Evaluating the Controls on Tourmaline Formation in Granitic Systems: a Case Study on Peraluminous Granites from the Central Iberian Zone (CIZ), Western Spain

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Tourmaline occurs in peraluminous granites from the Central Iberian Zone associated with two main AFM mineral assemblages: (1) muscovite + biotite ± cordierite ± andalusite in the Araya-type granites; (2) muscovite ± biotite ± garnet in leucogranites from the Alamo complex. When tourmaline is dominant, biotite is an accessory or absent, and vice versa. We present field and petrographic relations, mineral chemistry, and geochemical data for tourmaline-bearing and tourmaline-free granitic rocks from various localities in the Central Iberian Zone. Compositional phase diagrams are used to evaluate the factors controlling the occurrence of tourmaline relative to biotite in granitic rocks, with particular emphasis on the relationships between mineral assemblage and rock chemistry and its petrological implications. Although tourmaline stability in felsic magmas depends on the interplay between rates of changing environmental conditions such as bulk composition, T, and fO2, the principal factor dictating tourmaline formation is the B content of the melt, judging from phase relations. In short, regardless of other variables, granitic melts have to surpass a critical boron threshold to achieve tourmaline saturation. Experimental constraints, combined with petrographic and geochemical data, suggest minimum boron contents in the range of ~500–3000 µg g⁻¹ (depending on temperature) to saturate melt in tourmaline. Acting in concert with boron content, other variables such as Al₂O₃, mafic components, T, fO₂, and so on, control not only the formation of tourmaline during melt crystallization, but also the magnitude of boron loss from the magma to the surrounding rocks. The analysis of phase relations suggests that tourmaline granites usually form units distinct from biotite granites because common granitic melts have restricted accessibility to the three-phase Tur–Bt–Ms field.

KEY WORDS: tourmaline; biotite; peraluminous granites; stability

INTRODUCTION

In peraluminous granites (alumina saturation index, ASI >1.1, defined as the molecular ratio Al₂O₃/(Na₂O + K₂O + CaO) (Shand, 1943), excess alumina above that needed to form feldspars is incorporated into micas, especially muscovite and biotite, and Al-bearing minerals such as tourmaline, cordierite, Al₂SiO₅ polymorphs and garnet (Clarke, 1981). These mineral assemblages are sensitive to P, T, and bulk composition, and consequently provide information on the equilibrium relations, stability, and crystallization conditions of the host magma. Early crystallization of biotite and cordierite may be

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accompained by tourmaline depending on the boron concentration in the magma and other factors. As Hatch et al. (1972) stated, tourmaline is a mineral of outstanding interest from many points of view. Tourmaline is the dominant boron-bearing mineral in many crustal rocks and can be a liquidus phase in granitic magmas (Benard et al., 1985; Scaillet et al., 1995). Granites with relatively high B contents and magmatic tourmaline appear to be typical of continental collision zones, and seemingly require B-rich source regions (Leeman & Sisson, 2002). The abundance of B in melts is expected to hinge on the thermal history of their source regions and the stability of B-bearing minerals.

Tourmaline has been found in peraluminous leucogranites from several regions (e.g. Shearer et al., 1987; Scaillet et al., 1990; London & Manning, 1995; Pesquera et al., 2005; Buriánek & Novák, 2007). Magmas require a minimum amount of boron to achieve tourmaline saturation. However, boron preferentially partitions into the fluid phase relative to a granitic melt (Pichavant, 1981; Schatz et al., 2004), and therefore granites do not always reflect the actual magmatic boron contents. In some granitic complexes, tourmaline may coexist with biotite, but tourmaline-bearing rocks usually form distinct units from biotite-bearing rocks, which may be coeval or even cogetic units (e.g. Scaillet et al., 1990; Nabelek et al., 1992; Guillot & Le Fort, 1995; Dèzes, 1999; Visona & Lombardo, 2002; Pesquera et al., 2005). The antipathetic nature of tourmaline and biotite in granites was noted by Cech (1963). However, according to Scaillet et al. (1995) and Scarfe et al. (1997), tourmaline and biotite are not always mutually exclusive. Several factors, such as fO2, activity of H2O, alkalinity, and Al–Fe–Mg content have been considered to influence tourmaline stability with respect to other AFM phases (biotite, cordierite, muscovite, garnet) (Benard et al., 1985; Holtz & Johannes, 1991; London & Manning, 1995; Scaillet et al., 1995; Wolf & London, 1997). Opinions differ on the relative roles of those variables in controlling biotite and tourmaline stability in peraluminous granites. This study is concerned with this controversy, which is evaluated in Variscan peraluminous granites from the central and southern parts of the Central Iberian Zone (CIZ) (western Spain). We use composition phase diagrams as a tool for deciphering the effect of bulk composition on rock mineral assemblages. Based on a set of BFM, AFM, and ABF diagrams, a qualitative model is drawn up to explain why tourmaline granites tend to form distinct units from biotite granites.

**GEOLOGICAL OUTLINE**

The Central Iberian Zone (CIZ) is the innermost domain of the Variscan belt in the Iberian Massif and includes two subdomains: (1) the Ollo de Sapo Anticlinorium to the north, characterized by the occurrence of Cambro-Ordovician metavolcanic and metagranite rocks; (2) the Schist–Graywacke Complex (SGC) to the south, which consists of Neoproterozoic to early Palaeozoic metasediments with abundant intrusive granitoids (Fig. 1). Tectonomorphic domes (including high-grade tectonic metamorphic rocks, gneisses, migmatites, and leucogranites) are present in the northern part of the SGC.

The structure of the CIZ is the result of the superimposition of four phases (D1–D4) of Variscan deformation (see Ábalos et al., 2002, for an overview). The two main phases, D1 and D2, brought about heterogeneous ductile deformation and were accompanied by regional low- to high-grade metamorphism that evolved from intermediate (D1) to low-pressure (D2) conditions. The late deformation phases, D3 and D4, are more localized, but are responsible for the broad macrostructural outcrop patterns of the CIZ.

Syn- to late D2 granitoids, mostly of high peraluminosity (Bea et al., 1987), intrude the Neoproterozoic and early Palaeozoic metasediments and orthogneisses (Ferreira et al., 1987; López Plaza & Martínez Catalán, 1987). The granitoids can be grouped into three categories (for an overview see Castro et al., 2002). (1) The granodiorite suite includes quartz-gabbrodiorite, tonalite, granodiorite, and granite facies. This suite encompasses early syntectonic granitoids, associated with granites intruded during the Variscan D2 deformation, and granitoids represented by large batholiths that cross-cut the D2 structures. (2) The monzogranite suite (widespread in the southern sector of the CIZ) consists of zoned allochthonous plutons of variable size emplaced in an epizonal domain. They also occur as irregular patches with transitional contacts into biotite granodiorite. The granites of this suite are peraluminous, with little or no restite, and seem to have evolved by magmatic fractionation that led to leucocratic differentiates characterized by relatively high P and Li contents and by local Sn–W mineralization (Bea et al., 1992). Geochemical details and petrogenetic models for some granitoids from this suite have been given by Corretgé et al. (1983), Bea et al. (1994), Ramírez (1996), González-Menéndez (1998), and Ramírez & Grundvig (2000). (3) The leucogranite suite comprises early autochthonous and early to late allochthonous granitoids that are linked to the Variscan regional D2 deformation. They are peraluminous, with low CaO contents, and commonly show restitic enclaves of psammo-pelitic composition. Peraluminous leucogranites from the CIZ are interpreted as deriving from the partial melting of gneisses and schists during extension-related decompression (Díez-Balda et al., 1995; Castro et al., 1999, 2000). Geochemically and petrologically, there are many questions regarding these granitoids, particularly concerning the character of the protoliths and the physical conditions of melting and differentiation. In the central and southern part of the CIZ the source of the abundant granite magmatism has been attributed to metasediments of the SGC derived from Cadomian felsic
igneous rocks. This source layer would be characterized by high fertility and heat production (Bea et al., 2003).

Whereas the granodiorite suite is generally devoid of tourmaline, the monzogranite and leucogranite suites commonly contain tourmaline. For this study, we analysed rock samples from (1) the monzogranite suite (‘Araya-type’ granites), which mostly occurs in the southern part of the CIZ (Corretgé et al., 1985; Bea et al., 1987), particularly from the Alburquerque–Nisa batholith, Jálama pluton, and Cabeza de Araya batholith, and (2) the leucogranite suite that forms part of the ‘Alamo Complex’ in the central part of the CIZ (García de Figuerola et al., 1983) (Fig. 1).

**ANALYTICAL METHODS**

Modal compositions of biotite and tourmaline were determined by point counting on two to three mutually perpendicular thin sections of rocks, using an electromechanical point counter and the reliability criteria of van der Plas & Tobi (1965). Modal analyses of biotite and tourmaline in some porphyritic granites were performed involving: (1) an estimate of the volumetric proportion of the feldspar megacrysts on sawn, polished slabs on which a transparent grid is placed; (2) measurement of the components of the groundmass in thin sections.

Seventy-two granitic and 18 metamorphic rocks were analysed for major elements by X-ray fluorescence (XRF) on fused glass discs using a Philips PW1404/10 X-ray spectrometer at the University of Granada. Precision was ±2–5% for major elements, except MnO and P₂O₅ (5–10%), and ±2–5% for Zr. The trace element Zr was also measured by XRF on pressed powder pellets. Trace elements (except Zr) were determined by inductively coupled plasma mass spectrometry (ICP-MS) after HNO₃ + HF digestion of 100 mg of sample powder in a Teflon-lined vessel at 180°C and 200 p.s.i. for 30 min, evaporation to dryness, and subsequent dissolution in 100 ml of 4 vol. % HNO₃. Precision is better than ±5% for analytical concentrations of 10 µg g⁻¹. The international standards PM-8 and WS-E (Govindaraju et al., 1994) were used for calibration and dissolution (see Torres-Ruiz et al., 2003).

Mineral compositions were determined at the University of Granada with a Cameca SX100 electron microprobe.
equipped with five wavelength-dispersive spectrometers using both natural and synthetic standards: natural fluorite (F), natural sanidine (K), synthetic MnF₂O₃ (Ti, Mn), natural diopside (Ca), synthetic Fe₂O₃ (Fe), natural albite (Na), natural periclase (Mg), synthetic SiO₂ (Si), synthetic Cr₂O₃ (Cr), and synthetic Al₂O₃ (Al). An accelerating voltage of 15 kV, a beam current of 15 nA and a 2 μm focused electron beam were used to analyse tourmaline and associated minerals. Counting times on peaks were twice those of backgrounds: 15 s for Na and K; 20 s for Ti and Ca; 25 s for Fe, Si and Al; 30 s for Mg. Data were reduced using the procedure of Pouchou & Pichoir (1985). Analytical errors are estimated to be of the order of ±1–2% for major elements and ±10% for minor elements. The mineral chemistry database includes over 600 analyses of tourmaline, micas, cordierite, and garnet.

Several granitic and metamorphic rocks were analysed for boron and δ¹⁸O isotopes by prompt gamma neutron activation analysis and thermal ionization mass spectrometry (TIMS), respectively, at Activation Laboratories Ltd. (Actlabs, Canada). Eight tourmaline samples were also analysed by Mössbauer spectroscopy to assess the iron oxidation state. The Mössbauer analyses of powdered tourmaline samples were carried out in the Electricity and Electronics Department of the University of the Basque Country. Mössbauer spectra were obtained at room temperature using a standard spectrometer with a Co/Rh source. The isomer shift is reported relative to metallic iron. The spectra were collected in a multi-channel analyser with 512 channels, and the experimental data were evaluated by means of a least-squares fit.

Phase diagrams were developed with CSpace software (Torres Roldán et al., 2000), a program devised for analysing the composition and reaction spaces of mineral assemblages using algebraic techniques (singular value decomposition, SVD; Fisher, 1989, 1993). The generation of phase relations involves the manipulation of the composition space by means of a projection process (e.g. Thompson, 1957; Korzhinskii, 1959; Greenwood, 1975; Abbott & Clarke, 1979; Fisher, 1989). This is a complex issue because (1) most of the mineral phases are solid solutions, and (2) the rocks consist of high-variance mineral assemblages that are not amenable to straightforward projection owing to the lack of an adequate number of projection phases. To overcome these drawbacks, rocks and minerals were projected from actual mineral compositions using appropriate simple or coupled exchange vectors that allow condensation of the composition space. Even though this procedure masks the effects of bulk composition on mineral assemblage stability [it is not perfectly thermodynamically valid, paraphrasing Greenwood (1975)], it is still the best approach for the task of comparing high-variance mineral assemblages. We focus on this procedure to analyse tourmaline-bearing and -free assemblages in granites in an attempt to decipher the chemical variables that control tourmaline formation.

FIELD RELATIONSHIPS AND PETROGRAPHY

The Araya-type granites form allochthonous zoned plutons emplaced in low-grade SGC metasedimentary rocks during the Variscan orogeny. Although the monzogranites locally display fine- to medium-grained facies, as well as aplites and pegmatites, the most abundant facies is predominantly a medium- to coarse-grained granite with hypidiomorphic seriate to porphyritic textures. Based on the mineral association, the Araya-type granites are subdivided here into: (1) two-mica granites (MBG) with the assemblage quartz + K-feldspar + plagioclase + biotite + muscovite ± cordierite ± andalusite ± fibrolitic sillimanite; (2) tourmaline-bearing (generally tourmaline <1 vol. %) two-mica (muscovite + biotite) granites (MBTG) including quartz + K-feldspar + plagioclase ± cordierite ± andalusite ± fibrolitic sillimanite; (3) muscovite-tourmaline leucogranites (MTG) in which tourmaline is the main ferromagnesian mineral (up to 3 vol. %). MBG and MBTG show similar petrographic characteristics. Plagioclase grains are usually subhedral, in places including biotite, and zoned from An₂₂ to An₃₉ in the cores and An₅₋₁₀ in the rims. K-feldspar occurs as large (up to 8 cm in places) subhedral to anhedral grains, commonly containing inclusions of biotite, plagioclase, and muscovite. Quartz grains are often in anhedral aggregates. Fine- to coarse-grained cordierite is relatively common in the MBG and MBTG facies of the Araya-type granites. Where fresh cordierite occurs, it is subhedral to euhedral and is generally free of inclusions. However, cordierite is commonly replaced by a greenish, fine-grained aggregate of biotite + chlorite + white mica ± tourmaline (Fig. 2a), and also by intergrown muscovite and biotite grains. Some crystals with inclusions of biotite ± tourmaline are rimmed and partially replaced by muscovite that encloses subhedral andalusite grains. These textural features are similar to those described by Abbott & Clarke (1979) in the Musquodoboit pluton (southern Nova Scotia). Biotite is an ubiquitous phase in the MBG and MBTG facies, forming up to ~12 vol. % of the rock. It mainly occurs as fine- to medium-grained, reddish to yellowish brown, subhedral grains primarily including ilmenite, zircon, apatite and, in places, tourmaline (Fig. 2b). Chlorite and Ti-oxides may appear as a result of the alteration processes. White mica is relatively abundant in all granite facies, occurring as fine- to medium-grained prismatic crystals, comparable in size with biotite. Fine-grained muscovite replacing feldspars and cordierite is also relatively common. Fine-grained, euhedral to anhedral andalusite is usually mantled by prismatic or polycrystalline aggregates of...
muscovite, with mutual relations very similar to the textural types ($S_6\ S_8\ S_9\ $ and $C_2$) defined by Clarke et al. (2005). Tourmaline is unevenly distributed in the Araya-type granites and occurs as: (1) fine- to medium-grained, subhedral prismatic crystals to anhedral interstitial grains disseminated through the granite and coloured in various shades of khaki, greyish blue, and orange–brown to tan in thin section; (2) fine-grained, euhedral to subhedral, orange–brown to greyish blue crystals hosted in biotite and cordierite (Fig. 2a and b); (3) orangish brown or reddish brown to green tourmaline replacing pre-existing biotite and cordierite (Fig. 2c); (4) fine- to medium-grained, unzoned or slightly zoned, euhedral to anhedral crystals that are bluish green to khaki, typical of leucogranitic facies; (5) pale green to green amoeboidal tourmaline, commonly associated with muscovite, which replaces

![Fig. 2. Photomicrographs illustrating the occurrence of tourmaline in granitic rocks of the CIZ. (a) Tourmaline (Tur) hosted in biotite (Bt) and altered cordierite (Crd) (Alburquerque granite). (b) Euhedral tourmaline enclosed in biotite and feldspar (Cabeza de Araya granite). (c) Replacement of biotite by tourmaline (Alburquerque granite). (d) Elongate tourmaline grains coexisting with biotite and muscovite (Ms) in weakly foliated leucogranite from the Sierra del Alamo (Alamo complex). Tourmaline crystals are aligned according to the foliation defined by the micas. (e) Euhedral to subhedral, slightly zoned, tourmaline crystals in leucogranite from the Castellanos antiform (Alamo Complex).](https://academic.oup.com/petrology/article-abstract/54/3/609/1466271/Evaluating-the-Controls-on-Tourmaline-Formation-in-Granitic-Systems/613)
feldspars; (6) intergranular and microfracture-filling tourmaline. Mafic phosphates (e.g., magnetiortriple, childrenite) associated with biotite, cordierite, and tourmaline occur locally in the Alburquerque granite.

The Alamo complex leucogranites occur as numerous sheet-like and lenticular bodies (mostly from centimetre scale to 200 m thick and <3 km long) associated with schists, tourmalinites, gneisses, and migmatites within tectono-metamorphic domes in the northern part of the SGC (Fig. 1). The contact between the leucogranitic bodies and metamorphic rocks is sharp and concordant with the regional foliation. Some bodies have induced proximal boron metasomatism in the host-rocks, with the formation of late- to post-tectonic tourmaline. However, there are also leucogranitic bodies that lack evidence of fluid-induced wall-rock boron metasomatism. At several localities, tourmaline-bearing gneisses alternate with leucogranite sheets and pegmatoids (Fig. 3a). The gneisses are associated with migmatitic rocks and may be grouped into two main types: (1) leucocratic gneisses displaying tourmaline and feldspar porphyroclasts; (2) fine- to medium-grained melanocratic gneisses. The granitic rocks are mainly monzogranite in composition, but tonalitic compositions are also found. They show a range of microstructures from primary magmatic textures, with fine- to medium-grained (<1 to 5 mm) hypidiomorphic granular textures, through to textures indicative of subsolidus deformation, including local strong mylonitization. The Alamo complex leucogranites are a good example of tourmaline-bearing granites, with some having relatively high tourmaline contents (up to 12 vol. %). Three main leucogranite facies have been recognized: (1) two-mica leucogranites (MBL), with the assemblage muscovite + biotite + quartz + feldspars ± andalusite ± fibrolitic sillimanite; (2) tourmaline-bearing two-mica leucogranites (MBTL), with the assemblage muscovite + biotite + tourmaline (generally <0.2 vol. %) + quartz + feldspars + garnet (Fig. 2d), where the tourmaline/(tourmaline + biotite) ratio is mostly <0.15; (3) muscovite-tourmaline leucogranites (MTL), with the assemblage tourmaline (up to 10 vol. %) + muscovite + quartz + feldspars ± garnet (Fig. 2e). In places, compositional layering (<1 m) outlined by variations in the tourmaline/(tourmaline + biotite) ratio can be observed (Fig. 3b). Subhedral plagioclase is unzoned or weakly zoned from ÆAn0.8 in the interior zones to ÆAn0.3 in the rims. K-feldspar and quartz are commonly anhedral. Subhedral muscovite is ubiquitous in these granites and has magmatic textural characteristics. Biotite from the MBL and MBTL leucogranites is commonly less abundant than muscovite. Tourmaline occurs as black, fine- to medium-grained crystals (mostly <2 mm in cross-section) disseminated through the granite, and also concentrated in nodules (usually <1 cm diameter) and veinlets. In thin section, tourmaline commonly appears as unzoned to zoned, euhedral to anhedral crystals, generally with scarce inclusions (Fig. 2d and e). Characteristic colours are khaki, orange-brown, bluish green, and blue. Optically unzoned tourmaline crystals commonly coexist with zoned tourmaline crystals in the same sample. There is no regular distribution of colour zoning relative to the rim or core. The zones have mostly diffuse boundaries and in some cases form irregular patches in the interior of crystals. In m伊利itized granitic facies, tourmaline may contain quartz veinlets that completely transect the crystals. Subhedral to euhedral crystals of garnet, mostly very fine- to fine-grained, are common in MTL leucogranites, particularly in the Villaseco-Pereruela and Martinanmor leucogranites. In places, it includes very fine euhedral crystals of green tourmaline. Apatite is ubiquitous and zircon is present in most of the samples studied, particularly in biotite-bearing leucogranites. Ilmenite is rare in MTL. Accessory andalusite and sillimanite occur locally, particularly in fine-grained eastern leucogranites.

**WHOLE-ROCK CHEMISTRY**

We have analysed granitic rock samples to appraise the relationships between mineralogy and whole-rock composition. To this end, we have grouped the granitic rocks as they are classified above; that is, MBG, MBTG, and MTG within the Araya-type granites, and MBL, MBTL, and MTL within the Alamo complex leucogranites. Country-rock gneisses and schists associated with the granites are considered potential protoliths of the silicic magmas and, therefore, have also been analysed. Average bulk-rock compositions for major and trace elements of these granite groups and associated metamorphic rocks (average schist from the SGC and representative gneisses) are listed in Tables 1 and 2, respectively. All granite samples are peraluminous, with an aluminium saturation index that mainly ranges from 1.20 to 1.60. Except for the boron and Li contents, which are higher in MBT than in MBG, major- and trace-element distinctions between MBG and MBTG are in general subtle (Tables 1 and 2).

On average, MBG and MBTG are characterized by SiO2 = 71.7–72.8 wt %, Al2O3 = 14.4–14.3 wt %, K2O/Na2O = 1.47–1.44, and a B parameter (where B is the sum of Fe + Mg + Ti) in the range of 10–16 (Table 1). Rocks from the MTG group have similar whole-rock δ18O values of both types of granite overlap in the range of +10.6 to +13.0‰ (Table 1). Rocks from the MTG group have similar whole-rock δ18O values (+12.0 to +12.2‰), but a lower B parameter (average 17) and K2O/Na2O ratios (average 105) than those from the MBG and MBTG. There are, however, notable differences in trace element contents. Average MTG have higher Li, Rb, Sn, Ta, and U, and lower Ba, Sr, Y, Zr, Th, and ΣREE than average MBG and MBTG.
Fig. 3. (a) Melanocratic gneiss in contact with tourmaline-bearing leucogranite and pegmatoid in the Castellanos area (Alamo complex) (G, gneiss; L, tourmaline-bearing leucogranite; P, pegmatoid). (b) Outcrop showing compositional layering in leucogranite from the Martinamor area (Alamo complex). A tourmaline-rich leucogranite layer (MTL) is underlain by a two-mica leucogranite with tourmaline nodules (MBTL) and is abruptly overlain by a two-mica leucogranite with accessory tourmaline (MBTL).
higher Al$_2$O$_3$ contents, lower K$_2$O/Na$_2$O ratios (average 7.75 and 1.7, respectively), and whole-rock parameter values (average 23 and 17 for MBL and MTL, respectively). The average compositions of tourmaline, biotite, and muscovite are reported in Tables 3, 4, and 5, respectively.

Tourmalines from the two granitic suites belong mostly to the alkali group, according to the nomenclature of Henry et al. (2011), with (Na + K) >0.50 a.p.f.u. (based on 15T + Z + Y cations, exclusive of Na, Ca, and K; Table 3). The majority of the tourmaline compositions fall into the schorlitic field, with $\xi$Na/$\xi$Na + Na + K) ($\xi$Na = X-site vacancy) and Mg/(Mg + Fe) ratios in the range of 0.1–0.53 and 0.4–0.56, respectively (Fig. 4a). Tourmalines from Araya-type granites show a wider variation in the Mg/(Mg + Fe) ratio than tourmalines from the Alamo complex leucogranites. Mossbauer spectra (not shown) of some tourmalines from both granitic suites do not reveal the presence of Fe$^{3+}$. Laser ablation (LA)-ICP-MS data (unpublished) for tourmalines from these granites show very low Li contents (<250 μg g$^{-1}$). Although much of the chemical variability is in the Mg/(Mg + Fe) ratio, which would reflect the exchange vector MgFe$_{1}$ relating the compositions of schorl and dravite, the values of Σ(Fe + Mg) <3a.p.f.u. reveal the presence of Al in the Y site (Fig. 4b). Substantial amounts of Al may be incorporated into the Y site via the Al$^4$Si$^4$O$^8$(R$^{2+}$Na)$_{1.0}$ and Al$^4$O$^7$(R$^{2+}$OH)$_{1.0}$ substitutions where R$^{2+}$ = (Fe + Mg + Mn). The relative importance of these substitutions can be established by using the $\xi$Na vs Al diagram in which significant deviations from the Al$^4$Si$^4$O$^8$(R$^{2+}$Na)$_{1.0}$ exchange vector are observed (Fig. 4c). This means that, in addition to this

**MINERAL CHEMISTRY**

We analysed tourmaline, biotite, muscovite, cordierite, and garnet. The average compositions of tourmaline, biotite, and muscovite are reported in Tables 3, 4, and 5, respectively.

- **Table 1**: Average whole-rock major-element composition (wt %) and oxygen isotope composition (‰) of the rock groups

<table>
<thead>
<tr>
<th>Group</th>
<th>MBG (n = 23)</th>
<th>MBTG (n = 15)</th>
<th>MTG (n = 7)</th>
<th>MBL (n = 3)</th>
<th>BTL (n = 6)</th>
<th>MTL (n = 18)</th>
<th>Gneiss (n = 9)</th>
<th>Schist (n = 9)</th>
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<td>SiO$_2$</td>
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<tr>
<td>MgO</td>
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Table 2: Average whole-rock trace-element composition of the rock groups (ppm)

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<th>MBL (n=3)</th>
<th>MBTL (n=6)</th>
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The exchange mechanism, other substitutions contribute to the incorporation of Al into tourmaline. To further test whether the exchange mechanism $\text{Al}^3+/\text{Al}^2+$ accounts for the dispersion of the tourmaline data, the influence of the substitution $\text{Al}^3+/\text{Al}^2+$ is removed by condensing down that vector (Medaris et al., 2003) (Fig. 4d). However, the data still deviate significantly from the line. Accordingly, the compositional variability of the tourmalines associated with the CIZ granites seems to be controlled mainly by a combination of the $\text{Al}^3+/\text{Al}^2+$, $\text{Fe}^2+/\text{Fe}^3+$, and $\text{Fe}^2+/\text{Mg}^{2+}$ exchange vectors. Tourmalines from the MBTG and MTG have higher F contents than those from MBTL and MTL (Table 3), and a poor negative correlation of F vs $\text{Al}^3+$ (not shown) suggests that the increase in F on the W-site is accompanied by a decrease in Al on the Y-site. This trend is consistent with the fact that the higher the local charge at the Y sites, the lower the F in the tourmaline. However, the poor correlation reflects the strong influence of the occupancy and charge at the X-site, in addition to the environmental conditions, on the amount of F that can be incorporated into tourmaline (Henry & Dutrow, 2011). Likewise, the Ti contents tend to be higher in tourmalines from the Araya-type granites (~0.01–0.017 a.p.f.u.) than in tourmalines from the Alamo complex leucogranites (~0.01–0.018 a.p.f.u.).

Biocites from both Araya-type and Alamo complex granitic suites have $\text{Al}^{VI}$ > 2a.p.f.u. (based on 11 oxygens p.f.u., Table 4). The $\text{Mg}/(\text{Mg}+\text{Fe})$ ratio ranges from 0.14 to 0.46 and increases with decreasing $\text{Al}^{VI}$ (Fig. 5a), which is likely to reflect coupling between the effect of temperature and bulk composition on biotite crystallization. Biocites from MBG and MBL have lower average $\text{Mg}/(\text{Mg}+\text{Fe})$ values (0.35 and 0.32, respectively) than biocites from MBTG and MBTL (0.28–0.27). Overall, biocite compositions lie outside the annite–phlogopite–siderophyllite–castonite plane and plot in intermediate positions between triotahedral and dioctahedral micas (Fig. 5b). This reflects an enrichment in $\text{Al}^{VI}$ and, consequently, the presence of octahedral vacancies via the substitution.
The sum of the divalent cations (Mg\(^{2+}\)) (Fig. 5d). The amounts of Ti in biotite range from 0 to 3 to 2(Fe,F)\(^{2+}\) (Fig. 5c). The incorporation of Al\(^{3+}\) into biotite via the Al-Tschermak substitution seems to have been of minor importance as evidenced by the Al\(^{3+}\) vs Al\(^{4+}\) diagram (Fig. 5d). The amounts of Ti in biotite range from 0-0 to 0-24 a.p.f.u. and covary with the Ti content of tourmaline (Fig. 6a). The plot R\(^{2+}\) vs Ti (Fig. 5c) is not consistent with the Ti-deprotonation substitution in biotites from the granitic suites considered. However, biotites may have incorporated Ti in accordance with the exchange vectors Al\(^{4+}\)\(\text{T}||\text{Si}\text{Al}^{3+}\) and Ti\(^{3+}\)\(\text{Al}^{2+}\)\(\text{Al}^{4+}\) (Fig. 5f). In general, the average F content in biotite increases from tourmaline-free granites to tourmaline-bearing granites, from 0-27 and 0-14 a.p.f.u. in MBG and MBL to 0-32 and 0-27 a.p.f.u. in MBTG and MBTL, respectively. The Li concentrations vary between 1000 and 3750 µg g\(^{-1}\) (unpublished data from LA-ICP-MS). However, although biotites from MBTG have higher Li contents than in MBG, Li distributions between biotites from MBL and biotites from MBTL are subtle. Calculated distribution coefficients \(K_{D} = (\text{Mg}||\text{Fe})_{\text{H}_2\text{O}}/(\text{Mg}||\text{Fe})_{\text{H}_2\text{O}})\) between coexisting tourmaline and biotite range from ~1-25 to 2 (Fig. 6b), which are somewhat lower than those reported by Henry & Dutrow (2002).

Representative muscovite analyses are reported in Table 5. Muscovite is fine- to medium-grained and occurs as discrete subhedral grains, intergrown with biotite,
locally with K-feldspar, monocrystalline overgrowths on andalusite, or as very fine-grained masses in plagioclase, cordierite, and andalusite. Based on textural and compositional criteria (Miller et al., 1983; Monier et al., 1984; Speer, 1984), subhedral muscovite with grain sizes comparable with those of biotite and plagioclase is considered to be magmatic. On the Al-Si-M* diagram (Fig. 5b), the muscovites plot close to the end-member, and their compositions appear to be controlled by the celadonite and biotite (i.e. triocahedral) substitutions. The Na/(Na + K) ratio is mostly in the range of 0.6–0.9, and the Mg/(Mg + Fe) ratio for muscovites associated with biotite (~0.57) tend to be higher than in those coexisting with tourmaline ± biotite (~0.25–0.40). The average Ti content in muscovites decreases from MBG (0.04 a.p.f.u., based on 11 oxygens) to MTG (0.02 a.p.f.u.) and from MBL (0.03 a.p.f.u.) to MTL (0.01 a.p.f.u.). The average F content increases from MBG (0.1 a.p.f.u.) to MTG (0.03 a.p.f.u.); however, it decreases from MBL (0.15 a.p.f.u.) to MTL (0.05 a.p.f.u.). Overall, the Li content ranges from 120 to 1150 μg g⁻¹ (unpublished data from LA-ICP-MS), being higher in muscovites from Jalama-type granites than in granites from the Alamo complex.

Cordierite has a Mg/(Mg + Fe) ratio that varies between 0.41 and 0.49, low Mn contents (~0.02 a.p.f.u., based on 18 oxygens p.f.u.), and Na contents ranging from 0.17 to 0.34 a.p.f.u. These Na values are higher than those reported for metamorphic cordierites (Leake, 1960; Deer et al., 1997) and are consistent with a magmatic origin (Pereira & Bea, 1994). Garnet is almandine (69–72 mol %) with high spessartine (21–34 mol %) and low pyrope (14–28 mol %) and grossular (10–13 mol %) contents. In general, the garnet grains are not zoned except for some relatively large crystals, which show Mn enrichment from core to rim.

**DISCUSSION**

Tourmaline is a common mineral in peraluminous granites of the CIZ. In some granitic bodies it constitutes the main...
ferromagnesian phase (MTG and MTL), whereas in others it occurs as an accessory mineral coexisting with biotite and cordierite and muscovite (MBTG and MBTL). This prompts questions about its stability with respect to other AFM phases, the influence of bulk composition on phase relations, and the effect of the abundance and source of boron. The occurrence of two-mica and tourmaline leucograni...
Fig. 5. (a) Plot of Al$^{VI}$ vs Mg/(Fe + Mg) for biotites from MBG, MBTG, MBL, and MBTL. NNO, nickel–nickel oxide; FMQ, fayalite–magnetite–quartz. (b) Composition of biotites and muscovites plotted in the Al–M$^{+}$–Si diagram of Monier & Robert (1996). (c) Al$^{VI}$ vs $\psi^{VI}$. This plot reflects the importance of the substitution $\text{Al}^{+}R^{2+}R^{2+}$ which accounts for the incorporation of Al into biotite and results in the formation of octahedral vacancies ($\psi^{VI}$). (d) $\text{Al}^{IV}$ vs Al$^{VI}$. The data points should fall along the line $\text{Al}^{IV} = \text{Al}^{VI}$ if the incorporation of Al$^{VI}$ into biotite occurred only by the Al-Tschermak substitution. (e) R$^{2+}$ vs Ti. The Ti-Tschermak and Ti-deprotonation substitutions do not seem to have been operative in biotites from the studied granites. (f) (Ti + R$^{2+}$) vs Al$^{VI}$. Selected exchange vectors are shown for reference.
In addition to their peraluminous composition, the CIZ tourmaline-bearing granites are characterized by compositions with Sr$_2$O$_{10}$ (Linares et al., 1987; Ramirez, 1996; Gonzalez-Menendez, 1998) and $\delta^{18}$O $> +10\%$, suggesting that they were derived from magmas generated by partial melting of metasedimentary rocks. However, although a fractional crystallization model is tenable for the Araya-type granites (Ramirez, 1996; Gonzalez-Menendez, 1998), available data do not allow us to establish whether the two-mica and tourmaline leucogranites from the Alamo complex are cogenetic or whether they were generated under different anatectic conditions.

The granites in which tourmaline occurs are saturated in quartz and albite, so the SiO$_2$ activity is fixed and the Na activity is sufficiently high to promote tourmaline crystallization. In general, textural characteristics and chemical variations suggest that tourmaline formed during a relatively early magmatic stage through to subsolidus conditions. However, although a fractional crystallization model is tenable for the Araya-type granites (Ramirez, 1996; Gonzalez-Menendez, 1998), available data do not allow us to establish whether the two-mica and tourmaline leucogranites from the Alamo complex are cogenetic or whether they were generated under different anatectic conditions.

Influence of intensive variables

Temperature and pressure have a strong control on the stability of AFM phases. However, the fact that tourmaline is stable over a wide temperature-pressure range, from roughly surface to $\sim 900\,^\circ$C and ultra-high pressure conditions (Robbins & Yoder, 1962; Benard et al., 1985; Henry & Dutrow, 2002; Werding & Schreyer, 2002; Ota et al., 2008; Marschall et al., 2009; Ertl et al., 2010; van Hinsberg et al., 2011), suggests that temperature and pressure are not critical factors governing tourmaline stability. The Araya-type granites were emplaced under epizonal conditions ($\sim 200$–$300\,\text{MPa}$) at temperatures in the range of $800$–$650\,^\circ$C using the zircon saturation thermometry of Watson & Harrison (1983), and assuming that the granites represent melt compositions. Similar temperatures were calculated by Ramirez (1996) and Gonzalez-Menendez (1998) using the zircon and monazite thermometers of Watson & Harrison (1983) and Montel (1993), respectively. According to the experimental results of Scaillet et al. (1995) and Dal'Agno et al. (1999), plagioclase and biotite compositions from Araya-type granites yield temperatures in the range of $\sim 820$–$680\,^\circ$C and $\sim 750$–$650\,^\circ$C, respectively. Lower temperatures ($\sim 700$–$650\,^\circ$C) have been inferred from the average Ti contents in biotites (according to the calibrations of Henry et al. (2005)), probably owing to the effect of...
of late-stage chloritic alteration of biotite. Cordierite is stable below ~800°C and 400 MPa in peraluminous granitic melts (Barbey et al., 1999; Acosta-Vigil et al., 2003), which is consistent with inferred crystallization temperatures in the studied granites. In the case of the Alamo complex leucogranites, thermobarometric estimates based on mineral parageneses from the host-rocks (Díez-Balda, 1986) suggest that these granites were emplaced at minimum pressures of ~250–400 MPa and temperatures of ~650–700°C. These temperatures are in agreement with those obtained from Zr thermometry and plagioclase compositions (720–640°C and ~720–670°C, respectively). Inferred temperatures from biotite compositions are ~670–650°C, a little higher than the temperature (~620°C) calculated using the Ti-in-biotite geothermometer of Henry et al. (2005). Taking into account these temperature ranges, it appears that only the MBG are above the stability field for Fe-bearing tourmaline (van Hinsberg et al., 2011), which could account for the absence of tourmaline in this granitic facies. However, the MBTG and MTG granites, and those from the Alamo complex, are within the stability field of natural tourmaline and, consequently, temperature is not considered a crucial variable in controlling tourmaline formation relative to biotite.

Tourmaline stability has been found to be sensitive to $a$(H$_2$O), although the stability fields of tourmaline and biotite overlap in $T$–H$_2$O space (Scaillet et al., 1995). Biotite can coexist with peraluminous melts over a wide range of temperatures and H$_2$O melt contents, and crystallizes earlier at higher H$_2$O contents (Maaloe & Wyllie, 1975; Clemens & Wall, 1981). According to Guillot & Le Fort (1995) the crystallization of tourmaline or biotite in granites depends on the H$_2$O content of the liquid rather than on the nature of the metasedimentary source (i.e. bulk composition), with high H$_2$O contents favouring biotite formation. Plagioclase and biotite appear in the crystallization sequence earlier than K-feldspar and quartz. In general, tourmaline seems to have crystallized later than biotite, but the local occurrence of tourmaline as inclusions in biotite (Fig. 2b) shows that the former may start crystallizing before biotite. These observations, together with the experimental data of Scaillet et al. (1995), suggest a water content in the melt at the emplacement level in the range ~6–0.75 wt % H$_2$O. On the other hand, although it is conceivable that oxidizing conditions promote the formation of tourmaline at the expense of biotite (Scaillet et al., 1995), in our case oxygen fugacity is not considered a major factor in tourmaline stability because (1) ilmenite is the main oxide mineral in both granite suites, (2) Fe in tourmaline occurs as Fe$^{3+}$, and (3) crystallization took place at approximately $\Delta$FMQ = −0.5 (Fig. 5a) for the range of temperatures estimated above.

**Boron**

The saturation of a magma with respect to tourmaline depends on the initial concentration of B and the
crystallization sequence. However, there is no consensus on the boron concentration needed to saturate a melt with respect to tourmaline. The boron contents of tourmaline-saturated peraluminous melts produced in experiments range from about 0.15 to 6 wt % B2O3 (Benard et al., 1985; Scaillet et al., 1995; Wolf & London, 1997; Spicer et al., 2004; London, 2011), suggesting that relatively low B contents are sufficient to stabilize tourmaline upon peraluminous magma crystallization.

Benard et al. (1985) argued that tourmaline is favoured in strongly peraluminous melts with high Fe/Mg ratios. The BFM diagram (Fig. 8a), however, shows that the Fe/Mg ratio is not an outstanding factor in tourmaline stability in the compositional range considered here. Like tourmaline in metamorphic rocks, which may form by net-transfer reactions from B-bearing phyllosilicates, or by reactions of silicates with incoming B-bearing fluids (Dutrow et al., 1999; Henry & Dutrow, 2002), the critical component distinguishing tourmaline from other rock-forming minerals is of course boron. In appropriately B-rich systems the most important factors controlling tourmaline stability are the abundance of Al–Fe–Mg components and melt alkalinity (London & Manning, 1995). Accordingly, boron would be the primary factor. As expected, the tourmaline-free granites studied (MBG, MBL) have the lowest boron contents. The MBTG and MBTL groups have low boron contents, reflecting the accessory nature of the tourmaline, and the MTG and MTL groups have significant boron contents that overlap (owing to the projection effect) with the compositional space of tourmaline in the BFM diagram (Fig. 8a). It is worth emphasizing that the relations shown in the BFM diagram reflect the existence of a compositional gap between tourmaline-rich (MTL and MTG) and tourmaline-poor (MBTG and MBTL) granites, consistent with the petrographic observations (Fig. 7). However, although the Harney Peak and Himalayan granites show a gap in the modal Tur/ (Tur + Bt) ratio (Fig. 7), it is not mirrored by the bulk-rock composition (Fig. 8a).

The effect of boron can be further explored in the ABF diagram (Fig. 8b). In this diagram, the B2Al2FeO7 component is used instead of B2O3 as the apex of the triangular diagram to offer a close-up of the B-poor region. The procedure consists in defining the new component B2Al2FeO7 to offer a close-up of the B-poor region. The procedure consists in defining the new component B2Al2FeO7 (i.e. Al2O3 in excess of that of feldspars) and F (i.e. FeO + MnO + MgO) reflect, respectively, the degree of peraluminosity and the mafic nature of the projected compositions. This diagram clearly supports the hypothesis that the presence of tourmaline depends primarily on the B contents in granitic rocks with variable amounts of Al2O3 and (FeO + MnO + MgO). Tourmaline-free rocks (MBG, MBL) and tourmaline-bearing two-mica rocks (MBTG, MBTL) show similar large inverse covariations of projected Al2O3 and (FeO + MnO + MgO) contents (Fig. 8b), suggesting that the variation in peraluminosity and mafic character have a subordinate effect on tourmaline stability. Similar inferences are supported by the projected field of the MTG and MTL rocks in the ABF diagram (Fig. 8b). These rocks show significant variations in the projected Al2O3 content, indicating that peraluminosity is not a key factor in determining tourmaline formation instead of biotite. In addition, the bulk-composition fields for the tourmaline-bearing two-mica rocks (MBTG, MBTL) and tourmaline + muscovite rocks (MTG, MTL) reflect a gap (Fig. 8b), which suggests a compositional restriction for the three-phase (Ms–Bt–Tur) granitic rocks. This is extremely significant for the interpretation of tourmaline stability as discussed below.

On the other hand, it should be noted that the potential protoliths (schists and gneisses) of the granites have variable B contents (∼450–550 µg g⁻¹), with some orthogneisses having significant amounts of boron (Table 2; Fig. 8b). Minimum boron contents in the melt (∼200–400 µg g⁻¹) at which tourmaline could start to crystallize can be inferred from some MBTG and MBTL compositions. These values, nevertheless, are lower than those that would be expected by considering the following: (1) the buffering effect of equilibrium among tourmaline, biotite, cordierite, and melt (∼6200 µg g⁻¹B, Wolf & London, 1997); (2) the measured B concentrations in melts equilibrated with tourmaline versus temperature (∼500–6200 µg g⁻¹B, London, 2011); (3) the boron contents (>500 µg g⁻¹) derived from the experiments of Benard et al. (1985) and Scaillet et al. (1995). Experimental studies indicate that, regardless of other variables and at a temperature between 600 and 750°C, a critical boron threshold in the range of ∼500–3000 µg g⁻¹ must be achieved before tourmaline becomes stable in granitic melts. Lower boron contents would be indicative of boron mobility in exsolving fluids. Evidence in support of this comes from the widespread occurrence of tourmaline in the metamorphic aureoles associated with Araya-type granites. In the case of the Alamo complex the relatively low melt fractions produced during the formation of peraluminous leucogranites (∼20%, according to Castro et al., 2000) would yield a wide range in the boron content of ∼250–5000 µg g⁻¹. Accordingly, tourmaline-bearing leucogranites with boron contents lower than ∼500 µg g⁻¹ could reflect a significant loss of boron. Based on isotopic differences between late tourmalinite and granitic tourmaline, Pesquera et al. (2005) documented a boron loss of the order of 50% for the Martinamor leucogranite (location 2, Fig. 1). We are aware that these calculations are oversimplified given the mode of occurrence of the granitic bodies.
in the Alamo complex and the variability of the metasomatic effects produced in the surrounding rocks. However, tourmaline-bearing granitic sheets with relatively low boron contents, associated with tourmaline-free metasedimentary rocks, occur in some places. Based on these considerations, and on the range of temperatures estimated above, we infer that the boron content needed for tourmaline saturation in granitic melts may be as low as $\frac{C24}{500}^900^\circ\text{C}$. 

Peraluminosity and mafic components

Wolf & London (1997) stressed the influence of peraluminosity, measured by the parameter ASI, on tourmaline stability. They found that tourmaline becomes unstable in melts with ASI $<1.2$ at 700–750°C regardless of their boron content, and that more boron and/or higher ASI are required to stabilize tourmaline with increasing F contents. However, the ASI parameter cannot be used to monitor the activity of Al$_2$O$_3$ in mineral–melt systems because the solubility of alumina is affected by other components such as Fe, Mg, and B.

Further insights into the effect of peraluminosity and mafic components is revealed in the AFM diagram, which shows the Al$_2$O$_3$/(FeO + MgO + MnO) and MgO/(FeO + MgO + MnO) ratios (henceforth the mg-value) after projection from quartz, kfs, ap, ilmenite, and H$_2$O (Fig. 9a). It is important to realize that the projected Al$_2$O$_3$ content is that in excess of the Al$_2$O$_3$ needed to form feldspars, and that the new component FeO is in fact (FeO + MnO). Inasmuch as tourmaline plots between muscovite and cordierite, the degree of peraluminosity and the mafic nature do not appear to be of the utmost importance in dictating tourmaline formation (Fig. 9b). Such an intermediate position makes tourmaline potentially present in a number of relatively high-Al and low-Al compositions. This is clearly illustrated by the MBTG group, which ranges from moderate to high Al$_2$O$_3$(FeO + MnO + MgO) contents (Fig. 9b). The mg-values of associated minerals increase with increasing Mg contents in the bulk-rock compositions, as would be expected from the theory of phase relations in high-variance assemblages. A decrease in Mg is accompanied by an increase in the projected Al$_2$O$_3$ content of both biotite and coexisting tourmaline. This indicates that the differentiation trend involves an increase in FeO + MnO. High-Mg rocks contain cordierite + biotite $\pm$ tourmaline, suggesting that the presence of these phases is controlled by the bulk-rock composition, whereas low-Mg rocks contain Mn-rich garnet + tourmaline, but not biotite. Based on the AFM liquidus topology of Abbott & Clarke (1979) and Abbott (1985), the assemblage muscovite + biotite $\pm$ cordierite should evolve towards lower mg-values, through the three-phase assemblage Ms $+$ Bi $+$ Tur, until reaching the assemblage tourmaline + muscovite $\pm$ garnet upon decreasing temperature (Fig. 9c). The occurrence of Mn-rich garnet is attributable to the strong partitioning of Mn$^{2+}$ into the liquid relative to biotite, cordierite, or muscovite (Abbott, 1985). Consequently, the mg-value is not a overriding
Fig. 9. AFM diagrams (projected from Qtz, Kfs, Ilm, H₂O, and the indicated exchange vectors that allow condensation of the compositional space) showing mineral and bulk-rock composition fields for the studied granitic rocks (symbols as in Fig 8). Shaded areas show representative compositional ranges for various types of granites. The bulk-rock composition of gneisses and schists (possible protoliths), and granitic samples from the literature, are also plotted for comparison, in (d). It should be noted that tourmaline plots between muscovite and cordierite, and the MBTG group shows a wide range of Al₂O₃/(FeO + MgO + MnO) contents.

(continued)
Fig. 9. (Continued).
factor for tourmaline stability in peraluminous melts, but it is an important variable for the stability of coexisting cor-
dierite, biotite, and garnet. The assemblage Ms + Bt + Tur
is stable in leucocratic and relatively mafic rocks regardless
of their peraluminous nature, but field and petrographic
observations suggest that its stability field is very narrow.
This feature is also observed in the Harney Peak, Margeride, and Himalayan granites (Fig. 9d). The potential
protoliths (metapelites and gneisses) of Spanish
Variscan granites and leucogranites are relatively mafic and Mg-rich (Fig. 9d), and it is expected that partial
melting of these rocks produces Mg-poorer leucocratic to
mesocratic peraluminous melts, in agreement with experi-
mental work (e.g. Castro et al., 1999, 2000; Patiño-Douce,
1999).

On the other hand, some researchers have argued that Ti
concentrations in granitic melts are as important as B con-
centrations in controlling the relative stability of biotite
and tourmaline (Nabelek et al., 1992; Wilke et al., 2002). Ti
may stabilize biotite at the expense of tourmaline, even at
rather high B contents in granitic melts (Nabelek &
Bartlett, 1998). However, the effect of Ti on biotite-bearing
equilibria appears to be more complex than previously
thought, because the stabilizing effect of Ti becomes sig-
nificant only at temperatures characteristic of granuliteacies (Patiño-Douce, 1993). In the case of the CIZ
Variscan granites, and in other examples (e.g. the
Himalayan granites), there is a significant overlap in the
Ti contents of tourmaline-free (average 0-14-0-36 wt %,
Table 1) and tourmaline-bearing granites (average 0-06–
0-29 wt %, Table 1). Accordingly, it is difficult to support
the suggestion that high TiO2 contents in the melt prefer-
entially stabilize biotite instead of tourmaline, regardless
of the B content in melt.

EVOLUTIONARY MODEL
Based on the above considerations and phase relationships,
we have developed a generalized partial melting model
for the generation of boron-poor and boron-rich granitic
melts and magmatic fractionation.
Partial melting of gneiss or schist protoliths such as those
of the CIZ Variscan belt would produce a residue mostly
comprising Bt ± Crd ± Sil (e.g. Bea, 1991; Pereira & Bea,
1994) and a peraluminous granitic melt that may be satu-
rated in tourmaline or not. This is shown by the schematic
phase relations for subsolidus conditions, partial melting,
and crystallization from melts depicted in the ABF dia-
grams of Fig. 10a, b and c, respectively. Taking into account
that the reactions indicated below are based only on the
projected phase relations (i.e. the projection phases Qtz,
Kfs, Pl, and Ap, which should be present in the reactions
to maintain mass balance, are not considered), three pro-
cesses are considered.

1. Very low melt fractions during partial melting of
gneisses or schists, where B-rich melts (Fig. 10b) are likely
to be formed because of the low mineral/melt distribution
coefficient of boron, which behaves as an incompatible
element in most migmatitic or magmatic systems
(Lecman et al., 1992). In the case of the Alamo complex,
significant boron amounts may have been incorporated
into granitic melts by partial melting of local metamorphic
basement containing tourmaline-rich gneisses, such as has
been documented by Pesquera et al. (2005). This kind of
process would yield Ms–Tur magmas with variable
tourmaline/muscovite ratios upon crystallization via the
reaction L1 = Tur + Ms + L2 (Fig. 10c). Subsequent fraction-
ation of muscovite in these magmas contributes differ-
entiated muscovite–tourmaline granitic melts similar to
the MTL group (Fig. 10b and c). However, tourmaline
crystallization would interrupt the trend of increasing B
in the ABF diagram (small arrow in Fig. 10c).

2. Melts derived from higher fractions of partial melt-
ing are relatively rich in boron, but biotite is presumed to
form part of the crystallization assemblage. These melts
would be similar to those giving rise to the MBTG and
MBTL groups (Fig. 10c and d), and phase relations indi-
cate that the amount of tourmaline is relatively low. Tour-
malone should form after the reaction L1 = Tur + Bt +
Ms + L2 (B-rich melt Tur–Bt–Ms in Fig. 10c). Fractionation
of biotite from these magmas yields differentiated Ms–Tur
granitic melts as described above (Fig. 10b and c).

3. Finally, greater degrees of melting would form
B-deficient melts, from which only muscovite and biotite
are expected to crystallize (Fig 10b and c). These magmas
are similar to those that produced the MBG and MBL
groups (Fig. 10d). However, biotite and/or muscovite frac-
tionation can produce melts with higher B contents and,
consequently, give rise to Ms–Bt–Tur granitic bodies. In
this case, tourmaline would crystallize via the reaction
L1 = Tur + Bt + Ms + L2 (Fig 10c), as described above. If
fractionation allows a residual melt to have a composition
similar to the B-rich melt (i.e. MTG; Tur–Ms in Fig 10c),
tourmaline should form after the reaction L4 = Ms +
Tur + L5, as above. Any residual biotite that may be pre-
sent in this magma would react with the melt to produce
further tourmaline. This interpretation is similar to the
peritectic reaction L + biotite = tourmaline, progressively
displaced to the right with decreasing T and increasing B
activity, such as Shearer et al. (1987) proposed for the
Harney Peak granite. Those workers argued that the con-
tinuous FeMg± exchange reaction involving the crystal-
lization of garnet and biotite covers a wide range of Mg/
(Mg + Fe) compositions in the AFM projection that essen-
tially separates tourmaline-bearing assemblages from
biotite + muscovite assemblages. According to London &
Manning (1995) the very low mafic content of the
Hercynian granites from SW England relegates the
Fig. 10. A series of ABF diagrams depicting model phase relations for (a) pre-melting, (b) melting, and (c) crystallization conditions based on the studied granitic rocks. It should be noted that the predicted primary melt compositions marginally intersect the three-phase field Bt–Ms–Tur. The melt trends expected for fractional crystallization of muscovite±biotite are indicated in (b) and (c). Bulk-rock compositions of MBG and MBL, MBTG and MBTL, and MTG and MTL (shaded areas) are plotted in (d).

(continued)
Fig. 10. (Continued).
biotite–tourmaline reaction relationship to a very limited buffering capacity. Hence, there is not a wide range of overlap between ‘biotite granites’ and ‘tourmaline granites’ in terms of their mafic phases.

The phase relations and differentiation paths depicted in Fig. 10 reflect the antipathetic relationship between tourmaline and biotite in granitic systems. The bimodality in mineral assemblages (i.e. tourmaline granites and biotite granites) is a consequence of the restricted access to the three-phase field Tur–Bt–Ms of most granitic melts. That is, melts produced upon partial melting of common B-poor rocks have a composition undersaturated in B under supersolidus conditions (Fig. 10b). Upon crystallization, these compositions approach the B-saturation surface, which is depicted in Fig. 10b for supersolidus conditions and in Fig. 10c for solidus conditions. As shown in Fig. 10c, most primary magmas lie in the field of Tur–Ms or Bt–Ms, and only a very restricted range of compositions lie within the Tur–Bt–Ms field (very close to the Ms apex) above the B-saturation surface. Upon crystallization and fractionation, Bt–Ms magmas may yield small pods of Tur–Bt–Ms and Tur–Ms rocks, as seen for example in the Araya-type granites. Upon crystallization of Tur–Ms magmas, no biotite is formed. Upon crystallization of Tur–Bt–Ms magmas, small pods of Tur–Ms are formed. Therefore, melts of common composition are unlikely to produce Tur–Bt–Ms assemblages.

This explanation is consistent with the chemical characteristics and mineral assemblages of Variscan peraluminous granites from the CIZ. However, unravelling these kinds of complexities by using phase diagrams has proved to be difficult. Partitioning of boron between minerals and melt data are required to better define the evolution of the system, and thus to assess why partial melts have limited access to the three-phase Tur–Bt–Ms field. A small variation in the partial melting path defined by primary melts (blue arrow in Fig. 10b) would cause B-poor melts to evolve suddenly towards B-rich melts, which, in turn, would potentially yield tourmaline–muscovite-rich facies (Fig. 10c). If the melts evolve across the three-phase Ms–Bt–Tur field, mineral assemblages with continuous variations in modal Tur/(Tur + Bt) ratios are presumed to form. However, we do not observe such a transitional trend, nor does it seem to have been documented in other studies (e.g. Scaillet et al., 1990; Nabelek et al., 1992; Guillot & Le Fort, 1995; Searle et al., 1997; Visona & Lombardo, 2002), suggesting that the phase relations depicted in Fig. 10 closely approach the behaviour of natural systems.

Quantification of the evolution of boron and tourmaline trends in granitic systems requires further research on outstanding aspects, including the following: (1) boron partitioning between minerals, melts and fluids during melting, and crystallization from a melt (which depend on P, T, and bulk composition); (2) the minimum boron contents required for tourmaline stability in peraluminous granitic melts; (3) the influence of tourmaline on the melt–solid phase relations and thermodynamic modelling.

CONCLUDING REMARKS

Evaluating the occurrence of tourmaline in granitic rocks provides important insights into the evolution of boron in peraluminous granitic systems. Tourmaline may coexist with biotite in CIZ peraluminous granites, but never in similar modal proportions. When biotite is dominant, tourmaline is an accessory or absent, and vice versa, so that these minerals tend to show an antipathetic trend in granitic systems. Accordingly, two main AFM mineral assemblages can be defined in the CIZ peraluminous granites: (1) biotite + muscovite ± cordierite ± tourmaline ± andalusite, which occurs in Araya-type granites; (2) muscovite + tourmaline ± biotite ± garnet, typical of leucogranites from the Alamo complex. Relative to Araya-type granites, and for equivalent facies, the Alamo-complex leucogranites are characterized by slightly higher Al2O3 contents, lower K2O/Na2O ratios and ΣREE, and lower contents of several trace elements including Li, Rh, Ba, Y, Nb, Zr, U, and Th. The δ18O values of the studied granitic samples range from 10 to 13‰, but they do not correlate with the presence or absence of tourmaline.

The occurrence of tourmaline in granitic rocks is considered to be a function of (1) the B content of the protolith and (2) the extent of melting and fractionation. These processes govern the amount of boron in the melt, which is the primary variable dictating tourmaline formation in peraluminous granites. Minimum boron contents of the order of ~500–3000 μg g⁻¹, depending on the temperature of the melt, are required for tourmaline to become stable in granitic melts. Although the activities of Al, Fe, Mg, and Ti are important in controlling the stability of tourmaline relative to other AFM phases (biotite, cordierite, etc.), the phase relations portrayed in the AFM, BFM, and ABF diagrams are consistent with this boron threshold, which must be exceeded before other variables are effective. No matter what physical and chemical conditions exist, granitic melts with boron contents lower than the critical values will not form tourmaline. Tourmaline and biotite tend to show an antipathetic trend in granitic systems because common granitic melts have very restricted access to the three-phase Tur–Bt–Ms field, as evidenced from phase relations and differentiation paths depicted in the ABF diagram.

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