A CHEMICAL AND OPTICAL STUDY OF THE BLACK TOURMALINES*

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CONTENTS

HISTORICAL INTRODUCTION

The first analysis of tourmaline is attributed to A. Wondraschek.[1] Soon afterwards, in the early part of the eighteenth century, analyses were made by Vauquelin and Klaproth. The presence of lithium and boron was not shown until 1818, when Arfvedson[2] discovered the former and Lampardius[3] the latter. In 1827 Gmelin[4] and in 1845 Hermann[5] published good chemical analyses of tourmaline. Hermann pointed out for the first time that silica and boric oxide were in definite molecular proportions, four to one. In 1850 thirty analyses were published by Rammelsberg.[6] Recognizing the defects of his analyses he revised his paper in 1870.[7] From this revision Rammelsberg concluded that all tourmalines were derived from the acid H_6SiO_5. In 1888 Riggs[8] published twenty analyses and proposed as a general formula the simple boro-orthosilicate, $R_9BO_2 \cdot 2SiO_4$. Penfield and Foote[9] showed that

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[1] *Abhand. Bohm. Gest.*, **3**, 19, 1795.

[2] Schweiger's *Jour. d. Chem. u. Phys.*, **22**, 111.

[3] *Ann. d. Phys. u. Chem.*, **30**, 107.

[4] *Pogg. Ann.*, **9**, 127.

[5] *Journal für prakt. Chem.*, **35**, 232.

[6] *Ann. der Phys. u. Chem.*, **81**, 1.

[7] *Ann. der Phys. u. Chem.*, **215**, pp. 379 and 547.

[8] *Am. Jour. Sc.*, (III), **35**, 35.

[9] *Am. Jour. Sc.*, (IV), **157**, 100.

this formula reduces to that of Rammelsberg, namely, R_6SiO_5. Riggs further suggested that there are three tourmaline molecules representing a lithium, an iron, and a magnesium tourmaline, for which he gives formulae.

A short time later Wülfing[10] recalculated Riggs' analyses and decided that tourmalines are isomorphous mixtures represented by the two formulae:

Alkali tourmaline $12SiO_2 \cdot 3B_2O_3 \cdot 8Al_2O_3 \cdot 2Na_2O \cdot 4H_2O$, and Magnesium tourmaline $12SiO_2 \cdot 3B_2O_3 \cdot Al_2O_3 \cdot 12MgO \cdot 3H_2O$. However, there are certain inaccuracies and he suggests the need of a third formula.

Scharizer[11] about this time published three analyses of tourmaline from Schüttenhofen, Bohemia, and concluded with a very cumbersome formula.

Jannasch and Kalb[12] in 1889 estimated directly the water and boron in nine samples. They reached a general formula of $R_9 \cdot BO_2 \cdot (SiO_4)_2$, which reduces by Riggs' formula to Rammelsberg's acid, R_6SiO_5.

Various other investigators, notably, Goldschmidt[13] and Rheineck[14] in 1893, calculated analyses and all agreed that the tourmalines are isomorphous mixtures of alkali and magnesia molecules.

Alteration to muscovite, sericite, lepidolite, biotite and chlorite had been noted by investigators. Clarke in 1895[15] discussed the change of tourmaline to mica and upon this basis proposed formulae that would permit such an alteration.

Groth[16] adopted the formula of Jannasch with a slightly different interpretation. Penfield and Foote[17] made very careful analyses of a colorless and a green tourmaline from which they derived the acid $H_{20}B_2Si_4O_{21}$.

In 1899 Clarke[18] drew attention to the fact that his formula is identical with that of Penfield and Foote.

[10] *Mineralogische und petrographische Mittheilungen*, **10**, 161.

[11] *Zeitschr. für. Kryst.*, **15**, 343.

[12] *Ber. der deut. chem. Gesellschaft*, **22**, 216, and *Inaugural Dissertation*, G. W. Kalb, *Göttingen*.

[13] *Zeit. für Kryst.*, **17**, pp. 52 and 61.

[14] *Zeit. für Kryst.*, **22**, 52.

[15] *Bull. U.S.G.S.*, **125**, 66.

[16] *Tabellarische Uebersicht der Mineralien*, 4th edition, **1898**, 117.

[17] *Am. Jour. Sc.*, 7, **157**, 108.

[18] *Am. Jour. Sc.*, **158**, 8, 120

W. T. Schaller[19] and P. Reiner[20] avoided the difficulty of alteration to mica, that Clarke found in earlier analyses, by trebling their formula. Thus their formula would appear as $H_{60}Si_{12}B_6O_{63}$. Clarke[21] modified this to give a cumbersome formula that would make the tourmalines triboratotetraluminotetraorthosilicates.[22]

W. Vernadsky[23] assumed the tourmalines to be additive substances containing the kaolin ring, $R_4Al_2Si_2O_3$ with boron in place of the aluminum. This furnishes a nucleus, $R_4Al_2B_2Si_4O_{16}$, from which three groups were derived. These hypotheses are tentative and for the most part merely ingenious attempts at a solution of the riddle.

About this time attention was directed towards the optical properties of the tourmalines. P. Reiner,[24] Wülfing[25] and K. Becht have contributed a great deal of our available knowledge. An excellent compilation of the optical data can be found in Doelter.[26]

Only seven black tourmalines with optical data can be found in the literature and they give the following indices.

Location	ω	ϵ	$\omega-\epsilon$
Tirol[27]	1.6429	1.6195	0.0234
Tsilaisina[28]	1.6525	1.6279	0.0246
Madagascar[29]	1.6515	1.6281	0.0234
Ramona, San Diego[30]	1.669	1.6380	0.031
Auburn, Me.[31]	1.666	1.637	0.029
Brazil[31]	1.662	1.633	0.029
Haddam, Conn.[31a]	1.669	1.638	0.031

[19] Inaug. Diss. *Z. Kryst.*, **51**, 321, 1912.

[20] Inaug. Diss. (*Heidelberg*, **1913**).

[21] *Bull. U.S.G.S.*, **125**, 88.

[22] Mellor, *Inorganic and Theoretical Chemistry*, vol., **6**, 1925.

[23] *Z. Kryst.*, **53**, 273, 1914.

[24] P. Reiner, *op. cit.*

[25] E. A. Wülfing und K. Becht, *Sitzber. Heidelberg Ak.*, **1913**, Abh. 20.

[26] Doelter's *Handbuch der Mineralchemie*, Band **11**, Teil 2.

[27] K. Zimanyi, *Z. Kryst.*, **22**, 333, 1894.

[28] L. Duparc, M. Wunder und L. Sabot, *Mem. soc. phys. et d'hist. Nat. de Geneve*, **36**, Heft III, 283, 1910.

[29] R. Ch. Sabot, Diss. *Geneve*, **1914**.

[30] W. T. Schaller, Inaug. Diss., *Zeit. Kryst.*, **51**, 321, 1912.

[31] Riggs, *op. cit.*

[31a] Schaller, *op. cit.*, 332.

The following table from Shand's Eruptive Rocks,[32] indicates that tourmalines vary widely in composition.

SiO_2	34.63–41.16
B_2O_3	9.00–11.00
Al_2O_3	25.29–44.05
Fe_2O_3	nil – 6.60
Cr_2O_3	nil –10.80
FeO	nil –14.40
MgO	nil –14.90
CaO	nil – 5.10
Na_2O	nil – 3.59
K_2O	nil – 2.17
Li_2O	nil – 1.73
H_2O	nil – 4.61
F	nil – 1.19

Upon tourmalines in general a large number of optical observations have been made. Some of the investigators include M. Jerofejeff,[33] P. H. Schwehel,[34] A. Cossa and A. Arzruni,[35] G. B. d'Achiardi,[36] L. Duparc and his co-workers.[37]

According to E. A. Wülfing[38] the lithium tourmalines have the lowest indices of refraction; the magnesium tourmalines intermediate values, and the iron tourmalines possess the highest indices. A selection[39] of values from data furnished by the above mentioned investigators follows:

	Colorless	Dark green	Green	Red	Dark red	Straw yellow	Dark brown	Black
ω	1.6424	1.6424	1.6401	1.6394	1.6448	1.6430	1.6481	1.6525
ϵ	1.6223	1.6222	1.6220	1.6237	1.6251	1.6224	1.6250	1.6279
$\omega-\epsilon$	0.0201	0.0202	1.0181	0.0157	0.0197	0.0206	0.0231	0.0246

The optical character of tourmaline is negative. All colored tourmaline possesses well marked pleochroism. Usually in the black varieties, ω is green or blue and ϵ is brown or red; in green

[32] S. J. Shand, Eruptive Rocks, Thomas Murby and Co., *London.*

[33] M. Jerofejeff, *Proc. Russ. Min. Soc.,* **6,** 80, 1871.

[34] P. H. Schwehel, *Z. Kryst.,* **7,** 158, 1882.

[35] A. Cossa and A. Arzruni, *Z. Kryst.,* **7,** 9, 1882.

[36] G. B. d'Achiardi, *Atti. Soc. Toscana,* **13,** 229, 1894.

[37] L. Duparc and R. Sabot, *Bull. Soc. Min.,* **34,** 139, 1911.

[38] E. A. Wülfing, *Z. Kryst.,* **36,** 538, 1902.

[39] Mellor, *op. cit.,* p. 745.

varieties, ω is green or greenish-brown and ϵ is green of a different tint. The absorption of the ordinary ray is much greater than that of the extraordinary. Mellor and Doelter give excellent summaries of the work that has been done on tourmaline relating to the optical anomalies, absorption and reflection spectrums, radioactivity, electrostatic fields, cathode rays, radium rays, ultra-violet rays, pyroelectrification, dielectric constant, magnetic susceptibility, etc.

STATEMENT OF PROBLEM

The common, black, rock-forming tourmalines have received but little attention in the literature compared with the colored varieties. There is little optical data that can be correlated with an analysis of the same specimen. Most investigators have confined themselves to a study of formulae and for such work used chiefly the colored tourmalines other than black. It would seem, then, that a series of analyses, accompanied by their optical characteristics should prove of interest. Material was carefully selected and the optical data were determined upon the same sample of powder as that used for analysis. An effort has also been made to show how the optical properties of the various specimens analyzed vary with the composition. For such a correlation the data in the literature are very meager and the present study increases the data of that type about 100 per cent.

USES OF TOURMALINE

Tourmaline is of interest primarily because it is perhaps the most abundant and typical mineral developed in the pneumatolytic or fumarolic stage of igneous rock formation. This is indicated by the boron, hydroxyl and fluorine that it contains. Thus it is one of the most common and characteristic accessory minerals found in pegmatite dikes associated with intrusive granite. Its presence in rocks indicates as a rule nearness to the contact and it is very likely to appear in rocks that have suffered contact metamorphism. In this way it is frequently found associated with ore deposits and is a a criterion of their origin. The beautiful red, green and transparent varieties are valued as gems.

ACKNOWLEDGMENTS

Tourmalines have been obtained for this study from many sources. Many museums and private collectors have donated ma-

terial. To the following, who have contributed, grateful acknowledgment is made.

MATERIAL EXAMINED AND ITS SOURCE

All available tourmalines of the common black color were examined under the microscope before selections for analyses were made. Their color, pleochroism, zoning and indices of refraction were determined as recorded in Table I.

Tourmaline is common in slates, crystalline schists, pegmatites and granites, and in the zones of contact metamorphism adjacent to acid intrusives. The tourmalines listed below are from various sources, chiefly pegmatites, but in smaller number, from schists, granites and ore deposits.

TABLE I

No.	LOCATION	COLOR POWDER	ϵ (COLOR)	ω (COLOR)	$\omega-\epsilon$
1	Richville, N.Y.	light pinkish cinnamon	1.620 (white)	1.633 (light pinkish cinnamon)	0.013
2	San Diego, Calif.	pale grayish vinaceous	1.614 (white)	1.640 (white)	0.026
3	Little American Mine, Minn.		1.626 (vinaceous buff)	1.640 (olive black)	0.014
4	Bob Ingersoll Mine, Keystone, S. D.	gull gray	1.626 (white)	1.640 (gull gray)	0.014
			1.629 (white)	1.640 (gull gray)	0.011
			1.633 (light gull gray)	1.642 (deep gull gray)	0.009
			1.630 (light gull gray)	1.644 (deep gull gray)	0.014
5	Orford, N.H.	cartridge buff	1.620 (white)	1.644 (chamois)	0.024
6	Etta Mine, S.D.	mineral gray	1.633 (white)	1.645 (pale olive buff)	0.012
7	Monroe, Conn.	drab	1.622 (cartridge buff)	1.649 (honey yellow)	0.027
*8	Etta Mine, S.D.	mineral gray	1.630 (court gray)	1.649 (pea green)	0.019
9	Newry, Me.	light grayish olive	1.633+ (deep olive buff)	1.649 (citrine drab)	0.016
10	Paris, Me.	deep olive gray	1.622 (white)	1.649 (sage green)	0.027
			1.636 (white)	1.657 (dark olive gray)	0.021
			1.633 (vinaceous fawn)	1.662 (black)	0.029
			1.633 (pale smoke gray)	1.665 (olive gray)	0.032

* Selected for analysis.

TABLE I (*continued*)

No.	LOCATION	COLOR POWDER *	ϵ (COLOR)	ω (COLOR)	$\omega-\epsilon$
11		deep mouse gray	1.633 (smoke gray)	1.649 (dark olive gray)	0.016
			1.630 (vinaceous fawn)	1.655 (olive black)	0.025
			1.640 (vinaceous buff)	1.662 (olive black)	0.022
12		Saccardos umber	1.633 (pearl gray)	1.649 (hathis gray)	0.016
			1.633 (light pinkish cinnamon)	1.662 (bister)	0.029
13		drab	1.622 (pearl gray)	1.649 (hathis gray)	0.027
			1.628 (light pinkish cinnamon)	1.660 (bister)	0.032
14		pale king's blue	1.627 (pale king's blue)	1.649 (light king's blue)	0.022
15	Newtown, Conn.	drab	1.622 (cartridge buff)	1.649 (honey yellow)	0.027
16	San Diego, Calif.	white	1.620 (white)	1.649 (pale smoke gray)	0.029
17	Rocky Mountains	drab	1.633 (pale cinnamon buff)	1.649 (bister)	0.016
18	Delaware Co., Pa.	light gray	1.630 (pale smoke gray)	1.651 (grayish olive)	0.021
			1.635 (cinnamon buff)	1.655 (clay color)	0.020
19	Statesville, N.C.	slate gray	1.638 (green)	1.652 (blue)	0.014
			1.620 (pale olive gray)	1.655 (deep olive gray)	0.035

TABLE I (*continued*)

No.	LOCATION	COLOR POWDER	ϵ (COLOR)	ω (COLOR)	$\omega-\epsilon$
20	Tyrol	gray	1.638 (pale smoke gray)	1.653 (sage green)	0.015
21	Norberg, Sweden	light gray	1.633 (light vinaceous buff)	1.653 (dark olive buff)	0.020
22	Norberg, Sweden	smoke gray	1.640 (light blue)	1.653 (dark blue)	0.013
			1.633 (pale green)	1.655 (dark green)	0.022
*23	Wickes, Mont.	deep neutral gray	1.633 (tilleul buff)	1.655 (neutral gray)	0.022
			1.636 (vinaceous buff)	1.662 (olive brown)	0.026
24	Newlin, Pa.	deep neutral gray	1.630 (pale vinaceous fawn)	1.655 (dark purplish gray)	0.025
			1.627 (olive buff)	1.655 (deep olive)	0.028
			1.633 (vinaceous buff)	1.660 (olive black)	0.027
25	Middletown, Conn.	snuff brown	1.622 (cartridge buff)	1.655 (snuff brown)	0.033
26	Crown Point, Essex Co., N.Y.	dark grayish olive	1.640 (light drab)	1.655 (black)	0.015
27	Greenland	mouse	1.638 (tilleul buff)	1.655 (deep olive)	0.017
			1.635 (pale blue)	1.662 (deep blue)	0.027
28	Macomb, N.Y.	drab	1.633 (avellanceous)	1.655 (clay)	0.022
29	Stoneham, Me.	buffy brown	1.633 (olive buff)	1.655 (dark olive buff)	0.022

TABLE I (*continued*)

No.	LOCATION	COLOR POWDER	ϵ (COLOR)	ω (COLOR)	ω−ϵ
30	Rainy Lake, Minn.	olive black	1.633 (vinaceous cinnamon)	1.655 (olivaceous black)	0.022
31	Great Barrington, Mass.	dark olive gray	1.640 (light grayish olive)	1.655 (dark grayish olive)	0.015
			1.633 (pale smoke gray)	1.662 (dark grayish olive)	0.029
32		grayish olive	1.633 (pale smoke gray)	1.655 (slate olive)	0.022
			1.633 (smoke gray)	1.655 (olive brown)	0.022
33		hair brown	1.633 (light pinkish cinnamon)	1.655 (bister)	0.022
			1.633 (pearl gray)	1.662 (hathis gray)	0.029
34		hair brown	1.633 (light olive gray)	1.655 (deep olive gray)	0.022
			1.627 (light pinkish cinnamon)	1.662 (bister)	0.035
35		blackish slate	1.640 (puritan gray)	1.657 (artemisia green)	0.017
			1.633 (vinaceous buff)	1.665 (olive brown)	0.032
36	Custer, S.D.	olive gray	1.622 (pale olive gray)	1.657 (olive gray)	0.035
37		deep olive buff	1.630 (mineral gray)	1.657 (Vetiver green)	0.027
			1.640 (light gull gray)	1.665 (slate gray)	0.025
*38	Drummerstown, Vt.	buffy brown	1.633 (cartridge buff)	1.657 (honey yellow)	0.025

* Selected for analysis.

Table I (*continued*)

No.	Location	Color Powder	ϵ (Color)	ω (Color)	$\omega-\epsilon$
39	Baffinland	dark olive gray	1.638 (pale olive gray)	1.660 (deep olive gray)	0.022
			1.642 (pale olive buff)	1.662 (dark olive buff)	0.020
			1.635 (pale olive buff)	1.662 (dark olive buff)	0.027
			1.633 (pale olive buff)	1.662 (dark olive buff)	0.029
40	Mt. Grace, Warwich, Mass.	dark gull gray	1.633 (smoke gray)	1.662 (bluish slate)	0.029
41		olive gray	1.636 (drab gray)	1.660 (olivaceous black)	0.024
42	Harford Co., Md.	slaty black	1.638 (vinaceous fawn)	1.660 (black)	0.022
43		drab	1.627 (vinaceous buff)	1.660 (buffy brown)	0.033
			1.633 (vinaceous buff)	1.660 (buffy brown)	0.027
44	Ballewidden, St. Just, Cornwall	olive gray	1.638 (pale gull gray)	1.660 (slate)	0.022
45	Luxullianite, Cornwall	olive gray	1.633 (smoke gray)	1.660 (olive gray)	0.027
46	Oracle, Ariz.	slate	1.640 (avellanceous)	1.660 (blue black)	0.020
47		deep neutral gray	1.636 (smoke gray)	1.660 (black)	0.024
48		deep neutral gray	1.633 (vinaceous fawn)	1.660 (olive black)	0.027
49		dark neutral gray	1.637 (light grayish olive)	1.660 (black)	0.023

TABLE I (*continued*)

No.	LOCATION	COLOR POWDER	ϵ (COLOR)	ω (COLOR)	$\omega - \epsilon$
50		dark neutral gray	1.638 (vinaceous buff)	1.660 (black)	0.022
			1.640 (smoke gray)	1.664 (olivaceous black)	0.024
51		buffy brown	1.638 (pale smoke gray)	1.660 (olive brown)	0.022
			1.636 (pale smoke gray)	1.662 (slate gray)	0.026
52		olive brown	1.633 (pale smoke gray)	1.660 (slate olive)	0.027
			1.636 (smoke gray)	1.660 (olive brown)	0.024
			1.640 (light Tyrian blue)	1.664 (dark Tyrian blue)	0.024
53		olive green	1.640 (pale olive buff)	1.662 (dark olive buff)	0.022
			1.638 (pale olive buff)	1.662 (dark olive buff)	0.024
54	Sarapulka, Katharinenburg, Ural	slaty blue	1.640 (vinaceous fawn)	1.662 (black)	0.022
			1.640 (vinaceous fawn)	1.667 (black)	0.027
55	Chester, Mass.	slate	1.638 (pale smoke gray)	1.662 (artemisia green)	0.024
			1.633 (pale smoke gray)	1.662 (artemisia green)	0.029
56	Macon Co., N.C.	slate	1.633 (vinaceous buff)	1.662 (dark olive)	0.029
			1.644 (olive gray)	1.664 (storm gray)	0.020
57	Warwick, N. Y.	slate gray	1.633 (vinaceous buff)	1.662 (dark olive)	0.029
			1.638 (olive gray)	1.666 (storm gray)	0.028

TABLE I (*continued*)

No.	LOCATION	COLOR POWDER	ϵ (COLOR)	ω (COLOR)	$\omega-\epsilon$
58	Greenland	greenish gray	1.633 (olive buff)	1.662 (deep olive)	0.029
59	San Diego, Calif.	dull slate gray	1.633 (vinaceous buff)	1.662 (dark olive)	0.029
60	Greenland	mouse	1.645 (tilleul buff)	1.662 (deep olive)	0.017
61	Edinburgh, N. J.	grayish olive	1.640 (grayish olive)	1.622 (dark grayish olive)	0.022
62	Pierrepont, N. Y.	neutral gray	1.640 (pale smoke gray)	1.662 (black)	0.022
63	Springfield, Vt.	neutral gray	1.636 (smoke gray)	1.662 (black)	0.026
			1.636 (pale green blue slate)	1.662 (deep green blue slate)	0.026
64	Madagascar	slate	1.640 (pale smoke gray)	1.662 (black)	0.022
65	Haddam, Conn.	deep neutral gray	1.633 (drab gray)	1.662 (blackish slate)	0.029
66	Springfield, N.H.	slate	1.640 (drab gray)	1.662 (blackish slate)	0.022
67	East Hebron	buffy brown	1.633 (pale smoke gray)	1.662 (deep olive)	0.029
68	Sylvan Lake, S.D.	dark olive gray	1.638 (smoke gray)	1.662 (deep slate green)	0.024
			1.638 (pale smoke gray)	1.662 (dark olive buff)	0.024
			1.638 (pale smoke gray)	1.662 (black)	0.024
69	Chester, Phil.	slate	1.633 (pale smoke gray)	1.662 (olivaceous black)	0.029

TABLE I (*continued*)

No.	LOCATION	COLOR POWDER	ε (COLOR)	ω (COLOR)	ω−ε
*70	St. Lawrence Co.	deep neutral gray	1.636 (pale smoke gray)	1.662 (deep grayish olive)	0.026
71	Tate Quadrangle, Georgia	blue black	1.640 (light cinnamon drab)	1.662 (black)	0.022
72	North of Tate, Ga.	slate	1.638 (pale brownish drab)	1.662 (blue black)	0.024
73	Tate Quadrangle, Ga.	slate	1.640 (light cinnamon drab)	1.662 (blue black)	0.022
74	Filchburg, N.Y.	dark olive gray	1.636 (dark olive buff)	1.662 (dark olive)	0.026
75	Pringle, S.D.	deep neutral gray	1.640 (smoke gray)	1.662 (deep grayish olive)	0.022
76	Pine Creek, Idaho	slate color	1.640 (vinaceous fawn)	1.662 (bluish black)	0.022
77	Shoup area, Idaho	bluish black	1.640 (vinaceous fawn)	1.662 (bluish black)	0.022
78	Middletown, Conn.	slate	1.640 (vinaceous buff)	1.662 (black)	0.022
*79	Custer, S.D.	buffy brown	1.633 (olive buff)	1.662 (olive brown)	0.029
80	Eastern Manitoba	slate	1.638 (vinaceous buff)	1.662 (slate black)	0.024
81	Freemont Co., Colo.	slate	1.633 (vinaceous fawn)	1.662 (black)	0.029
82	10 miles S.E. Custer, S.D.	slate	1.640 (pale green blue slate)	1.662 (green blue slate	0.022
			1.633 (pale smoke gray)	1.664 (grayish olive)	0.031

* Selected for analysis.

TABLE I (*continued*)

No.	LOCATION	COLOR POWDER	ϵ (COLOR)	ω (COLOR)	$\omega-\epsilon$
83		dark olive gray	1.638 (smoke gray) 1.640 (pale vinaceous fawn)	1.662 (deep olive) 1.664 (dark neutral gray)	0.024 0.024
84	Westport, Ontario	dark neutral gray	1.633 (vinaceous buff)	1.662 (dark olive)	0.029
85			1.638 (pale smoke gray) 1.640 (pale smoke gray)	1.662 (dark gull gray) 1.664 (tawny olive)	0.024 0.024
86	Ash River Falls, Minn.	light slate	1.636 (drab gray)	1.662 (black)	0.026
87	Rainy Lake, Minn.	slate	1.638 (drab gray)	1.662 (olivaceous black)	0.024
88	Giant's Range, Minn.	deep neutral gray	1.640 (vinaceous buff)	1.662 (black)	0.022
89	Southern California	slate	1.640 (pale smoke gray) 1.640 (pale smoke gray 1.640 (pale smoke gray)	1.662 (dark grayish olive) 1.662 (slate gray) 1.662 (storm gray)	0.022 0.022 0.022
90	Cripple Creek, Colo.	drab	1.638 (white) 1.640 (chamois)	1.662 (chamois) 1.662 (Isabella color)	0.024 0.022
91	Bamhe, Norway	dark olive gray	1.633 (pinkish cinnamon)	1.662 (dark olive)	0.029
92	Auburn, Me.	slate	1.640 (light Varley's gray)	1.662 (blue black)	0.022
93	Oracle, Ariz.	deep olive	1.640 (deep olive buff)	1.662 (dark olive)	0.022

TABLE I (*continued*)

No.	LOCATION	COLOR POWDER	ε (COLOR)	ω (COLOR)	ω–ε
94	Oracle, Ariz.	bluish slate	1.638 (avellanceous)	1.662 (black)	0.024
95	Oracle, Ariz.	slate	1.640 (vinaceous fawn)	1.662 (black)	0.022
96	Oracle, Ariz.	bluish slate	1.638 (vinaceous buff)	1.662 (black)	0.024
97	Oracle, Ariz.	blackish slate	1.638 (vinaceous fawn)	1.662 (black)	0.024
98	Oracle, Ariz.	blackish slate	1.640 (vinaceous fawn)	1.662 (black)	0.022
99	Oracle, Ariz.	blackish slate	1.636 (vinaceous fawn)	1.662 (black)	0.026
100	Oracle, Ariz.	blackish slate	1.638 (vinaceous buff)	1.662 (black)	0.024
101	Hornpayne, Ontario	drab	1.633 (pale smoke gray) 1.638 (vinaceous buff)	1.662 (slate gray) 1.664 (olive black)	0.029 0.026
102	Jellicoe, Ontario	chaetura drab	1.638 (pale smoke gray) 1.640 (vinaceous buff)	1.662 (deep gull gray) 1.664 (chaetura drab)	0.024 0.024
103		mouse gray (center)	1.640 (pale neutral gray 1.633 (cinnamon buff)	1.662 (neutral gray) 1.665 (tawny olive)	0.022 0.032
		slate color (edge)	1.640 (pale purplish gray)	1.665 (slate color)	0.025
104		blackish slate	1.640 (vinaceous buff) 1.649 (gull gray)	1.662 (black) 1.665 (slate gray)	0.022 0.016

TABLE I (*continued*)

No.	LOCATION	COLOR POWDER	ϵ (COLOR)	ω (COLOR)	$\omega-\epsilon$
105		deep mouse gray	1.633 (vinaceous buff)	1.662 (black)	0.029
			1.636 (pallid neutral gray)	1.665 (neutral gray)	0.029
106		deep gull gray	1.636 (light gull gray)	1.662 (slate gray)	0.026
107	Botallack, St. Just, Cornwall	drab	1.636 (pale olive buff)	1.662 (dark olive buff)	0.026
			1.640 (gull gray)	1.665 (slate)	0.025
108	Westport, Ontario	deep neutral gray	1.644 (smoke gray)	1.662 (olivaceous black)	0.018
109	Hugo Mine, Keystone, S.D.	cinnamon drab	1.636 (pinkish buff)	1.662 (clay)	0.026
110	Keystone, S.D.	slate gray	1.640 (gull gray)	1.665 (slate)	0.025
111		dark neutral gray	1.640 (deep gull gray)	1.662 (slate)	0.022
			1.636 (vinaceous buff)	1.665 (blue black)	0.029
			1.636 (tilleul buff)	1.668 (blue black)	0.032
112	St. Malo, France	snuff brown	1.633 (light pinkish cinnamon)	1.662 (snuff brown)	0.029
113	Haddam Neck, Connecticut	slate	1.640 (light drab)	1.664 (dark grayish olive)	0.024
114	New York City	lily green	1.640 (light drab)	1.664 (dark grayish olive)	0.024
115	Oxford, Me.	slate gray	1.638 (pale smoke gray)	1.664 (black)	0.026

TABLE I (*continued*)

No.	LOCATION	COLOR POWDER	ϵ (COLOR)	ω (COLOR)	$\omega-\epsilon$
116	Snarum, Norway	light neutral gray	1.640 (pale smoke gray)	1.664 (light brownish olive)	0.024
117	Lawrenceville, N.J.	dark olive gray	1.637 (vinaceous buff)	1.664 (dark olive)	0.027
118	Greener, Tyrol	mineral gray	1.635 (smoke gray)	1.664 (olive green)	0.029
119	Hebron, Me.	buffy brown	1.635 (olive buff)	1.664 (dark olive buff)	0.029
		buffy brown	1.649 (cinnamon buff)	1.672 (sepia)	0.023
120	Acworth, N.H.	blue gray	1.640 (smoke gray)	1.664 (slate gray)	0.024
121	Hayward, S.D.	hair brown	1.633 (dark olive buff)	1.664 (dark olive)	0.031
122	Fitchburg, Mass.	chaetura drab	1.638 (pale smoke gray)	1.664 (grayish olive)	0.026
123	Harney Peak, S.D.	slate gray	1.640 (pale smoke gray)	1.664 (grayish olive)	0.024
124		slate color	1.649 (light neutral gray)	1.664 (slate)	0.025
			1.640 (vinaceous buff)	1.668 (black)	0.028
			1.638 (vinaceous buff)	1.668 (black)	0.030
			1.649 (light neutral gray)	1.664 (slate)	0.015
125	Grassy Island, Rainy Lake, Minn.	slate	1.636 (pale smoke gray)	1.664 (deep grayish olive)	0.028
126	Round Lake, Minn.	slate	1.640 (vinaceous buff)	1.664 (black)	0.024

TABLE I (*continued*)

No.	Location	Color Powder	ϵ (Color)	ω (Color)	$\omega-\epsilon$
127	Auburn, Me.	slate	1.636 (smoke gray)	1.664 (slate)	0.028
128	Canyon City, Colo.	dark neutral gray	1.640 (smoke gray)	1.664 (black)	0.024
129	Pierrepont, N.Y.	dark grayish olive	1.640 (light drab)	1.664 (dark grayish olive)	0.024
130	Saxony	deep olive gray	1.640 (pale smoke gray)	1.664 (deep grayish olive)	0.024
131	Pechofen, Saxony	olive gray	1.640 (pale smoke gray)	1.664 (deep grayish olive)	0.024
132		buffy brown	1.640 (smoke gray)	1.664 (olive brown)	0.024
133	Springfield, N.H.	blue gray	1.640 (pale olive gray)	1.664 (green blue slate)	0.024
			1.644 (light olive gray)	1.675 (dark olive gray)	0.031
134	Königsberg, Norway	greenish slate	1.640 (pale vinaceous buff)	1.664 (dark olive)	0.024
			1.649 (citrine drab)	1.670 (deep olive)	0.021
135		deep mouse gray	1.640 (vinaceous fawn)	1.665 (bluish black)	0.025
			1.640 (pale smoke gray)	1.665 (bluish black)	0.025
			1.640 (light blue)	1.665 (medium blue)	0.025
			1.640 (tilleul buff)	1.665 (deep olive)	0.025
136		dark grayish olive	1.649 (deep gull gray)	1.665 (slate gray)	0.016
			1.633 (vinaceous buff)	1.668 (deep olive)	0.035

TABLE I (*continued*)

No.	LOCATION	COLOR POWDER	ϵ (COLOR)	ω (COLOR)	$\omega-\epsilon$
137	Bristol, Conn.	dark olive gray	1.649 (light olive gray)	1.665 (deep olive gray)	0.016
138	Custer, S.D.	deep neutral gray	1.633 (pale smoke gray)	1.665 (deep grayish olive)	0.032
			1.640 (pale green blue slate)	1.672 (deep green blue slate)	0.032
139		slate	1.640 (pale smoke gray)	1.665 (deep grayish olive)	0.025
		slate	1.640 (pale violet gray)	1.665 (blackish violet gray)	0.025
140			1.640 (light vinaceous fawn)	1.665 (bluish black)	0.025
141		slate gray	1.640 (pallid neutral gray)	1.665 (slate gray)	0.025
142		Payne's gray	1.633 (pale smoke gray)	1.665 (Payne's gray)	0.032
143	Luxulyan, St. Austell, Cornwall	neutral gray	1.640 (pale gull gray)	1.665 (slate color)	0.025
144	St. Lawrence Co., N.Y.	slate gray	1.633 (pale neutral gray)	1.665 (neutral gray)	0.032
145	Birse Lake, Manitoba	pale neutral gray	1.633 (pale smoke gray)	1.665 (smoke gray)	0.032
146	Harney Peak, S.D.	slate	1.636 (pale smoke gray)	1.665 (black)	0.029
147		slate	1.638 (vinaceous buff)	1.665 (black)	0.027
			1.658 (celandine green)	1.672 (artemisia green)	0.014
148	Deadwood, S.D.	olive gray	1.633 (smoke gray)	1.665 (olive gray)	0.032

TABLE I (*continued*)

No.	LOCATION	COLOR POWDER	ϵ (COLOR)	ω (COLOR)	$\omega-\epsilon$
149	Las Vegas, N.M.	slate	1.640 (pale neutral gray)	1.665 (neutral gray)	0.025
150	Bob Ingersoll Mine, Keystone, S.D.	deep mouse gray	1.633 (smoke gray)	1.665 (olive gray)	0.032
			1.640 (light gull gray)	1.665 (slate color)	0.025
151	Moravia	beaver brown	1.638 (pale maize yellow)	1.666 (mars-yellow)	0.028
			1.640 (maize yellow)	1.668 (mars-yellow)	0.028
			1.645 (light orange yellow)	1.668 (cad-mium yellow)	0.023
152	Newhouse, Utah	slate	1.640 (vina-ceous buff)	1.668 (black)	0.028
153		deep mouse gray	1.633 (pale smoke gray)	1.668 (deep grayish olive)	0.035
154		slate	1.649 (vina-ceous fawn)	1.668 (black)	0.019
155	Portugal	neutral gray	1.649 (pale smoke gray)	1.670 (clear Payne's gray)	0.021
			1.640 (white)	1.670 (smoke gray)	0.030
			1.649 (celan-dine green)	1.672 (artemi-sia green)	0.023
156	Hebron, Me.	slate	1.640 (vina-ceous buff)	1.672 (black)	0.032
157	Haddam, Conn.	smoky gray	1.640 (smoke gray)	1.672 (deep olive)	0.032
*158	Thousand Islands, St. Lawrence River	blue slate	1.644 (vina-ceous fawn)	1.672 (black)	0.028

* Selected for analysis.

TABLE I (continued)

159	Koma Gori, Kai Province, Japan	slate (edge)	1.649 (light grayish olive) 1.649 (pale gray)	1.672 (deep olive) 1.677 (alizarin blue)	0.023 0.028
		(center)	1.644 (light grayish olive) 1.646 (pale smoke gray)	1.674 (deep olive) 1.674 (alizarin blue)	0.030 0.028
160	DeKalb, N.Y.	blue slate	1.640 (smoke gray)	1.672 (blue black)	0.032
161	Kai, Japan	blue gray	1.649 (light gull gray)	1.672 (slate gray)	0.023
162	Kinkles Quarry, N.Y.	dark purplish olive	1.646 (pale smoke gray)	1.672 (dark grayish olive)	0.026
163	Pierrepont, N.Y.	slate	1.640 (light drab)	1.672 (dark grayish olive)	0.032
164	Syme, N.H.	slate	1.649 (pale smoke gray)	1.672 (black)	0.023
165	Chester, Pa.	deep neutral gray	1.640 (light drab)	1.672 (black)	0.032
166	Cornwall, Eng.	slate	1.644 (pale smoke gray)	1.672 (black)	0.028
167	Sonnenberg, Hartz Mts.	neutral gray	1.636 (pale smoke gray)	1.672 (black)	0.036
168	Johnsberg, N.Y.	olivaceous black	1.655 (light drab)	1.672 (olivaceous black)	0.017
169	San Diego, Calif.	slate blue	1.640 (pale smoke gray)	1.672 (slate blue)	0.032
170	Bernice Lake, Man.	dark olive gray	1.640 (pale smoke gray)	1.672 (grayish olive)	0.032

TABLE I *(continued)*

171	Cecil Co., Md.	gray	1.635 (cinnamon)	1.672 (black)	0.027
172	N. of Bernice Lake Man.	dark olive gray	1.640 (pale smoke gray)	1.672 (grayish olive)	0.032
173	Elba	blue black	1.649 (pale Russian blue)	1.677 (delft blue)	0.028
			1.651 (Russian blue	1.677 (deep delft blue)	0.026
174	Cactus Mine, Utah	slate	1.653 (vinaceous buff)	1.674 (olive black)	0.019
175	Herman, N.Y.	iron gray	1.655 (vinaceous buff)	1.674 (olive brown)	0.019
			1.640 (smoke gray)	1.677 (deep grayish olive)	0.037
176	Predazzo, Tyrol	dull greenish black	1.649 (vinaceous buff)	1.675 (black)	0.026
			1.650 (smoke gray)	1.677 (artemisia green)	0.027
177	Grafton, N.H.	slate	1.640 (vinaceous fawn)	1.677 (black)	0.037
178	Crown Pt. N.Y.	slate (center)	1.662 (light pinkish cinnamon)	1.677 (black)	0.015
		(edge)	1.662 (light pinkish cinnamon)	1.677 (black)	0.015
			1.675 (light pinkish cinnamon)	1.685 (black)	0.010
179	Moriah, Essex Co., N.Y.	deep grayish olive	1.662 (light grayish olive)	1.682 (black)	0.020

* Selected for analysis.

Powder colors in Table 1, were determined by taking powder crushed to 80 mesh and comparing with Ridgway's Standard Colors.[40] The pleochroic colors listed are also according to the nomenclature of Ridgway. Pleochroism is strong in practically all colored tourmalines.

Indices were compared by the Becke method with oils standardized upon a refractometer. Absorption is always $\omega > \epsilon$. So great is the absorption that the index of refraction of the ordinary ray was determined in some cases with the greatest difficulty. Only by selecting very thin fragments which allowed a little light to pass through could the measurement be made.

Zoning is quite marked and readily determined when present. In the table where more than one value is given for a specimen, values so recorded represent different zones in the same crystal. As the powder method was adopted it is impossible to state the zoning sequence except in the large crystals. In some of the larger crystals the indices, and sometimes also the colors, were different. A variation was also noticed in fragments of the same color. The difference was not large but sufficient to be noticed. All fragments that possessed more than one color displayed a distinct line of demarcation between the color zones, although a Becke effect could not be obtained between the differently colored parts. In a few cases colors "fingered" into each other, but gradational effects were not observed.

The tourmalines examined ranged from minute crystals to masses up to four inches. The small tourmalines were separated with difficulty from their gangue. In a few cases heavy liquids were resorted to.

SELECTION OF MATERIAL FOR ANALYSIS

To avoid the uncertainty of composition in a zoned crystal, material was selected for the most part from samples that were not zoned. The only tourmaline available in sufficient amounts from an ore deposit was, however, somewhat zoned.

The first five analyses in the table of analyses were made upon good crystals that were mechanically separated from all gangue. Microscopic examination made it certain that all extraneous material was removed, except in one case where a yellowish-brown al-

[40] *Color Standards and Color Nomenclature*, R. Ridgway, Curator of the Division of Birds, United States National Museum, Washington, **1912**.

teration product was observed. This specimen was treated separately as appears later.

The samples were ground to pass an 80-mesh sieve and in the main the methods of Hillebrand, *Bulletin* **700,** *United States Geological Survey,* were followed. In the case of ferrous iron and alkalis, reduction to an impalpable powder was resorted to. Some investigators[41] state that fine grinding in air produces a negligible quantity of ferric iron from ferrous. Clarke,[42] on the other hand, states that ferrous iron in tourmaline is readily changed to ferric and that fine comminution results in some oxidation. To determine the accuracy of the method several tourmaline crystals were powdered under absolute alcohol to prevent oxidation of the ferrous iron.[43] This is the best medium that has been suggested other than inert gases. With such a procedure no more ferrous oxide was found than when the grinding was done in air. It would appear that the amount of oxidation that has taken place in the preparation of the powdered tourmalines in air is negligible.

TABLE II. ANALYSES
G. W. Ward, *Analyst*

	8	38	70	158	179	79	23
H_2O-	0.62	0.22	0.18	0.06	0.16	0.28	0.10
H_2O+	1.42	1.18	1.78	2.30	3.38	1.48	1.28
SiO_2	38.26	36.66	36.18	34.70	34.38	35.68	35.22
CaO	0.18	1.18	4.02	0.38	2.36	0.38	2.02
MgO	1.41	7.24	4.72	2.82	3.68	2.23	7.36
Fe_2O_3	1.94	2.48	5.09	5.04	6.88	5.15	5.49
FeO	6.22	3.87	5.10	8.02	14.73	7.07	5.59
Al_2O_3	36.40	35.95	32.95	37.75	24.53	34.18	31.25
TiO_2	0.14	0.71	0.72	0.27	0.80	0.80	0.71
MnO	0.28	0.02	0.04	trace	trace	trace	0.16
Na_2O	1.46	0.92	0.80	0.84	1.45	2.18	2.34
K_2O	0.65	0.37	0.19	0.31	0.17	0.57	0.32
Li_2O	0.13	0.09	trace	trace	nil	0.11	trace
B_2O_3	11.32	9.91	8.85	7.56	8.28	9.90	8.64
Cr_2O_3	0.10	0.04	trace	trace	nil	nil	trace
F	trace	nil	trace	nil	nil	trace	nil
Total	100.53	100.84	100.62	100.05	100.80	100.01	100.48
O for F_2	—	—	—	—	—	—	—

[41] Hillebrand, F. W., *Bull.,* **700,** *U.S.G.S.*

[42] Clarke, F. W., *Bull.,* **588,** *U.S.G.S.*

[43] Hillebrand, *op. cit.,* p. 191.

Sp. Gr. =	3.097	3.089	3.075	3.104	3.091	3.100	3.000
ϵ	1.630	1.633	1.636	1.644	1.662	1.633	1.636
ω	1.649	1.655	1.662	1.672	1.682	1.662	1.662
$\omega-\epsilon$	.019	.022	.026	.028	.020	.029	.026
Powder color	mineral gray	buffy brown	deep neutral gray	blue slate	deep grayish olive	buffy brown	deep neutral gray

Pleochroic formulae

ϵ	court gray	cartridge buff to cream buff	pale smoke gray	vinaceous fawn	light grayish olive	olive buff	tilleul buff
ω	pea-green	honey-yellow	deep grayish olive	black	black	olive brown	neutral gray

Location of material
    8. Etta Mine, S.D.—pegmatite.
    38. Drummerstown, Vt.—pegmatite.
    70. St. Lawrence Co., N.Y.—pegmatite.
    158. Thousand Islands, St. Lawrence,—pegmatite.
    179. Moriah, Essex Co., N.Y.—pegmatite.
    79. Custer, S.D.—schist.
    23. Wiches, Montana—ore.

ALTERATION OF A HIGH-IRON TOURMALINE

Evidences of alteration were seen upon a hand specimen from Moriah, Essex County, New York, in the form of a brownish stain. Material for analysis was selected so as to avoid most of the altered portions. Completion of the chemical work produced the figures shown in column A, Table III.

Attention was at once drawn to the very low silica and alumina content and the extreme values of both ferrous and ferric iron. Boron, too, is low, but a reference to Doelter's[44] admirable compilation of tourmaline analyses reveals one specimen with boron as low as 5.40 per cent. Several have values of 7.5 per cent or less. A microscopic examination indicated that much altered material was present.

Purifying with acid was resorted to next. The material was di-

[44] Doelter, *op. cit.*

TABLE III. ANALYSIS OF ALTERED TOURMALINE NO. 179.
G. W. Ward, *Analyst*

	A	B	C	D
H_2O-	0.34⎫	2.16	0.16⎫	+0.98
H_2O+	4.18⎭		3.38⎭	
SiO_2	30.82	38.18	34.38	−3.56
CaO	2.00	4.70	2.36	−0.36
MgO	4.12	5.14	3.68	+0.44
Fe_2O_3	10.65	11.08	6.88	+3.77
FeO	16.22	11.19	14.73	+1.49
Al_2O_3	22.05	18.38	24.53	−2.48
TiO_2	0.89	0.89	0.80	+0.09
MnO	trace	0.05	trace	
Na_2O	0.94	2.20	1.45	−0.51
K_2O	0.95	0.93	0.17	+0.78
Li_2O	nil	nil	nil	
B_2O_3	6.12	5.76	8.28	−2.16
Cr_2O_3	trace	trace	trace	
F	nil	nil	nil	
Total	99.28	100.65	100.80	

A. Original specimen.
B. Acid treated.
C. Hand picked.
D. Difference between original and hand picked.

gested with cold, 1:4 hydrochloric acid until all soluble portions were removed.

Treatment with hydrofluoric acid, as reported by Penfield and Foote,[45] was omitted, because it was found that finely ground tourmaline is attacked by the acid. After filtering and thorough washing the material was air-dried. Column B gives the analysis of this acid treated material. The unexpected high percentage of silica led to the conclusion that residual silica must have remained after the acid treatment. A microscopic examination confirmed this. More silica, however, was apparent than would have represented the amount of alteration as indicated in A. Thus, it would appear that tourmaline had been altered by cold, dilute, hydrochloric acid. This is contrary to our knowledge of the chemistry of tourmaline. The suggestion then is advanced that some of the tour-

[45] Penfield and Foote, *Am. Jour. Sc.*, **157**, 7, 1899.

maline has undergone alteration, producing a product similar under the microscope to the unaltered tourmaline, but soluble in dilute hydrochloric acid.

What was left of the original sample was crushed to pass a 40 mesh sieve, and the unaltered material carefully selected by means of a hand lens. This was further crushed to pass 80 mesh and the few altered pieces then visible were discarded. This separation excluded all altered material. Upon this material a chemical analysis was made and it appears as sample 179, Table II. It is believed that this composition represents very closely the unaltered tourmaline.

These analyses were recalculated to 100 per cent and appear below.

CALCULATIONS BASED ON DATA OF TABLE III*

	I	II	III	IV	V
H_2O-	0.16	0.34	0.37	$+0.21$	47
H_2O+	3.29	4.14	4.55	$+1.26$	79.5
SiO_2	33.56	30.49	33.48	-0.08	110.0
CaO	2.30	1.98	2.18	-0.12	116.1
MgO	3.59	4.07	4.47	$+0.88$	88.2
Fe_2O_3 FeO	22.71	28.36	31.14	$+8.43$	80.1
Al_2O_3	23.95	21.82	23.95	0.00	110.2
TiO_2	0.78	0.88	0.92	$+0.14$	88.6
Na_2O	1.41	0.93	1.06	-0.35	151.9
K_2O	0.17	0.94	1.04	$+0.87$	18.1
B_2O_3	8.08	6.05	6.64	-1.44	133.6
Total	100.00	100.00	109.8	$+9.80$	

   I.   Unaltered tourmaline analysis recast.
  II.   Altered tourmaline analysis recast.
III.   Altered tourmaline expressed in grams per 100 grams of unaltered mineral, assuming total alumina to have remained constant during alteration.
IV.   Losses and gains in grams during alteration of 100 grams of tourmaline, assuming total alumina constant.
 V.   Relative gains and losses expressed as quotients by dividing the percentage in the unaltered phase by its percentage in the altered and multiplying by 100.

   * The above table and explanation is according to Leith and Meade, *Metamorphic Geology*, pp. 8 and 288, 1915.

Using the values in column V, a graph has been constructed, see Fig. 1. The graph shows only relative gains and losses. If any
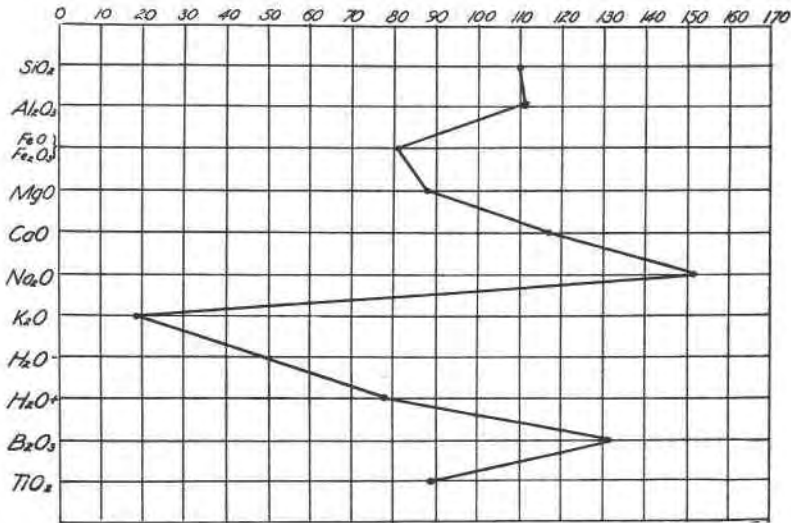
constituent can be considered as constant, not decreasing or increasing, during alteration, then all constituents to the right of this point upon the graph represent losses, and all to the left represent gains.

The assumption has been made that the total alumina is constant. Interpreting Fig. 1 under these conditions, water, potash, iron, magnesia, and titanium have been added. Silica and alumina are practically constant. Lime, boric oxide and soda have been lost. Such a change suggests conditions of alteration by weathering. Optically the alteration product is of a yellowish-brown color, nonpleochroic and possesses a very low birefringence. Good interference figures are difficult to obtain but the indication is that the fragments are uniaxal. The indices vary, for ϵ from 1.661 to 1.695 and for ω from 1.712 to 1.722.

DISCUSSION OF ANALYSES

Isomorphous Relationships

Certain isomorphic relationships have to be considered. All investigators are agreed that the fluorine and hydroxyl radicles replace each other. Mutual replaceability of the oxides, such as lime, magnesia, manganous oxide and ferrous oxide, is conceded. The alkalis are isomorphous. Ferric oxide and chromic oxide can replace alumina. Titanium has always presented difficulties in the tourmalines. Some analysts consider that it is trivalent replacing aluminum, while others look upon it as tetravalent and include it with the silicon. Penfield and Foote[46] consider it as being trivalent, simply because it gives them a better ratio in their attempts at deriving formulae.

In crystal structure work it has been found that silicon possesses four valence co-ordinates. These co-ordinates in the case of silicon unite oxygen atoms to the silicon. The structure is such that the oxygen occupies the four corners of a tetrahedron, with silicon in the centre of such a so'id figure. Aluminum has six valence co-ordinates in crystal structures like the spinels, which tie six oxygen atoms to the central aluminum atom. The figure is that of an octahedron with the oxygens occupying the corners.

Titanium compounds so far investigated have six coordinates, and never four; and thus resemble aluminum in arrangement of oxygen atoms. Rutile exhibits a somewhat distorted octahedron with titanium in the center surrounded by six oxygen atoms, placed one at each corner of the figure. In anatase the arrangement is the same as for rutile but much more distorted. The aluminum in garnet has recently been shown by Menzer[47] to be surrounded by oxygen atoms in much the same manner as titanium in rutile and anatase. From such considerations, remembering that chemical valence and valence co-ordinates are not the same, one concludes that titanium cannot be isomorphous with silicon but that it replaces aluminum. Most investigators have adopted the idea of Penfield and Foote, considering for what seems to be the same reason as theirs, titanium isomorphous with aluminum.

When the analyses of Table II are recalculated, taking into account relationships expressed above and then plotted against their respective birefringence, a series of graphs result. These appear

[46] Penfield and Foote, *op. cit.*, p. 117.
[47] G. Menzer, *Z. Kryst.*, **69**, 300–397, 1928.

in Fig. 2. The recalculated analyses are shown in Table IV and may be identified by the letter "W" following the original number.
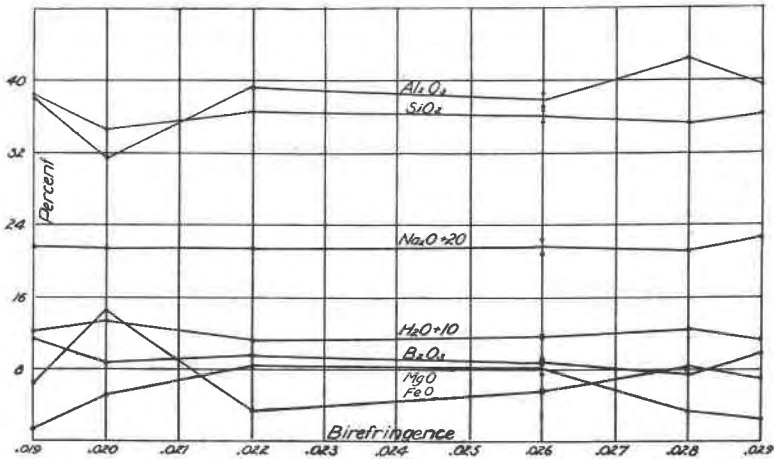

Fig. 2.

INTERPRETATION OF RECAST ANALYSES

The irregular lines in Fig. 2 bring out several interesting relationships. The soda curve varies little, with a tendency to increase as the birefringence increases. Magnesia also increases toward the right, until birefringence 0.026 is reached. It decreases from this point on. Alumina and silica follow each other except for birefringence 0.020 and 0.028. Low silica and alumina with high ferrous oxide is not out of accord with the literature. But one would expect a higher birefringence for specimen 179, since it is claimed[48] that an increase in iron is the cause of an increase in birefringence. Again the divergence between silica and alumina at birefringence 0.028 appears anomalous. The alumina is unusually high but early analyses do not indicate that such a condition is irregular. A specimen from Elba has been analyzed by two investigators independently, Schaller[49] and Rammelsberg[50] and each found approximately 44 per cent alumina. Doelter's compilation has many

[48] Kunitz, (Halle,) *Centralbl. für Mineralogie*, 1926.
   Wülfing, E. A., *op. cit.*
   Schaller, W. F., *op. cit.*
[49] Schaller, W. F., *op. cit.*, p. 324.
[50] Rammelsberg, *Abh. Berliner Ak.*, p. 74, 1890.

analyses with over 40 per cent alumina. With high alumina, as
a rule, the iron is not over 6 per cent, but in sample number 158
the iron is 8 per cent. This is not excessive for an iron tourmaline
but is too high when associated with a large percentage of alumina.
The curve for ferrous oxide is very irregular, particularly in speci-
men 179. The boric oxide and the water increase and decrease
together except at birefringence 0.020, here they diverge, the
water increases and the boric oxide decreases. In the main both of
these last curves are irregular. The remaining oxides are not ab-
normal.

In general, specimens 158 and 179 are not compatible with the
others. For number 179 the silica and alumina are very low, but
the ferrous iron is high. When number 158 is considered, the
alumina and iron have both increased and the magnesia decreased.
The silica does not follow the alumina curve but decreases slightly.

From the above, it apparently requires a combined increase in
ferrous oxide and magnesia to offset a decrease in both alumina
and silica. An increase in alumina alone is nullified by a decrease
in magnesia, provided the ferrous oxide is constant or nearly so,
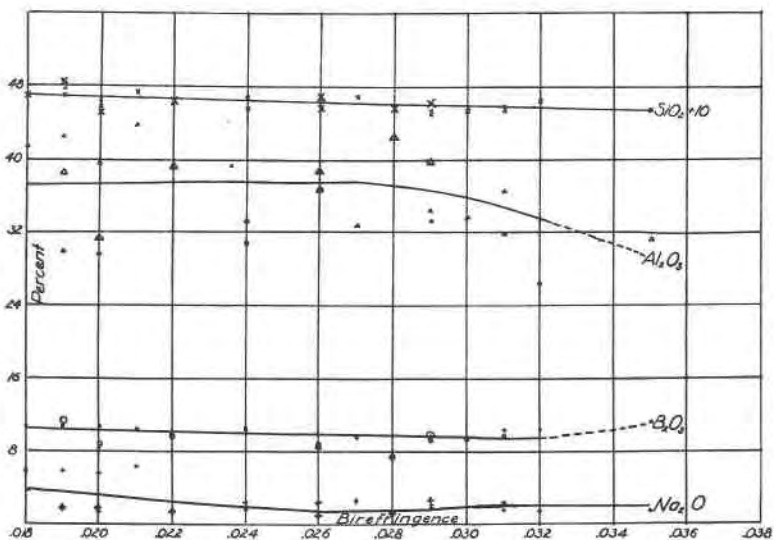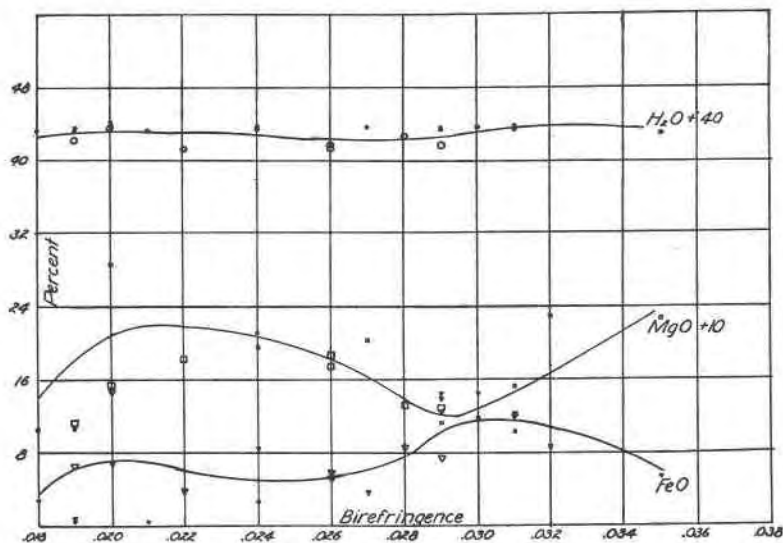as may be assumed in specimen 158.

Fig. 3.

Fig. 4.

RECAST ANALYSES COMPARED WITH THOSE IN THE LITERATURE

Eighteen analyses were taken from the literature, recast, and plotted along with the black tourmalines analyzed here. Arbitrary curves were drawn and these appear in Figs. 3 and 4. Not all additional analyses are of black tourmalines. For the most part the seven tourmalines of this paper agree with earlier results. Silica and soda are represented by straight lines. The alumina decreases surprisingly when the birefringence has passed 0.029. The boric oxide is normal until near the end where it takes a sudden jump upwards. The curve for water indicates slight variation. Magnesia and ferrous oxide curves are extremely irregular, their increase and decrease is suggestive of isomorphous replacement. The decrease in ferrous oxide may be enough to make up for the sudden rise in magnesia. Analyses and optical data used in plotting the curves of Figs. 3 and 4 are shown in Table IV.

Wm. M. Agar[51] has determined the refractive indices for a number of minerals from the Adirondacks. Among these are a few tourmalines which he relates to chemical analyses given in Dana. Agreement with the curves drawn here is very close.

[51] *Am. Phil. Soc.*, vol. **62**, 95, 1923.

TABLE IV. RECAST ANALYSES

NUMBER ON GRAPH	ORIGINAL NUMBER	$\omega-\epsilon$	SiO_2	Al_2O_3	B_2O_3	Na_2O	H_2O	MgO	FeO
1	3S	.018S	36.72	41.31	10.60	5.93	3.33	0.64	2.63
2	34R	.019S	36.87	29.83	10.85	1.29	3.43	17.50	0.23
3	2S	.019S	37.57	42.18	10.65	5.95	3.38	0.84	0.49
4	8W	.019W	38.34	38.28	11.35	2.05	2.05	1.56	6.51
5	35R	.020S	35.88	29.22	10.64	1.08	3.53	18.57	0.88
6	5S	.020S	36.38	39.77	8.12	5.73	4.29	—	6.97
7	179W	.020W	34.83	31.21	8.41	1.57	3.58	5.47	14.93
8	1S	.021S	37.89	43.85	10.28	6.03	3.49	0.06	0.22
9	38W	.022W	36.55	39.07	9.88	1.17	1.40	8.05	3.88
10	27R	.024W	35.47	30.86	10.49	1.87	3.61	9.45	8.25
11	29R	.024W	36.70	33.03	10.08	2.57	3.79	11.33	2.50
12	70W	.026W	36.70	38.54	8.98	0.91	1.99	7.67	5.21
13	23W	.026W	35.66	36.87	8.75	2.58	1.39	8.91	5.86
14	28R	.027W	36.80	32.65	9.76	2.84	3.83	10.28	3.84
15	158W	.028W	35.28	42.39	7.67	1.05	2.40	3.15	8.15
16	15R	.029W	35.05	34.02	9.64	2.23	3.63	1.12	14.31
17	19R	.029S	34.87	33.13	9.70	2.46	3.58	2.38	13.91
18	79W	.029W	36.00	39.97	9.99	2.60	1.77	2.53	7.14
19	17J	.030S	35.28	33.67	9.10	2.32	3.55	1.70	14.38
20	21R	.031S	35.07	31.90	9.96	2.39	3.63	5.05	12.00
21	6S	.031S	35.21	36.24	10.43	1.92	3.51	0.39	12.11
22	31R	.032W	36.17	26.34	10.31	1.67	3.53	13.66	8.32
25	5	.035	35.15	31.30	11.29	1.48	2.93	12.72	5.21

S—Schaller
J—Jannasch-Kalb
R—Riggs
W—Ward

It is claimed by some investigators that the birefringence is a function of the density. The denser the mineral the higher its birefringence. An investigation along this line was suggested by Dr. Gruner. He derived for each element its "ion number." These numbers are simply the atomic numbers of the elements plus or minus their valence electrons. Hence, oxygen, which is a negative element, has an ion number of 8 plus 2, or 10; potassium's ion number, since potassium is a positive element, is 19 minus 1, or 18. Their total is obtained by multiplying the necessary ion numbers by the proper percentages of the analyses shown in Table II.

This sum is an indication of the packing of the ions. If the structure is "close-packed" an increase in the sum would mean an increase in density, and an increase in optical refraction and birefringence. A number of analyses from the literature as well as those analyzed here were treated in this way but did not reveal any relationship with respect to optical properties. Neither could a close relationship between density and birefringence be detected.
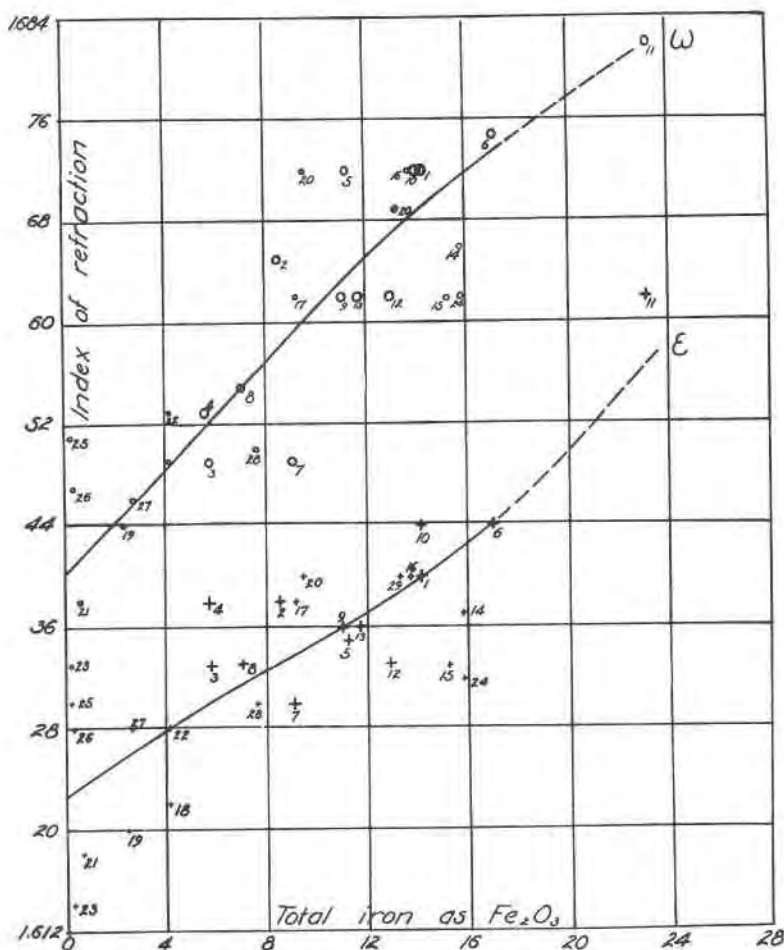

Fig. 5.

Total Iron Compared with Optical Data

The micas[52] and pyroxenes[53] have been found to increase in index and birefringence as the percentage of iron increases. The suggestion was obtained from the above papers that perhaps in the tourmaline group some such relationship might be found. This prompted the curves plotted in Fig. 5.

In Fig. 5 the refractive indices for the ordinary and extraordinary rays are plotted against the total iron. With low birefringence and low indices the per cent of iron is likewise low, as the iron increases so do the indices and birefringence. A maximum birefringence is apparently reached for tourmalines containing between 12 per cent and 16 per cent total iron, whereas the indices continue to increase. These facts are brought out in the table below. The decrease in birefringence, however, is based almost wholly on one specimen from Moriah, New York, specimen 179.

Percent of Total Iron as Fe_2O_3	ω	ϵ	$\omega - \epsilon$
0–10	1.650	1.629	.021
10–20	1.667	1.637	.030
20–30	1.680	1.662	.020

The increase in either ferrous or ferric iron does not seem to be separately the cause of increase in index. This probably is mainly due to the lack of a constant ratio between these oxides. In the compilation of the above data literature upon the subject was freely consulted and the following information derived and plotted.

No relationship could be discerned between the powder color and the chemical composition. Nor can any relationship be seen with the optical properties. An attempt was made to correlate the colors of ϵ and ω rays with the indices and birefringence. No connection between these properties was revealed. This much may be stated however, from 179 tourmalines examined 142 gave a powder color that was some shade of gray; 10 were drab; 9 were blue-black; 16 were brown and two were green. As to the pleochroic formula, 69 specimens were buff colored for ϵ; 84 were gray; 12 were drab; 5 were blue; 8 were pinkish cinnamon and 1 was white. The color

[52] Grout, F. F., *Am. Mineral.*, vol. 9, No. 8, p. 159, 1924.
[53] Winchell, A. N., *Am. Jour. Sc.*, vol. 111, p. 504, 1923.

TABLE V

NUMBER	ANALYST	TOTAL FE AS Fe_2O_3	BIREF.	ϵ	ω	SPOT ON GRAPH
169	Ward	14.33%	.032	1.640	1.672	1
60	"	8.63	.017	1.638	1.655	2
9	"	5.93	.016	1.633	1.649	3
20	"	5.83	.015	1.638	1.653	4
171	"	11.15	.037	1.635	1.672	5
166	"	17.10	.031	1.644	1.675	6
8	"	9.11	.019	1.630	1.649	7
38	"	7.04	.022	1.633	1.655	8
70	"	11.01	.026	1.636	1.662	9
158	"	14.21	.028	1.644	1.672	10
179	"	23.22	.020	1.662	1.682	11
79	"	13.00	.029	1.633	1.662	12
23	"	11.70	.026	1.636	1.662	13
15	Riggs and Schaller[1]	15.90	.029	1.637	1.666	14
19	"	15.45	.029	1.633	1.662	15
21	"	13.69	.032	1.640	1.672	16
27	"	9.13	.024	1.638	1.662	17
28	"	4.22	.027	1.622	1.649	18
29	"	2.78	.024	1.620	1.644	19
31	"	9.54	.032	1.640	1.672	20
35	"	0.98	.020	1.618	1.638	21
VII	"	4.07	.028	1.628	1.653	22
34	Penfield and Foote[2]	0.25	.019	1.614	1.633	23
17	Jannasch-Kalb[3]	15.98	.030	1.632	1.662	24
1	Schaller[4]	0.24	.021	1.630	1.651	25
2	"	0.42	.019	1.628	1.647	26
3	"	2.93	.018	1.628	1.646	27
5	"	7.74	.020	1.630	1.650	28
6	"	13.45	.031	1.638	1.669	29

[1] Schaller, W. T., Inaug. Diss., *Zeit. Kryst.*, **51**, 332, 1912.
  Riggs, R. B., *Am. Jour. Sci.*, Series III, vol. **35**, p. 49.
[2] Penfield and Foote, *Am. Jour. Sci.*, Series IV, vol. **7**, p. 107.
[3] Jannasch-Kalb, see Reiner, *op. cit.*
[4] Schaller, W. T., *op. cit.* pp. 324–332.

of ω is somewhat different, 82 were grayish; 63 were black; 9 were green; 8 were blue; 5 were yellow; 9 were brown; one was white and one pinkish cinnamon. One specimen showed a gradation in color for ω, from sage green to black.

In general when values for ω are below 1.662 the colors of the fragments are light. Above 1.660 buffs come in and a general darkening results.

Considering the composition of the black tourmalines and the color of the hand specimens the conclusion is reached that a mixture of ferrous and ferric iron apparently is the cause of the color, the same as in the micas and other ferromagnesium minerals.

COMPARISON OF ANALYSES OF TOURMALINES FROM VARIOUS SOURCES

It was hoped that some fundamental difference could be observed in the analysis of a black tourmaline from an ore deposit when compared with similarly colored tourmalines from schists and pegmatites. Analysis 23 records the composition of a black tourmaline from an ore deposit. Numbers 8 and 79 are from a pegmatite and a schist, respectively. The outstanding feature of the tourmaline from an ore deposit is its high magnesia content, but tourmalines of pegmatitic origin may have as high or even higher percentages of this oxide. Number 38, in Table II, is from a pegmatite and practically equals the magnesia content of tourmaline No. 23. The soda in analyses 79 and 23 is slightly higher than that found in the pegmatites, but other analyses of pegmatitic tourmalines that have been published show even greater amounts in many cases.

The tourmalines taken from a schist and from a pegmatite are from the same general region, namely, Custer, South Dakota. Tourmaline in schists is the result of contact action. It can be stated that the tourmaline in the schist,[54] from which specimen No. 79 was taken was due to contact action of the pegmatite that produced specimen No. 8. Differences in the two analyses are so slight and it would be impossible to state from an analysis the nature of the rock from which the tourmaline came.

ATTEMPTS AT FORMULA

In considering the formula, certain isomorphous relationships have to be taken into consideration. These are referred to under the discussion of chemical analyses. Table IV contains the figures used in the following considerations.

[54] Schwartz, G. M., Geology of the Etta spodumene mine, *Econ. Geol.*, Nov. **1925**, p. 652.

Schwartz and Leonard, Contact action of Pegmatite on schist, *Bull. Geol. Soc. Am.*, Dec. **1927**.

Taken in chronological order the most favored and often re-
peated formulae are those of Rammelsberg suggested in 1890.
As so well stated by Shand,[55] there seems to be little preference for
any one formula and that of Rammelsberg has the advantage of
simplicity. It represents all the tourmalines as salts of the acid
(H_6SiO_5). Rammelsberg[56] also found that the ratio of R to Si
was approximately as 6 to 1. According to him all tourmalines
could be represented by mixtures of three molecules.

$$x \text{ equals } R_6' \quad SiO_5$$
$$y \text{ equals } R_3'' \quad SiO_5$$
$$z \text{ equals } R_2''' \quad SiO_5$$
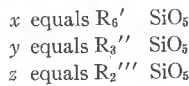
R', R'', and R''' representing, respectively, monad, dyad and triad
elements. He then calculated a number of existing analyses re-
sulting in a series of nine groups,[57] of which I, II, III, IV, V and
VI are illustrated by many examples.

	$x : y : z$	$R' : R'' : R''' : Si$
I	1:2: 6	1 : 1 : 2 : 1.5
II	1:2: 9	1 : 1 : 3 : 2
III	1:1: 6	2 : 1 : 4 : 2.66
IV	1:1: 9	2 : 1 : 6 : 3.66
V	3:1:18	6 : 1 : 12 : 7.33
VI	3:1:27	6 : 1 : 18 :10.33

Such a calculation applied to the analyses of black tourmalines
listed in Table IV appears below and is in good agreement with
Rammelsberg's theory.

Number of Specimen	$x : y : z$	$R' : R'' : R''' : Si$	$R : Si$
8	1 :1 :12	2.3:1 : 8.3 :4.9	5.96: 1
38	1 :2 :15	1 : 1.3 : 5.3 : 3.2	6.1 : 1
70	1 :2 :12	1 : 1 : 3.8 : 2.4	6.0 : 1
158	4 :5 :39	1.6:1 : 5.3 : 3.1	6.3 : 1
179	1.3:2 : 7.5	1.3:1 : 2.5 : 1.7	6.3 : 1
79	1 : 2.6 :12.3	1 : 1.3 : 4.1 : 2.5	6.3 : 1
23	1.8 : 2.2 : 19.5	1.8:1 : 6.5 : 3.7	6.2 : 1

[55] Shand, S. J. *op. cit.*, p. 34.

[56] Rammelsberg, C. F., *Abh. Berliner Ah.*, **1890**, p. 14, and Doelter, *Handbuch
der Mineralchemie*, Band II, Teil 2., p. 765.

[57] Doelter, *op. cit.*, p. 765.

Numbers 8, 158 and 23 of the above compare favorably with Rammelsberg series IV and the remainder agree with series II. The ratio R to Si, where R is the monovalent sum of $R'+R''+R'''$, is an approximation of 6 to 1.

TABLE VI. CALCULATION OF TABLE II TO HYDROGEN EQUIVALENTS

	8	38	70	158	179	79	23
SiO_2	.638	.611	.603	.578	.573	.592	.587
B_2O_3	.162	.142	.126	.108	.118	.141	.123
Al_2O_3	2.141	2.115	1.938	2.221	1.443	2.011	1.838
FeO	.173	.108	.142	.223	.409	.196	.156
Fe_2O_3	.072	.092	.189	.187	.255	.191	.203
MgO	.070	.362	.236	.141	.184	.112	.365
CaO	.006	.042	.144	.014	.077	.014	.072
Na_2O	.047	.030	.026	.027	.047	.070	.076
K_2O	.014	.009	.004	.007	.004	.012	.007
H_2O	.227	.155	.218	.262	.393	.195	.153
MnO	.008	—	—	—	—	—	—
Ti_2O_3	.010	.053	.053	.021	.060	.060	.053
Total	2.768	2.966	2.950	3.103	2.872	2.861	2.923

RATIO OF SiO_2 TO B_2O_3 TO REPLACEABLE HYDROGEN

SiO_2	4	4	4	4	4	4	4
B_2O_3	1.01	0.93	0.84	0.75	0.83	0.95	0.84
H	17.52	19.44	19.57	21.46	20.05	19.24	19.91

Riggs [57] proposed three formulae in 1888, as follows:

Lithia tourmaline	$H_8Si_{12}B_6Al_{16}(Na,Li)_4O_{63}$
Iron	$H_8Si_{12}B_6Al_{14}Fe_4Na_2O_{63}$
Magnesia tourmaline	$H_8Si_{12}B_6Al_{10}Mg_{28/3}Na_{4/3}O_{62}$

If the lithia molecule is considered as containing only sodium and no lithium, then these apply fairly well to the analyses recorded here. The last three analyses of black tourmalines, numbers 179, 9 and 23, fit such formulae only approximately.

[57] Riggs, *op. cit.*, p. 50.

Penfield and Foote claimed that tourmalines are derived from the acid $H_{20}B_2Si_4O_{21}$. The seven analyses mentioned in Table II, calculated to their hydrogen equivalents for each constituent, are given in Table VI.

Penfield and Foote find that the hydrogen equivalents vary. Analyses by Scharizer, Riggs and Engelmann, and analyses from various other miscellaneous sources give hydrogen equivalents that are not constant. For boron they vary from 0.70 to 1.01, and for the total replaceable hydrogen the equivalents vary from 17.4 to 21. An attempt was made by Penfield and Foote to explain the extreme values by errors in the analysis. The average ratio upon which they base their formula is, $SiO_2 : B_2O_3 : H$ as $4 : 0.95 : 19.88$. In the black tourmalines here tested the average ratio is, $4 : 0.88 : 19.60$. These are fairly close to $4 : 1 : 20$.

It is interesting to note here, that the special formulae of Riggs, Wülfing, Jannasch and Kalb, all reduce by the substitution of hydrogen equivalents to $H_{20}B_2Si_4O_{21}$.

If the assumption is made that SiO_2 and B_2O_3 are in a constant ratio of 4 to 1, and knowing that all tourmalines contain over 20 per cent alumina with various other oxides in minor amounts, a relationship can be shown between alumina and the other oxides that are present. Comparing their hydrogen equivalents it can be shown that the sum of the oxides present in minor amounts, plus the hydrogen equivalent of alumina, equals approximately a constant. The hydrogen equivalents are given in Table VI.

Specimen Number	M	N	M+N
8	0.627	2.141	2.768
38	0.851	2.115	2.966
70	1.012	1.938	2.950
158	0.882	2.221	3.103
179	1.429	1.443	2.872
79	0.850	2.011	2.861
23	1.085	1.838	2.923
		Average	2.920

M is the sum of the hydrogen equivalents of all the oxides present except SiO_2, Al_2O_3 and B_2O_3.

N is the hydrogen equivalent of Al_2O_3.

$M+N$ is the sum of M and N.

Five analyses by Schaller[58] give an average value for $M+N$ of 3.045. The hydrogen equivalents are obtained by reducing the molecular weight of the oxides to a value equivalent to one hydrogen, and then dividing the oxide percentages by the value so obtained. Thus alumina, since each Al is trivalent, would be divided by one-sixth of its molecular weight, or seventeen.

Wülfing[59] recalculated Riggs' analyses and showed that the sum of the molecular proportions varied between 2.35 and 2.42. When such a calculation is made for the tourmalines analyzed in this investigation, it is found that only two are in good agreement, the remainder are only approximate.

Specimen Number	
8	2.214
38	2.335
70	2.339
158	2.073
179	2.218
79	2.124
23	2.108

Reiner[60] proposed three molecules which are as follows:

I	$Si_{12}B_6Al_{16}Na_4H_8O_{63}$
II	$Si_{12}B_6Al_{12}Fe_8H_8O_{63}$
III	$Si_{12}B_6Al_{10}Mg_{12}H_6O_{63}$

These also correspond to the acid, $H_{20}B_2Si_4O_{21}$. He reduced these molecules to actual percentage of the oxide present. Thus the percentage composition of a pure soda molecule, a pure iron molecule and a pure magnesia molecule is obtained. Then, by calculation, the relative amounts of each molecule present can be determined on the basis of the proportion of soda, iron and magnesia in the analysis. Such a computation was made for the seven analyses given here. There was found, however, a deficiency of from 20 per cent to 40 per cent in all cases except in numbers 179 and 23. These two are in fair agreement as the following reveals.

Not only do his molecules prove deficient in the total but when compared with analyses in Table II wide differences are seen. It

[58] Schaller, *op. cit.*

[59] *Tschermak, Min. und pet., Mitth.* 1888–1889, **10**, pp. 161 to 173.
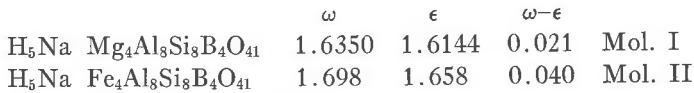
[60] Reiner, *op. cit.*, p. 15.

CALCULATED COMPOSITIONS ACCORDING TO REINER'S MOLECULES

Analyses	8	38	70	158	179	9	23
Mol. I	30%	18%	14%	16%	25%	41%	40%
II	25	15	20	31	57	27	22
III	6	33	31	33	22	10	26
SiO_2	21.57	23.69	23.12	20.92	36.12	27.79	35.27
B_2O_3	6.26	6.87	6.70	6.17	10.48	8.06	10.23
Al_2O_3	21.14	20.26	19.46	18.73	32.10	27.35	32.23
FeO	6.51	3.88	5.21	8.15	14.93	7.14	5.86
MgO	1.56	8.05	7.67	3.15	5.47	2.53	8.91
Na_2O	1.91	1.17	0.91	1.05	1.57	2.60	2.58
H_2O	2.09	2.06	2.03	1.96	3.40	2.67	3.18
Total	61.04	65.98	65.10	60.13	104.07	78.14	98.26

seems, therefore, that the molecules set forth by Reiner do not apply to the seven analyses of black tourmalines reported here.

Recently Kunitz[61] has proposed a set of new molecules, an isomorphous series for the iron-magnesium tourmalines, the end members of which are as follows.

		ω	ϵ	$\omega - \epsilon$	
H_5Na	$Mg_4Al_8Si_8B_4O_{41}$	1.6350	1.6144	0.021	Mol. I
H_5Na	$Fe_4Al_8Si_8B_4O_{41}$	1.698	1.658	0.040	Mol. II

In an attempt to test his theory when applied to our analyses, the first step was to calculate his formulae into percentages of oxides.

OXIDE	MOLECULE I	MOLECULE II
SiO_2	37.96	34.48
B_2O_3	11.09	10.06
Al_2O_3	32.28	29.31
FeO	—	20.69
MgO	12.66	—
Na_2O	2.45	2.23
H_2O	3.56	3.23
	100.00	100.00

[61] Kunitz, W., (Halle), *Centralbl. für Min. und Pet.*, Abst. A, **11**, p. 377, 1926.

The percentage composition obtained, several excellent analyses taken from the literature were proportioned according to the relative amounts of magnesia and ferrous oxide. The above molecules did not satisfy the conditions. The analyses made in the course of this paper were then tried. They also failed to even approximate the composition given above. Doelter reports several analyses with a percentage of magnesia much in excess of 12.66 and it would appear that the extreme value had not been selected for this molecule.

Certain relationships between a number of the elements in tourmaline have been stated. In the majority of analyses the ratio SiO_2 to B_2O_3 has been found to be about 4 to 1. This was first noted by Hermann[62] in 1845. Later in 1889, Clarke[63] found a variation that he states cannot be due to an error in the chemical analysis. The Table that follows is abstracted from Clarke's paper, to which has been added other data.

Riggs' Analyses	SiO_2	B_2O_3 found	B_2O_3	to	SiO_2
Rumford, red	38.07	9.99	1	to	4.44
Paris, black	35.03	9.02	1	"	4.53
Monroe, brown	36.41	9.65	1	"	4.40
Brazil, Green	36.91	9.87	1	"	4.36
Auburn, Colorless	38.14	10.25	1	"	4.35
Jannasch and Kalb					
Snarum	35.64	9.93	1	"	4.18
Mursinka	34.88	8.94	1	"	4.54
Buckworth	35.50	8.34	1	"	4.97
Brazil	37.05	9.09	1	"	4.75
Doelter's, Handbach					
No. 74, S. Diego, red, Wittich (1914)	37.54	9.12	1	"	4.81
No. 82, Von Camp, Schweiz, Engelmann (1877)	39.26	9.40	1	"	4.88
No. 95, Madagascar, dark red, Duparc, etc., (1910)	37.72	9.58	1	"	4.58
Z. Kryst., **V**, *57*					
Ceylon, dark, Becht (1913)	35.15	11.29	1	"	3.64
Zucherhandl, black	37.38	9.20	1	"	4.81
Rajamaki, brown	35.48	8.90	1	"	4.65

[62] Hermann, *op. cit.*, p. 1.
[63] Clarke, *op. cit.*, p. 120.

Ward

8	38.26	11.32	1	"	3.94
38	36.66	9.91	1	"	4.30
70	36.18	8.85	1	"	4.78
158	34.70	7.56	1	"	5.35
179	34.38	8.28	1	"	4.87
79	35.68	9.90	1	"	4.18
23	35.22	8.64	1	"	4.77

It does not appear possible that the lack of uniformity in the ratio is due to inaccuracies in analysis as was thought to be the case in the early days. Analyses that have been made by reliable investigators do not always show the ratio $SiO_2:B_2O_3 = 4:1$.

SUMMARY

One hundred and seventy-four specimens of black tourmaline and a few colored ones were examined under the microscope. Variation in color of the powdered mineral, pleochroic formula, indices of refraction, birefringence, zoning and occurrence were determined and recorded. Analyses were made of seven black tourmalines selected to show the variation in optical properties.

The tourmalines analyzed were shown to agree fairly well with Rammelsberg's formula, $(R_6SiO_5)_x$, specifically, with series II and IV. Fair agreement was observed with Riggs' formula when the lithium was eliminated from the "lithia molecule." Penfield and Foote proposed the acid $H_{20}B_2Si_4O_{21}$ which agrees with the analyses made in the course of this work. Reiner's molecules prove inaccurate when an attempt is made to relate them to the analyses of this paper or to some of those published elsewhere. The black tourmaline analyses made during this investigation, or appearing in the literature, do not agree with the interpretation of Kunitz's isomorphous series. Penfield and Foote claim that the ratio SiO_2 to B_2O_3 is always as 4 is to 1. Analyses made here and in the literature show that this ratio is not constant.

There is little doubt but that the acid from which all tourmalines are derived is represented by $H_{20}B_2Si_4O_{21}$. The complexity and number of possible substitutions for the hydrogen and other atoms are disputed points. There may even be distinct silicic and boric acids. It would be futile at this time to propose new molecules. The literature is full of them and many peculiar specimens will fail to fit any proposed formula. Possibly x-ray work may prove

suggestive but the data at present are too complex to permit representation by any simple formula.

It was shown that variation in the chemical composition of the tourmalines was independent of geologic occurrence.

The alteration of a high iron tourmaline was investigated. This specimen proved abnormal in many ways and further work is being done upon it.

It was also discovered that values below 1.662 for ω gave light colors in the pleochroic formula.

Relationships between the chemical composition and the optical data were plotted. It was indicated that an increase in the indices and birefringence was largely due to increase in total iron.