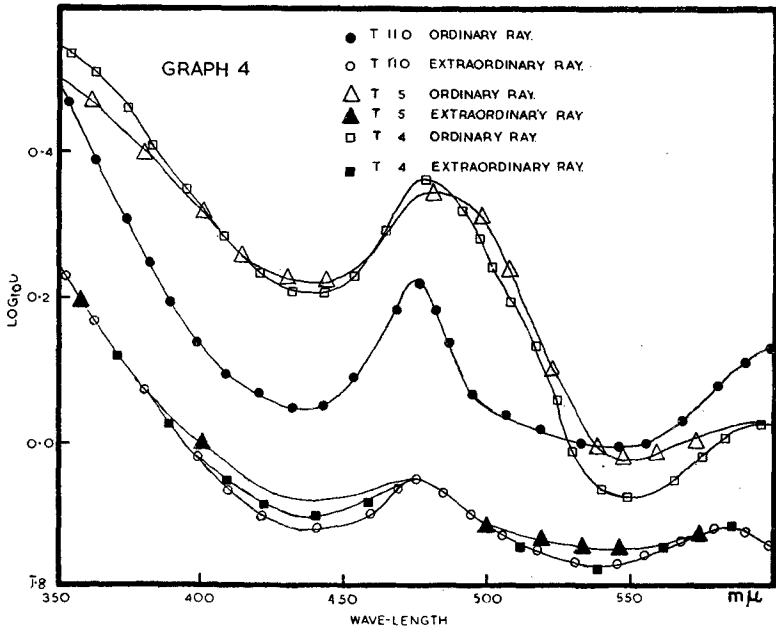


FIG. 4. Comparison of absorption curves for three crystals of pink tourmaline.

## Effect of heating.

When the colour of a crystal is caused by a lattice-defect or colour-centre type of structure, the colour tends to be destroyed by quite moderate heating (300° C. or thereabouts). The tourmaline crystals are quite unaffected by heating at less than 800° C.; between 800° and 1000° C. the pink crystals are decolorized with some loss in weight and with partial destruction of the lattice.[1] This suggests that the colouring material is an essential and integral part of the lattice.

Some experiments were carried out to see whether the green and pink forms reacted differently on heating. The tourmaline crystals were heated at 900–1000° C. for 1–3 hours, i.e. until the weight was constant. The results are summarized in table I. After heating the pink crystals were white and opaque; the green crystals were also opaque, but

[1] F. Machatschki, Notiz über die Entwässerung des Turmalins. Zentralblatt Min., Abt. A, 1941, pp. 135–137. [M.A. 8–382.]

brownish—the depth of colour depending on the intensity of colour in the original. Where the green crystal was unevenly coloured, this colour-zoning was preserved in the heated specimen. In almost all the experiments the green crystals lost more weight than the pink. In one experiment, where the crystals were weighed after one, two, and three

TABLE I. Pink and green tourmaline: loss of weight on heating to 900–1000° C.

| Crystal. | Time. | Loss %. | Crystal. | Time. | Loss %. |
|---|---|---|---|---|---|
| T. 4. pink | 3 hrs. | 3·49 3·71 | T. 4. green | 3 hrs. | 4·19 |
| T. 13. pink | 3 hrs. | 2·61 | T. 13. green | 3 hrs. | 4·08 |
| T. 110. strong pink | 3 hrs. | 6·29 | T. 110. pale green | 3 hrs. | 3·11 |
| T. 12. colourless-pink | 3 hrs. | 3·59 3·98 4·08 | | | |
| T. 8. strong pink | 1 hr. | 4·27 | | | |
| | | | T. 7. dull green-colourless | 1 hr. | 3·84 |
| | | | T. 9. green-yellow green-colourless | 1 hr. | 4·49 |
| | | | T. 10. pale green | 3 hrs. | 4·53 |
| | | | T. 111. dark green, opaque | 3 hrs. | 4·02 |
| Mean (excluding T. 110) | | 3·68 | Mean (not T. 110) | | 4·18 |

hours heating, the green crystal also lost weight more quickly than its pink counterpart. T. 110 was again anomalous, since the pink part of the crystal lost twice as much weight as the green. There is no constant value for the weight loss, which must depend on something variable in the atomic structure and chemical composition. The structure is undoubtedly destroyed in part by the heating. One of the hydroxyl groups in the crystal is more loosely bound than the others, and it may be that the loss in weight is due—at least in part—to the removal of this hydroxyl group. The magnitude of the effect (3–4 %) is compatible with this hypothesis.

### Lattice structure.

The atomic lattice pattern of tourmaline has only recently been determined.[1,2] There is still some disagreement on minor points of symmetry, but the essential structure is satisfactorily established. The basic unit is a ring of six silicon atoms, with the appropriate oxygen

[1] G. E. Hamburger and M. J. Buerger, The structure of tourmaline. Amer. Min., 1948, vol. 33, pp. 532–540. [M.A. 10–541.]

[2] T. Ito and R. Sadanaga, A Fourier analysis of the structure of tourmaline. Acta Cryst., 1951, vol. 4, pp. 385–390. [M.A. 11–429.]

groupings, and with three $(BO_3)$ groups and three $(OH)$ groups symmetrically placed in relation to it. Each silicon ring is linked to the neighbouring ring structures by six aluminium atoms. The large central cavity of the six-sided ring is the main focus of interest for this investigation, since it is here that replacement occurs. The centre of this cavity is filled with large, loosely bonded atoms, Na, Ca, and OH or F. (It is suggested that this central $(OH)$ group may be the one that is displaced on heating.) Symmetrically arranged around the central cavity are three more sites where replacement can occur, and where iron and manganese, if present, will be situated—according to the structural analyses. The formula for the unit cell is $NaR''_3Al_6(BO_3)_3(OH)_4Si_6O_{18}$; Ca can replace Na if valency conditions are satisfied. $R''$ can be $Fe''$, Mn, Mg, $(Al+Li)$, $Fe'''$ (if valency conditions are satisfied), &c.

### Chemical composition.

Table II gives the results of partial chemical analyses of one of the crystals used for the absorption measurements. At first sight, it is somewhat disconcerting to observe that both the pink and green portions of T. 4 contain both iron and manganese. The green portion contains more ferrous iron, more ferric iron, and considerably more manganese than the pink. Both crystals contain lithium, the green one rather more than the pink, although it is doubtful if the difference is significant.

TABLE II. Partial analyses of a tourmaline crystal from San Diego County, California. (Analyst, W. H. Herdsman.)

|  |  | Pink. T. 4. % |  | Green. T. 4. % |
|---|---|---|---|---|
| Fe (ferrous) | ... | 0·12 | ... | 0·58 |
| Fe (ferric) | ... | 0·36 | ... | 0·67 |
| Mn | ... | 0·24 | ... | 1·12 |
| Al | ... | 22·75 | ... | 21·84 |
| Si | ... | 17·56 | ... | 17·32 |
| Li | ... | 0·82 | ... | 0·94 |

These results may be considered together with table III which is a collection of analyses[1, 2, 3] of tourmaline from different localities. The data used to compile the tables is by no means comprehensive, but

[1] T. N. Agafonova, Chemical composition and colour of tourmalines from the Borshchovochnoi Mts. Compt. Rend. (Doklady) Acad. Sci. URSS, 1947, vol. 55, pp. 849–852. [M.A. 10–317.]

[2] E. S. Dana, System of Mineralogy, 6th edit., 1892, p. 555.

[3] W. Kunitz, Die Mischungsreihen in der Turmalingruppe. . . . Chemie der Erde, 1929, vol. 4, pp. 208–251. [M.A. 4–203.]

TABLE III. Chemical composition of pink, green, and dark green to black tourmalines.

| | Colour. | Si. | Al. | Si:Al ratio. | Mn. | Fe$^{++}$. | Fe$^{+++}$. | Fe+Mn. | Li. | Mg. | F. | H$_2$O. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Siberia. (Agafonova, anal. 1) | rose | 17·86 | 22·20 | 1:1·243 | 0·45 | 0·12 | 0·06 | 0·63 | 0·06 | 0·21 | 0·96 | 5·33 |
| Siberia. (Agafonova, anal. 2) | rose | 17·37 | 22·67 | 1:1·305 | 0·36 | 0·17 | — | 0·53 | 0·07 | 0·37 | 0·80 | 4·15 |
| Siberia. (Agafonova, anal. 3) | rose | 18·27 | 22·26 | 1:1·218 | 0·20 | 0·10 | 0·05 | 0·35 | 0·11 | 0·14 | 0·32 | 2·98 |
| Rumford, Maine. (Dana, anal. 36) | rose | 17·77 | 22·89 | 1:1·256 | 0·27 | 0·20 | — | 0·47 | 0·74 | 0·04 | 0·58 | 4·26 |
| Brazil. (Dana, anal. 37) | pink | 17·36 | 22·47 | 1:1·294 | 0·61 | 0·40 | — | 1·01 | 0·82 | — | — | 3·90 |
| Murminsk, Urals. (Kunitz) | red | 17·74 | 21·97 | 1:1·238 | 1·15 | 0·21 | — | 1·36 | 0·83 | — | 0·96 | 3·18 |
| Rožná, Moravia. (Kunitz) | pale red | 17·61 | 21·83 | 1:1·240 | 0·67 | 0·94 | — | 1·61 | 0·65 | — | 0·64 | 3·16 |
| Penig, Saxony. (Kunitz) | red | 17·44 | 21·75 | 1:1·247 | 1·29 | 0·40 | — | 1·69 | 0·67 | 0·07 | 0·81 | 3·44 |
| Nerchinsk, Siberia. (Kunitz) | dark red | 17·59 | 21·20 | 1:1·206 | 1·58 | 0·40 | — | 1·98 | n.d. | n.d. | n.d. | n.d. |
| NaLi$_{1.5}$Al$_6$(BO$_3$)$_3$(OH)$_4$Si$_6$O$_{18}$ | — | 17·71 | 21·25 | 1:1·200 | — | — | — | — | 1·12 | — | — | — |
| NaMgLiAlAl$_6$(BO$_3$)$_3$(OH)$_4$Si$_6$O$_{18}$ | — | 17·84 | 20·00 | 1:1·121 | — | — | — | — | 0·736 | 2·58 | — | — |
| Siberia. (Agafonova, anal. 4) | green | 16·62 | 20·46 | 1:1·231 | 3·50 | 0·26 | 0·59 | 4·35 | 0·14 | 0·37 | 0·76 | 3·53 |
| Siberia. (Agafonova, anal. 5) | green | 16·31 | 19·95 | 1:1·223 | 2·53 | 0·90 | 4·58 | 8·01 | 0·14 | 0·24 | 0·41 | 3·38 |
| Siberia. (Agafonova, anal. 6) | green | 16·81 | 20·46 | 1:1·217 | 3·97 | 1·56 | 0·15 | 5·68 | 0·06 | 0·35 | 0·64 | 3·86 |
| Siberia. (Agafonova, anal. 7) | green | 16·61 | 19·95 | 1:1·201 | 4·87 | 1·55 | 0·29 | 6·71 | 0·08 | 0·30 | 0·77 | 3·88 |
| Siberia. (Agafonova, anal. 8) | green | 16·96 | 19·76 | 1:1·162 | 3·66 | 1·00 | 0·96 | 5·62 | 0·07 | 0·34 | 0·80 | 4·74 |
| Abuurn, Maine. (Dana, anal. 38) | colour-less | 17·80 | 20·97 | 1:1·178 | 1·07 | 1·07 | 0·22 | 2·36 | 0·64 | — | 0·62 | 4·16 |
| Brazil. (Dana, anal. 39) | pale green | 17·45 | 20·99 | 1:1·203 | 1·14 | 1·78 | 0·11 | 3·03 | 0·81 | — | 0·32 | 3·63 |
| Auburn, Maine. (Dana, anal. 40) | pale green | 17·67 | 19·97 | 1:1·131 | 0·39 | 3·02 | 0·31 | 3·42 | 0·64 | 0·02 | 0·62 | 4·18 |
| Brazil. (Dana, anal. 41) | olive-green | 17·23 | 20·18 | 1:1·171 | 1·72 | 2·48 | 0·23 | 4·43 | 0·77 | 0·02 | 0·14 | 3·64 |
| Nerchinsk, Siberia. (Kunitz) | green brown | 16·81 | 19·92 | 1:1·184 | 6·36 | — | — | 6·36 | 0·37 | — | — | — |

TABLE III (*continued*).

| | Colour. | Si. | Al. | Si:Al ratio. | Mn. | $Fe^{++}$ | $Fe^{+++}$ | Fe+Mn. | Li. | Mg. | F. | $H_2O$. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Chesterfield, Mass. (Kunitz) | ... green | 17·92 | 18·20 | 1:1·075 | 8·36 | 5·48 | — | 8·84 | 0·48 | 0·08 | — | 3·94 |
| South-West Africa. (Kunitz) | ... blue-green | 16·85 | 21·07 | 1:1·251 | 0·56 | 3·79 | — | 4·35 | 0·56 | 0·51 | 1·01 | 2·89 |
| $NaLiAlFe_{0.5}Mn_{0.5}Al_6(BO_3)_3(OH)_4Si_6O_{18}$ | | 17·28 | 19·35 | 1:1·120 | — | — | — | 5·68 | 0·71 | — | — | — |
| $NaMgLi_{0.5}Al_{0.5}Fe_{0.5}Mn_{0.5}Al_6(BO_3)_3(OH)_4Si_6O_{18}$ | | 17·14 | 17·85 | 1:1·042 | — | — | — | 5·64 | 0·35 | 2·48 | — | — |
| Siberia. (Agafonova, anal. 9) | ... black | 16·10 | 27·46 | 1:1·169 | 0·23 | 9·30 | 1·78 | 10·31 | 0·04 | 0·57 | 0·19 | 3·44 |
| Siberia. (Agafonova, anal. 10) | ... black | 16·26 | 26·64 | 1:1·136 | 1·07 | 8·92 | 1·33 | 11·32 | 0·02 | 0·21 | 0·43 | 3·74 |
| Siberia. (Agafonova, anal. 11) | ... black | 15·82 | 26·18 | 1:1·154 | 0·71 | 9·51 | 0·79 | 11·01 | 0·03 | 0·76 | 0·41 | 3·47 |
| Siberia. (Agafonova, anal. 12) | ... black | 15·82 | 24·68 | 1:1·168 | 0·99 | 8·43 | 1·49 | 10·91 | 0·07 | 0·46 | 0·17 | 3·17 |
| Siberia. (Agafonova, anal. 13) | ... black | 16·12 | 24·32 | 1:1·086 | 0·81 | 9·06 | 2·07 | 9·94 | 0·07 | 0·96 | 0·64 | 2·99 |
| Rumford, Maine. (Dana, anal. 42) | dark green | 17·05 | 20·18 | 1:1·183 | 0·25 | 5·00 | — | 5·25 | 0·45 | — | 0·16 | 3·52 |
| Auburn, Maine. (Dana, anal. 43)... | dark green | 16·92 | 19·43 | 1:1·148 | 0·56 | 5·49 | 0·11 | 6·16 | 0·50 | 0·10 | 0·71 | 4·05 |
| Auburn, Maine. (Dana, anal. 45)... | black | 16·92 | 18·07 | 1:1·104 | 0·04 | 11·06 | — | 11·10 | — | 0·06 | — | 3·62 |
| Brazil. (Dana, anal. 46) | ... black | 16·16 | 17·32 | 1:1·070 | 0·09 | 10·64 | 0·23 | 10·96 | 0·04 | 1·28 | 0·06 | 3·42 |
| $NaLi_{0.5}Al_{0.5}FeMnAl_6(BO_3)_3(OH)_4Si_6O_{18}$ | | 16·54 | 17·19 | 1:1·040 | — | — | — | 10·86 | 0·34 | — | — | — |
| $NaMgFeMnAl_6(BO_3)_3(OH)_4Si_6O_{18}$ | | 16·47 | 15·86 | 1:0·962 | — | — | — | 10·84 | — | 2·38 | — | — |

Na, Ca, K, and B percentages have been omitted. All figures are percentages except the Si:Al ratio.

neither is it at all selective. The percentage compositions of some 'ideal' crystals thought to approximate fairly closely to the pink, green, and black types have been given for reference. The boron, sodium, potassium, and calcium figures have been omitted from the tables since none of these was expected to contribute directly to the colour. The important elements giving rise to colour are those having internal electron orbits which are normally unoccupied, i.e. the transition elements, the rare-earths, and elements allied to the rare-earths. The rare-earths (both groups) give line-like absorption spectra and fluorescence; the transition elements give broad bands and never any fluorescence. The boron content of the crystals was reasonably constant and there was always considerably more sodium than calcium or potassium.

Iron and manganese are present in the pink, green, and black crystals. The pink tourmalines have from 0·2–1·5 % Mn and up to 1 % ferrous iron. Generally speaking, the ferric iron content is low, although it is important not to place too much emphasis on this, since it is difficult to distinguish accurately between the two valency states when both are present in such small quantities. The lowest manganese content quoted is equivalent to one Mn atom to each twenty unit cells. The black crystals also contain about 1 % of manganese; the green crystals have the highest Mn content up to 5 %. Both the green and black tourmalines may contain an appreciable amount of ferrous iron in addition to ferric; the total iron content of the green crystals is always in excess of the pink.

Magnesium and lithium are present throughout in small and variable amounts. The lithium content seems to depend in part on the locality, since, for example, all tourmaline analysis quoted by Agafonova (from the Borshchovochnoi Mts., Siberia) are low in lithium.

The silicon:aluminium ratio has been calculated for the recorded analysis and for the ideal composition. It is interesting to observe that the amount of aluminium is almost always higher than that given by the theoretical formulae, suggesting a limited amount of replacement of Si by Al in the basic silicon-ring structure. There is no evidence from the analyses that this proxying occurs to a greater or lesser extent in the pink or green forms, although this does not preclude the possibility of it being more random in one case than the other.

The spectroscopic data required that the pink crystals should carry divalent manganese and the green ones ferrous iron. These conditions are fulfilled by the chemical analyses, but this is by no means the complete story. It is still necessary to account for the ferrous iron in the pink crystals and the high manganese content of the green crystals. In

the one case it is the manganese that controls the colouring and in the other the ferrous iron is responsible. The simplest explanation would be one of differing valency states. Quensel and Gabrielson[1] attempted to determine whether any of the manganese present in the pink tourmaline was in a higher state of oxidation but could obtain no evidence for this. They also suggested that the iron in pink tourmaline is trivalent and that in green mainly divalent; once again the experiments designed to test this theory gave no positive results. Carobbi and Pieruccini (1947, loc. cit.) provide a useful summary of earlier theories relating to colour. From a review of the data provided by emission spectra they suggest that the green colour is due to divalent iron, the pink colour to manganese plus caesium and lithium. Any satisfactory theory of colour must explain the mutual exclusiveness of the pink and green forms. It is here suggested, tentatively, that the solution may lie in the peculiar nature of the manganese atom which only gives rise to colour under certain rather restricted conditions. These conditions are not often satisfied, but when they are—as in potassium permanganate—the colouring can be very strong indeed. (In this case it is thought to be due to the tetrahedral co-ordination of four oxygen atoms around the manganese.) Manganese sulphate crystals are a very pale pink; the colour is somewhat strengthened in solution, possibly because of the tetrahedral co-ordination of four water molecules. The pink colour of a tourmaline crystal is more intense than that of any solution of manganese sulphate. Presumably the site provided for the Mn atom in a tourmaline lattice satisfies the stringent electronic conditions required for the production of colour in manganese. Even so, the strength of the colour is much less than the theoretical maximum, which is nearly attained in $MnO_4'$.

The pink colour is shown by crystals with as little as $0.2 \%$ Mn. The green colour, on the other hand, is only seen when the total iron content (ferrous plus ferric) is $1\%$ or more. This amount of iron seems to inhibit the production of the manganese colouring, possibly because of some slight distortion of the lattice. Note the analysis of a colourless crystal (Dana, analysis 38) which contains about $1\%$ of both Fe and Mn: the iron content is adequate to inhibit the manganese colour, but is not sufficient to produce a distinct green colour. One interesting point to remember is the absorption of the extraordinary ray of pink tourmaline (graph 3), which is like that of green tourmaline but less intense—as

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[1] P. Quensel and O. Gabrielson, Minerals of the Varuträsk pegmatite. XIV. The tourmaline group. Geol. För. Förh. Stockholm, 1939, vol. 61, pp. 63–90. [M.A. 7–335.]

would be expected from the low iron content: a similar low absorption of the ordinary ray is masked by the strong pink colour. Environmental conditions appear to have much less effect on the strength of absorption in the case of iron.

Lithium is commonly believed to play some part in the production of a pink colour, but it is not possible to confirm or deny this from these results. Lithium is certainly present in all the pink crystals, but the green and black ones also contain lithium, although sometimes in lesser amount. It is perhaps worth noting that the lowest lithium recorded for the pink tourmaline—0·06–0·07 %—would provide one Li atom for ten unit cells.

In marked contrast to the pink and green forms there appears to be a complete gradation chemically between green and black tourmaline. The black crystals are characterized by a high ferric iron content, low manganese, and low lithium.