

Synthesis and characterization of tourmaline in the system $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{B}_2\text{O}_3-\text{H}_2\text{O}$

PHILIP E. ROSENBERG, FRANKLIN F. FOIT, JR., VANAVAN EKAMBARAM*
Department of Geology, Washington State University, Pullman, Washington 99164-2812

ABSTRACT

Na-Al tourmalines have been synthesized in assemblages with albite, quartz, H_3BO_3 , and aqueous fluid in the system $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{B}_2\text{O}_3-\text{H}_2\text{O}$ between 450 and 600°C at 1 kbar in the presence of excess SiO_2 , B_2O_3 , and H_2O . Fusion above 600°C limits the stability of Na-Al tourmalines, which have been characterized by their optical properties, X-ray diffraction patterns, and partial chemical (electron microprobe, EMP, and analytical electron microscope, AEM) analyses.

Refractive indices, $N_e = 1.639(2)$ and $N_o = 1.642(2)$ are higher than those of elbaite and dravite but conform to the density vs. mean refractive index trend for the tourmaline group. Refined cell parameters, $a_0 = 15.885(2)$ Å, $c_0 = 7.104(1)$ Å, are similar to those of aluminous dravites and elbaite. The synthetic Na-Al tourmalines approach the composition of the ideal endmember, $\text{NaAl}_3\text{Al}_6(\text{BO}_3)_3\text{Si}_6\text{O}_{21}(\text{OH})$, but are somewhat more aluminous, alkali deficient, and proton enriched. These compositions may be metastable with respect to the ideal endmember. With the synthesis of Na-Al tourmaline, it is possible to define the compositional field of tourmaline in the system $\text{Na}_2\text{O}-\text{MgO}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{B}_2\text{O}_3-\text{H}_2\text{O}$.

INTRODUCTION

The substitutions $\text{R}^{2+} + \text{H}^+ = \text{R}^{3+}$ and $\text{R}^+ + 2\text{H}^+ = \text{R}^{3+}$, which result in partial dehydroxylation, are important in the tourmaline group (Foit and Rosenberg, 1977, 1979). These substitutions, which are extensive in natural dravites, schorls, and elbaite, represent solid solution toward an R^{3+} -rich (principally Al^{3+}), proton-deficient endmember, $\text{R}^+\text{R}_3^+\text{R}_6^+(\text{BO}_3)_3\text{Si}_6\text{O}_{21}(\text{OH})$. Although an Fe^{3+} -rich variety, buergerite [$\text{NaFe}_3^+\text{Al}_6(\text{BO}_3)_3\text{Si}_6\text{O}_{21}(\text{OH})$], occurs in nature, the Al-rich endmember, Na-Al tourmaline, has not been reported as a mineral.

Because dehydroxylation substitutions are common and extensive in natural tourmaline and because buergerite is known to exist, endmember Na-Al tourmaline was expected to occur as a phase in the system $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{B}_2\text{O}_3-\text{H}_2\text{O}$. Although Maitrallet (1976) was unable to synthesize tourmaline from a granite, water, and H_3BO_3 mixture at 2 kbar, Voskresenskaya and Barsukova (1968) reported the synthesis of tourmaline in the system $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{B}_2\text{O}_3-\text{H}_2\text{O}$. A limited experimental investigation of this system in the presence of excess B_2O_3 , SiO_2 , and H_2O has been undertaken to confirm this synthesis and to characterize Na-Al tourmaline.

SYNTHESIS

Although the structural formula $\text{NaAl}_3\text{Al}_6(\text{BO}_3)_3\text{Si}_6\text{O}_{21}(\text{OH})$ for tourmaline in the system $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{B}_2\text{O}_3-\text{H}_2\text{O}$ was predicted by analogy with buergerite, a starting composition with excess Na_2O (as well as SiO_2 , B_2O_3 , and

H_2O) was prepared to compensate for alkali lost to the fluid phase during crystallization. Mechanical mixture 54—having the bulk composition Na_2O , 13.33; Al_2O_3 , 13.33; SiO_2 , 53.34; and B_2O_3 , 20.00 mol%—was prepared from Na_2O (dessicated after thermal decomposition of sodium oxalate), $\gamma\text{-Al}_2\text{O}_3$ (Linde 0.05 μm powder), Cab-O-Sil (preheated to 1000°C), and B_2O_3 (spec-pure).

After preliminary results of this investigation had been reported (Ekambaram et al., 1981), M. Pichavant (1982, written comm.) informed us that tourmaline may have been synthesized in small amounts in his experimental study of the system $\text{SiO}_2\text{-KAlSi}_3\text{O}_8\text{-NaAlSi}_3\text{O}_8\text{-B}_2\text{O}_3\text{-H}_2\text{O}$ (Pichavant, 1981) from a gel approximating the composition of the "ternary" minimum in the system Q-Or-Ab at 1 kbar. Following this suggestion, a second mechanical mixture, M, representing a projection of the composition of this minimum into the system $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$ with excess B_2O_3 was prepared using the same starting materials as for mixture 54. The bulk composition of this mixture is SiO_2 , 68.00; Al_2O_3 , 6.00; Na_2O , 6.00; and B_2O_3 , 20.00 mol%.

Samples of these mixtures together with small amounts of water (solid/water weight ratio $\sim 5/1$) were sealed into gold tubes and equilibrated in the temperature range 450–650°C at 1 kbar for one to two months using conventional hydrothermal techniques. The air-dried products of these experiments were identified by X-ray diffractometry and optical microscopy. More than 200 experiments were carried out using mixtures 54, M, and others (Ekambaram, 1978; Ekambaram et al., 1981; Rosenberg, unpub. data). Experiments at 600°C and lower temperatures yielded

* Present address: Department of Geophysical Sciences, University of Chicago, Chicago, Illinois 60637.

Table 1. X-ray* data for Na-Al tourmaline

hkl	Na-Al tourmaline				DeKalb dravite (Borg and Smith, 1969)	
	54		M		d _{calc} Å	I/I ₀
	d _{obs} Å	I/I ₀	d _{obs} Å	I/I ₀		
101	6.369	47	6.43	82	6.413	44
021	4.929	31	4.91	8	4.998	31
300	4.543	18	4.56	10	4.605	46
211	4.283	14	4.26	20	4.235	41
220	4.024	100	4.05	100	3.998	33
012	3.475	86	3.48	12	3.502	23
131	3.365	35	3.29	13	3.386	8
401	3.127	42	----	---	3.117	9
410	2.998	25	3.02	26	3.014	33
122	2.950	30	2.94	64	2.975	100
321	2.907	13	----	---	2.903	1
330	2.670	25	----	---	2.659	4
312	2.613	26	2.65	15	2.631	8
051	2.547	98	2.55	44	2.581	90
042	2.499	10	----	---	2.499	6
003	2.426	10	----	---	2.413	11
232	2.378	45	2.38	18	2.384	14
511	2.357	22	2.36	9	2.347	22
502	2.201	15	2.18	9	2.196	6
303	2.138	20	----	---	2.138	4
422	2.122	15	----	---	2.117	15
152	2.085	85	2.08	8	2.047	51
440	1.986	11	----	---	1.993	8

*Ni-filtered CuK_α radiation

Table 2. Chemical data (mole percent); partial compositions recalculated to 100%

	Tm 54 (EMP) [†]	Tm 54 (AEM) [‡]	Tm M (AEM)	Ideal Na-Al Tm
SiO ₂	41.88	41.72	53.95	54.55
Al ₂ O ₃	53.48	53.82	42.52	40.90
Na ₂ O	4.64	4.46	3.53	4.55

[†] EMP = Electron microprobe[‡] AEM = Analytical electron microscope

cell dimensions and chemical composition. The characteristics of tourmalines synthesized in two experiments are reported in this paper: mixture 54 crystallized at 500°C for 60 days and mixture M crystallized at 550°C for 63 days. Because the latter experiment yielded only a trace of tourmaline, only partial characterization was possible. Tourmalines crystallized from mixtures 54 and M are referred to as tourmalines 54 and M, respectively.

X-ray data for Na-Al tourmalines 54 and M are compared with those for DeKalb dravite (Table 1; Borg and Smith, 1969, p. 455). Partial chemical analyses were obtained using the electron microprobe (EMP) and/or the analytical electron microscope (AEM) (Table 2).

Optical properties

Tourmaline 54 occurs as isolated acicular crystals or sheaflike aggregates of radiating acicular or bladed crystals up to 200 μm long and 5 μm wide (Fig. 1). Much smaller yields of isolated acicular crystals up to 20 μm and 2 μm wide were synthesized from mixture M. Most crystals were far smaller than the maximum size recorded.

Na-Al tourmaline crystals are colorless and display no observable pleochroism. Single crystals exhibit parallel extinction and are length fast, indicating elongation parallel to the c-axis. Refractive indices determined in white light for tourmaline 54 are $N_e = 1.639 \pm 0.002$, $N_o = 1.642 \pm 0.002$. Na-Al tourmaline 54 lies on the density vs. mean refractive index trend for schorl, dravite, uvite, liddicoatite, and many tourmalines of intermediate composition (Fig. 2), further evidence that it has the tourmaline structure.

X-ray data

The X-ray-powder diffraction patterns of both Na-Al tourmalines were weak and not suitable for refinement of unit-cell dimensions because of the poor crystallinity and the small proportion of tourmaline present in these samples. However, least-squares refinement of the cell parameters of a comparable Na-Al tourmaline having fewer but better-defined reflections (Ekambaran, 1978) yielded $a_0 = 15.885(2)$ Å, $c_0 = 7.104(1)$ Å, $V = 1552.57$ Å³, and a calculated density of 3.087 g/cm³.

Although the X-ray diffraction data for Na-Al tourmaline and dravite (Table 1) are sufficiently similar to suggest that they have the same basic structural configuration, differences in reflection intensities are apparent. More specifically, there are significant differences in the

quartz, B-bearing albite, H₃BO₃, and minor amounts of tourmaline, but tourmaline is absent in all experiments at temperatures of 625°C and above. Fusion occurred in these higher-temperature experiments yielding B-bearing glass and albite, quartz, and H₃BO₃. Glass predominated particularly in the products of experiments with mixture M. Tourmaline was later crystallized from the solid products of these experiments by re-equilibration at or below 600°C in sealed gold tubes to which small amounts of water were added. Attempts to synthesize the hypothetical alkali-free Al tourmaline □Al₃Al₆Si₆(BO₃)₃O₂₀(OH)₂ at 500°C and above from a mixture with nearly stoichiometric SiO₂ and Al₂O₃ in the presence of excess B₂O₃ and H₂O were unsuccessful.

The experimental data of Ekambaran (1978) indicate that melting occurs at 612 ± 12 °C in the system Na₂O-Al₂O₃-SiO₂-B₂O₃-H₂O in the presence of excess SiO₂, B₂O₃, and H₂O at 1 kbar. These results are in accord with those of Chorlton and Martin (1978), who reported that the addition of 5 wt% B₂O₃ to granitic bulk compositions lowers melting temperatures to approximately 600°C. Furthermore, Pichavant (1981) observed that the melting of quartz-alkali feldspar assemblages begins at 600°C in the presence of excess water at 1 kbar with 15 wt% B₂O₃ in the aqueous-fluid phase.

CHARACTERIZATION

Synthetic Na-Al tourmalines were identified by their optical properties and X-ray powder-diffraction patterns and were characterized, where possible, by refined unit-

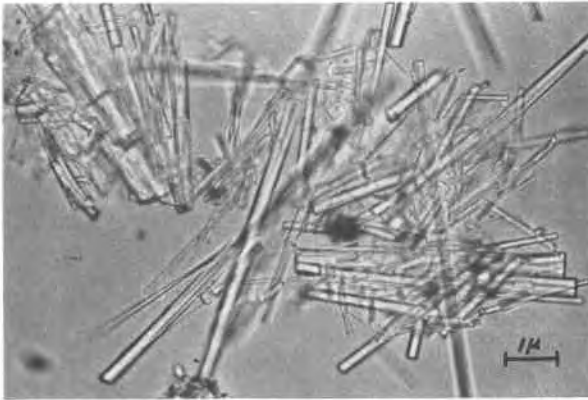


Fig. 1. Photomicrograph of synthetic Na-Al tourmaline (Tm 54).

relative order of the four most intense reflections not only between the Na-Al tourmalines and dravite but between the Na-Al tourmalines 54 and M. This may merely reflect variations in the degree of preferred orientation due to differences in crystal morphology and/or sample preparation.

Chemistry

The small size of even the largest crystals synthesized made chemical analyses difficult. However, the composition of Na-Al tourmaline 54 was determined by EMP and AEM techniques, whereas that of tourmaline M could be determined only using the AEM. Natural dravite from Dobruwa, Corinthia, Austria (NMNH 103791, Swanson et al., 1964; Rosenberg and Foit, 1979) was used as a standard in all analyses (Table 2).

The EMP and AEM (Champness et al., 1982; Rosenberg and Foit, 1979) analyses reported in Table 2 are based, respectively, on 16 and 8 random point analyses of well-formed crystals in which compositional zoning was not observed. Only relative oxide percentages could be obtained using the AEM because crystals vary in thickness and absorption corrections are not possible. Thus, all analyses (Table 2) have been recalculated to 100 mol%. EMP and AEM analyses of tourmaline 54 are nearly identical. The composition of tourmaline M lies close to that of ideal endmember Na-Al tourmaline.

The three-phase triangle (Fig. 3) shows solid-phase compositions projected into the system $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$ for the assemblages synthesized. Albite and Na-Al tourmaline are represented by the composition of the ideal endmembers. Mixture 54 yielded the same solid assemblage as mixture M, suggesting that excess Na_2SiO_3 was leached into the fluid phase (Flower, 1974), which changed the effective composition of the solid assemblage so that it was also within the three-phase triangle (Fig. 3).

Tourmaline M is considerably richer in SiO_2 and poorer in Al_2O_3 than is tourmaline 54 (Table 2; Fig. 3) reflecting the higher Si/Al ratio of mixture M relative to mixture 54. A solid-solution series probably exists between ideal

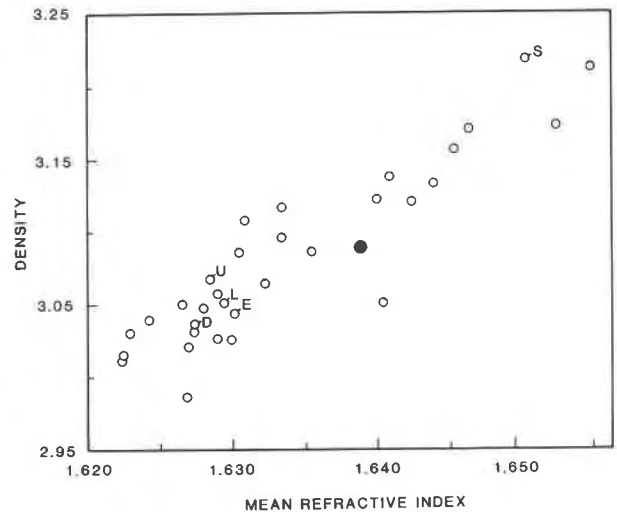


Fig. 2. Variation of mean refractive index with density for tourmalines. ● = Na-Al tourmaline, U = uvite, D = dravite, E = elbait, L = liddicoatite, S = schorl. Data taken from Bridge et al. (1977), Cossa and Arzruni (1883), Dunn et al. (1977), Kitahara (1966), Kunitz (1929), Quensel and Gabrielson (1939), Sahama et al. (1979), Schaller (1913), Simpson (1931), Slivko (1959), and Tomisaka (1968).

endmember Na-Al tourmaline and the Al-rich, Si-deficient composition synthesized from mixture 54.

Structural formulae

By adopting the conventional assumption that B is present in stoichiometric quantities and by varying the number of protons, structural formulae may be calculated for Na-Al tourmalines based on $31(\text{O},\text{OH})$. Variation in the

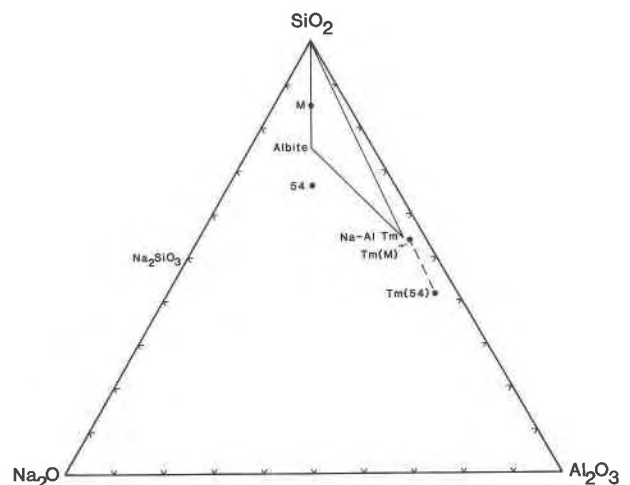


Fig. 3. Ternary diagram showing compositions (in mole percent) of starting mixtures and Na-Al tourmalines projected into the system $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$. Starting mixtures: 54 and M. Na-Al tourmalines: Na-Al Tm, ideal; Tm(M), tourmaline M; Tm(54), tourmaline 54. Albite, ideal.

Table 3. Si/Al ratios in starting mixtures and in tetrahedral coordination in Na-Al tourmaline

Mixture	Starting Composition	Tourmaline
54	2.01	2.37
M	5.62	5.56

number of protons results in concomitant changes in the numbers of Na, Al, and Si atoms in the calculated formulas. Cation site assignments follow procedures commonly used in tourmaline structural studies (e.g., Donnay and Barton, 1972; Rosenberg and Foit, 1979): (1) Si⁴⁺ is supplemented by enough Al³⁺ to fill the tetrahedral site. (2) In the absence of divalent cations, both the 18c and 9b octahedral sites must be occupied by Al³⁺; full occupancy is assumed. The requirement of a definite number of Al³⁺ cations permits selection of a unique structural formula. (3) Since the total Na⁺ available for both structural formulas is less than unity, the remaining portion of the 3a alkali site is assumed to be vacant, which is frequently the case in natural tourmalines (Foit and Rosenberg, 1979).

The structural formulas calculated using this procedure are



for tourmaline crystallized from mixture 54 (according to the EMP analysis; Table 2) and



for tourmaline crystallized from mixture M.

DISCUSSION

Stability of Na-Al tourmaline

Since ideal Na-Al tourmaline, NaAl₃Al₆(BO₃)₃Si₆O₂₁(OH), is the Al³⁺ analogue of buergerite, its stability in the system Na₂O-Al₂O₃-SiO₂-B₂O₃-H₂O was anticipated. As in buergerite, the presence of R³⁺ in the 9b octahedral site is compensated for by proton deficiency relative to dravite [NaMg₃Al₆(BO₃)₃Si₆O₁₈(OH)₄]. The Na-Al tourmalines synthesized in this study compensate for Al³⁺ in the 9b octahedral site by the presence of tetrahedrally coordinated Al as well as by proton- and alkali-deficiency. Na-Al tourmaline may also be considered to be a proton-deficient, Al-rich, Li-free elbaite. Li-deficient elbaite, common in nature (Foit and Rosenberg, 1977), represent solid solution toward ideal Na-Al tourmaline. Thus, Na-Al tourmaline is an important endmember of the tourmaline group.

In Na-Al tourmalines 54 and M, ^{iv}(Si/Al) ratios closely reflect Si/Al ratios in their respective starting mixtures (Table 3), suggesting that Si and Al are incorporated into tetrahedral coordination on a random basis and that alkali-site occupancy and numbers of protons are varied to provide charge balance. Thus, it may be possible to synthesize tourmalines somewhat more aluminous than those

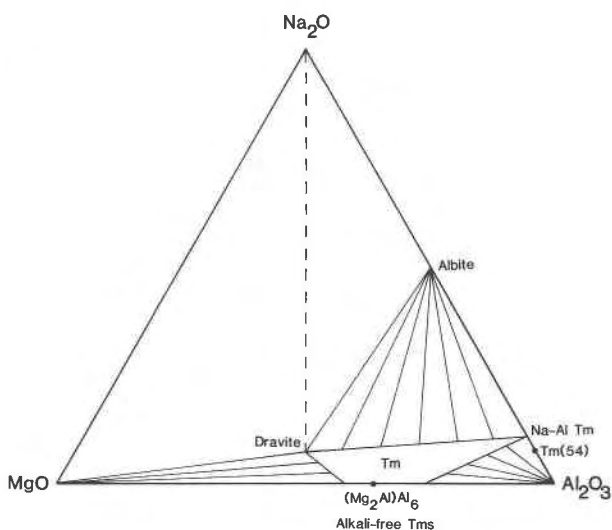


Fig. 4. Hypothetical, "isothermal," isobaric ternary diagram showing the compositional field of tourmaline (Tm) in the system Na₂O-MgO-Al₂O₃-SiO₂-B₂O₃-H₂O in the presence of excess SiO₂, B₂O₃, and H₂O. Alkali-free Mg-Al tourmalines (Rosenberg and Foit, 1979, 1985); Na-Al tourmalines, this study; Na-Al Tm, ideal composition; Tm(54), tourmaline 54. See text for details.

reported in this study by starting with mixtures having even lower Si/Al ratios. The near absence of tetrahedral Al in most natural tourmalines implies a strong site preference for Si, suggesting that the Na-Al tourmalines synthesized in this study may be metastable with respect to the ideal endmember.

Metastability of the Na-Al tourmalines synthesized in this study relative to the ideal endmember may also be inferred from crystal-chemical considerations. Since each octahedron in the cluster of three edge-sharing 9b octahedra shares two vertices with two adjacent tetrahedra of the T₆O₁₈ ring, any size mismatch between the tetrahedral and tetrahedral portions will tend to strain the structure. The smaller size of the Al-containing 9b octahedral cluster in Na-Al tourmaline as compared to that in dravite, buergerite, or even elbaite should favor a smaller ring size. Thus, the preference of Si over Al in the tetrahedral ring should be even stronger in Na-Al tourmaline than in other members of the tourmaline group. It follows that the ideal endmember, which contains no ^{iv}Al, is probably the stable Na-Al tourmaline composition.

Compositional field of tourmaline in Na₂O-MgO-Al₂O₃-SiO₂-B₂O₃-H₂O system

The compositional field of tourmaline in the system Na₂O-MgO-Al₂O₃-SiO₂-B₂O₃-H₂O in the presence of excess quartz, B₂O₃, and H₂O may be inferred from the results of this study and those of Rosenberg and Foit (1979, 1985). The field (Fig. 4) is defined by the endmembers dravite, NaMg₃Al₆(BO₃)₃Si₆O₁₈(OH)₄; ideal alkali-free tourmaline, □(Mg₂Al)Al₆(BO₃)₃Si₆O₁₈(OH)₄, and solid solutions from this composition toward talc and mullite

(Rosenberg and Foit, 1985); and ideal Na-Al tourmaline, $\text{NaAl}_3\text{Al}_6(\text{BO}_3)_3\text{SiO}_6\text{O}_{21}(\text{OH})$, and the more aluminous, presumably metastable compositions synthesized in the present study. The linear boundaries of the tourmaline field imply that the endmembers are related by coupled substitutions: dravite and Na-Al tourmaline, $\text{Mg}^{2+} + \text{H}^+ = \text{Al}^{3+}$; dravite and ideal alkali-free tourmaline, $\text{Na}^+ + \text{Mg}^{2+} = \square + \text{Al}^{3+}$; and ideal alkali-free tourmaline and Na-Al tourmaline, $2\text{Mg}^{2+} + 3\text{H}^+ = \text{Na}^+ + 2\text{Al}^{3+}$.

Crystalline phases lying in the five-component system without B_2O_3 (e.g., phlogopite, glaucophane, paragonite, cordierite) are not represented in Figure 4 because they are thought to be unstable in the presence of excess B_2O_3 . Tourmaline is expected to coexist with phases that would plot at the apices of the ternary diagram: MgO represented by talc (or anthophyllite) possibly with some substitution of the type $\text{B}^{3+} + \text{H}^+ = \text{Si}^{4+} + \text{H}_2\text{O}$; Al_2O_3 represented by andalusite (mullite in synthetic systems), probably B bearing, although dumortierite, $\text{Al}_7(\text{BO}_3)(\text{SiO}_4)_3\text{O}_3$, is possible; and Na_2O represented by reedmergnerite, NaBSi_3O_8 . Extensive solid solution from albite, which also coexists with tourmaline, toward reedmergnerite has been reported (Eugster and McIver, 1959), but the series may be limited by a miscibility gap (Chorlton and Martin, 1978). The diagram (Fig. 4) is actually polythermal since reedmergnerite melts incongruently to quartz and liquid at 567°C (Eugster and McIver, 1959), and synthetic tourmalines (Rosenberg and Foit, 1979, 1985, and this study) represent various temperatures between 500 and 700°C. Although endmember compositions are known, the existence of complete solid-solution series between dravite and both alkali-free and Na-Al tourmalines is conjectural. The ternary diagram shows an extensive one-phase area of tourmaline solid solutions, which implies widely variable tourmaline compositions in the six-component system.

CONCLUSIONS

Na-Al tourmalines have been synthesized with B-bearing albite, quartz, H_3BO_3 , and aqueous fluid in the system $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{B}_2\text{O}_3-\text{H}_2\text{O}$ between 450 and 600°C at 1 kbar. Extensive melting above 600°C appears to account for the absence of tourmaline at higher temperatures.

Two samples of Na-Al tourmaline have been characterized by their optical properties, X-ray diffraction data, and partial chemical analyses. Refractive indices, $N_e = 1.639 \pm 0.002$ and $N_w = 1.642 \pm 0.002$ are higher than those of elbaite and dravite but, nevertheless, conform to the general density versus mean refractive index trend for the tourmaline group. Refined unit-cell dimensions $a_0 = 15.885(2) \text{ \AA}$, $c_0 = 7.104(1) \text{ \AA}$ (Ekambaram, 1978) are similar to those of aluminous dravites and elbaites. The synthetic Na-Al tourmalines are more aluminous than the ideal endmember $\text{NaAl}_3\text{Al}_6(\text{BO}_3)_3\text{Si}_6\text{O}_{21}(\text{OH})$, having the structural formulas $(\square_{0.06}\text{Na}_{0.94})\text{Al}_3\text{Al}_6(\text{Si}_{4.22}\text{Al}_{1.78})(\text{BO}_3)_3\text{O}_{19.2}(\text{OH})_{2.8}$ and $(\square_{0.24}\text{Na}_{0.76})\text{Al}_3\text{Al}_6(\text{Si}_{5.82}\text{Al}_{0.18})(\text{BO}_3)_3\text{O}_{20.6}(\text{OH})_{1.4}$, but these solid solutions may be metastable with respect to the ideal endmember.

The compositional field of tourmaline in the system $\text{Na}_2\text{O}-\text{MgO}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{B}_2\text{O}_3-\text{H}_2\text{O}$ in the presence of excess $\text{SiO}_2, \text{B}_2\text{O}_3$, and H_2O based on data from Rosenberg and Foit (1979, 1985) and this study appears to define an extensive field of solid solutions, implying widely variable tourmaline compositions.

ACKNOWLEDGMENTS

We thank Michel Pichavant for calling to our attention the possible existence of a tourmaline-like phase in the silica-rich portion of the system $\text{K}_2\text{O}-\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{B}_2\text{O}_3-\text{H}_2\text{O}$. Analytical studies were carried out in the Department of Geology at the University of Manchester, England. We are indebted to Graham Cliff for technical assistance.

REFERENCES

- Borg, I.Y., and Smith, D.K. (1969) Calculated X-ray powder patterns for silicate minerals. Geological Society of America Memoir 122.
- Bridge, P.J., Daniels, J.L., and Pryce, M.S. (1977) The dravite crystal bonanza of Yinnietarra, Western Australia. Mineralogical Record, 8, 109–110.
- Champness, P.E., Cliff, G., and Lorimer, G.W. (1982) Quantitative analytical electron microscopy of metals and minerals. Ultramicroscopy, 8, 121–132.
- Chorlton, L.B., and Martin, R.F. (1978) The effect of boron on the granite solidus. Canadian Mineralogist, 16, 239–244.
- Cossa, A., and Arzruni, A. (1883) Ein Chromturmalin aus den Chromeisenlagern des Urals. Zeitschrift für Kristallographie, 7, 1–16.
- Donnay, G., and Barton, R., Jr. (1972) Refinement of the crystal structure of elbaite and the mechanism of tourmaline solid solution. Tschermarks Mineralogische und Petrographische Mitteilungen, 18, 273–276.
- Dunn, P.J., Appleman, D., Nilen, J.A., and Norbery, J. (1977) Uvite, a new (old) common member of the tourmaline group and its implications for collectors. Mineralogical Record, 8, 100–108.
- Ekambaram, V. (1978) Stability relations and crystal chemistry of tourmaline in the system $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{B}_2\text{O}_3-\text{H}_2\text{O}$. M.S. thesis, Washington State University, Pullman.
- Ekambaram, V., Rosenberg, P.E., and Foit, F.F., Jr. (1981) Synthesis and characterization of tourmaline in the system $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{B}_2\text{O}_3-\text{H}_2\text{O}$. (abs.) EOS, 62, 1065.
- Eugster, H.P., and McIver, N.L. (1959) Boron analogues of alkali feldspars and related silicates. (abs.) Geological Society of America Bulletin, 70, 1598–1599.
- Flower, M.F.J. (1974) Phase relations of titanacmite in the system $\text{Na}_2\text{O}-\text{Fe}_2\text{O}_3-\text{Al}_2\text{O}_3-\text{TiO}_2-\text{SiO}_2$ at 1000 bars total water pressure. American Mineralogist, 59, 536–548.
- Foit, F.F., Jr., and Rosenberg, P.E. (1977) Coupled substitutions in the tourmaline group. Contributions to Mineralogy and Petrology, 62, 109–127.
- (1979) The structure of vanadium-bearing tourmaline and its implications regarding tourmaline solid solutions. American Mineralogist, 64, 788–798.
- Kitahara, J. (1966) On dravite (Mg-tourmaline) from the Hirose Mine, Tottori Prefecture. Japanese Association of Mineralogists, Petrologists and Economic Geologists Journal, 56, 228–233 (Japanese with English summary).
- Kunitz, W. (1929) Beiträge zur Kenntnis der magmatischen Assoziationen I. Die Mischungsreihen in der Turmalinsgruppe und die genetischen Beziehungen zwischen Turmalinen und Glimmern. Chemie der Erde, 4, 208–251.
- Maitrallet, P. (1976) Les nodules à tourmaline des granitoides dans quelques gisements de France et d'Italie. Thèse 3e cycle,

- University of Pierre et Marie Curie, Paris (not seen; extracted from Chorlton and Martin, 1978, listed above).
- Pichavant, Michel. (1981) An experimental study of the effect of boron on a water-saturated haplogranite at 1 kbar vapor pressure. *Contributions to Mineralogy and Petrology*, 76, 430–439.
- Quensel, P., and Gabrielson, O. (1939) Minerals of the Varutrask pegmatite XIV. The tourmaline group. *Geologiska Föreningens Stockholm Förhandlingar*, 61, 63–90.
- Rosenberg, P.E., and Foit, F.F., Jr. (1979) Synthesis and characterization of alkali-free tourmaline. *American Mineralogist*, 64, 180–186.
- (1985) Tourmaline solid solutions in the system $MgO-Al_2O_3-SiO_2-B_2O_3-H_2O$. *American Mineralogist*, 70, 1217–1223.
- Sahama, Th.G., Knorring, V., Ragnar, O., and Ragnar, T. (1979) On tourmaline. *Lithos*, 12, 109–114.
- Schaller, W.T. (1913) Beitrag zur Kenntnis der TurmalinGruppe. *Zeitschrift für Kristallographie*, 51, 321–343.
- Simpson, E.S. (1931) Contributions to the mineralogy of Western Australia. IV. *Royal Society of Western Australia Journal*, 17, 137–149.
- Slivko, M.M. (1959) Manganese tourmalines. *Mineralogicheskii Sbornik (Lvov)*, 13, 139–148.
- Swanson, H.E., Morris, M.C., Evans, E.H., and Verner, L. (1964) Standard X-ray diffraction patterns. *National Bureau of Standards Monograph*, 25, Sec. 3, 47–48.
- Tomisaka, Takeshi. (1968) Synthesis of some end-members of the tourmaline group. *Mineralogical Journal (Japan)*, 5, 355–364.
- Voskresenskaya, I.E., and Barsukova, M.L. (1968) Synthesis and properties of some iron and iron-free varieties of tourmaline. In A.N. Lobachev, Ed. *Gidrothermal'nyi Sintez Kristallov*, 175–192. *Academia Nauk SSSR, Institut Kristallograph, Moscow* (transl. Consultants Bureau, Inc., New York, 1971).

MANUSCRIPT RECEIVED JUNE 11, 1985

MANUSCRIPT ACCEPTED MARCH 18, 1986