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Revision 1

Petrogenetic controls on the origin of tourmalinite veins from Mandrolisai igneous massif (central Sardinia, Italy): insights from tourmaline crystal chemistry

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Abstract

An inclusive study of tourmaline, a well-known petrogenetic indicator, allowed the reconstruction of late-stage evolution of B-bearing Variscan granodioritic magmas in Sardinia batholith (Italy). Tourmaline samples from Mandrolisai igneous massif were chemically and...
structurally investigated by electron microprobe analysis, single-crystal X-ray diffraction, Mössbauer, infrared and optical absorption spectroscopy.

Tourmaline aggregates occur both as large crystals displaying graphic textures with quartz, in aplite layers and pegmatite dykes within tonalitic granodiorite, and as fine-grained assemblages, in tourmalinite veins crystallized along fractures within metamorphic country rocks. Tourmaline was identified as schorl in pegmatites and as dravite in veins, both with relevant foitite and magnesiofoitite components. Petrological and mineralogical constraints based on mineral oxythermomobarometry and tourmaline crystal chemistry converged towards crystallization temperatures in the range 650-400 °C at about 2.2 kbar, under NNO conditions that remained almost unvaried during the whole magma crystallization path. In the reconstructed scenario, Mandrolisai tourmaline recorded the late stages of consolidation of a single granodioritic magma batch, whose crystallization path locally led to residual concentration of B in the melt. Due to melt/hydrous fluid immiscibility processes, B enrichment promoted the crystallization of the large tourmaline + quartz assemblages in pegmatites. Late B-bearing fluids triggered metasomatic reactions and favored the precipitation of fine-grained tourmaline in tourmalinite veins under a brittle solid-state regime, which overprinted a fracture network of the country rocks previously formed under magmatic flow conditions.

Mandrolisai granodiorites are metaluminous (ASI = 0.93-0.95), that is far from the compositional characters of typical B-bearing magmas, mostly felsic and markedly peraluminous (ASI > 1.2). The uncommon occurrence of tourmaline-bearing rocks in Mandrolisai may be an evidence of the limited control exerted by Al₂O₃ saturation on the origin of tourmaline. Conversely, a more important role of B contents, likely coming from crustal sources, may be invoked for tourmaline saturation in the magma.

1. Introduction
Tourmaline is very stable over a wide range of $P$-$T$ conditions and in recent years has recorded an increasing interest as petrogenetic indicator. It occurs in a wide range of crustal rocks and is able to constrain physical-chemical conditions as temperature, composition and oxidation state of metamorphic fluids (van Hinsberg and Schumacher, 2011; van Hinsberg et al., 2011a,b, 2017; Berryman et al., 2017; Dutrow and Henry 2018). In magmatic rocks, tourmaline is found mainly in peraluminous granites, occurring in a full range of crystallization conditions, from near-liquidus to pegmatitic-related phases, where it commonly shows intergrowths with quartz (London et al., 1996; Pesquera et al., 2013). In magmatic systems, tourmaline saturation mainly depends on B saturation of melts (London et al., 1996), $\text{Al}_2\text{O}_3$ Saturation Index (ASI, Wolf and London, 1997), Fe/Mg ratio of magmas (Bernard et al., 1985), $\text{H}_2\text{O}$ contents (Acosta-Vigil et al., 2003) as well as oxygen fugacity (Scaillet et al., 1995; Dutrow and Henry, 2000). Partial melting processes of B-bearing protoliths have been invoked to promote the B saturation of anatectic melts (Pesquera et al., 2013). Several magmatic to post-magmatic hydrothermal options are available to explain the tourmaline crystallization as follows: (1) Primary magmatic origin mainly based on observed quartz/tourmaline graphic intergrowths in granitic pegmatites (London et al., 1996; Grew et al., 2008; Wadoski et al., 2011); (2) Origin by fluids/boron-silicate melts immiscibility processes, on account of melt inclusions as well as field observations: i.e. tourmaline aggregates at the cores of pegmatitic bodies, or as miaroles and orbicules in granites (Trumbull et al., 2008; Drivenes et al., 2015, Hulsbosch et al., 2017, 2018); (3) Origin by hydrous and B-rich fluids exsolved from granitic melts (Sinclair and Richardson, 1992; Trumbull et al., 2008; Hong et al., 2017); (4) Metasomatic replacement by B-rich late- to post-magmatic hydrothermal fluids migrating along grain boundaries and microfractures to explain the growth and distribution of tourmaline nodules in granites (Rozendaal and Bruwer, 1996); (5) Origin by cooling of B-rich late- to post-magmatic hydrothermal fluids in fractures, to form tourmaline-rich or, less frequently, tourmalinite veins found close to the intrusions (Trumbull and Chaussidon, 1999; Slack and Trumbull, 2011; Xydous et al., 2016).
Tourmaline-bearing rocks typically derive from B-rich magmas, which are mostly felsic and markedly peraluminous (ASI > 1.2, London et al., 1996; Wolf and London, 1997). In the Late-Variscan magmatism of Sardinia, tourmaline is documented not only in peraluminous (ASI > 1) but also in metaluminous (ASI < 1) intrusions, mainly occurring in pegmatites within granodiorites and granites belonging to the old magmatic peak (OMP sensu Conte et al., 2017). Detailed information is only available for the weakly peraluminous Arbus igneous complex (southwestern Sardinia) in which tourmaline crystallization has been related to late-stage evolution of cordierite-bearing granitic melts at shallow crustal levels (Bosi et al., 2018). An example of tourmaline-bearing rocks related to metaluminous granodioritic magmas is offered by the Mandrolisai igneous massif (central Sardinia). In Mandrolisai igneous massif tourmaline occurs both in pegmatites within granodiorites and in thin tourmalinite veins at the contact with metamorphic basement (Fig. 1). Notably, the tourmaline-enriched rocks found in the Mandrolisai igneous massif represent the unique occurrence with tourmalinite veins reported in the Sardinia batholith so far (Zucchetti 1965; Matteucci and Zucchetti, 1965). No detailed information is currently available to relate those tourmalines to their hosting migmatic rocks.

In the present study, tourmaline samples from the Mandrolisai igneous massif and metamorphic country rocks were chemically and structurally investigated to be tentatively related to the evolution of magma pulse and post-collisional Variscan tectonics. Obtained results suggested a late-stage magmatic evolution, with crystallization temperatures below 700 °C at shallow conditions during the cooling of the pluton.

2. Geological setting and tourmaline occurrence

2.1. Regional setting of Mandrolisai region

The Mandrolisai region is schematically made up by tectonic units belonging to the inner (Gennargentu Unit) and outer (Meana Sardo Units, Castello Medusa and Grighini Units) nappe
zones of the Variscan basement of Sardinia (Carmignani et al., 2015). These units are intruded by the granitoids of the Mandrolisai igneous massif, which locally are unconformably covered by Permian undeformed rhyolitic volcanics (Fig. 1). The Mandrolisai igneous massif is an OMP-related, monophasic, E-W ellipsoidal body of about 100 km², emplaced along extensional-trastensional faults including thrusts reactivated as low angle normal shears, at about 300 Ma, according to U/Pb data obtained on zircons from a nearby granodiorite intrusion emplaced at the same structural level (299 ±3 Ma; Meloni et al., 2017). The pluton is almost entirely composed of biotite amphibole granodiorites, intruded northwestward by leucogranitic magmas. Remarkably, along the western contacts with the low-grade metamorphics, granodiorite grades to tonalitic granodiorite enriched in tonalitic dark enclaves, with local and discontinuous sub-vertical veins and pods of tourmaline-bearing pegmatites. In this sector, the irregular contacts with basement are marked by low-angle injections of foliated biotite granodiorite into the metamorphics. As generally recognized in OMP-related plutons of Sardinia (Casini et al., 2015; Cuccuru et al., 2016), the geometry of the Mandrolisai igneous massif resembles a laccolithic body, as documented by general contact field relationships and by flat magmatic foliation evidenced by dark enclaves.

2.2. Petrographic features

The only whole-rock chemical data for the Mandrolisai granodiorites available in literature are from Negretti (1966). They plot at the boundary between magnesian and ferroan rock-series and in the calc-alkalic field in the Frost and Frost (2008) classification diagrams (Fig. 2a,b). In general, Mandrolisai granodiorites show a metaluminous character with a homogeneous ASI index in the range of 0.93-0.95.

The main petrographic characters of granodiorites belonging to Mandrolisai igneous massif are reported in Table 1. Hypidiomorphic granular textures are by far dominant; porphyritic varieties are locally observed at the top of the intrusion. Textural evidences indicate the early appearance of a well-developed (up to 1cm), twinned and zoned calcic amphibole coupled with oscillatory zoned
plagioclase, followed by dark mica, K-feldspar and quartz. Amphibole composition, reported in Table S1 of the Supplementary material, may be referred to magnesio-ferric-hornblende (Hawthorne et al., 2012). The Fe# [Fe/(Fe+Mg)] is in the restricted range of 0.43-0.52, while Ti contents display an appreciable variability decreasing from 0.17 (core) to 0.04 (rim) atoms per formula unit (apfu). Plagioclase shows an average andesinic composition, displaying a slight reverse zoning from An$_{41}$ to An$_{48}$. Dark mica composition, reported in Table S2, falls in the field of the biotite series (annite-phlogopite; Rieder et al., 1998).

Among accessories phases, magnetite, zircon and apatite are ubiquitous; in particular, apatite commonly appears as inclusion in quartz. Large allanite grains (up to 5 mm), ilmenite and sulfides occur as minor accessories. Late-stage mineral phases consist of small euhedral amphibole grains associated with dark mica and small prismatic rutile grains forming discontinuous rims around dark mica. In addition, quartz mortar textures are commonly observed in tonalitic granodiorites and increase in foliated facies at the contacts with the metamorphic basement.

2.3. Tourmaline occurrence

Tourmaline occurrence is mainly documented in the western part of the Mandrolisai pluton, close to the intrusive/metamorphic contacts (Fig. 1). Unfortunately, the widespread occurrence of volcanic and sedimentary cover of different ages does not allow detailed geological observations and precise reconstructions. Type tourmaline occurrence may be outlined as follows: (a) fine-grained tourmaline bands, in tourmalinite thin veins, firstly recognized by Zucchetti (1965) and Matteucci and Zucchetti (1965) in Fustiarbu region, southwestward of the small town of Busachi; (b) large tourmaline nests and fan-like aggregates in pegmatites associated with tonalitic granodiorite and (c) blastic tourmaline aggregates in meta-igneous hornfelsed xenoliths included in tonalitic granodiorite.

In the field, type (a) tourmalines are discontinuously exposed for some hundreds of meters on roof pendants of low-grade felsic meta-volcanics (e.g., pyroxene-bearing hornfels), at the contact
with tonalitic granodiorites (Fig. 3a,b). Indeed, tourmalinite veins occur as closely spaced sub-
parallel EW trending veinlets (0.3-10 cm thick) crosscutting the pervasive foliation of the
metamorphic country rock and displaying a dark massive and dominantly microcrystalline texture
(sub-millimetric up to 1 mm). Tourmalinite veins are delimited, at both contacts with the host rock,
by thin (1-2 cm), white bands made of quartz and feldspar (both K-feldspar and albite), which grade
in turn to the host rocks through an irregular border, marked by quartz infillings into the foliation
planes of the meta-volcanics (Fig. 3b). Under the polarizing microscope, tourmalinite veins reveal a
quite simple texture made of subhedral tourmaline grains and accessory quartz filling a
microfracture network (Fig. 4a,b). Tourmaline grain size is in the range of 0.2-1.0 mm and mostly
0.5 mm. SEM investigation revealed the spotted occurrence of interstitial white mica flakes
associated with tourmaline (sample BUP4, Fig. S1a,b).

Type (b) tourmaline belongs to NE trending pegmatitic dikes locally observed in tonalitic
granodiorites, mainly close to the outcrops of tourmalinite veins (Fig. 1). In the field, they mostly
occur as aplite-pegmatite dikes, with fine-grained aplite layers commonly grading into coarse-
grained pegmatite bands, both having a dominant quartz-feldspar composition with local
enrichment in dark tourmaline and minor flakes of white mica. In aplite layers, tourmaline occurs as
thin bands of fine-grained crystals, whereas in pegmatite bands it occurs as nests and fan-like
aggregates up to 7 cm in size made of elongated acicular to prismatic crystals (Fig. 3c,d). Under the
polarizing microscope, tourmaline occurs as aggregates of large crystals showing graphic textures
with quartz (Fig. 4c). Moreover, occasional large, optically-zoned tourmaline crystals are observed,
as well as bands of cataclastic tourmaline and fine-grained aggregates of tourmaline and quartz up
to 300 μm, which suggest brittle deformation (Fig. 4d,e).

The described picture is completed by local occurrence of tourmaline granoblastic aggregates
(type-c tourmaline) observed in hornfelsed meta-igneous xenoliths in tonalitic granodiorite close to
the western contacts with the basement. Under the polarizing microscope, these tourmaline grains
occur as porphyroblastic aggregates in quartz-feldspatic-chlorite layers (Fig. 4f).
2.4. Tourmaline formula and site population

The general structural formula of tourmaline, $XY_3Z_6T_6O_{18}(BO_3)_3V_3W$, encompasses many constituents: $X = Na^+$, $K^+$, $Ca^{2+}$, $\square$ (= vacancy); $Y = Al^{3+}$, $Fe^{3+}$, $Cr^{3+}$, $V^{3+}$, $Mg^{2+}$, $Fe^{2+}$, $Mn^{2+}$, $Li^+$, $Ti^{4+}$, $\square$; $Z = Al^{3+}$, $Fe^{3+}$, $Cr^{3+}$, $V^{3+}$, $Mg^{2+}$, $Fe^{2+}$; $T = Si^{4+}$, $Al^{3+}$, $B^{3+}$; $B = B^{3+}$; $V = (OH)^-$, $O^{2-}$; $W = (OH)^-$, $F^-$, $O^{2-}$. Note that the not italicized letters X, Y, Z and B represent groups of cations at the $[9]X$, $[6]Y$, $[6]Z$, $[4]T$ and $[3]B$ crystallographic sites (identified with italicized letters). V and W represent groups of anions accommodated at the [3]-coordinated O(3) and O(1) crystallographic sites, respectively.

3. Materials and methods

Six macroscopic rock samples containing tourmaline were chosen to represent the various tourmaline types: samples BUP4 and BUP13 for type a), BUP8A, BUP14A and BUP14B for type b), and BUP8B for type c). Tourmaline samples were investigated by Scanning Electron Microscopy (SEM) and Electron MicroProbe Analysis (EMPA). Specifically, tourmaline single crystals were handpicked from sample BUP4 for X-ray diffraction and structure refinement (SREF), Mössbauer spectroscopy (MS), Fourier-transform infrared (FTIR) spectroscopy and Optical-absorption spectroscopy. Details of the various experimental procedures may be found in Supplementary materials.

The information resulting by the inclusive, multi-analytical characterization of sample BUP4 was extended, when possible, to the other samples to close the gap due to missing information.

4. Results

4.1 Fe oxidation state in tourmaline
The Mössbauer spectrum of BUP4 is dominated by a major absorption doublet with high quadrupole splitting typical for Fe$^{2+}$ (Fig. 5). However, the asymmetry of the doublet with a stronger low-velocity component indicates that some amounts of Fe$^{3+}$ are also present, so that the spectrum was fitted with four doublets assigned to Fe$^{2+}$ and one doublet assigned to Fe$^{3+}$. Assuming similar recoil-free fractions for both iron species, an Fe$^{3+}$/ΣFe ratio of 0.075 was obtained (Table S5). In agreement with Andreozzi et al. (2008), the measured hyperfine parameters are consistent with Fe$^{2+}$ occurring mainly at the Y site.

4.2. Tourmaline atomic fractions

For sample BUP4, both the site-scattering results and the bond distances of B and T sites are consistent with the B site fully occupied by B$^{3+}$ and the T site without B$^{3+}$ (e.g., Bosi and Lucchesi, 2007). Accordingly, in agreement with SREF results (Table S4), the boron content was assumed to be stoichiometric (B$^{3+}$ = 3.00 apfu). As the Mössbauer spectroscopy showed that more than 92% of Fe is in the divalent oxidation state, all Mn can be assumed as Mn$^{2+}$. The (OH)$^-$ contents were then calculated by charge balance under the assumption of $T + Y + Z = 15$ apfu and 31 anions. These constraints were also applied to the point analyses of all the other samples. In these latter samples, Li$_2$O contents were estimated by the procedure proposed by Pesquera et al. (2016) for analyses with MgO $<$ 2%. The results of atomic fractions are reported in Table 2.

Tourmaline site populations at the X, Y, Z, T, B, O(3) (≡ V) and O(1) (≡ W) sites were obtained by following the standard site preference suggested by Henry et al. (2011). As for sample BUP4 the SREF results were available, the Y and Z site populations were optimized according to the procedure of Bosi et al. (2017a), fixing the minor elements Ti$^{4+}$, Mn$^{2+}$, Zn$^{2+}$ and Li$^+$ at Y. The resulting empirical structural formula of BUP4 tourmaline is:

$$X_{(Na_{0.49\pm0.03}Ca_{0.42}K_{0.01})\Sigma1.00}^{Y(Al_{1.27}Fe^{2+}_{0.94}Mg_{0.67}Fe^{3+}_{0.08}Ti_{0.03}Mn_{0.01})\Sigma3.00}^{Z(Al_{5.40}Mg_{0.60})\Sigma6.00}\times(Si_{6}O_{18})(BO_3)_3\times(O^{(3)})(OH)_3\times[(OH)_{0.47}F_{0.05}O_{0.48}]\times1.00$$
Although this empirical formula would correspond to a schorl \((\text{Fe}^{2+} > \text{Mg} \text{ at the } Y \text{ site})\), on the basis of the structural formula derived from the procedure of Henry et al. (2011) for hydroxy-tourmalines sample BUP4 was named dravite as the total of Mg is higher than \(\text{Fe}^{2+}\) (Table 2). This is another example of ambiguity in the tourmaline nomenclature, derived by naming tourmaline species by using either the empirical or the calculated formula (for further details see Bosi et al., 2017b; Bosi, 2018).

4.3. **FTIR spectra in the (OH)-stretching region and band assignment**

The infrared spectrum recorded parallel to the \(c\)-axis direction of sample BUP4 shows a broad and very intense band centered around 3530 cm\(^{-1}\) and two more narrow bands at 3635 and 3732 cm\(^{-1}\) (Fig. 6). As often observed for tourmaline spectra in the (OH)-range, the main band is off-scale for the \(E//c\) direction due to excessive absorption (e.g., Gebert and Zemann, 1965). This band is normally assigned to (OH) at the \(O(3)\) site of the tourmaline structure (e.g., Bosi et al., 2015a). Spectra obtained perpendicular to the \(c\)-axis direction show considerably weaker absorption bands at 3475 and 3556 cm\(^{-1}\), which reflects that the (OH) dipoles in the tourmaline structure are closely aligned to the \(c\)-axis direction.

On account of previous tourmaline studies, the relatively weak vibrational bands above \(\sim 3600\) cm\(^{-1}\) can be assigned to the \(O(1)\) site, whereas the strong bands below 3600 cm\(^{-1}\) can be assigned to the \(O(3)\) site (e.g., Gonzalez-Carreño et al., 1988; Skogby et al, 2012; Gatta et al., 2014). Assignment of bands to specific atomic arrangements in the (OH)-region may be just tentatively done because the relation between occupants and band positions is very complex (Hawthorne, 2016). Based on the studies of Bosi et al. (2015b, 2018), and Watenphul et al. (2016), the main FTIR bands of the studied tourmaline can be considered to be related to the following atomic arrangements:
~3732 cm$^{-1}$ is assigned to $^Y(R^{2+}R^{2+}Al)^{-O(1)}(OH)^{-X}(Na)$

~3635 cm$^{-1}$ is assigned to $^Y(R^{2+}R^{2+}Al)^{-O(1)}(OH)^{-X}(\parallel)$

~3556 cm$^{-1}$ is assigned to $(^YR^{2+}ZAl^{2+}Al)-(^YR^{2+}ZAl^{2+}Al)-(^YR^{2+}ZAl^{2+}Al)-O(3)(OH)_3$

~3475 cm$^{-1}$ is assigned to $(^YR^{2+}ZAl^{2+}Al)-(^YR^{2+}ZAl^{2+}Al)-(^YAl^ZAl^{2+}Al)-O(3)(OH)_3$

where $R^{2+}$ is Mg and Fe$^{2+}$. It should be noted that occurrence of these bands is consistent with the presence of (OH) at both the O(1) and O(3) in the structural formula of sample BUP4.

4.4. Optical spectrum

The optical absorption spectra recorded for tourmaline BUP4 (Fig. 7) show two relatively broad and intense absorption bands, polarized in $\mathbf{E}\perp \mathbf{c}$ ($\mathbf{E}\parallel \mathbf{O}$) at 1130 nm (8800 cm$^{-1}$) and 730 nm (13700 cm$^{-1}$), and an additional very broad band, also polarized in $\mathbf{E}\perp \mathbf{c}$ ($\mathbf{E}\parallel \mathbf{O}$) at 445 nm (22450 cm$^{-1}$). In the visible spectral range, the band at 445 nm is the dominating spectral feature of sample BUP4. In addition to the three strong, broad and O-polarized absorption bands, $\mathbf{E}\parallel \mathbf{c}$ ($\mathbf{E}\parallel \mathbf{E}$) spectra show a set of weak and sharp absorption bands at ca. 7300, 7100, 6970 and 6910 cm$^{-1}$ that are due to overtones of the fundamental (OH)-stretching modes recorded in the range 3500-3750 cm$^{-1}$. The broad and intense absorption bands at 1130 and 730 nm recorded in the $\mathbf{E}\parallel \mathbf{O}$-polarized spectrum are assigned, in agreement with previous optical absorption studies on tourmalines (e.g., Mattson and Rossman, 1987), to Fe$^{3+}$-enhanced spin-allowed $d$-$d$ transitions in six-coordinated Fe$^{2+}$. These previous studies have demonstrated that Fe$^{3+}$ sample concentrations enhance intensities of these two bands in $\mathbf{E}\parallel \mathbf{O}$-spectra. Hence, the $I_O/I_E$-ratios for these two bands are related to the [Fe$^{3+}$]/[Fe$^{2+}$] concentration product in tourmaline. This is in agreement with Fe$^{3+}$/Fe$_{tot}$-ratio of BUP4 as determined by Mössbauer spectroscopy. The very broad O-polarized absorption band at 445 nm is assigned, in accordance with previous studies (e.g., Taran et al., 1993), to a Fe$^{2+}$-Ti$^{4+}$ intevalence charge transfer (IVCT) process. The strong intensity of this band as recorded in the O-spectrum of
sample BUP4 confirms the \([\text{Fe}^{2+}]\cdot[\text{Ti}^{4+}]\) concentration product as determined by EMP and Mössbauer analyses.

5. Discussion

5.1. Tourmaline crystal chemistry

Chemical composition of tourmaline grains from the six investigated samples display a marked difference between type a) and the other two types b) and c). Indeed, the tourmaline from tourmalinite veins (samples BUP4 and BUP13) is the richest in Mg (1.35 apfu) and Ca (0.10 apfu) and the poorest in \(\text{Fe}^{2+}\) (0.94 apfu), \(\text{W}^\text{F}^{-}\) (0.05 apfu) and \(\text{W}^\text{(OH)}^{-}\) (0.47 apfu) with respect to the other investigated samples. Conversely, tourmaline from pegmatitic dykes and granoblastic aggregates (samples BUP8A, BUP14A, BUP14B and BUP8B) are generally enriched in \(\text{Fe}^{2+}\) (up to 1.87 apfu), Na (up to 0.60 apfu) and Li (up to 0.24 apfu), showing a relatively limited compositional variability (Table 2; Fig. S1c,f). All the analyzed crystals are rather chemically homogenous in terms of major elements (Table 2). The occurrence of frequently observed optical zoning (e.g., tourmaline crystals BUP8A_1z and BUP8A_2, Fig. 4c and S1d,e) can be related to variable contents of Ti (from 0.02 to 0.78 wt% \(\text{TiO}_2\)), which trigger and variably intensify the \(\text{Fe}^{2+}\cdot\text{Ti}^{4+}\) IVCT process responsible for optical absorption in the visible spectral range.

Previous chemical analysis classified the tourmalines from the Mandrolisai igneous massif as K-dominant (Matteucci and Zucchetti, 1965), whereas the present data show that the studied tourmalines are dominated by Na and then by \(\square\) at the \(X\) site (Fig. 8). The anomalous high K contents measured by Matteucci and Zucchetti (1965) is likely due to lack of purity degree of tourmaline used for their wet chemical analysis, probably mixed with fine-grained white mica (e.g., sample BUP4, Fig. S1a,b). All the presently studied samples are hydroxy-species and, according to their representative compositions, belong to the alkali group of the tourmaline supergroup (Table 2). In spite of that, all spot analyses documented the occurrence of a large number of \(X\)-site vacancies,
pointing towards the fields of foitite and magnesio-foitite (Fig. 8). Accordingly, the studied tourmalines were identified as dravite (BUP4 and BUP13) and schorl (BUP8A, BUP14A, BUP14B and BUP8B), both with a significant foititic component up to (and sometimes, as in sample BUP14A_2, slightly higher than) 50%. This finding is of particular relevance, as tourmalines occurring in rocks that have interacted with hydrothermal fluids are usually characterized by a significant number of vacancies at the X site (Fošt, 1989; Francis et al., 1999; Henry and Dutrow, 1996; Medaris et al., 2003).

In the tourmaline sample studied by SREF (BUP4), the incorporation of Mg occurs at expenses of Fe$^{2+}$ through the homovalent substitution Fe$^{2+} \leftrightarrow$ Mg; both Fe$^{2+}$ and Fe$^{3+}$ are ordered at the Y site, whereas Al and Mg are disordered over the Y and Z sites. The observed cation order-disorder scheme is consistent with the Z site partly occupied by Mg, as documented by Z mean atomic number (m.a.n.) less than 13 and by mean bond distance <Z-O> of 1.921 Å (Table S4). In fact, the latter distance is larger than 1.904(3) Å, a value typically observed in tourmalines with the Z site fully occupied by Al (Bosi, 2018).

As already mentioned, chemical composition of tourmaline samples BUP4 and BUP13 is markedly distinct from that of BUP8A, BUP14A, BUP14B and BUP8B, which are partly overlapping and continuously scattered along the main substitutional trend (Na + Fe$^{2+}$) ↔ (□ + Al), following a schorlitic-foititic series (Fig. 9). At the scale of the Sardinia batholith, comparisons may be made between the Mandrolisai massif and the Arbus igneous complex, both emplaced at a shallow structural level (Bosi et al., 2018). Tourmalines from Mandrolisai and Arbus show similar schorlitic-foititic evolutionary trends (Fig. 9), which suggests crystallization paths referable to analogous thermobaric conditions, likely, from moderately fractionated granitoid magmas (e.g., Novák et al., 2004; Roda et al., 1995). Constraints on the crystallization temperature range for Mandrolisai tourmalines may be offered by preliminary studies on temperature-dependent Mg-Fe intersite disorder over the Y and Z sites, for which Mg tends to order at Y and Fe at Z with increasing temperature (Bosi et al., 2019, and references therein). In the present case, the ordering
of Fe at the $Y$ site in sample BUP4 indicates a temperature of origin below 700 °C for tourmalinite veins. More specifically, according to Henry and Dutrow (1996) and Ertl et al. (2012), the relevant number of $X$-site vacancies and the absence of Al at the $T$ site indicate a formation temperature for BUP4 below 450 °C. All these findings converge to a crystallization scenario for the Mandrolisai tourmalines in the range 650-400 °C, consistent with the temperature limits previously obtained for tourmalines of the Arbus pluton (Bosi et al., 2018). The parallel though not overlapping trends observed in Figure 9 may be explained in terms of the peraluminous character of the Arbus pluton (ASI < 1.16) with respect to the metaluminous character of Mandrolisai. Interestingly, the same parallel trend is an indication that the alumina saturation of the magma played a limited role in the Mandrolisai igneous massif, mainly affecting tourmaline crystal-chemistry rather than its stability.

In the Late Variscan European magmatism, a subordinate effect of ASI variations on tourmaline stability has been documented by Pesquera et al. (2013) for peraluminous granites from Central Iberian zone.

Similarly to what observed in the Arbus igneous complex, in the Mandrolisai igneous massif, the evolution shown by type b) and c) tourmaline is typical of non-extremely evolved magmas and represents the early steps of crystallization usually observed in tourmalines from granitic pegmatites (e.g., Federico et al., 1998; Jolliff et al., 1986; London, 2011). Furthermore, type a) tourmaline from tourmalinite veins is analogous to Arbus tourmaline from veinlets and nests disseminated into the contact aureole of the pluton, as both of them show a relative enrichment of cation vacancies (and minor Ca) at the $X$ site accompanied by a relevant dravitic component, likely due to Mg uptake from the country rock. In fact, this last feature is commonly observed in tourmalinite veins, where ferromagnesian minerals are selectively replaced by tourmaline (Trumbull and Chaussidon, 1999; Slack and Trumbull, 2011).

5.2. Mineralogical and petrological constraints on the origin of tourmalinite veins
Mandrolisai tourmaline compositions plot in the region of Li-poor granitoids of the classical Henry and Guidotti (1985) Al-Fe-Mg diagram, showing environmental fields of tourmalines from various rock types (Fig. 10). This is an indication that the granodioritic magma was very poor in Li, as further supported by the absence of elbaite and other Li-bearing minerals in the pegmatitic veins and pods. Moreover, pegmatitic samples BUP8A, BUP14A, BUP14B and BUP8B are characterized by smaller Fe$^{2+}$ content and larger Mg content with respect to pegmatitic tourmalines of the Arbus igneous complex. Such a difference is consistent with the different serial character and the more oxidizing crystallization conditions of Mandrolisai magmas with respect to Arbus magmas, which belongs to an ilmenite series reaching a true ferroan character in peraluminous (and tourmaline-bearing) granitic terms (Fig. 2a,b). Notably, homogeneous redox conditions corresponding to nickel-nickel oxide (NNO) buffer during the entire crystallization path of Mandrolisai granodioritic magma may be inferred from chemical composition of dark micas (Fig. 11). According to Anderson and Smith (1995), NNO conditions are also confirmed by amphiboles, whose Fe# < 0.65 (Table S1). Yet, conditions more oxidizing than Arbus but just below NNO are suggested by tourmaline BUP4 from tourmalinite vein, whose Fe$^{3+}$/Fe$^{2+}$ ratio is \(\sim 0.1\) (Table S5), while Fe$^{3+}$/Fe$^{2+}$ > 0.1 would be expected for NNO conditions (Fuchs et al., 1998).

The geological scenario in which the crystallization of Mandrolisai tourmaline took place is schematically related to the emplacement of a single pulse of granodioritic magma at shallow crustal levels. Magma arose along tectonic contacts during post-collisional phases in which a transtensive regime was still active (Casini et al., 2012; 2015). Tourmaline growth recorded the late-stages of consolidation of a single magma batch, whose crystallization locally led to residual concentration of B in the melt. Similarly to what recently described for the Arbus pluton (Bosi et al., 2018), in layered aplite/pegmatite rocks the enrichment of B promoted the crystallization of tourmaline + quartz at the cores of pegmatitic bodies as a response of melt/hydrous fluid immiscibility processes (Hulsbosch et al., 2017; 2018). The early generation of tourmaline (b- and c-type) was followed by emplacement of tourmalinite veins, made of fine-grained tourmaline (a-
type) crystallized along fractures within metamorphic country rock. In particular, fine-grained schorl-dravite tourmaline crystallized in the central part of the fractures, and lateral diffusion of the remaining B-free, Si-Al-rich hydrothermal fluids produced the centimetric quartz-feldspar bands observed at both sides of tourmalinite veins. The emplacement mechanism of tourmalinite veins documents the strong tendency of B to escape from magma melt, while tourmaline composition (e.g., samples BUP4 and BUP13) reflects the intense interaction between B-bearing hydrothermal fluids and Mg-Fe-rich mineral phases of the country rock (e.g., amphibole and biotite). In fact, hydrothermal fluids triggered metasomatic reactions, and then tourmaline have likely grown at the expense of these mineral phases, which reasonably made available the Fe and, above all, the Mg. The commonly observed appearance of abundant, fine-grained tourmaline crystals is in favor of a precipitation from a fast-cooled hydrothermal fluid, under high nucleation and low crystal-growth rates. This is also in good agreement with a poorly developed thermal aureole, which suggests that thermal flux related to the intrusion was not very high.

The Mandrolisai igneous massif shows an elliptical, EW trending shape similar to the Arbus igneous complex, for which a local NS extension was constrained (Cuccuru et al., 2016). Mandrolisai granodiorite grades westward to a less felsic rock-type (i.e., tonalitic granodiorite, Fig. 1) which records some degree of solid state deformation (i.e., mortar quartz textures). In tourmaline-bearing aplite/pegmatite veins associated with granodiorites, brittle deformation is also documented by the occurrence of a fine-grained tourmaline-quartz cataclastic matrix (e.g., tourmaline sample BUP8A_2), which follows a primary tourmaline showing graphic intergrowths with quartz (e.g., sample BUP8A_1). Brittle deformation may have involved the western contact of the pluton, producing a discrete, roughly EW trending sub-vertical fracture network that was locally filled up by sub-centimetric to centimetric discontinuous tourmalinite veins. More precise indications on shallow conditions of Mandrolisai magma emplacement may be obtained by the Al-in hornblende geobarometer on late-crystallizing amphiboles in granodiorites. Assuming a temperature value close to the haplogranite solidus, these amphiboles fulfill the constraints required
by the calibration recently proposed by Mutch et al. (2016) for low-pressure near-solidus felsic systems. They gave an average value of 2.2 kbar (Table S1) with an uncertainty of ±0.6 kbar, in good agreement with the above-mentioned geological constraints. This value is slightly higher than 1.7 kbar recently proposed for tourmaline-bearing rocks of the Arbus pluton (Bosi et al., 2018). Taking into account of calculated pressure value of 2.2 kbar, a successive refinement of the Al-in-hornblende geobarometer by using the Anderson and Smith’s (1995) calibration for late-stage amphiboles suggested average temperature values for late-magmatic granodioritic magmas and contact metamorphic aureole of about 700 and 550 °C, respectively (Table S1). The latter value matches the estimates obtained for garnet from skarn deposits within the thermal aureole around nearby granodiorites, emplaced at the same structural level below the Gennargentu tectonic Unit southeastward of the studied region (Meloni et al., 2017).

Sub-liquidus temperature may also be estimated by the use of plagioclase-amphibole pairs. The revised calibration proposed by Holland and Blundy (1994) was used to constrain the open/closed evolution of the magmatic system in which Mandrolisai tourmaline crystallization took place. On basis of the calculated confining pressure of 2.2 kbar, temperatures obtained for core compositions of magnesio-ferric-hornblende and plagioclase (An42) gave average value of 775 °C (sample BUP11A, Table S1), that is in the field of temperatures previously found for coeval amphibole-bearing granodioritic magmas from central Sardinia (Secchi et al., 1991). Textural evidences (i.e., hypidiomorphic granular textures, lack of xenocrystic phases) indicate that granodiorites arose in the upper crust as almost molten magma pulses, in agreement with processes widely observed for many Sardinia intrusions (Conte et al., 2017). In these conditions, Mandrolisai magmas match the constraints imposed by the P₂O₅ saturation calibration suggested by Harrison and Watson (1984). Assuming that the granodiorites are not far from melt compositions, temperature estimates obtained on the basis of the granodiorite whole-rock analyses (Negretti, 1966) are in the range of 900-930 °C, higher than those obtained by plagioclase/hornblende pairs. According to Harrison and Watson (1984), this difference in temperature may be an evidence of
P₂O₅ in excess of that required to saturate the granodioritic melt, indicating in turn contamination by a crustal component. The obtained model for the origin of Sardiania late-Variscan granodiorites agrees with the model proposed for Sardinia and Corsica batholith by Cocherie et al. (1994), involving a mixed mantle/crustal scenario in which the interaction with crustal materials may likely represent the source of boron.

6. Conclusions

In the Mandrolisai igneous massif, tourmaline-bearing pegmatites and associated tourmalinite veins mainly occur at the contact with basement, where tourmaline crystallization was promoted by residual B enrichment and interaction with country rocks. They formed during magmatic to hydrothermal evolution of a metaluminous granodioritic magma pulse. This scenario favored: (1) the production of tourmaline-bearing pegmatites at the top of the intrusion, and (2) the infilling of B-rich hydrothermal fluids in an E-W trending network of fractures in metamorphic country rocks, forming thin tourmalinite veins. The fracture system infilled by tourmalinite veins is located at the intrusive/basement contact and represents a local extensional joint developed at the end of consolidation stages of granodioritic magma, in agreement to what observed for other OMP-related intrusions of Sardinia batholith (Casini et al., 2015; Cuccuru et al., 2016). When comparing tourmaline from Mandrolisai igneous massif with that from Arbus intrusives, a similar schorl to foitite crystallization sequence may be observed in the same range of temperature (600-450 °C) and at a pressure of about 2 kbar. The main differences regard the less pronounced Al and the more pronounced Mg contents shown by Mandrolisai tourmaline, and are related to different granodioritic magma evolution and magma-country rock interaction. Notably, these parameters are responsible for the metaluminous character of the igneous complex (ASI ≤ 0.95 vs ASI < 1.16 for Arbus), and drive the crystallization of tourmalinite veins.
At a regional scale, the occurrence of tourmaline-bearing rocks in OMP-related plutons suggest the existence of a B-bearing rock-series, dominated by granodioritic magmas and evolved at middle-to-upper crustal levels with complex contamination processes such as magma mixing and assimilation of crustal materials, as already demonstrated for the Variscan batholith of Corsica (Cocherie et al., 1994). Plutons related to younger magmatic peak (YMP) were likely dominated by partial melting of deeper (B-poor) meta-igneous materials, promoted by mantle delamination and astenospheric input (Conte et al., 2017, and reference therein), producing magmas marked by a F-bearing character coupled with granophile metallogenic signature (Naitza et al., 2017). Consequently, as argued by Bosi et al. (2018), an early B-bearing followed by a late F-bearing batholithic stage can be proposed for the post-collisional growth of Sardinia batholith.

Magmas that gave rise to the Mandrolisai igneous massif derived from meta-sedimentary sources and were far from the compositional characters of typical B-rich magmas, commonly felsic and strongly peraluminous. The uncommon occurrence of tourmaline-bearing rocks in the metaluminous Mandrolisai granodiorites may be an evidence of the limited control exerted by Al2O3 saturation on the origin of tourmaline. A similar evidence was reported by Pesquera et al. (2013) for granites from Central Iberian zone. Conversely, a more important role of B contents, likely coming from crustal sources, may be invoked for tourmaline saturation in the magma.

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References


Table Captions

Table 1. Summary of geological and petrographical features of late-Variscan intrusives from Mandrolisai igneous massif (central Sardinia, Italy).

Table 2. Representative chemical composition for tourmalines from Mandrolisai igneous massif and contact metamorphite (central Sardinia, Italy).

Figure Captions

Figure 1. Schematic geological map of Mandrolisai igneous massif (central Sardinia, Italy). Simplified after Carmignani et al. (2015). 1-3: Paleozoic Basement (low-grade metamorphites). (1) Castello Medusa and Monte Grighini tectonic Units. (2) Meana Sardo tectonic Unit. (3) Gennargentu tectonic Unit. 4-7: Late-Variscan magmatism. (4) biotite amphibole granodiorites grading westward to (5) biotite amphibole tonalitic granodiorites. (6) Leucogranites and associated porphyries stocks. (7) Late dike activity. Aplites and porphyries (a), mafic dikes (mainly spessartites; b) and quartz hydrothermal veins (c). (8) Permian volcanic covers. (9) Undifferentiated post-Permian covers. Other symbols: main Variscan thrust (10). Numbers in square boxes refer to analyzed samples of tourmaline-bearing rocks (BUP4, BUP8A-B, BUP13, BUP14A-B). White-colored numbers refer to samples of granodiorite (BUP10, 11 and 12) and hornfels (BUP5) of which amphiboles and dark micas were analyzed.

Figure 2. Serial characters of late-Variscan intrusives from OMP-related Mandrolisai igneous massif in the Frost and Frost’s (2008) classification diagrams. Open squares refer to whole rock
data after Negretti (1966). Additional data are reported for comparison: arrow refers to magmatic evolutive trend (from monzogabbroic rocks to peraluminous granites) of the OMP-related Arbus igneous complex (data after Secchi et al., 1991), in which the solid part of the arrow refers to appearance of tourmaline in pegmatites associated to monzogranitic granodiorites; shaded area refers to YMP-related granodioritic up to leucogranitic rocks from southern Sardinia (whole rock data after Conte et al., 2017).

Figure 3. Field aspects of tourmaline-bearing rocks from Mandrolisai igneous massif and their surroundings (central Sardinia, Italy). a) Sub-vertical EW trending thin tourmalinite veinlets (dark gray) of Fustiarbu region. b) Particular of tourmaline vein crosscutting the contact metamorphites foliation of hosting meta-igneous rocks (Sample BUP4; Fustiarbu). c) Fan-like tourmaline aggregates at the core of layered pegmatites hosted in tonalitic granodiorites (Su Pitighe). d) Massive tourmaline aggregates at the core of layered pegmatites hosted in tonalitic granodiorites (Su Pitighe).

Fig. 4 Petrographic characters of tourmaline-bearing rocks from Mandrolisai igneous massif (central Sardinia, Italy). a) Fine-grained tourmaline in tourmalinite veins (a-type tourmaline, sample BUP4, Fustiarbu, crossed polarized light). b) Fine-grained tourmaline band and sparse crystals in quartz (a-type tourmaline, sample BUP13, Fustiarbu, plane polarized light). c) Tourmaline-quartz intergrowths in pegmatitic vein associated to tonalitic granodiorite (b-type tourmaline, sample BUP8A, Su Pitighe, plane polarized light). d) Detail of large unzoned tourmaline crystal (Tur₁, sample BUP8A_1), zoned tourmaline crystal (Tur₁z, sample BUP8A_1z) and fine-grained assemblage of quartz and tourmaline (Tur₂, sample BUP8A_2) related to brittle deformation (Su Pitighe, plane polarized light). e) Large unzoned tourmaline crystals rimmed by cataclastic band of tourmaline and quartz due to brittle deformation (b-type tourmaline, sample BUP14A, Su Pitighe, crossed polarized
light). f) Blastic pseudoparamorphs of tourmaline on acidic meta-igneous hornfelsed xenoliths in tonalitic granodiorite (c-type tourmaline, sample BUP8B, Su Pitighe, crossed polarized light).

Figure 5. $^{57}$Fe Mössbauer spectrum for the tourmaline sample BUP4 obtained at room-temperature. Fitted absorption doublets assigned to Fe$^{2+}$ and Fe$^{3+}$ are indicated in green and red colors, respectively. Diamonds denote measured spectrum and black curve represents summed fitted spectra.

Figure 6. Polarized FTIR absorption spectra in the (OH) stretching frequency region for the tourmaline sample BUP4. Spectra are vertically off-set for clarity. The main band around 3530 cm$^{-1}$ is truncated in the E$\parallel$C direction due to excessive absorption. Sample thickness 61 μm.

Figure 7. Polarized optical absorption spectra in E$\perp$C and E/C for the tourmaline sample BUP4 from Mandrolisai igneous massif (central Sardinia, Italy).

Figure 8. Compositions of tourmalines from Mandrolisai igneous massif plotted in terms of $\frac{X{\square}}{X{\square}+Na}$ and Fe/(Fe$^3+$Mg). Symbols represent the various types of tourmaline occurrence: blue full circle = type a) tourmaline in tourmalinite veins within country rock (samples BUP4 and BUP13); blue full square = type b) tourmaline in pegmatites associated with tonalitic granodiorite (samples BUP8A, BUP14A, BUP14B); blue full diamond = type (c) blastic tourmaline aggregates in meta-igneous hornfelsed xenoliths included in tonalitic granodiorite (sample BUP8B). Tourmalines from Arbus pluton are plotted for comparison: black open circle = tourmaline within country rock; black open square = tourmalines within
Figure 9. \([\text{Na} + \text{Fe}^{2+} + \text{O}(1)(\text{OH},\text{F})] \text{ versus } [\text{X}^{2+} + \text{Al} + \text{O}(1)\text{O}]\) chemical evolution in tourmalines from Mandrolisai igneous massif (blue full symbols, as in Fig. 8) and Arbus pluton (black open symbols; Bosi et al. 2018). Blue arrow indicates the change in temperature during tourmaline chemical variation (Bosi et al., 2018).

Figure 10. Al-Fe\(^{2+}\)-Mg triangular diagram showing the principal chemical variation in tourmalines from Mandrolisai igneous massif (blue full symbols, as in Fig. 8) and Arbus pluton (black open symbols; Bosi et al. 2018). Rock stability fields (modified after Henry and Guidotti, 1985) are reported for comparison: (1) Li-rich granitoid pegmatites and aplites, (2) Li-poor granitoids and their associated pegmatites and aplites, (3) Fe\(^{3+}\)-rich quartz-tourmaline rocks (hydrothermally altered granites), (4) Metapelites and metapsammites coexisting with an Al-saturating phase, (5) Metapelites and metapsammites not coexisting with an Al-saturating phase, (6) Fe\(^{3+}\)-rich quartz-tourmaline rocks, calc-silicate rocks, and metapelites, (7) Low-Ca metalultramafics and Cr, V-rich metasediments, and (8) Metacarbonates and metapyroxenites.

Figure 11. Fe\(^{2+}\)-Fe\(^{3+}\)-Mg diagram showing the evolution trend of dark micas in granodiorites from Mandrolisai igneous massif (blue open squares). Black line represents NNO buffer conditions (Eugster and Wones, 1962). The blue arrow represents the evolution trend of dark micas from monzogabbroic rocks to peraluminous granites of Arbus igneous complex, interpolated from data reported in Secchi et al. (1991).
Supplementary Materials: Table and Figure Captions

Table S1. Representative chemical analyses of amphibole from Mandrolisai igneous massif and contact metamorphites.

Table S2. Representative chemical analyses of dark micas from granodioritic rocks from Mandrolisai igneous massif and contact metamorphite.

Table S3. X-ray diffraction data for tourmaline from sample BUP4.

Table S4. Fractional atomic coordinates (x, y, z), equivalent displacement parameters (U_{eq} in Å^2), mean atomic number (m.a.n.) and selected bond distances (Å) for tourmaline from sample BUP4.

Table S5. Mössbauer parameters for tourmaline from sample BUP4 obtained at room-temperature.

Figure S1. SEM-BSE images for tourmaline crystals from Mandrolisai igneous massif: (a-c) tourmalinite veinlet of Fig. 4a (sample BUP4); (b) detail of the a) image showing muscovite flakes; (c) detail of the a) image showing large euhedral tourmaline crystals; (d-e) tourmaline from pegmatitic veins reported in Fig. 4c (sample BUP8A); (d) large euhedral optically-zoned tourmaline crystals, (e) quartz-tourmaline fine-grained assemblage; (f) fine-grained blastic aggregates of tourmaline (red dashed areas) reported in Fig. 4d (sample BUP8B).
Table 1. Summary of geological and petrographical features of late Variscan intrusives from Mandrolisai igneous massif (central Sardinia, Italy)\(^a\)

<table>
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<tr>
<th>Rock Units</th>
<th>General geological features and essential petrographic characters</th>
<th>Mineral assemblage</th>
<th>Accessory phases</th>
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<tr>
<td>Dikes</td>
<td>Sub-vertical porphyritic dikes occasionally crosscutting felsic dikes</td>
<td>Hbl → Ca-Pl + Hbl + Bt + Qz</td>
<td>Mag + Ilm + Sulph + Ap + Zrn</td>
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<td>Qz + Kfs + Na-Pl + Bt + Ms</td>
<td>Mag + Zrn + A.n</td>
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<td></td>
<td>Pl(_{\text{An41-55}}) + Qz + Kfs + Bt + Mg-Hbl</td>
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<td>Pl(_{\text{An41-55}}) + Qz + Kfs + Bt + Mg-Hbl</td>
<td>Mag + Aln + Ilm + Sulph + Ap + Zrn</td>
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</table>

\(^a\) Integrated and modified after Negretti (1966). Hypidiomorphic granular textures are by far dominant. Feldspars, amphiboles and dark micas from granodiorites were analyzed by EMPA. Dark micas and amphiboles were classified according to Rieder et al. (1998) and Hawthorne et al. (2012), respectively. All analyzed dark micas belong to the biotite series (annite-phlogopite). All analyzed amphiboles are calcium amphiboles showing \(B(Ca) > 1.5\) apfu, in agreement with observed optical features. C.I. (= color index expressed in weight %) and A.S.I. (= molar
alumina saturation index) were calculated according to whole-rock analytical data reported in Negretti (1966).

Abbreviations list according to Kretz (1983) and Whitney and Evans (2010): Pl = plagioclase; Qz = quartz; Kfs = K-feldspar; Bt= biotite; Hbl = hornblende; Ms = muscovite; Ilm = ilmenite; Ap = apatite; Aln = allanite; Zrn = zircon; Sulph = sulphides (mainly pyrrotite); Mag = magnetite; Rt = rutile; Ab = albite; Hem = hematite; Ep = epidote; Ser = sericite; Tur = tourmaline.
Table 2. Representative chemical composition for tourmalines from Mandrolisai igneous massif and contact metamorphic (central Sardinia, Italy).

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<tr>
<th></th>
<th>BUP4</th>
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<td>0.27(11)</td>
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<td>0.15(3)</td>
<td>0.07(3)</td>
<td>0.05(2)</td>
<td>0.05(2)</td>
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Site populations

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Number of atoms (atomic fractions) normalized to 31 anions (O, OH, F). Errors for oxides and F (in bracket) are standard deviation of 10 spot analyses; n = number of individual analytical points used in the average; apfu = atoms per formula unit. Ion allocation in the formula XY3Z6(T6O18)(BO3)3V3W according to Henry et al. (2011).

a Calculated in accordance with the SREF results.
b Determined by Mössbauer spectroscopy.
c Estimated with the procedure of Pesquera et al. (2016).
d Calculated by stoichiometry (see text).
e Confirmed by infrared spectroscopy.
Highlights

- Mandrolisai igneous massif tourmalines correspond to dravite and schorl.
- Schorl occurs in pegmatites and dravite occurs in tourmalinite veins, both compositions have a relevant foititic component.
- Mandrolisai tourmalines follow the trend formerly reconstructed for tourmalines of the Arbus igneous complex (SW Sardinia, Italy): crystallization temperatures in the range 650-400 °C.
- Mandrolisai tourmalinite veins, were likely formed under a brittle solid-state regime, which overprinted a previous deformation under magmatic flow conditions.
Figure 7

BUP4

Absorbance

Wavenumber (cm\(^{-1}\))
Figure 8
Figure 9

Graph showing the relationship between $[\text{Na} + \text{Fe}^{2+} + \text{O}^{1}(\text{OH, F})]$ (apfu) and $[\text{X□} + \text{Al} + \text{O}^{1}(\text{O}^{2-})]$ (apfu) with indications for temperatures of approximately 400 °C and 650 °C.