

# Tourmaline the Indicator Mineral: From Atomic Arrangement to Viking Navigation

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**T**ourmaline *sensu lato* has been known for at least two thousand years, and its unique combination of physical properties has ensured its importance to human society, from technical devices (such as a possible Viking navigational aid and early piezoelectric gauges in the 20<sup>th</sup> century) to attractive and popular gemstones. The chemical diversity and accommodating nature of its structure combine to make tourmaline a petrogenetic indicator for the wide range of rocks in which it occurs. Recent advances in understanding the structure, site assignments, and substitution mechanisms have led to a new nomenclature for the tourmaline supergroup minerals. Eighteen species have been described to encapsulate the chemical variety found in this intriguing structure.

**KEYWORDS:** tourmaline, crystal structure, crystal chemistry, pyroelectricity, piezoelectricity, tourmaline nomenclature, gemstone

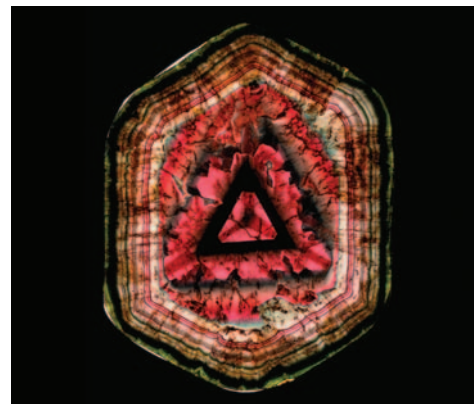
## INTRODUCTION

For many years, tourmaline *sensu lato* (i.e. minerals of the tourmaline supergroup) was not taken seriously by mineralogists, petrologists, and geochemists. The problem lay primarily in our lack of understanding of these minerals. They have recondite crystal chemistry, a fairly complicated crystal structure, and a chemical composition that is almost Byzantine in its complexity. Moreover, they can exhibit extremely convoluted chemical zoning, and several of their more important chemical constituents (H, Li, B, Fe<sup>2+</sup>, Fe<sup>3+</sup>) were not easily determined by standard analytical techniques (specifically, electron microprobe analysis). Tourmaline was essentially a “Saturday afternoon” mineral, something that was fun to look at but wasn’t to be taken too seriously. This situation began to change about 20 years ago, as systematic examination of its crystal chemistry and paragenesis began to illuminate the mysteries of this hitherto exotic mineral. Tourmaline is the epitome of the thesis that the more complicated a mineral, the more information it contains about its crystallization and subsequent evolution, and our increased understanding of its crystal chemistry is turning this mineral into an important petrogenetic indicator (van Hinsberg et al. 2011).

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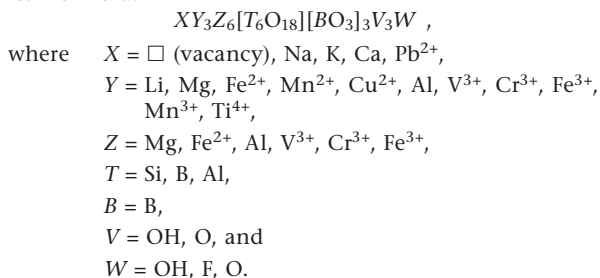
Tourmaline as a  
constituent of jewelry.  
FROM THE TOURMALINE  
COLLECTION OF  
DR. E. SOKOLOVA



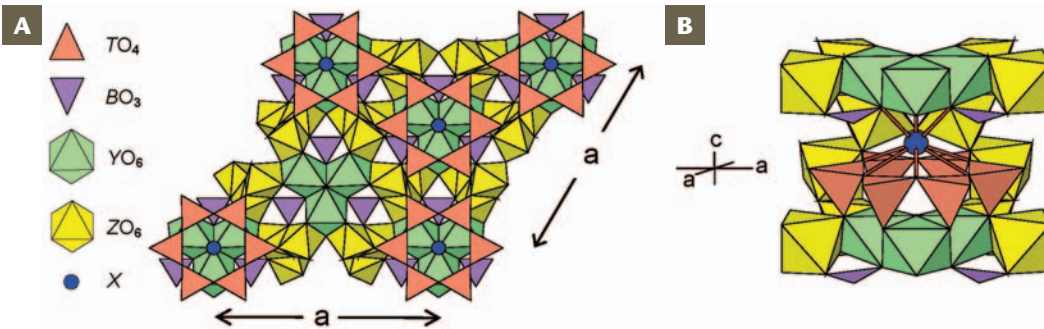
**FIGURE 1** A complexly zoned slice of fluor-liddicoatite cut parallel to (001), from Anjanabonoina, Madagascar. This slice measures approximately 10 cm in its longest dimension, and displays a trigonal star pattern and “aggregate-type” zoning. The outer region consists of fine-scale color zoning roughly parallel to the prism faces.  
PHOTO © HAROLD & ERICA VAN PELT

## CHEMICAL COMPOSITION

Our first indication of the complexity of the minerals of the tourmaline supergroup arises from their general chemical formula:



The letters in the general formula correspond to groups of cations or anions that occupy the same sites in the structure. These occupancies are well established, except perhaps for the presence of Fe<sup>2+</sup> at the Z site where some differences of opinion still exist (e.g. Ertl et al. 2006; Andreozzi et al. 2008). The crystal chemistry of tourmaline has taken a long time to unravel, a result of the combination of a complicated structural arrangement and a flexible structure that can incorporate many different cations and anions. In particular, the above formula can include three light lithophile elements (H, Li, B) that can occur in variable quantities and Fe that can occur as both Fe<sup>2+</sup> and Fe<sup>3+</sup>. These constituents cannot be analyzed easily with the more common analytical techniques, and either (often dubious) stoichiometric assumptions are necessary to calculate a chemical formula or less common and more difficult analytical techniques (see below) are required for accurate chemical analysis. These problems are compounded by the fact that tourmaline is often zoned on a fine scale (Fig. 1; see Pezzotta and Laurs 2011 this issue), and bulk analytical



**FIGURE 2** The crystal structure of tourmaline: (A) projected onto (001); (B) oblique view

techniques are not appropriate. Thus an adequate understanding of the chemical variations in tourmaline minerals has been dependent on the development of suitably advanced milli- and microbeam analytical techniques, accounting for why the tourmaline minerals are perhaps the last of the common silicates to be adequately understood.

### THE CRYSTAL STRUCTURE OF TOURMALINE

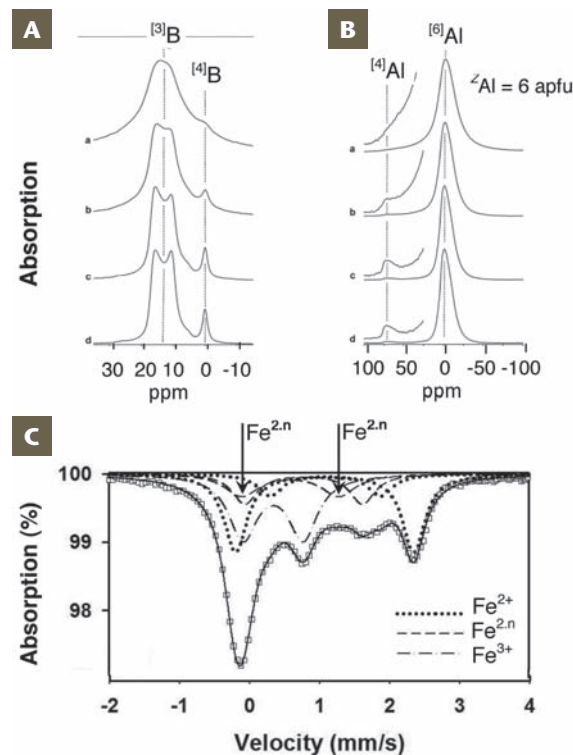
In the structure of tourmaline (FIG. 2), there is one tetrahedrally coordinated site, labelled *T*, which is predominantly occupied by Si but also can contain Al and B. Six  $TO_4$  tetrahedra join corners to make a  $[T_6O_{18}]$  ring, forming a cyclosilicate structure. There is one triangularly coordinated site that is fully occupied by B. There are two octahedrally coordinated sites, labeled *Y* and *Z*, respectively. Three *Y* octahedra share edges to form a  $[Y_3\phi_{13}]$  trimer ( $\phi$  = unspecified anion). The *Z* octahedra share edges around the periphery of this trimer, the  $BO_3$  group providing additional linkage (FIG. 2A). The *X* site is [9]-coordinated and lies out of the plane of the  $[T_6O_{18}]$  ring.

Tourmaline has point-group symmetry  $3m$ , which is both noncentrosymmetric (i.e. does not have a center of symmetry) and polar (i.e. the unit cell of the structure has a net electric dipole moment). Thus tourmaline is both pyroelectric and piezoelectric (see below). The principal atomic-scale contribution to the piezoelectric and pyroelectric effects is the attitude of the tetrahedra in the tourmaline structure. All tetrahedra point along  $-c$  (FIG. 2B), and the resulting noncentrosymmetry and polar character strongly affect the growth, morphology, internal texture, and chemical zoning of tourmaline (e.g. van Hinsberg et al. 2011).

Much of the chemical complexity of tourmaline arises because of the variety of sites in the structure and the ease with which several of these sites can incorporate a wide variety of chemical species. In particular, H, Li, B,  $Fe^{2+}$ , and  $Fe^{3+}$  are common variable constituents, and their quantitative analysis can require careful crystal-structure refinement (e.g. Ertl et al. 1997, 2005), SIMS (secondary-ion mass spectrometry: H, Li, B), MAS NMR (magic-angle-spinning nuclear magnetic resonance:  $^{14}B$  and  $^{14}Al$ ; i.e. [4]-coordinated B and Al replacing Si at the *T* site), and  $^{57}Fe$  Mössbauer spectroscopy ( $Fe^{2+}$  and  $Fe^{3+}$  at the *Y* and *Z* sites).  $^{11}B$  and  $^{27}Al$  MAS NMR are sensitive to the coordination numbers of B and Al (FIG. 3A, B). There is a strong signal from  $^{11}B$  at  $\sim 13$ – $20$  ppm and a well-resolved signal at  $\sim 0$  ppm (FIG. 3A) due to  $^{14}B$  that replaces Si at the *T* site in the tourmaline structure (Tagg et al. 1999; Lussier et al. 2008), and there is a strong signal from  $^{11}Al$  at  $\sim 0$  ppm and a well-resolved signal at  $\sim 60$ – $70$  ppm (FIG. 3B) due to  $^{14}Al$  that replaces Si (Lussier et al. 2009). Thus  $^{11}B$  and  $^{27}Al$  MAS NMR allows detection of low levels ( $\sim 0.02$  apfu, atoms per formula unit) of  $^{14}B$  and  $^{14}Al$  in tourmalines that contain only small amounts of (ferromagnetic) transition metals (which tend to quench the NMR signal).  $^{57}Fe$  Mössbauer spectroscopy

is sensitive to valence state and coordination of Fe. FIGURE 3C shows the spectrum of an Fe-bearing elbaite with signals from  $Fe^{2+}$ ,  $Fe^{3+}$ , and a mixed state,  $Fe^{2,n}$ , which indicates intervalence charge transfer, the dynamic transfer of charge between locally adjacent Fe cations in the structure that gives rise to intense pleochroism in many tourmalines. The relative intensities of the peaks are related to the amounts of the different Fe species, and Fe at the *Y* and *Z* sites gives rise to different doublets in the spectrum (Andreozzi et al. 2008). Consequently, the combination of several analytical methods can give more complete chemical information about tourmaline, but problems still exist with regard to detecting and accurately measuring  $^{14}B$  and  $^{14}Al$  in Fe-rich ( $FeO > 2$  wt%) tourmaline.

Tourmaline shows extensive short-range order (local clustering of specific cations and anions; e.g. Taylor et al. 1995) due to the operation of the local valence-sum rule (Hawthorne 1997; Bosi 2011). As a result, the chemical constituents of tourmaline have extremely slow diffusion rates, and tourmaline from many environments is



**FIGURE 3** Spectroscopy and site occupancy in tourmaline. (A)  $^{11}B$  MAS NMR spectra of a series of tourmalines with the amount of  $^{14}B$  increasing downward (a to d) in accord with the peak at  $\sim 0$  ppm (B)  $^{27}Al$  MAS NMR spectra of a series of tourmalines with the amount of  $^{14}Al$  increasing downward in accord with the peak at  $\sim 65$  ppm (C)  $^{57}Fe$  Mössbauer spectrum of tourmaline (elbaite) showing peaks (doublets) due to  $Fe^{2+}$ ,  $Fe^{3+}$ , and mixed-valence  $Fe^{2,n}$ . SPECTRA FROM LUSSIER ET AL. (2008, 2011)

**FIGURE 4** Miner Ailton Barbosa kneeling with a large elbaite tourmaline (variety rubellite) cluster, which he discovered at the Jonas mine, Minas Gerais, Brazil, in 1978. PHOTO ©JULIO CESAR MENDES MENDES



extremely optically, chemically, and isotopically zoned. Such zoning preserves details of the crystallization history of the tourmaline, gives major insight into the petrologic processes affecting the host rocks (e.g. Henry and Guidotti 1985; Henry and Dutrow 1992; van Hinsberg and Marschall 2007; van Hinsberg and Schumacher 2009; van Hinsberg et al. 2011), and provides a record of the evolving fluids from which the tourmaline crystallized (e.g. Dutrow et al. 1999; Marschall et al. 2008; Marschall and Jiang 2011 this issue). In particular, the occurrence of B in both [3]- and [4]-coordination has major ramifications with regard to B isotope signatures in rocks (Marschall and Jiang 2011).

### MORPHOLOGICAL CRYSTALLOGRAPHY AND HABIT

Tourmaline is rhombohedral, ditrigonal pyramidal (point group  $3m$ ) and has space-group symmetry  $R3m^*$ . It commonly occurs as large crystals (FIG. 4), typically euhedral and showing a bewildering variety of forms (Goldschmidt 1922). Doubly terminated crystals are common and frequently exhibit *hemimorphic* character, that is, they have different morphological forms at each end of the  $c$  crystallographic axis (FIG. 5A). Tourmaline is pyroelectric due to the polar character of its symmetry and structure: when the crystal is heated, the *antilogous pole* of the crystal (the end that occurs along the  $+c$  crystallographic axis; FIG. 5A) acquires a negative charge, and the *analogous pole* (the end that occurs along the  $-c$  crystallographic axis) acquires a positive charge (Dietrich 1985). The pyramidal faces are much steeper on the antilogous end than on the analogous end, and the pedion (single basal face) at the antilogous end is highly reflective whereas the pedion at the analogous end has a rather matt luster. Crystal growth is much more rapid in the  $+c$  direction than in the  $-c$  direction, and authigenic crystals growing on detrital tourmaline cores are extended toward the antilogous end compared to the analogous end (e.g. Henry and Dutrow 1992).

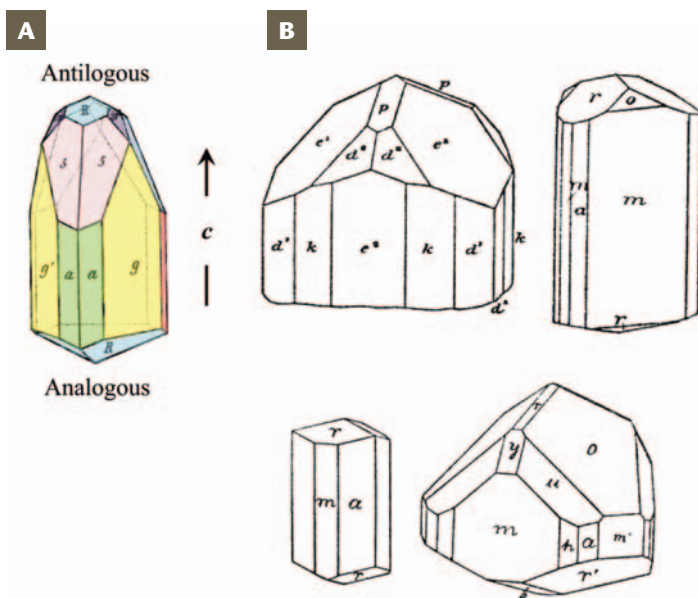
Tourmaline shows extremely diverse habits and is commonly morphologically complicated (FIG. 5B). Crystals are predominantly prismatic, varying from stubby to very acicular or fibrous, but can be tabular. Moreover, prism faces are commonly grooved parallel to the  $c$  axis, a characteristic feature for the identification of tourmaline in hand specimen. The change from prismatic to fibrous habit can be particularly spectacular when accompanied by a color change (Lussier et al. 2008).

**TABLE 1** COMMON PHYSICAL PROPERTIES OF THE TOURMALINE MINERALS

Color	Commonly black, also brownish, reddish pink to pink, pale green to dark green, yellow, shades of blue, mauve to purple, white, colorless
Streak	White to brown, greyish blue
Luster	Usually vitreous, occasionally resinous
Hardness (Mohs)	7–7½
Cleavage	Indistinct, poor on both {110} and {101}
Fracture	Uneven to conchoidal
Density (g cm <sup>-3</sup> )	2.8–3.3
Morphology	{110}, {111}, {11̄1}, {101}, {101̄}, {001}, {001̄} common
Habit	Crystals are frequently prismatic and often form divergent aggregates in granitic pegmatites.
Unit-cell dimensions	$a = b = 15.7\text{--}16.2 \text{ \AA}$ , $c = 7.05\text{--}7.25 \text{ \AA}$ , $\alpha = \beta = 90^\circ$ , $\gamma = 120^\circ$
Optic sign	Uniaxial negative
Refractive indices	$\epsilon = 1.610\text{--}1.650$ , $\omega = 1.635\text{--}1.675$
Birefringence	0.018–0.040
Pleochroism	Colored tourmaline minerals can be strongly pleochroic: shades of green and bluish green, pale blue to dark blue, pale pink to red, various shades of brown

### PHYSICAL PROPERTIES AND THEIR IMPORTANCE

Its hardness and lack of cleavage make tourmaline an important resistate mineral in clastic sediments, where it can be used as a provenance indicator (Henry and Guidotti 1985; Henry and Dutrow 1992; Morton et al. 2005; Marschall et al. 2008). Such detrital tourmaline typically serves as a nucleus for authigenic crystallization of tourmaline, which, with continued increase in temperature, can grade into subsequent metamorphic growth (e.g. Henry and Dutrow 1996 and references therein) in a wide variety of metamorphic rocks (van Hinsberg et al. 2011). Its multitude of colors and its hardness combine to make tourmaline a spectacular gemstone (Pezzotta and Laurs 2011). Standard physical properties are listed in TABLE 1.



**FIGURE 5** (A) Hemimorphic morphology (after Goldschmidt 1922) and the antilogous–analogous ends of a crystal. (B) Typical morphological forms of tourmaline (from Goldschmidt 1922)

\* There are some reports of tourmaline, or sectors within tourmaline crystals, having orthorhombic, monoclinic, or even triclinic symmetry (e.g. Akizuki et al. 2001).

## Pyroelectricity

On heating, materials that are pyroelectric attract other materials. In 314 BCE, Theophrastus noted that tourmaline attracts ash and straw when it is heated (Dietrich 1985). This property of tourmaline gave rise to the name *Aschentrecker*, or ash puller, and Dutch traders of the 18<sup>th</sup> century used long prismatic crystals of tourmaline to clean ash from their meerschaum pipes. The term *pyroelectricity* is derived from the Greek *pyr*, meaning fire, and the word *electricity*, and describes the ability of certain materials to produce a temporary voltage when they are heated (or cooled). The change in temperature causes a corresponding change in the positions of the atoms such that the net polarization of the crystal changes, and this change results in a voltage across the crystal. Consequently, only polar crystals can be pyroelectric. Polar materials do not normally have a net dipole moment because the intrinsic dipole moment of the crystal is neutralized by electric charge that builds up on the surface of the crystal by conduction or electrostatic attraction. Polar crystals only show pyroelectricity when disturbed in some way (e.g. heating) that perturbs their interaction with the neutralizing surface charge (Nye 1957).

## Piezoelectricity

When subjected to a mechanical stress, materials that are piezoelectric accumulate an electric charge. The piezoelectric effect was first shown by the brothers Pierre and Jacques Curie in 1880, using tourmaline, quartz, and topaz (Dietrich 1985). The term *piezoelectricity* is derived from the Greek *piezo*, meaning to squeeze, and the word *electricity*. In solid materials, an ion in an asymmetric environment has a dipole moment. In a centrosymmetric crystal, the symmetry results in zero net dipole moment. In a noncentrosymmetric crystal, the net dipole moment is nonzero. If a noncentrosymmetric crystal is mechanically stressed, the atoms in the crystal move in response to that stress, and the resulting strain induces a change in the net dipole moment. In turn, an electric charge is generated by this change in dipole moment, resulting in piezoelectricity. This gave rise to the use of Malagasy tourmaline as pressure gauges in submarines during WWI (Carl Francis, personal communication).

## Tourmaline: the Viking Sunstone?

The Icelandic saga *Rauðúlfs þáttr* tells us that Viking sailors used crystals as a navigational aid—a *sólarsteinn* (sunstone) that allowed them to locate the sun in cloudy and foggy weather. The story describes the visit of Olav Haraldsson II, king of Norway from 995 to 1030 (also known as St. Olav), to Eystridalir, a remote part of Norway where a wise man named Rauðúlfr was accused of stealing cattle. Rauðúlfr and his family lived in a rather special house that rotated with the movement of the sun across the sky. King Olav asked Rauðúlfr how the house managed to follow the sun when the sky was obscured by cloud and fog. So Rauðúlfr showed the king his sunstone, which allowed him to locate the sun through cloud and fog. Subsequently, Rauðúlfr and his family were found innocent of the cattle theft, and Rauðúlfr's two sons, who were skilled astronomers, joined the king's retinue (Faulkes 1966).

The identity of Viking sunstone is strongly debated, the principal candidates being tourmaline (presumably elbaite), cordierite, and calcite (Karlsen 2000), all of which strongly polarize light. The atmospheric requirements for such navigation are as follows: (1) the degree of linear polarization, *p*, of the light from the sky should be high; and (2) at a given position of the sun, the pattern of the angle of polarization,  $\alpha$ , of the foggy/cloudy sky should be similar to that of the clear sky (Hegedüs et al. 2007). Requirement (2) is always satisfied, but if the fog layer is illuminated by direct sunlight, requirement (1) is usually satisfied only if the sky is cloudy. Presumably, the effectiveness of this method is also strongly dependent on the optical quality of the specific crystal in the possession of the navigator.

## HOW TO NAME A TOURMALINE

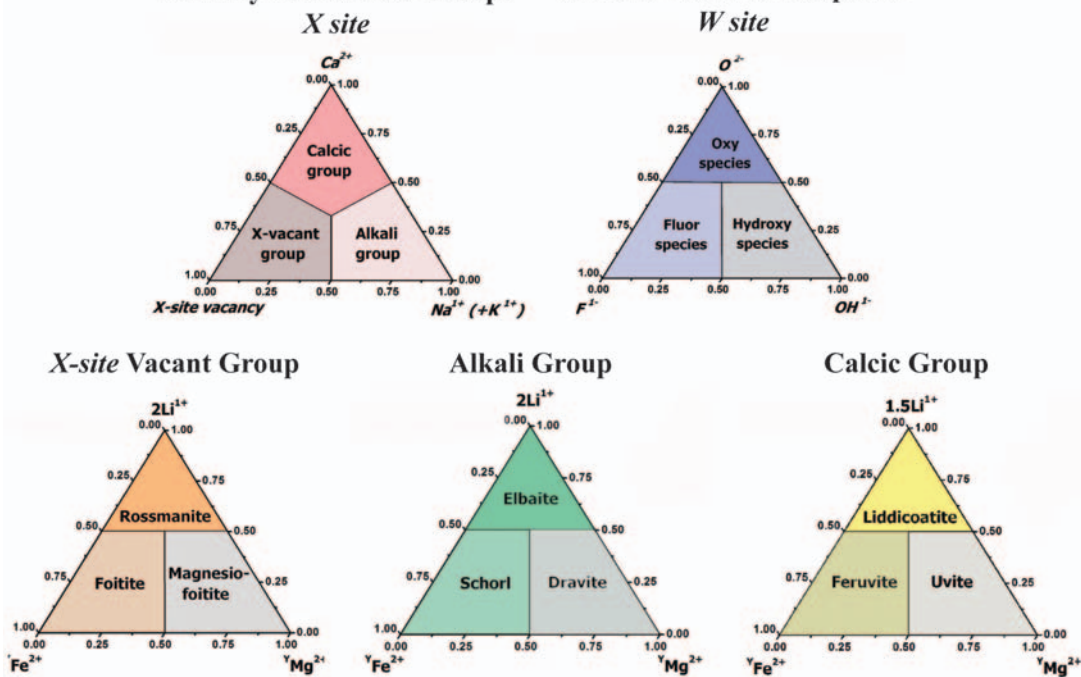
The numerous chemical constituents and their ability to occupy a variety of sites in the tourmaline structure has given rise to a modest number of recognized species in the past, but this number has been increasing significantly in the last few years. Tourmaline species are defined in terms of chemical composition, and the primary criterion is the dominance of a particular chemical constituent at a given crystallographic site. The result is that each distinct mineral species can be associated with an end-member composition

**TABLE 2** IMA-ACCEPTED TOURMALINE SPECIES AND THEIR END-MEMBER COMPOSITIONS

General formula	(X)	(Y <sub>3</sub> )	(Z <sub>6</sub> )	T <sub>6</sub> O <sub>18</sub>	(BO <sub>3</sub> ) <sub>3</sub>	V <sub>3</sub>	W
<b>Alkali Group</b>							
Dravite	Na	Mg <sub>3</sub>	Al <sub>6</sub>	Si <sub>6</sub> O <sub>18</sub>	(BO <sub>3</sub> ) <sub>3</sub>	(OH) <sub>3</sub>	(OH)
Schorl	Na	Fe <sup>2+</sup> <sub>3</sub>	Al <sub>6</sub>	Si <sub>6</sub> O <sub>18</sub>	(BO <sub>3</sub> ) <sub>3</sub>	(OH) <sub>3</sub>	(OH)
Chromium-dravite	Na	Mg <sub>3</sub>	Cr <sub>6</sub>	Si <sub>6</sub> O <sub>18</sub>	(BO <sub>3</sub> ) <sub>3</sub>	(OH) <sub>3</sub>	(OH)
Vanadium-dravite	Na	Mg <sub>3</sub>	V <sub>6</sub>	Si <sub>6</sub> O <sub>18</sub>	(BO <sub>3</sub> ) <sub>3</sub>	(OH) <sub>3</sub>	(OH)
Fluor-dravite	Na	Mg <sub>3</sub>	Al <sub>6</sub>	Si <sub>6</sub> O <sub>18</sub>	(BO <sub>3</sub> ) <sub>3</sub>	(OH) <sub>3</sub>	F
Fluor-schorl	Na	Fe <sup>2+</sup> <sub>3</sub>	Al <sub>6</sub>	Si <sub>6</sub> O <sub>18</sub>	(BO <sub>3</sub> ) <sub>3</sub>	(OH) <sub>3</sub>	F
Elbaite	Na	Li <sub>1.5</sub> Al <sub>1.5</sub>	Al <sub>6</sub>	Si <sub>6</sub> O <sub>18</sub>	(BO <sub>3</sub> ) <sub>3</sub>	(OH) <sub>3</sub>	(OH)
Povondraite	Na	Fe <sup>3+</sup> <sub>3</sub>	Mg <sub>2</sub> Fe <sup>3+</sup> <sub>4</sub>	Si <sub>6</sub> O <sub>18</sub>	(BO <sub>3</sub> ) <sub>3</sub>	(OH) <sub>3</sub>	O
Chromo-alumino-povondraite	Na	Cr <sub>3</sub>	Mg <sub>2</sub> Al <sub>4</sub>	Si <sub>6</sub> O <sub>18</sub>	(BO <sub>3</sub> ) <sub>3</sub>	(OH) <sub>3</sub>	O
Fluor-buergerite	Na	Fe <sup>3+</sup> <sub>3</sub>	Al <sub>6</sub>	Si <sub>6</sub> O <sub>18</sub>	(BO <sub>3</sub> ) <sub>3</sub>	(O) <sub>3</sub>	F
Olenite	Na	Al <sub>3</sub>	Al <sub>6</sub>	Si <sub>6</sub> O <sub>18</sub>	(BO <sub>3</sub> ) <sub>3</sub>	(O) <sub>3</sub>	(OH)
<b>Calcic Group</b>							
Fluor-uvite	Ca	Mg <sub>3</sub>	MgAl <sub>5</sub>	Si <sub>6</sub> O <sub>18</sub>	(BO <sub>3</sub> ) <sub>3</sub>	(OH) <sub>3</sub>	F
Feruvite	Ca	Fe <sup>2+</sup> <sub>3</sub>	MgAl <sub>5</sub>	Si <sub>6</sub> O <sub>18</sub>	(BO <sub>3</sub> ) <sub>3</sub>	(OH) <sub>3</sub>	(OH)
Uvite	Ca	Mg <sub>3</sub>	MgAl <sub>5</sub>	Si <sub>6</sub> O <sub>18</sub>	(BO <sub>3</sub> ) <sub>3</sub>	(OH) <sub>3</sub>	(OH)
Fluor-liddicoatite	Ca	Li <sub>2</sub> Al	Al <sub>6</sub>	Si <sub>6</sub> O <sub>18</sub>	(BO <sub>3</sub> ) <sub>3</sub>	(OH) <sub>3</sub>	F
<b>Vacancy Group</b>							
Foitite	□	Fe <sup>2+</sup> <sub>2</sub> Al	Al <sub>6</sub>	Si <sub>6</sub> O <sub>18</sub>	(BO <sub>3</sub> ) <sub>3</sub>	(OH) <sub>3</sub>	(OH)
Magnesio-foitite	□	Mg <sub>2</sub> Al	Al <sub>6</sub>	Si <sub>6</sub> O <sub>18</sub>	(BO <sub>3</sub> ) <sub>3</sub>	(OH) <sub>3</sub>	(OH)
Rossmannite	□	Li Al <sub>2</sub>	Al <sub>6</sub>	Si <sub>6</sub> O <sub>18</sub>	(BO <sub>3</sub> ) <sub>3</sub>	(OH) <sub>3</sub>	(OH)

## Primary Tourmaline Groups

## General Tourmaline Species



**FIGURE 6** Classification of the tourmaline supergroup minerals by chemical composition. The primary division (TOP, LEFT) is made according to the dominant occupancy of the X site to give the X-site vacant, alkali, and calcic groups. The secondary division (BOTTOM) is made according to the dominant occupancy of the Y site (Mg, Fe<sup>2+</sup>, 2Li or 1.5 Li) with the Z site = Al dominant and V = OH dominant for each primary group, giving the root names shown here and in TABLE 2. The tertiary divisions (TOP RIGHT) are made according to the dominant occupancy of the Z site (Al, Cr<sup>3+</sup>, V<sup>3+</sup>, not shown) and the W anions (OH, F, O<sup>2-</sup>); the names involve the use of prefixes attached to root names and other trivial names and are listed in TABLE 2. FIGURES MODIFIED FROM HENRY ET AL. (2011)

that is irreducible, that is, it cannot be expressed in terms of two constituents of simpler composition and with the same atomic arrangement (Hawthorne 2002). For the majority of atomic arrangements and chemical compositions, this results in end-member formulae that have a single chemical species at each site, e.g. dravite:  ${}^X\text{Na} {}^Y\text{Mg}_3 {}^Z\text{Al}_6 ({}^T\text{Si}_6\text{O}_{18}) ({}^B\text{BO}_3)_3 {}^V(\text{OH})_3 {}^W(\text{OH})$ . However, electroneutrality can require some end-members to have two constituents of different valence (and in a fixed ratio) at one site in their structure (the remaining sites having only one constituent each), e.g. elbaite:  $\text{Na} {}^Y(\text{Li}_{1.5}\text{Al}_{1.5}) \text{Al}_6 (\text{Si}_6\text{O}_{18}) (\text{BO}_3)_3 (\text{OH})_3 (\text{OH})$ , in which the Y site is occupied by both Li and Al in a 1:1 ratio. This point is of particular relevance to the tourmalines, as the end-member compositions of the Li-bearing tourmalines rossmanite, elbaite, and liddicoatite have the Y site occupied by  $\text{LiAl}_2$ ,  $\text{Li}_{1.5}\text{Al}_{1.5}$ , and  $\text{Li}_2\text{Al}$ , respectively (TABLE 2). These chemical and structural complexities were recently evaluated to develop the currently IMA-accepted tourmaline minerals and their end-member compositions (TABLE 2; Henry et al. 2011). The tourmaline minerals are now referred to as a supergroup. Compositional variation in tourmaline may involve cations (or anions) of the same valence (homovalent variation) or cations (or anions) of different valence (heterovalent variation). Several common-mineral classifications are now based on the premise that distinct arrangements of formal charges at the sites in a structure are distinct root compositions, warrant distinct *root names*, and are distinct species (listed in TABLE 2). For a specific root name, different homovalent cations (e.g. Mg versus Fe<sup>2+</sup>) or anions (e.g. OH versus F) are indicated by prefixes (e.g. magnesiofoitite:  $\square (\text{Mg}_2\text{Al}) \text{Al}_6 (\text{Si}_6\text{O}_{18}) (\text{BO}_3)_3 (\text{OH})_3 (\text{OH})$ ; fluor-dravite:  $\text{Na} \text{Mg}_3 \text{Al}_6 (\text{Si}_6\text{O}_{18}) (\text{BO}_3)_3 {}^V(\text{OH})_3 {}^W\text{F}$ . Earlier established names are retained (e.g. schorl instead of “ferro-dravite”), but newly introduced tourmaline minerals, where appropriate, are named using prefixes, as indicated previously.

The tourmaline minerals show extensive compositional variation at the X, Y, Z, and W sites, and less variation at the T site. As a result, the tourmaline supergroup is divided into groups and subgroups according to compositional variation at these sites. The primary subdivision involves variation at the X site, resulting in the X-site vacant, alkali, and calcic groups (FIG. 6, TOP LEFT). For each group, the occu-

pancy of the Y site is considered in terms of the constituents  ${}^Y\text{Fe}$ ,  ${}^Y\text{Mg}$ , and  ${}^Y\text{Li}$  (FIG. 6, BOTTOM). Next, the anion occupancy of the O(1) site (the W anions) is considered: W may be occupied by (OH), F, or O<sup>2-</sup>, and this forms the basis of the next division (FIG. 6, TOP RIGHT) into the hydroxy-, fluor-, and oxy- species, defined as follows: hydroxyl- if  $\text{OH} + \text{F} \geq \text{O}^{2-}$  and  $\text{OH} \geq \text{F}$ ; fluor- if  $\text{OH} + \text{F} \geq \text{O}^{2-}$  and  $\text{F} > \text{OH}$ ; and oxy- if  $\text{O}^{2-} > \text{OH} + \text{F}$ . Variation in Z site constituents is expressed in terms of prefixes (TABLE 2). It should be emphasized that this classification is designed specifically for tourmalines that have been chemically analyzed.



**FIGURE 7** Tourmaline as eye candy. The Candelabra tourmaline is one of the stunning crystal clusters found in the legendary blue-cap tourmaline pocket at the Tourmaline Queen mine of Pala, California, in 1972. This rare blue-cap cluster (25 cm wide) of three elbaite crystals on quartz is now part of the Smithsonian Institution’s collection. PHOTO © HAROLD & ERICA VAN PELT

## AESTHETICS

Despite the intellectual fascination of tourmaline, we should not lose sight of the fact that there are other (aesthetic) reasons to appreciate this mineral. It forms mineral specimens so beautiful that they acquire their own names and are well known worldwide (FIG. 7). In addition, tourmaline gemstones show a bewildering array of spectacular colors (FIG. 8) and large stones are common (although expensive). Color and zoning can combine to form beautiful *objets d'art* and jewelry, and wealthy socialites collect tourmaline jewelry. It is fitting that such an interesting mineral has such a beautiful appearance.

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**FIGURE 8**

A selection of faceted (1.28–3.02 ct; 6.75 mm round to 8.9 × 8.3 mm cushion), unheated, Cu-bearing tourmalines from Mozambique showing the vivid colors typical of the deposit.

GEMSTONES COURTESY OF PALA INTERNATIONAL; PHOTOGRAPHER: ROBERT WELDON ©GEMOLOGICAL INSTITUTE OF AMERICA, REPRINTED WITH PERMISSION



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