

# The Variation of Tourmaline Chemistry with Metamorphic Grade in Southwest Maine

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## INTRODUCTION

Metamorphic tourmaline can provide useful information about its host rock and the conditions under which it grew. Nevertheless, studies on metamorphic tourmaline are scarce even though tourmaline forms in virtually all grades of metamorphism and only needs boron plus the usual rock-forming elements to grow (Henry and Guidotti, 1985; Henry and Dutrow, 1996). Indeed, tourmaline compositions closely reflect the bulk composition of the rock in which they are formed. For metamorphic rocks of the same bulk composition, changes in tourmaline composition can be related to changes in metamorphic grade (Henry and Guidotti, 1985; Henry and Dutrow, 1996). The goal of our project was to determine the variation of tourmaline chemistry with metamorphic grade for rocks in southwest Maine. To this end we analyzed tourmaline from three formations (Smalls Falls, Rangeley, and Perry Mountain), each of which is relatively homogeneous and uniform in bulk composition. The Perry Mountain and Rangeley Formations have fairly similar compositions, but the Smalls Falls Formation is sulfide-rich, so the iron is concentrated into sulfide minerals (mainly pyrrhotite), leaving little for the silicate minerals in the rock (Mohr and Newton, 1983). Tourmaline in this formation is therefore iron-poor.

## GEOLOGIC SETTING

Western Maine has undergone at least two complex tectonometamorphic events, the Taconic Orogeny and the Acadian Orogeny. Taconian metamorphism was caused by the North American continental plate colliding with another plate during the Ordovician period (Robinson et al., 1986; DeYoreo et al., 1989). The Devonian to Carboniferous Acadian metamorphism in Maine involves a series of spatially and temporally overlapping regional events that resulted largely from heating by shallow-dipping tabular plutons. These plutons developed from the melting of the lower crust due to crustal thickening (DeYoreo et al., 1989), and were intruded in a series of pulses ranging from early middle Devonian into Carboniferous time. It is believed that the metamorphisms associated with these intrusive pulses are responsible for the latest growth of the tourmaline found (personal communication, M. D. Dyar, 1996). Moreover, chemical equilibrium was closely approached during the final metamorphism at any given locality (e.g. Henry and Guidotti, 1985; Guidotti and Holdaway, 1993). Hence, major-element compositions of tourmaline should vary as a result of changing metamorphic grade. Each of the three formations sampled exhibits metamorphic grades ranging from staurolite zone to K-spar + sillimanite zone. The few samples collected at the southernmost portion of the area crystallized in response to intrusion of the Carboniferous Sebago Pluton. All of the remainder formed in response to heat imparted by the middle Devonian Mooselookmeguntic Pluton (Guidotti and Holdaway, 1993).

## MATERIALS AND METHODS

With the guidance of Professor Charles Guidotti, we sampled outcrops across southwest Maine from the Perry Mountain, Rangeley, and Smalls Falls formations. We were able to sample each formation in four metamorphic zones: Staurolite Zone (StZ), Lower Sillimanite Zone (LSZ), Upper Sillimanite Zone (USZ), and K-feldspar Sillimanite Zone (KSZ). We tried to choose samples for which the tourmaline would be saturated with Si, Al, and Ti (indicated by the presence of quartz, staurolite or sillimanite, and rutile or ilmenite, respectively) (Guidotti et al., 1977; Guidotti, 1978; Henry and Guidotti, 1985). Although we looked closely for tourmaline at each outcrop, it was

difficult or impossible to see tourmaline in hand sample. Because we were also unable to find tourmaline in crushed portions of our samples, we could not pick tourmaline separates for analysis of isotopes, the lighter elements, and the oxidation state of iron. Thin sections were made of all our samples and we did find tourmaline in most thin sections. Major element chemistry of the tourmaline in thin section was determined using the scanning electron microscope (SEM) at Amherst College and its energy dispersive x-ray spectrometer (EDS). We also analyzed garnet and biotite grains in each thin section and made sure that each rock contained the saturating minerals.

## RESULTS AND DISCUSSION

Chemical analyses of our samples are listed in Table 1, expressed as mineral formulas. Tourmaline analyses are normalized on the basis of 24.5 oxygens (assuming 2 H<sub>2</sub>O and 1.5 B<sub>2</sub>O<sub>3</sub> per 31 oxygen formula). Garnet is normalized on the basis of 12 oxygens. Biotite is normalized on the basis of 11 oxygens (assuming 1 H<sub>2</sub>O per 12 oxygen formula). All Fe is assumed to be Fe<sup>+2</sup>. The data are summarized graphically in Figure 1, which shows the Mg/(Mg+Fe) values for tourmaline, biotite, and garnet for each of the four metamorphic zones. Tourmaline composition is shown on the bottom axis. Both garnet and biotite compositions are shown on the top axis because the garnet is systematically lower in Mg/(Mg+Fe). Compositions of minerals that occur together are connected by tie lines. Because the partitioning of elements normally decreases with increasing temperature, we expected the tie lines on Figure 1 to become more nearly vertical with increasing metamorphic grade. This was our observation for the StZ, LSZ, and USZ. However, the tourmaline in the KSZ does not follow this trend and seems anomalous. Because the composition of tourmaline is so complex, chemical reactions not involving Fe and Mg might affect the Fe-Mg distribution among tourmaline, garnet and biotite. Nonetheless, the fact that the Fe-Mg distribution among these minerals generally appears to be systematic supports the use of tourmaline in cation exchange geothermometers. It is also interesting to note that the three-phase triangle, Tour-Bio-Gar shifts to lower Mg/(Mg+Fe) values as the grade increases.

X-ray intensity maps were collected for tourmaline crystals in two samples: Ru-C-1, a Smalls Falls rock in the Staurolite Zone; and Ru-U, a Smalls Falls rock from the K-felspar-Sillimanite Zone. Intensity maps for Fe and Ca in the StZ sample are shown in Figures 2a and 2b, respectively. Lighter colors indicate a higher concentration of the element. The chemical zoning shown in these maps is complex and may be due to growth of tourmaline during more than one metamorphic event or to growth of tourmaline on a detrital core. We have not shown the intensity maps for the KSZ tourmaline because there is no chemical zoning visible. This suggests that either the zoning has been eliminated by diffusion at the higher temperatures of the KSZ or that new tourmaline crystals have nucleated and grown in the KSZ.

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Formation	SF	SF	SF	SF	PM	PM	PM	RF	RF	RF	RF
Sample	C-1	T	K	U	B-2	jack's	J-2	Ru-A	Ru-F	Ru-N	Ru-R4
Grade	STZ	LSZ	USZ	KSZ	STZ	LSZ	USZ	STZ	LSZ	USZ	KSZ
	<b>Tourm.</b>	<b>Tourm.</b>	<b>Tourm.</b>	<b>Tourm.</b>	<b>Tourm.</b>	<b>Tourm.</b>	<b>Tourm.</b>	<b>Tourm.</b>	<b>Tourm.</b>	<b>Tourm.</b>	<b>Tourm.</b>
<b>Wt% Total</b>	87.77	87.44	88.68	87.31	89.44	89.73	86.57	87.42	88.82	89.18	87.14
Si	5.92	5.92	5.90	5.87	5.90	6.03	5.87	5.82	5.88	5.84	5.85
Al	6.34	6.29	6.41	6.49	6.27	6.11	6.46	6.46	6.43	6.49	6.48
Ti	0.07	0.05	0.07	0.07	0.10	0.11	0.11	0.07	0.10	0.12	0.07
Mg	2.30	2.24	2.16	2.18	1.58	1.48	1.33	1.66	1.54	1.44	1.52
Fe	0.19	0.33	0.29	0.23	1.04	1.10	1.09	0.97	0.91	0.96	1.06
Mn	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Ca	0.13	0.18	0.10	0.13	0.09	0.07	0.06	0.07	0.08	0.09	0.04
Na	0.75	0.67	0.73	0.73	0.78	0.73	0.69	0.62	0.72	0.71	0.61
K	0.01	0.00	0.00	0.01	0.01	0.09	0.01	0.00	0.00	0.00	0.00
<b>Mg/Fe+Mg</b>	0.92	0.87	0.88	0.91	0.60	0.58	0.55	0.63	0.50	0.48	0.59
<b>Mg/Fe</b>	12.34	6.74	7.48	9.61	1.51	1.35	1.21	1.71	1.68	1.50	1.42
			<b>Biotite</b>	<b>Biotite</b>	<b>Biotite</b>	<b>Biotite</b>	<b>Biotite</b>	<b>Biotite</b>	<b>Biotite</b>	<b>Biotite</b>	<b>Biotite</b>
<b>Wt% Total</b>			99.02	96.30	96.94	96.14	95.78	93.99	96.83	98.33	96.76
Si			2.75	2.81	2.63	2.61	2.65	2.66	2.67	2.66	2.57
Al			1.70	1.64	1.85	1.77	1.80	1.81	1.81	1.78	1.81
Ti			0.06	0.11	0.09	0.08	0.12	0.10	0.11	0.15	0.18
Mg			1.83	1.83	1.03	1.10	0.83	0.93	0.94	0.91	0.77
Fe			0.51	0.42	1.26	1.46	1.45	1.37	1.34	1.34	1.54
Mn			0.02	0.02	0.01	0.00	0.00	0.00	0.01	0.00	0.00
Ca			0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00
Na			0.15	0.10	0.16	0.14	0.14	0.09	0.09	0.11	0.08
K			0.75	0.79	0.77	0.68	0.79	0.85	0.81	0.80	0.86
<b>Mg/Fe+Mg</b>			0.78	0.81	0.45	0.43	0.36	0.40	0.41	0.40	0.33
<b>Mg/Fe</b>			3.58	4.39	0.82	0.75	0.57	0.68	0.71	0.68	0.50
					<b>Garnet</b>	<b>Garnet</b>		<b>Garnet</b>	<b>Garnet</b>	<b>Garnet</b>	<b>Garnet</b>
<b>Wt% Total</b>					103.83	101.83		98.18	103.71	104.31	98.45
Si					2.97	2.96		3.04	2.96	2.96	3.04
Al					2.02	2.00		2.05	2.00	2.00	2.04
Ti					0.00	0.00		0.00	0.00	0.00	0.00
Mg					0.28	0.30		0.22	0.31	0.30	0.20
Fe					2.34	2.43		2.26	2.33	2.37	2.36
Mn					0.28	0.22		0.26	0.31	0.28	0.27
Ca					0.07	0.08		0.09	0.10	0.08	0.05
Na					0.13	0.10		0.00	0.06	0.10	0.00
K					0.00	0.00		0.00	0.00	0.00	0.00
<b>Mg/Fe+Mg</b>					0.11	0.11		0.09	0.12	0.11	0.08
<b>Mg/Fe</b>					0.12	0.12		0.10	0.13	0.13	0.08

Table 1. EDS analyses of tourmaline, biotite, and garnet in polished thin sections. Analyses have been normalized to cation numbers (mineral formulas) on the basis of 24.5 oxygens for tourmaline, 11 oxygens for biotite, and 12 oxygens for garnet because no data were available for water or boron. Samples are from the Smalls Falls Formation (SF), the Perry Mountain Formation (PM), or the Rangeley Formation (RF). Metamorphic grades are the Staurolite Zone (STZ), the Lower Sillimanite Zone (LSZ), the Upper Sillimanite Zone (USZ), and the K-feldspar Sillimanite Zone (KSZ).

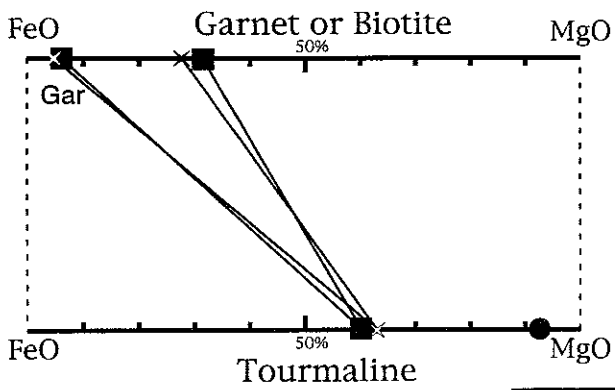


Figure 1a. StZ

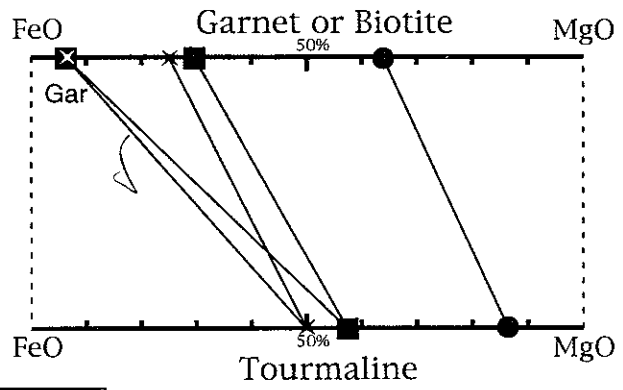


Figure 1b. LSZ

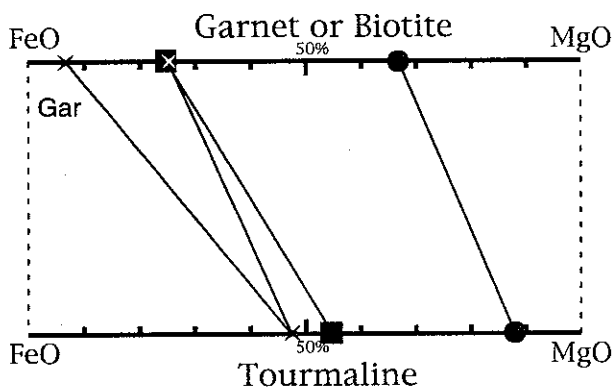


Figure 1c. USZ

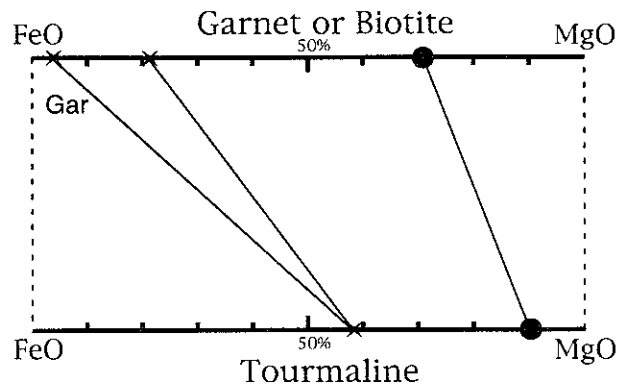


Figure 1d. KSZ



Figure 2a. Fe x-ray map of a tourmaline from the Smalls Falls Fm. in the StZ.

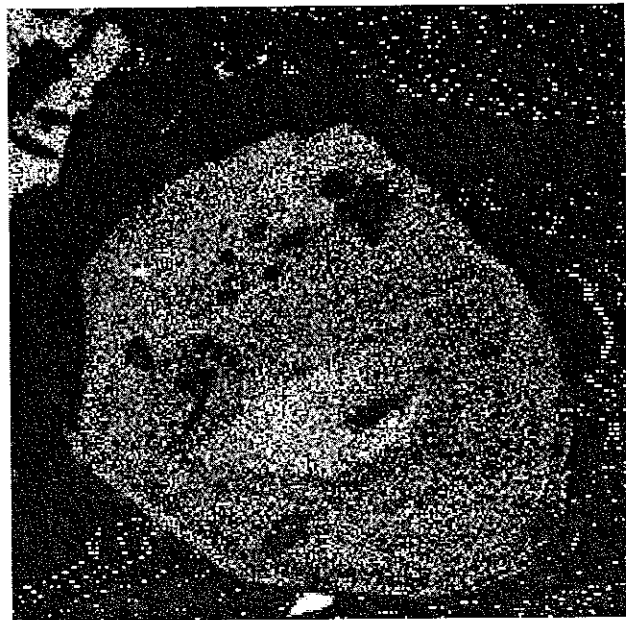


Figure 2b. Ca x-ray map of a tourmaline from the Smalls Falls Fm. in the StZ.