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Lithium tourmalines from the Meldon aplite, Devonshire, England

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SUMMARY. Seven chemical analyses of pink or green tourmalines belonging to the elbaite-schorl series, along with their physical, optical, and X-ray data are presented. Linear variation diagrams showing the relationship between composition and refractive indices, specific gravities, and cell parameters are constructed. Relationship between colour and chemical composition is also discussed.

THE Meldon aplite, Devonshire, is a soda-lithia aplite dyke about 60 to 80 ft in thickness, occurring three-quarters of a mile north-west of the main Dartmoor granite (Worth, 1920). The aplite has been cut and metasomatized by a multitude of successive generations of thin (2 to 7 cm) K- and Li-rich veins containing tourmaline crystals. The magmatic veins of earlier generations and surrounding contemporaneously metasomatized aplites contain green tourmalines whereas the later pneumatolytic-hydrothermal veins and associated or contemporaneously metasomatized aplite contains pink tourmaline (rubellite). Four samples (Table I), M.P.T., M18, M200, and M17 belong to the rubellite variety of elbaite (M17 being paler pink than the others) and three samples, M5, MK653, and R. A. H. are verdelites (green-coloured elbaites).

The samples M18 and M.P.T. are from veins composed of orthoclase, lepidolite, quartz, and rubellite; the sample M200 comes from a very late greisen-like vein composed chiefly of rubellite, lepidolite, quartz, and a subordinate amount of feldspar; the samples M17, MK653, M5 and R. A. H. have been obtain from reconstituted aplite, composed mainly of albite, quartz, and lepidolite.

Chemistry. The green tourmalines are richer in iron and poorer in aluminium than the pink tourmalines. In the green tourmalines ferrous iron and manganese are inversely related. There is no clear difference in the lithium or manganese content of the two groups. At first sight there is poor correspondence between the theoretical and the calculated formulae (Table I) as there is so much Al included in the R_3 group that, despite 0·74 to 0·96 Li, the total valency of the R_3 group is around 7. In the formula $NaR_3Al_6B_3Si_6O_{27}(OH)_4$, R_3 should have only a total of 6 valencies; however, the deficiency of Si, B, and OH restores the over-all balance. From an examination of published analyses of tourmalines, Foit and Rosenberg (1974) have identified several analyses that show a variation of the trivalent ions (R^{3+}) with (R^{+}+OH^{-}+F^{-}). This

TABLE I. *Chemical analyses and physical properties of tourmalines*

	Pink				Green		
	M17	*M18*	*M200*	*M.P.T.*	*MK653*	*M5*	*R. A. H.*
SiO_2	37·08	37·52	37·14	36·86	36·86	36·64	36·36
TiO_2	0·08	0·12	0·00	0·12	0·00	0·38	tr.
Al_2O_3	41·72	42·43	44·24	43·59	35·49	37·43	40·48
Fe_2O_3	0·00	0·09	0·00	0·07	0·48	0·51	—
FeO	1·12	1·18	0·06	0·21	6·03	6·71	3·64
MnO	0·00	0·00	0·00	0·27	0·30	0·06	1·05
MgO	0·21	0·37	0·33	0·51	0·35	0·31	0·09
CaO	1·80	0·32	0·32	0·68	2·51	0·36	0·67
Na_2O	2·61	2·27	2·50	2·27	2·61	2·40	2·20
K_2O	0·41	0·36	0·31	0·26	0·41	0·23	0·44
Li_2O	1·19	1·34	1·52	1·33	1·12	1·17	1·27
H_2O^+	3·31	3·28	3·05	3·47	3·58	3·43	3·64
H_2O^-	0·12	0·13	0·07	0·12	0·08	0·16	0·08
B_2O_3	10·54	10·52	10·78	10·42	10·35	10·15	10·30
Total	100·19	99·93	100·32	100·18†	100·17	99·94	100·28*
ω	1·641	1·642	1·638	1·639	1·646	1·648	1·644
ϵ	1·622	1·623	1·618	1·620	1·625	1·626	1·623
D	3·02	3·03	3·01	3·01	3·10	3·13	3·096
a(A°)	15·84	15·84	15·85	15·85	15·93	15·94	—
c(A°)	7·09	7·09	7·10	7·10	7·12	7·13	—
c/a	0·448	0·448	0·448	0·448	0·447	0·447	—
	Numbers of ions on the basis of 31(O, OH, F)						
Si	5·899	5·829	5·843	5·815	6·036	5·989	5·841
B	2·905	2·915	2·925	2·836	2·925	2·862	2·855
Al	6·000	6·000	6·000	6·000	6·000	6·000	6·000
Al	1·825	2·028	2·198	2·105	0·851	1·212	1·664
Fe^{3+}	0·000	0·012	0·000	0·008	0·059	0·063	—
Mg	0·050	0·089	0·078	0·119	0·086	0·076	0·021
Ti	0·010	0·015	0·000	0·014	0·000	0·047	—
Li	0·761	0·864	0·962	0·844	0·738	0·770	0·821
Fe^{2+}	0·149	0·158	0·008	0·028	0·826	0·917	0·488
Mn	0·000	0·000	0·000	0·036	0·041	0·079	0·143
Na	0·805	0·706	0·761	0·694	0·829	0·760	0·685
Ca	0·307	0·055	0·062	0·115	0·441	0·063	0·115
K	0·084	0·074	0·054	0·053	0·087	0·047	0·090
ΣXY	3·99	4·00	4·12	4·02	3·96	4·03	4·03
OH	3·513	3·513	3·199	3·652	3·911	3·740	3·950†

* Includes F 0·10, less O = F 0·04. † Includes F 0·050.

relationship can be resolved into two competing substitutions: $R^{2+}+H^+ = R^{3+}$ and $R^{2+}+R^+=R^{3+}$—in the Meldon elbaites a very slight trend towards this second, alkali-deficient end-member can be seen, with (Na+K) totalling 0·74 to 0·92. The ionic balances also demonstrate that the analyses fit better to this formula (Donnay and Buerger, 1950; Ito and Sadanaga, 1951) with 19 cations to 31 (O,OH) rather than to the formula $NaR_9B_3Si_6(O,OH)_{30}$ (Belov and Belova, 1949) with 19 cations to 30

(O,OH); e.g. specimen M17 has 18·8 cations to 31 (O,OH) or 18·2 cations if calculated to 30 (O,OH).

Cell Parameters. The cell parameters of the pink tourmalines range from $a = 15{\cdot}84$ to 15·85 Å and $c = 7{\cdot}09$ to 7·10 Å, which are distinctly lower than the green iron-rich elbaites with $a = 15{\cdot}93$ to 15·94 and $c = 7{\cdot}12$ to 7·13 Å. The difference in the axial ratio c/a between the two groups is, however, very small. The a and c parameters of these tourmalines have been plotted against each other on fig. 1, in which Epprecht's (1953) results have been replotted after conversion from kX to Ångstrom units. The pink tourmalines lie close to the elbaite end and the green tourmalines lie approximately half-way between elbaite and schorl end as required by their respective compositions.

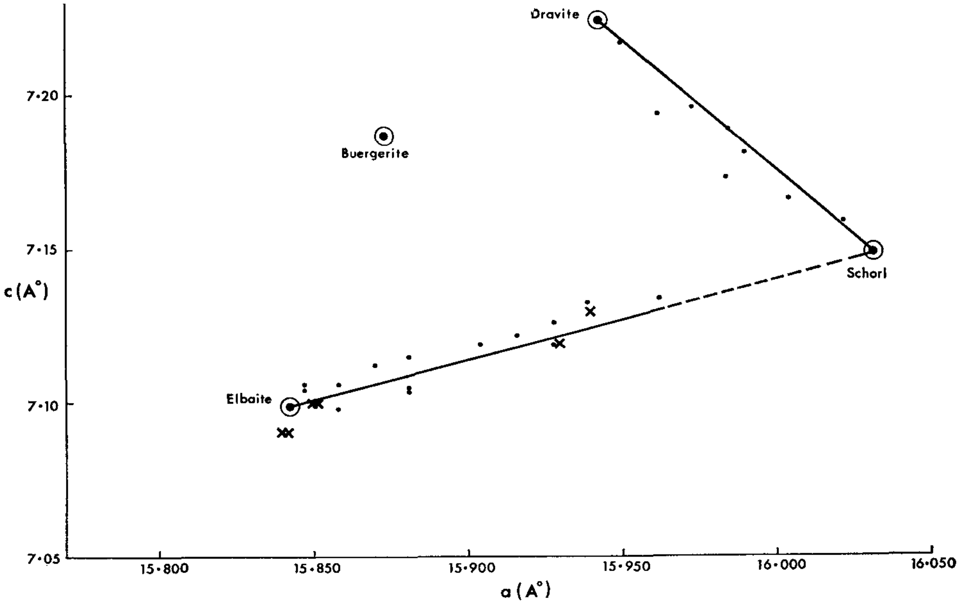

FIG. 1. Cell dimensions of the Meldon elbaites (X) plotted on a new diagram of the results of Epprecht (1953) converted from kX to Å (·) and the values for buergerite given by Donnay *et al.* (1966).

Optical and physical properties. Linear variation diagrams showing the relationship between the number of ions of ($Fe^{2+}+Fe^{3+}+Mn^{2+}$) on the basis of 31 (O,OH) and the refractive indices and the specific gravities are presented in fig. 2.

Colour variation in tourmalines, especially elbaites, has invoked much interest. According to Quensel and Gabrielson (1939) the pink tourmalines contain iron dominantly in trivalent and the green tourmalines in divalent form. The present work does not lend support to this view, because ferrous iron is dominant in both the pink and the green elbaites. Carobbi and Pieruccini (1947) regard pink colour as due to divalent manganese plus lithium and caesium, whereas green colour is due to divalent iron. This idea is inapplicable here because three of the pink tourmalines, M18, M200, and

M17, contain neither a detectable amount of manganese nor of caesium, and so far as lithium is concerned both the pink and the green tourmalines contain similar amounts. Manning (1969) has suggested that the colour of pink tourmaline is due to *d-d* electronic transitions in octahedrally-bonded Mn^{3+}; they have an absorption band at 19 000 cm^{-1} (520 nm). But although most pink tourmalines (including that studied by Manning) contain appreciable manganese, the virtual absence of this element in three out of four Meldon rubellites make this explanation of the pink colour improbable for these particular tourmalines. The green colouration of some elbaites has been tentatively ascribed to the $Fe^{2+} \rightarrow Ti^{4+}$ charge-transfer giving rise to a band in the 22 000 to 24 000 cm^{-1} range, whereas the intensity of the $Fe^{2+} \rightarrow Fe^{3+}$ band at around 18 500 cm^{-1} is a good indicator of the degree of oxidation of iron (Faye *et al.*, 1974). For other recent work on the crystal field spectra and dichroism of tourmaline see Wilkins *et al.*, (1969) and Hermon *et al.* (1973).

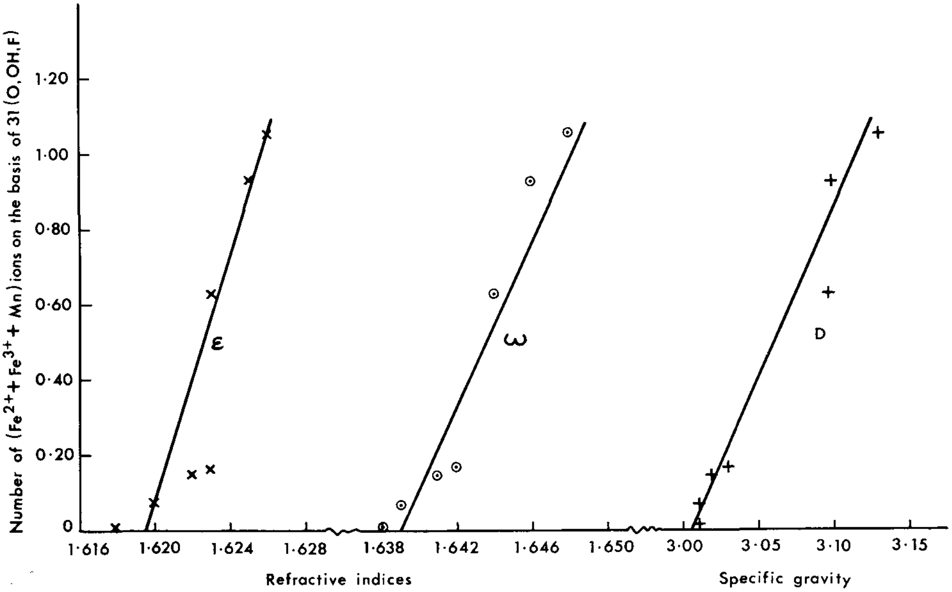

FIG. 2. The refractive indices and specific gravities of elbaites from Meldon in relation to the number of $(Fe^{2+}+Fe^{3+}+Mn)$ ions on the basis of 31(O,OH,F).

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