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THE INCORPORATION OF FLUORINE IN TOURMALINE: INTERNAL CRYSTALLOGRAPHIC CONTROLS OR EXTERNAL ENVIRONMENTAL INFLUENCES?

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Abstract

The manner in which F is incorporated into the tourmaline structure depends on internal influences such as crystallographic constraints and on external influences such as temperature, pressure, local mineral assemblage and fluid composition. Tourmaline has a general formula $XY_3Z_6(T_6O_{18})(BO_3)_3V_3W$, with the most common site-occupancies being: $X = Ca^{2+}$, Na^{1+}, K^{1+}, $^X\square$ (vacancy); $Y = Li^{1+}$, Mg^{2+}, Fe^{2+}, Mn^{2+}, Al^{3+}, Cr^{3+}, Fe^{3+}; $Z = Al^{3+}$, Mg^{2+}, Fe^{3+}, Cr^{3+}; $T = Si^{4+}$, Al^{3+}; $B = B^{3+}$; $V \equiv [O(3)] = OH^{1-}$, O^{2-}; $W \equiv [O(1)] = OH^{1-}$, F^{1-}, O^{2-}. Of particular importance for understanding F^{1-} incorporation in tourmaline is that F^{1-} occurs solely at the O(1) site. Substitution of F^{1-} at this site is influenced by the occupancy (total charge) of the *X* and the *Y* sites. The *X* site is generally occupied by cations of variable charge (+1 or +2) or is vacant (zero charge). There are three *Y*-site cations, which can have charges of +1, +2, +3 or +4. However, the charge of the local bond-valence arrangements of the *Y*-site cations are most commonly between +6 (*e.g.*, Mg_3) and +7 (*e.g.*, Mg_2Al). Because of local bonding of the O(1)-site anion to three neighboring *Y*-site cations and an *X*-site cation, the charges at the *X* and *Y* sites affect the F^{1-} occupancy at the *W* site. Disorder of Mg and Al at the *Y* and *Z* sites influences the local charge, and consequently, the F content. The accumulated data on tourmaline verify the general crystallographic influences. A summary of >8800 tourmaline compositions from different lithologic environments illustrates that for tourmaline with an average *X*-site charge exceeding +0.9, there is a range from 0 to a maximum of 1.0 *apfu* F. As the *X*-site charge decreases, the maximal amount of F decreases, with the maximal amount of F being less than 0.2 *apfu* for those tourmalines with an *X*-site charge of less than +0.5. Petrological factors superimpose local environmental influences on F concentrations. The presence of minerals with a fixed high F content, such as fluorite, local assemblages of minerals and the degree of fractionation in a magma or fluid control the amount of F that is available to tourmaline within the crystallographic constraints imposed by local *X*- and *Y*-site charge.

Keywords: tourmaline, crystal chemistry, fluorine, F-rich assemblages, fractionation, database.

Sommaire

Le mode d'incorporation structurale du fluor dans la tourmaline dépend de contrôles internes, par exemple les contraintes cristallographiques, ainsi que des influences externes, par exemple la température, la pression, l'assemblage local des minéraux et la composition de la phase fluide. Une tourmaline possède la formule générale $XY_3Z_6(T_6O_{18})(BO_3)_3V_3W$, l'occupation la plus commune des sites étant: $X = Ca^{2+}$, Na^{1+}, K^{1+}, $^X\square$ (lacune); $Y = Li^{1+}$, Mg^{2+}, Fe^{2+}, Mn^{2+}, Al^{3+}, Cr^{3+}, Fe^{3+}; $Z = Al^{3+}$, Mg^{2+}, Fe^{3+}, Cr^{3+}; $T = Si^{4+}$, Al^{3+}; $B = B^{3+}$; $V \equiv [O(3)] = OH^{1-}$, O^{2-}; $W \equiv [O(1)] = OH^{1-}$, F^{1-}, O^{2-}. Pour comprendre le comportement du fluor, il faut réaliser que le F^{1-} ne peut se trouver que sur le site O(1). La substitution du F^{1-} à ce site serait influencée par le taux d'occupation (la charge totale) associé aux sites *X* et *Y*. Le site *X* contient généralement des cations de charge variable (+1 ou +2) ou bien est vacant (aucune charge). Il y a trois cations présents au site *Y*, ce qui peut donner une charge de +1, +2, +3 ou +4. Toutefois, la charge générée par les arrangements locaux des valences de laison des cations au site *Y* est en général entre +6 (*e.g.*, Mg_3) et +7 (*e.g.*, Mg_2Al). Comme conséquence de la coordinence locale de l'anion du site O(1) à trois cations du site *Y* et à un atome du site *X*, les charges aux sites *X* et *Y* exercent un contrôle sur le taux d'occupation du site *W* par le fluor. Un désordre de Mg et Al impliquant les sites *Y* et *Z* influence la charge locale et, par conséquent, la teneur en F. Les compositions accumulées dans une banque de données servent à vérifier le bien-fondé de ces prédictions cristallochimiques. Les compositions disponibles, au delà de 8800, provenant de divers milieux lithologiques montrent qu'une tourmaline ayant une charge moyenne au site *X* de plus de +0.9 peut contenir de 0 à un maximum de 1.0 *apfu* F. À mesure que la charge associée au site *X* diminue, la quantité maximale de F diminue, la teneur maximale étant inférieure à 0.2 *apfu* pour les tourmalines ayant une charge au site *X* de moins de +0.5. Les facteurs pétrologiques imposent une influence environnementale locale sur les concentrations de F possibles. La présence de minéraux à teneur en F élevée fixe, la fluorite par exemple, l'assemblage local des minéraux, et le

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degré de fractionnement des magmas ou fluides régissent la quantité de F disponible à la tourmaline, compte tenu des contraintes cristallographiques imposées par la charge aux sites *X* et *Y*.

(Traduit par la Rédaction)

Mots-clés: tourmaline, cristallochimie, fluor, assemblages riches en F, fractionnement, banque de données.

INTRODUCTION

Representatives of the tourmaline supergroup of minerals are encountered in a wide variety of rock types, largely because they are the primary mineral host for boron, they can accommodate a large array of chemical constituents, and they are stable over an extreme range of temperature, pressure and fluid compositions (*e.g.*, Henry & Dutrow 1996). A tourmaline also can serve as an effective monitor of the pressure – temperature – fluid evolution of a rock in which the tourmaline develops. For example, in metapelitic rocks, it is commonplace to find tourmaline grains that preserve textures and compositions that mark growth and, in some cases, dissolution representing different stages of development of the metamorphic rocks (Henry & Dutrow 1992, 1996). The manner in which chemical constituents are incorporated into the tourmaline structure depends on external influences such as temperature, pressure, the local assemblage of minerals, and fluid composition. It also depends on internal influences such as crystallographic and surface-energy constraints. The crystallographic control on incorporation of certain cations and anions has been well documented in other minerals, such as Ti in biotite and amphibole, or Cl and F in biotite and amphibole (Guidotti *et al.* 1977, Volfinger *et al.* 1985, Oberti *et al.* 1992, Makino *et al.* 1993, Robert *et al.* 1993, Hawthorne *et al.* 1998, Boukili *et al.* 2001, Henry & Guidotti 2002, Henry *et al.* 2005). Consequently, the proper interpretation of the texture and composition of tourmaline-supergroup minerals is dependent on the relative impact of the competing effectiveness of internal and external influences. In this paper, we will establish the general systematics of F contents in tourmaline-supergroup minerals and consider the relative importance of the crystallographic constraints within the petrological environment in which a tourmaline forms.

TOURMALINE: CRYSTALLOGRAPHIC BACKGROUND

The crystallography of tourmaline has a significant influence on the amount of F that can be incorporated in the structure. However, the nuances of the relevant crystallographic features that enhance or inhibit F incorporation warrant a review of the crystallographic background of tourmaline. A large part of this complexity relates to the wide range of substitutions leading to many possible tourmaline species (Table 1).

Tourmaline is a crystallographically acentric borosilicate mineral with the generalized structural formula $XY_3Z_6(T_6O_{18})(BO_3)_3V_3W$ (Hawthorne & Henry 1999). The structure is based on a six-membered ring of tetrahedra in which the tetrahedra are pointing in the same direction (Fig. 1). In turn, this leads to polar and asymmetric morphological, electrical and chemical properties in the crystal (Dietrich 1985, Henry & Dutrow 1996). The *T* site is primarily occupied by Si, possibly some Al and, less commonly, B. Interspersed in the structure are triangularly coordinated (BO_3) clusters in which B is the only occupant.

The nine-coordinated *X*-site cations (or vacancies) sit in the center of the six-membered ring of tetrahedra. This site generally contains Na^{1+}, K^{1+}, Ca^{2+} or is vacant ($^{X}\square$), *i.e.*, with local charges ranging from 0 to +2. The different substituents at the *X* site form a basis for the chemical groups of tourmaline, *i.e.*, alkali, calcic and *X*-site-vacant groups (Hawthorne & Henry 1999, Henry *et al.* 2009). Further, the type of cation (or vacancy) at the *X* site has previously been considered to have an important influence on the amount of F incorporated into the structure, such that only minor F is expected in a tourmaline that has dominant vacancy at the *X* site (Robert & Benoist 1993, Robert *et al.* 1997, Henry 2005).

The *Y* and *Z* sites are octahedrally coordinated and are occupied by a variety of cations with charges of +1, +2, +3 and +4. However, local bond-valence arrangements for the three *Y*-site cations most commonly have a cumulative local charge of +6 (*e.g.*, Mg_3) to +7 (*e.g.*, Mg_2Al) in tourmalines in which the *W*-site anions are predominantly occupied by OH^{1-} or F^{1-} (Hawthorne 2002). Nonetheless, local charges at the three *Y*-site cations as low as +5 (*e.g.*, Li_2Al) and as high as +9 (*e.g.*, Al_3) are known to occur in tourmaline (Table 1). Robert *et al.* (1997) proposed that the existence of higher combined charges at the *Y* site inhibits the incorporation of F in tourmaline. There are six *Z*-site cations in slightly distorted octahedra. This site is most commonly occupied by trivalent cations (Al^{3+}, Cr^{3+}, V^{3+} and Fe^{3+}), but can contain divalent species, most commonly Mg^{2+}, and possibly some Fe^{2+} (Bosi 2008). Order–disorder in tourmaline affects the actual location of cations and anions in the tourmaline structure (Hawthorne & Henry 1999). For example, Hawthorne (2002) showed that the occurrence of Mg at the *Z* site and Al at the *Y* site is due to disorder associated with the occurrence of O^{2-} at the *W* site and can be expressed as $2^{Y}Mg^{2+} + {}^{Z}Al^{3+} + {}^{W}(OH)^{1-} = 2^{Y}Al^{3+} + {}^{Z}Mg^{2+} + {}^{W}O^{2-}$.

TABLE 1. NOTEWORTHY TOURMALINE SPECIES

Species	(*X*)	(*Y*$_3$)	(*Z*$_6$)	*T*$_6$O$_{18}$	(BO$_3$)$_3$	(*V*)$_3$	(*W*)
			Alkali group				
Schorl	Na	Fe^{2+}_3	Al_6	Si_6O_{18}	$(BO_3)_3$	$(OH)_3$	(OH)
Fluor-schorl	Na	Fe^{2+}_3	Al_6	Si_6O_{18}	$(BO_3)_3$	$(OH)_3$	(F)
*"Oxy-schorl"**	Na	Fe^{2+}_2 Al	Al_6	Si_6O_{18}	$(BO_3)_3$	$(OH)_3$	(O)
Dravite	Na	Mg_3	Al_6	Si_6O_{18}	$(BO_3)_3$	$(OH)_3$	(OH)
Fluor-dravite	Na	Mg_3	Al_6	Si_6O_{18}	$(BO_3)_3$	$(OH)_3$	(F)
*"Oxy-dravite"**	Na	Mg_2 Al	Al_6	Si_6O_{18}	$(BO_3)_3$	$(OH)_3$	(O)
Chromium-dravite	Na	Mg_3	Cr_6	Si_6O_{18}	$(BO_3)_3$	$(OH)_3$	(OH)
Vanadium-dravite	Na	Mg_3	V_6	Si_6O_{18}	$(BO_3)_3$	$(OH)_3$	(OH)
Povondraite	Na	Fe^{3+}_3	Fe^{3+}_4 Mg_2	Si_6O_{18}	$(BO_3)_3$	$(OH)_3$	(OH)
Elbaite	Na	$Li_{1.5}$ $Al_{1.5}$	Al_6	Si_6O_{18}	$(BO_3)_3$	$(OH)_3$	(OH)
*"Fluor-elbaite"**	Na	$Li_{1.5}$ $Al_{1.5}$	Al_6	Si_6O_{18}	$(BO_3)_3$	$(OH)_3$	(F)
Fluor-buergerite**	Na	Fe^{3+}_3	Al_6	Si_6O_{18}	$(BO_3)_3$	$(O)_3$	(F)
Olenite**	Na	Al_3	Al_6	Si_6O_{18}	$(BO_3)_3$	$(O)_3$	(OH)
			Calcic group				
Uvite**	Ca	Mg_3	Al_5 Mg	Si_6O_{18}	$(BO_3)_3$	$(OH)_3$	(OH)
Fluor-uvite**	Ca	Mg_3	Al_5 Mg	Si_6O_{18}	$(BO_3)_3$	$(OH)_3$	(F)
Feruvite**	Ca	Fe^{2+}_3	Al_5 Mg	Si_6O_{18}	$(BO_3)_3$	$(OH)_3$	(OH)
*"Fluor-feruvite"**	Ca	Fe^{2+}_3	Al_5 Mg	Si_6O_{18}	$(BO_3)_3$	$(OH)_3$	(F)
Liddicoatite**	Ca	Li_2 Al	Al_6	Si_6O_{18}	$(BO_3)_3$	$(OH)_3$	(OH)
Fluor-liddicoatite**	Ca	Li_2 Al	Al_6	Si_6O_{18}	$(BO_3)_3$	$(OH)_3$	(F)
			X-site-vacant group				
Foitite	□***	Fe^{2+}_2 Al	Al_6	Si_6O_{18}	$(BO_3)_3$	$(OH)_3$	(OH)
Magnesio-foitite**	□	Mg_2 Al	Al_6	Si_6O_{18}	$(BO_3)_3$	$(OH)_3$	(OH)
Rossmanite	□	Li Al_2	Al_6	Si_6O_{18}	$(BO_3)_3$	$(OH)_3$	(OH)

* Hypothetical species of tourmaline identified by the Subcommittee on Tourmaline Nomenclature of the International Mineralogical Association's Commission on New Minerals, Nomenclature and Classification, but not currently approved by IMA (Henry *et al.* 2009). ** End-member formula modified from the initial formula (Hawthorne & Henry 1999). *** *X*-site vacancy.

The disorder increases the amount of Mg at the *Z* site and decreases the amount of Al at the *Y* site. This will effectively decrease the local charge at the *Z* site and increase the local charge at the *Y* site, and will potentially influence F incorporation.

There are four anion sites that have two distinctly different local environments. The three *V*-site anions are coordinated to two *Z*-site cations and one *Y*-site cation, typically with combined cation charges of +8 to +9. The *V* site [≡ O(3)] is most commonly occupied by OH^{1-}, and occasionally O^{2-}. There is a single *W*-site [≡ O(1)] anion that is coordinated to three *Y*-site cations with combined cation charges of +5 to +9, but most commonly +6 to +7. The *W*-site anions include OH^{1-}, O^{2-} and F^{1-}. Significantly, this is the only anion site that is known to accommodate F. In terms of classification of the tourmaline groups based on *W*-site occupancy, the dominant-valency rule, adopted by the International Mineralogical Association's Commission on New Minerals, Nomenclature and Classification, states that in a relevant site, the dominant ion of the dominant valence state at the site is considered for nomenclature (Hatert & Burke 2008). Consequently, the occupancy of the *W* site forms the basis for the secondary groups: hydroxy, fluor and oxy groups; these are defined as follows: hydroxy: $OH^{1-} + F^{1-} \geq O^{2-}$ and $OH^{1-} \geq F^{1-}$; fluor: $OH^{1-} + F^{1-} \geq O^{2-}$ and $F^{1-} \geq OH^{1-}$, and oxy: $O^{2-} > OH^{1-} + F^{1-}$ (Henry *et al.* 2009).

Spectroscopic studies of tourmaline reveal aspects of the local environment of the two distinct types of anion sites (*V* and *W* sites), each being influenced by the local configurations of cations that potentially can influence F incorporation (Gonzalez-Carreño *et al.* 1988). Because the *V* anions are bonded to cations that typically have +8 to +9 charge, the proton of an OH^{1-} typically shares its charge with neighboring atoms of oxygen in the tetrahedra. This scenario is considered to make the F^{1-}-for-OH^{1-} substitution unlikely at the *V* site (Robert *et al.* 1997). In the case of the *W* site, if OH^{1-} occurs at the site, the hydrogen bond extends toward the *X* site (Cámara *et al.* 2002). Occupancy of the *X* site by a cation (+1 or +2) causes repulsion of the H away from the *X* site. Robert *et al.* (1997) proposed that the charge environment of the O(1) site is more similar to a symmetrical point-charge; as a result, F is much more likely to substitute for OH. Higher charge at the *Y* site produces a higher incident bond-valence charge at the O(1) site, and this promotes stronger hydrogen bonding

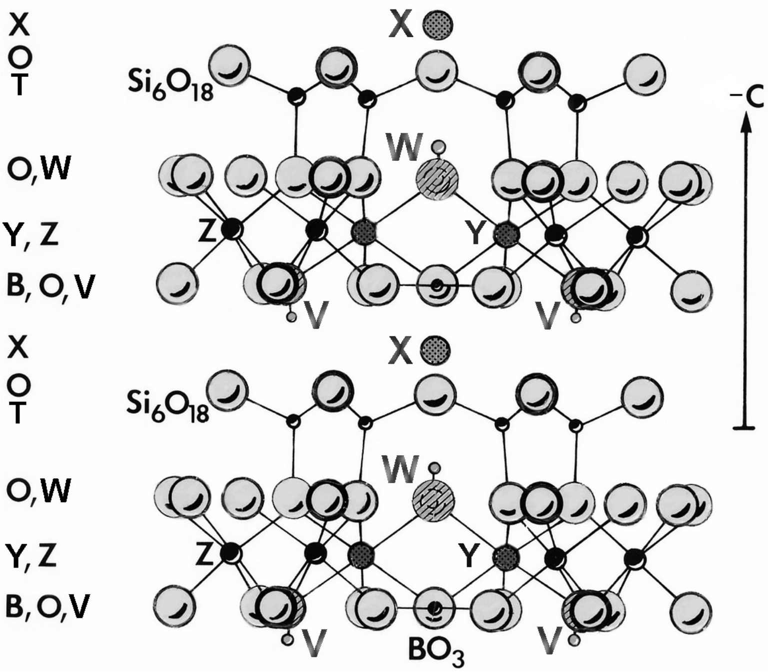

FIG. 1. Generalized structure of tourmaline showing the relations among the *X*, *Y*, and *W* sites. Of particular note is the bonded H in the *W* site, shown as being oriented toward the *X* site.

between the proton and the bridging anions of the tetrahedra which, in turn, inhibits substitution of F^{1-} for OH^{1-}. Consequently, there will be a potential interaction among the *X*, *Y* and *W* sites depending on the charge and size of the cations and anions occupying the sites.

THE TOURMALINE DATASET

To examine the range of F content as a function of different chemical, structural and petrological parameters in tourmaline and the predicted crystallographic constraints, an extensive dataset (>8800 entries) from a variety of rock types was culled from the literature and from unpublished sources, and screened using a series of analytical total and structural formula criteria to provide high-quality analytical data for examination of tourmaline systematics. In addition, a subset of the data also includes results of structure refinements, such that the influence of the actual site-occupancy due to disorder can be addressed.

Data sources for tourmaline from different generalized rock-types are listed in Table 2 under the following headings: (1) Li-rich pegmatites, granitic rocks and surrounding host rocks, (2) Li-poor pegmatites, granitic rocks and surrounding host-rocks, (3) metapelitic schists and gneisses, (4) mafic eclogites, mafic granulites, amphibolites and blackwalls, (5) tourmalinites, quartz–tourmaline veins and greisens, (6) calcareous metasediments and magnesite rocks, (7) metamorphosed sandstones and conglomerates, (8) metamorphosed ultramafic rocks, (9) metamorphosed evaporitic rocks, (10) metamorphosed ironstones, (11) hydrothermal vents and veins, (12) anorthosites, and (13) undetermined or multiple sources.

Normalization and quality control of tourmaline data

The manner in which these tourmaline data are normalized can have a significant effect on the accuracy of the structural formula calculated for tourmaline. For tourmalines with complete analytical data, those data are normalized on the basis of 31 anions. However, most tourmaline analyses are done with the electron microprobe, and do not include Li, B, H or the oxidation state of Fe. As such, they require special consideration for normalization procedures. For tourmaline from petrological environments in which Li is likely to be present (*e.g.*, highly fractionated pegmatites), tourmaline compositions are normalized on the basis of 31 atoms of oxygen with Li being estimated by iteration as 3 minus the sum of the *Y*-site cations (Burns *et al.* 1994, Henry & Dutrow 1996). For tourmaline from

TABLE 2. SOURCES OF DATA FOR TOURMALINE, ACCORDING TO ROCK TYPE

1) **Li-rich pegmatites, granitic rocks and adjacent host-rocks**

Bowman (1902), Slivko (1955), Rath & Puchelt (1957), El-Hinnawi & Hofmann (1966), Donnay & Barton (1972), Chaudhry & Howie (1976), Dunn *et al.* (1978), Foord & Mills (1978), Sahama *et al.* (1979), Povondra *et al.* (1985), Jolliff *et al.* (1986), Bloomfield (1997), Deer *et al.* (1997), Lyckberg & Hawthorne (1997), Ahn & Buseck (1998), Federico *et al.* (1998), Aurisicchio *et al.* (1999a, 1999b), Dyar *et al.* (1999), Keller *et al.* (1999), Morgan & London (1999), Teertstra *et al.* (1999), Dutrow & Henry (2000), Akizuki *et al.* (2001), Ertl *et al.* (2003a), Tindle *et al.* (2003, 2005, 2006, 2008), Bosi *et al.* (2005a, 2005b), Breaks *et al.* (2008), Soares *et al.* (2008), Ertl *et al.* (2010a, 2010c)

2) **Li-poor pegmatites, granitic rocks, and adjacent host-rocks**

Otroshchenko *et al.* (1971), Neiva (1974), Povondra (1981), Pieczka & Kraczka (1988), Kretz *et al.* (1989), Němec (1989), Sinclair & Richardson (1992), Grew *et al.* (1995), Povondra & Vrána (1996), Deer *et al.* (1997), Novák (1998), Povondra *et al.* (1998), Novák & Taylor (2000), Ertl *et al.* (2003b), Zhang *et al.* (2004), Marschall & Ludwig (2006), Trumbull *et al.* (2008), Novák *et al.* (2011)

3) **Metapelitic schists**

Bridge *et al.* (1977), Foit & Rosenberg (1979), Henry (1981), Povondra (1981), Henry & Guidotti (1985), Grew (1986), Grew *et al.* (1990, 1991b), Henry & Dutrow (1992), Jiang *et al.* (1995), Visser (1995), Povondra & Vrána (1996), Losos & Selway (1998), Novák *et al.* (1998), Dyar *et al.* (1999), Groat *et al.* (2002), Marschall *et al.* (2008), Trumbull *et al.* (2008, 2009), D.J. Henry, unpubl. data

4) **Eclogites, mafic granulites, amphibolites and blackwalls**

Morgan & London (1987), Henry & Dutrow (1990), Marschall *et al.* (2006), Bosi *et al.* (2010)

5) **Tourmalinites, quartz–tourmaline veins and greisens**

Abraham *et al.* (1972), Willner (1992), London & Manning (1995), Laurs *et al.* (1996), Houzar *et al.* (1998), Béziat *et al.* (1999), Francis *et al.* (1999), Pesquera *et al.* (1999), Henry *et al.* (2002), Yu & Jiang (2003), Henry & de Brodtkorb (2009)

6) **Calcareous metasediments and magnesite rocks**

Donnay *et al.* (1967), Otroshchenko *et al.* (1971), Dunn (1977a, 1977b), Sahama *et al.* (1979), Schmetzer *et al.* (1979), Povondra & Novák (1986), Cotkin (1989), Grew *et al.* (1991a), Deer *et al.* (1997), Modreski *et al.* (1997), Henry & Dutrow (2001), Pertlik *et al.* (2003), Ertl *et al.* (2010a)

7) **Metamorphosed sandstones and conglomerates**

Henry *et al.* (1994), Van den Bleeken *et al.* (2007)

8) **Metamorphosed ultramafic rocks**

Peltola *et al.* (1968), Dunn (1977b), Challis *et al.* (1995)

9) **Metamorphosed evaporitic rocks**

Jiang *et al.* (1997), Henry *et al.* (2008)

10) **Metamorphosed ironstones**

Cleland *et al.* (1996), D.J. Henry, unpubl. data

11) **Hydrothermal vents and veins**

Moore *et al.* (2004), Mlynarczyk & Williams-Jones (2006)

12) **Anorthosites**

Hietanen (1987)

13) **Undetermined or multiple sources**

Frondel *et al.* (1966), Mattson & Rossman (1984), MacDonald *et al.* (1993), Deer *et al.* (1997), Dyar *et al.* (1998), Lussier *et al.* (2009), Ertl *et al.* (2010b) petrological environments in which Li is likely to be relatively low, tourmalines are normalized on the basis of 15 $Y + Z + T$ cations (Henry & Dutrow 1996, 2001, Clark 2007)

A series of compositional criteria were used to screen the data to identify the better-quality tourmaline data for further consideration. For those samples for which a complete chemical analysis has been made (or can be calculated), the dataset is considered unacceptable if the sum of the oxides is outside the range 98.3–101.7%. In all samples in which the optimal procedure of normalization is used, several additional criteria are used eliminate questionable datasets. A tourmaline composition is not accepted if any of the following characteristics are exhibited: (1) Si > 6.15 atoms per formula unit (*apfu*), (2) B < 2.85 *apfu*, (3) the sum of the $Y + Z + T$ cations >15.5 *apfu*, (4) the sum of the *X*-site cations exceeds 1.1 *apfu*, or (5) the sum of OH + F at the *W* and *V* sites is greater than 4.2 *apfu*. Those analytical datasets that met these criteria are included here.

RESULTS

The cumulative dataset

The cumulative data on tourmaline from these diverse petrological environments can be examined in terms of the F content in *apfu* relative to the occupancy of the *X* site to investigate the presence of any overarching trends. The Na–F diagram shows a high concentration of tourmaline with chemical compositions between 0.5 and 0.8 *apfu* Na (Fig. 2a). However, that data cluster reflects the Na-dominant nature of most of the tourmaline in the overall dataset. More significantly, there is a full range of F at the *W* site (0–1 *apfu*). Likewise, the Ca–F diagram shows a complete range of Ca contents (0–1 *apfu*), with a full range of F (0–1 *apfu*) at the *W* site (Fig. 2b). In contrast, as the number of vacancies at the *X* site increases, the maximal amount of F decreases to <0.15 F *apfu* at a proportion of *X*-site vacancies greater than 0.6 *pfu* (Fig. 2c). Because this dataset is derived from a wide variety of

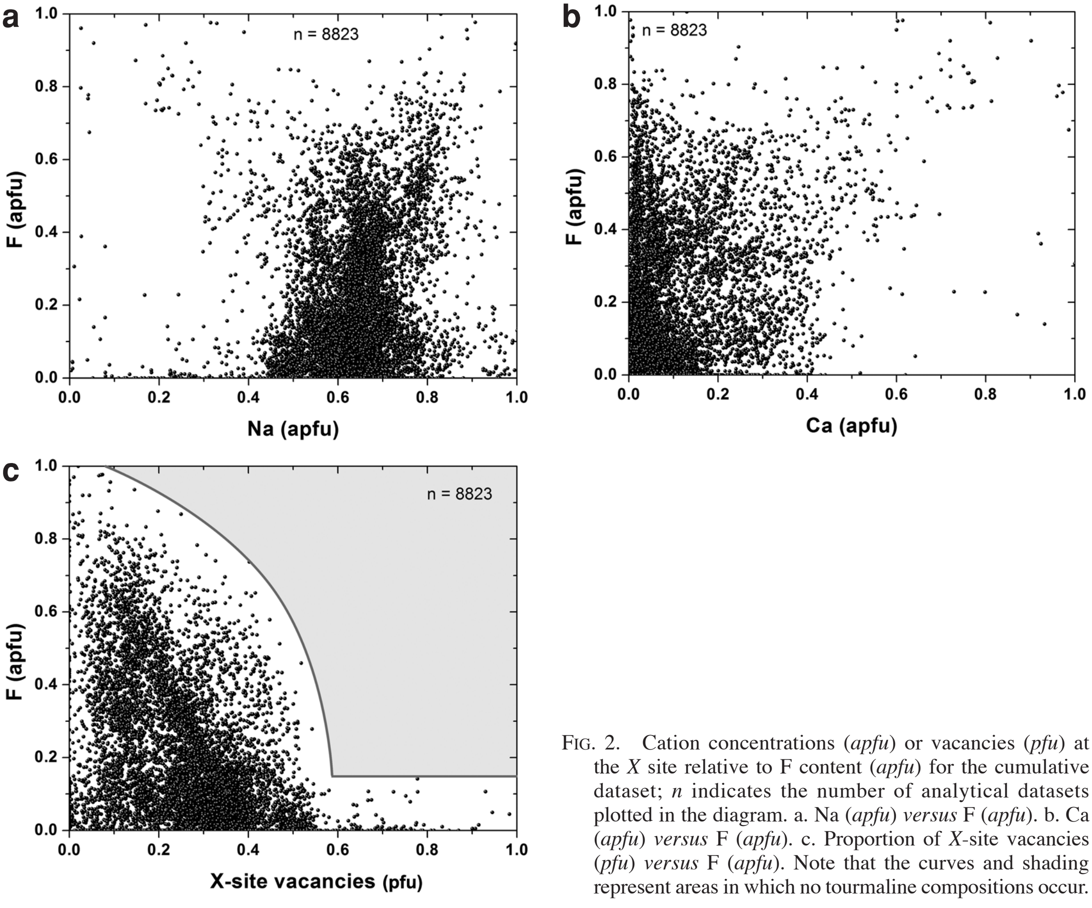

FIG. 2. Cation concentrations (*apfu*) or vacancies (*pfu*) at the *X* site relative to F content (*apfu*) for the cumulative dataset; *n* indicates the number of analytical datasets plotted in the diagram. a. Na (*apfu*) *versus* F (*apfu*). b. Ca (*apfu*) *versus* F (*apfu*). c. Proportion of *X*-site vacancies (*pfu*) *versus* F (*apfu*). Note that the curves and shading represent areas in which no tourmaline compositions occur.

petrological environments, it is likely that the drastic diminution of maximal F with *X*-site vacancy represents a fundamental crystallographic influence consistent with conjectures of earlier spectroscopic studies (Robert *et al.* 1997). Nonetheless, within the Na- and Ca-rich regions, there is a complete spectrum of F content (0–1 *apfu*), indicating that local petrological environment must also have a fundamental influence on the extent of F incorporation.

The total charge at the *X* site may be a better measure of the influence of the *X* site on the incorporation of F at the *W* site (Fig. 3). For tourmalines that have an average *X*-site charge of greater than +0.9, there is a complete range of 0 to 1 *apfu* F. However, at lower *X*-site charge, the maximal F content decreases markedly, falling below 0.15 *apfu* F for tourmalines with *X*-site charge below +0.5. This upper limit presumably reflects a crystallochemical limitation. Comparable to the *X*-site vacancy – F data (Fig. 2c), there is a significant dispersion of data for those tourmalines with higher *X*-site charge such that it likely reflects the influence of local petrological environment.

The other potential contribution to the charge environment around the *W* site is related to the charge at the *Y* site. Because of the uncertainty related to the disorder of the divalent and trivalent cations at the *Y* and *Z* sites, data were used strictly from those studies in which structural formulae were determined by optimizing the crystallographic constraints established by structural refinements of the tourmaline (MacDonald *et al.* 1993, Ertl *et al.* 2003a, 2003b, Pertlik *et al.* 2003, Bosi *et al.* 2005a, 2005b, Bosi & Lucchesi 2007, Ertl *et al.* 2008, Lussier *et al.* 2009, Bosi *et al.* 2010, Ertl *et al.* 2010a, 2010b). A plot of *Y*-site charge *versus* F content shows that there is quite a bit of dispersion of the data, but there is a general maximal threshold F content, which decreases as the *Y*-site charge increases from +6.5 to +8.3 (Fig. 4). This finding is generally consistent with the speculations of Robert *et al.* (1997). The scattered data below the maximal curve likely reflects the petrological environment. The exceptional data above the maximal curve pertain to the more unusual tourmalines fluor-buergerite and Cr-rich tourmalines, which exhibit atypical structural characteristics (Bosi & Lucchesi 2007).

These cumulative data can also be examined in terms of the potential existence of the disparate fluor-tourmaline species (see Table 1). Tourmaline can be classified into groups based on the dominant occupancy at the *X* site (Henry *et al.* 2009). Tourmalines have been described that contain dominant Na^{1+}, Ca^{2+}, $^{X}\square$ and, rarely, K^{1+}. However, because of the rare occurrence of K-rich tourmalines, it is practical to combine the cations with like charge, Na^{1+} and K^{1+}, as an alkali group. This results in primary groups that are termed the alkali, calcic and *X*-site-vacant groups. Within the restriction of the dominant-valency rule (see above), the dominant anion of the dominant valency at the *W* site defines secondary tourmaline groups: hydroxy, fluor and oxy groups (Henry *et al.* 2009). A histogram of F contents in alkali-group tourmalines in this dataset shows that even though more of the tourmaline samples have a relatively low F content, there are a significant number of tourmalines that have dominant F at the *W* site (Fig. 5a). Examination of the datasets, especially those of Tindle *et al.* (2002, 2003, 2006, 2008) and Breaks *et al.* (2008), reveals the existence of the

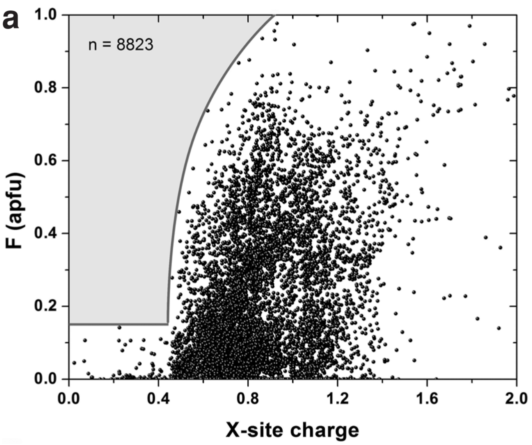

FIG. 3. Average *X*-site charge relative to F content (*apfu*) for the cumulative dataset. The curves and shading represent areas in which no tourmaline compositions occur.

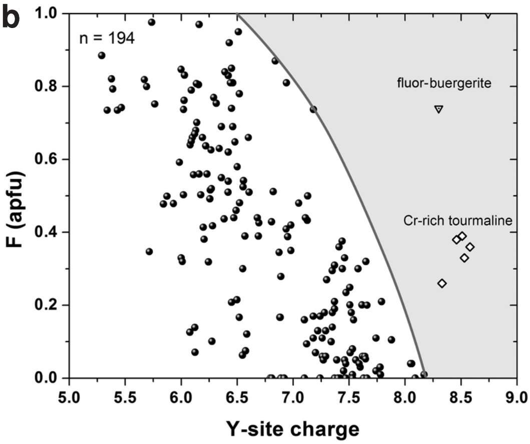

FIG. 4. Average *Y*-site charge relative to the F content (*apfu*) for the dataset in which the structural formulae were optimized based on structural refinement constraints. The curves and shading represent areas in which only the unusual tourmalines fluor-buergerite and Cr-rich tourmaline plot.

F-dominant alkali-group tourmalines: fluor-dravite, fluor-schorl, “fluor-elbaite” and fluor-buergerite (Table 1). A histogram of the calcic-group tourmalines exhibit an F distribution that is slightly skewed toward higher F content (Fig. 5b). The dataset confirms the existence of all of the fluor- and hydroxy-dominant calcic tourmaline species listed in Table 1. A histogram of the F contents in *X*-site vacant tourmaline shows that there are typically minor amounts of F, mostly <0.01 *apfu*, with a few reaching above 0.2 *apfu* F (Fig. 5c). There is no F-dominant *X*-site-vacant tourmaline species in this dataset, but owing to extended possibilities of F-dominance in accordance with the dominant-valency rule, such species may be forthcoming.

DISCUSSION

Within the context of the crystallographic thresholds for F incorporation in tourmaline, specific petrological environments have a fundamental control on the actual F content attained in tourmaline. Subsets of the cumulative dataset that are derived from distinct petrological settings illustrate this aspect.

Evolution of F content in fractionating granitic pegmatites

The subset of tourmaline data from the McCombe granitic pegmatite provides evidence of magmatic fractionation trends as they relate to F incorporation in tourmaline (Tindle *et al.* 2003, 2005). The McCombe pegmatite is a complex type and spodumene subtype member of the LCT family pegmatites exposed along the Uchi – English River subprovincial boundary-zone, Ontario, in the Superior Province of the Canadian Shield. The pegmatite dike cuts mafic metavolcanic country-rocks. The compositional signatures in tourmaline developed in the wallrocks of the dikes are interpreted as being formed at the expense the wallrocks. However, primary magmatic tourmaline developed in the late-fractionating granitic magmas is associated with the spodumene, lepidolite and aplite zones. The tourmaline species evolve progressively from foitite to schorl to elbaite to “fluor-elbaite” to fluor-liddicoatite (Fig. 6a). The trend of increasing F as a function of increasing *X*-site charge or decreasing *X*-site vacancy roughly follows a slope of +1 and –1, respectively

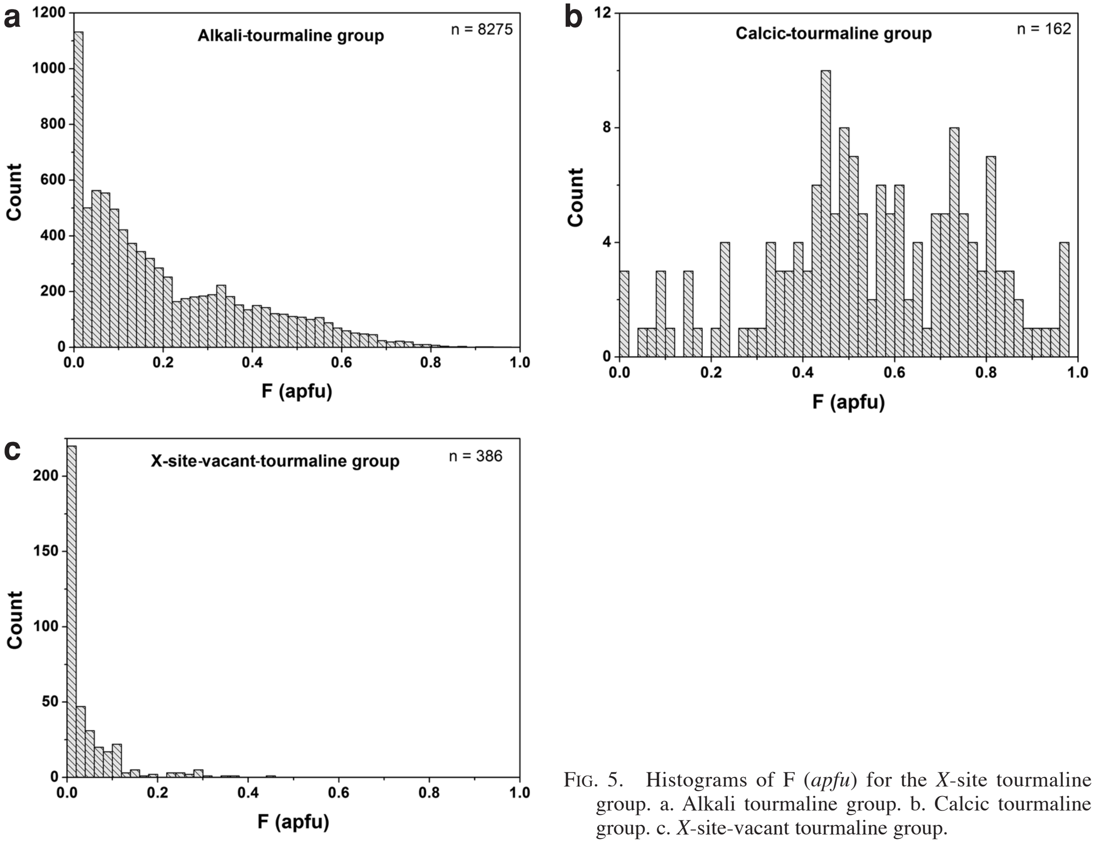

FIG. 5. Histograms of F (*apfu*) for the *X*-site tourmaline group. a. Alkali tourmaline group. b. Calcic tourmaline group. c. *X*-site-vacant tourmaline group.

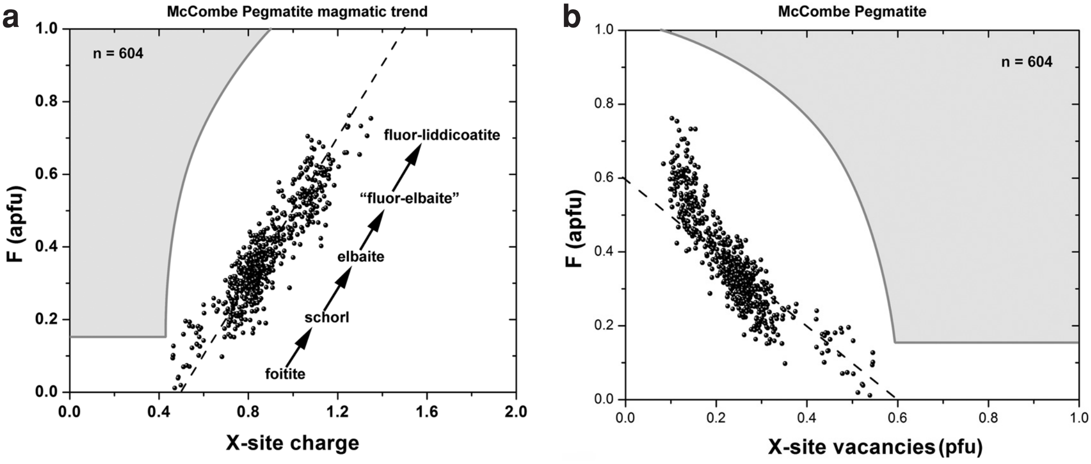

FIG. 6. Fluorine content relationships of tourmaline in the McCombe pegmatite, reflecting magmatic fractionation zones. The gray field represents the region in which no tourmaline compositions have been found in the cumulative dataset (Figs. 2c, 3) a. *X*-site charge *versus* F (*apfu*). The tourmaline species progressively change to more Li-enriched and F-enriched species upon fractionation. The dashed line is a reference line with a slope of +1. b. *X*-site vacancy *versus* F (*apfu*). The dashed line is a reference line with a slope of –1.

(Figs. 6a, b). The general compositional progression of the magmatic tourmaline is generally characterized by coequal participation of the substitutions: $^{X}\square$ + Fe^{2+} = Na + Li and $\mathrm{OH}^{1-} = \mathrm{F}^{1-}$. These data fall well within the boundaries of the compositional range of tourmaline, and the chemical variation is likely related to environmental influences rather than crystallographic constraints. The pegmatite-forming melt is interpreted as having undergone fractionation accompanied by increased activity of F and Li (Tindle *et al.* 2005). The buildup of Ca in the pegmatite in the late-formed zones is considered to reflect contamination *via* a fluid phase.

Evolution of F content in a fractionating fluid in a pocket in a granitic pegmatite

A similar petrological environment, but one that involves the development of fibrous tourmaline on coarse elbaite, is found in a pegmatite pocket at the Cruzeiro mine, Brazil. The pegmatite contains Li-rich minerals and shows evidence for pocket rupture, followed by additional stages of fractionating, reactive fluids. The response is that silver-gray tourmaline fibers partially replace pink elbaite in pegmatite pockets (Dutrow & Henry 2000). The pegmatite contains quartz, albite, muscovite, tourmaline, beryl, garnet, columbite–tantalite, spodumene, lepidolite and amblygonite. Textures indicate that an interaction with reactive fluids caused the development of the tourmaline fibers (0.05-0.3 mm). Three distinct generations of tourmaline replacement developed within individual tourmaline fibers, each generation of tourmaline being partially dissolved and replaced by the subsequent generation. Generation-1 tourmaline, preserved as dark blue anhedral enclaves in the fiber interior, consists of foitite that typically has <0.01 *apfu* F (Fig. 7a). Generation-2 tourmaline is blue-gray, partially replaces Generation-1 tourmaline, and becomes progressively more Na- and F-enriched, having compositions that range from schorl to elbaite. Generation-3 tourmaline is yellow-green, partially replaces the previous two generations of tourmaline, and has a composition of "fluor-elbaite". Similar to the tourmaline in the fractionating McCombe pegmatite, the general compositional progression of the Cruzeiro fibers is characterized by the substitutions: $^{X}\square$ + Fe^{2+} = Na + Li and $\mathrm{OH}^{1-} = \mathrm{F}^{1-}$. The difference between the two systems is that the fibers must develop in a fluid-dominant environment in the pegmatite pocket, and there are oscillations between tourmaline stabilization and destabilization overprinted by chemical fractionation. The increasing trend in F content is most likely related to tourmaline growth in an environment of increased F activity in the fractionating fluids.

Fluorine-enriched petrological environments, with fluorine-dominant minerals

If tourmaline is responsive to the local petrological environment, it should contain maximal amounts of F if it is in equilibrium with a high-F mineral with fixed proportion of F. This mineral should hold the F contents of coexisting F-bearing minerals at maximal levels for the local environmental conditions. Topaz and fluorapatite typically are F-rich minerals, but do not necessarily indicate maximal contents of F owing to the possibility of incorporation of OH^{1-} for F^{1-} in their

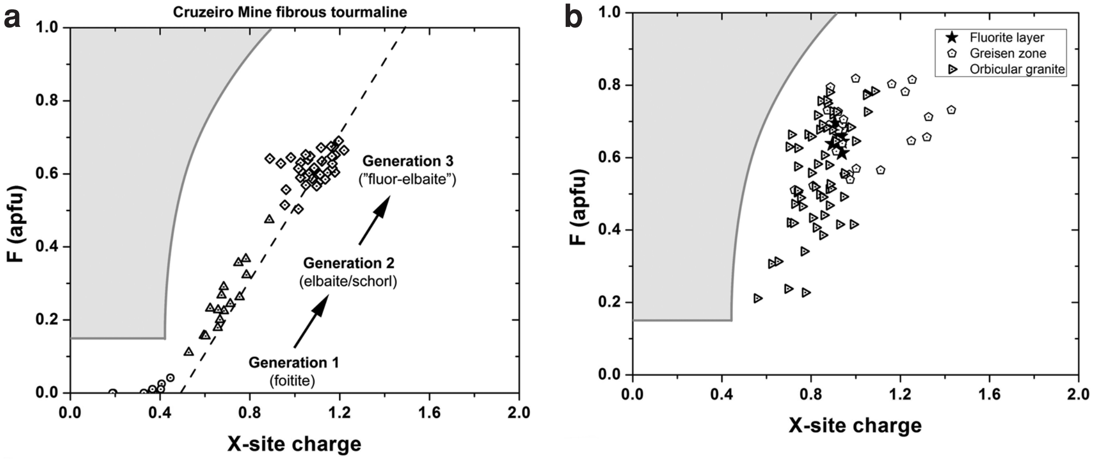

FIG. 7. The *X*-site charge *versus* F content (*apfu*) in disparate petrological environments. The gray field represents the region in which no tourmaline compositions have been found in the cumulative dataset (Fig. 3). a. Tourmaline data for the progressive evolution of tourmaline fibers developed in a pegmatite of the Cruzeiro mine, Brazil. The dashed line is a reference line with a slope of +1, and it is in the same location as the reference line shown for tourmaline from the McCombe pegmatite (Fig. 6b). The progressive change in tourmaline composition associated with the three generations is punctuated by tourmaline destabilization and partial replacement by subsequent generations of tourmaline. b. Tourmaline data from three diverse fluorite-bearing localities: fluorite-rich layer in an orthogneiss (Novák *et al.* 1998), greisen-style metasomatic pegmatite and host-rock amphibolite (Laurs *et al.* 1996), and orbicular granite (Trumbull *et al.* 2008).

structures. However, fluorite is an appropriate mineral with a fixed high level of fluorine. Consequently, it is useful to examine representative compositions of tourmaline in petrological environments containing fluorite.

Tourmalines found in fluorite-bearing assemblages from three distinct petrological environments generally exhibit maximal or near-maximal F-content within the crystallochemical boundaries of tourmaline (Fig. 7b). Novák *et al.* (1998) documented tourmaline from a metamorphosed fluorite-rich layer in a leucocratic orthogneiss from Nedvědice, western Moravia, Czech Republic. These tourmaline compositions generally fall in the ranges of fluor-schorl to fluor-dravite. Laurs *et al.* (1996) included information on tourmaline related to emerald mineralization and greisen-style metasomatism of an amphibolite at the Khaltaro granitic pegmatite, Haramosh Mountains, northern Pakistan. Tourmaline associated with fluorite is found in metasomatically altered pegmatite and host-rock amphibolite; the compositions found are fluor-dravite to fluor-schorl. Trumbull *et al.* (2008) described tourmaline from orbicular granites from the Erongo granite in the Damara Belt, Namibia. The tourmaline-rich orbicules are interpreted as having been formed late in the crystallization history from an immiscible Na–B–F-rich hydrous melt. The tourmaline in the fluorite-bearing rocks is generally fluor-schorl. Significantly, the tourmalines associated with fluorite in these petrological environments generally outline the boundary of the F range defined by the cumulative dataset, implying that crystallochemical constraints limit these tourmaline compositions as well. Those tourmalines that deviate from the maximal F content likely lack local equilibrium with fluorite.

CONCLUSIONS

The extensive compositional dataset obtained to describe tourmaline from a wide variety of rocks demonstrate several significant features.

(1) There are limits to the amounts of F that can be incorporated into tourmaline at the *W* site, and this is strongly associated with the occupancy and charge at the *X* site. For an average *X*-site charge exceeding +0.9, there is a range from 0 to a maximum of 1.0 *apfu* F. As the *X*-site charge decreases, the amount of F decreases, with the maximal amounts of F being <0.2 *apfu* for those tourmalines with an *X*-site charge less than +0.5.

(2) There is a threshold level of F that is dictated by the average charge of the *Y*-site cations such that the higher the local charge at the *Y* sites, the lower the F in the tourmaline.

(3) Our survey of tourmaline compositions shows that within this dataset, fluor species are relatively common in the alkali-group and calcic-group tourmalines, but have not been found in the *X*-site-vacant tourmalines.

(4) Within the limitations of crystallographic constraints, petrological factors superimpose local envi-

ronmental influences on F concentrations. Features such as fractionating magmas and fluids or the presence of a F-rich phase like fluorite control the amount of F that is available to and can be incorporated in tourmaline. In turn, the variable amounts of F in tourmaline are useful indicators of local chemical environmental conditions and can help to constrain these conditions.

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