Multistage boron metasomatism in the Alamo Complex (Central Iberian Zone, Spain): Evidence from field relations, petrography, and ⁴⁰Ar/³⁹Ar tourmaline dating

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ABSTRACT

The Alamo Complex consists of structural-metamorphic domes surrounded by low-grade metasedimentary rocks of Upper Proterozoic to Lower Cambrian age that form part of the Schist Graywacke Complex (Central Iberian Zone, Spain). Tourmaline is ubiquitous throughout the domes, in which it occurs in tourmalinites, psammo-pelitic schists, quartzites, gneisses, migmatites, leucogranites, aplo-pegmatites, and quartz veins. Overall, tournaline compositions can be described within the four component system schorl-dravite-foitite-magnesiofoitite, with $K_2O < 0.23\%$, low Ca contents, Mg/(Mg+Fe) = 0.25-0.71 and X/(X+Na) = 0.18-0.43, where X = vacancies in the X site. Field relations and petrographic observations, combined with tourmaline ⁴⁰Ar/³⁹Ar data, provide evidence of intense boron metasomatism affecting this region. Tournaline ⁴⁰Ar/³⁹Ar step-heating spectra for Cambrian-Ordovician orthogneisses are complex, yielding a pseudo-plateau age of ~370 Ma that is interpreted to reflect Variscan rejuvenation of older tourmaline. Tourmaline ⁴⁰Ar/³⁹Ar data for mylonitized and folded tourmalinites yield disturbed spectra with pseudo-plateau ages of ~355-342 Ma that are unsuitable for precise age determination. These ages, however, are consistent with published ages (340-350 Ma) for the second Variscan deformation (D₂). Tournaline from fine-layered tournalinite and metasedimentary rocks yield well-defined plateau ages of 317 and 315 Ma, respectively, recording an additional metasomatic event concomitant with anatexis and evolution of B-bearing granites, pegmatites, and hydrothermal fluids. The different tourmaline-forming stages reflect significant boron cycling within the continental crust of the Central Iberian Zone, driven by deformation, metamorphism, and magmatism during the Variscan orogeny. Boron-rich aqueous fluids related to Cambro-Ordovician magmatism are considered to be the primary source of boron.

Keywords: Tourmaline, petrography, chemical composition, ³⁹Ar/⁴⁰Ar dating, Alamo Complex, Central Iberian Zone, Spain

INTRODUCTION

Although boron is one of the less abundant elements of the Earth, it is nevertheless a widespread constituent of the continental crust, being enriched in sedimentary, igneous, and metamorphic rocks. The preference of boron for aqueous fluids and its susceptibility to fractionation make boron a useful tracer for hydrologic and magmatic/hydrothermal processes (Leeman and Sisson 1996). The formation of boron-bearing fluids involves several crustal processes such as metamorphic devolatilization and magmatism. Boron is believed to largely reside in minerals such as clays, micas, and tourmaline (Leeman and Sisson 1996). The latter is by far the main sink for boron in crustal rocks with a wide physical and chemical stability and mode of occurrence (Henry and Dutrow 1996). This is due, in part, to the ability of the tourmaline structure to accommodate various elements of different sizes and valence states (Hawthorne and Henry 1999). The chemical variability, together with its refractory character and ubiquity, make tourmaline a powerful tool in petrology and a potentially important geochemical monitor.

This work builds upon previous studies of tourmaline-rich rocks in the Central Iberian Zone (Pesquera et al. 2005). It aims to contribute to an understanding of the relationships between tourmalinization and geological processes, based on field and petrographic observations in conjunction with ⁴⁰Ar/³⁹Ar tourmaline data. In this regard, there is conflicting evidence concerning the reliability of the ⁴⁰Ar/³⁹Ar dating method in tourmaline. Ring-silicates have been generally considered the least retentive minerals for Ar and tend to trap excess Ar (Dalrymple and Lanphere 1969; Fortier and Giletti 1989). However, Andriessen et al. (1991) found K-Ar ages to be consistent with the known age constraints, suggesting a closure temperature similar to that of hornblende (~500–550 °C). Some studies indicate that tourmaline is able to yield reasonably acceptable ages of tourmalinization and metamorphism (Fitch and Miller 1972; De Jong 1991). Further difficulties arise because (1) of the very low K₂O contents, except for some tourmalines with >2 wt% K₂O such as the "potassium-dravites" from high-P terrains (e.g., Shimizu and Ogasawara 2005) and (2) the tourmaline may develop different growth stages during metamorphism (Henry and Dutrow 1996). Despite these problems, and due to the small variations in Rb/ Sr and Sm/Nd ratios in tourmaline, the 40Ar/39Ar dating method

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might be a good option. It is with this purpose that we have studied pre-Variscan tourmaline-bearing orthogneisses, Variscan leucogranites, and several spatially associated tourmaline-rich rocks and veins that occur in Upper Proterozoic metasediments from the Central Iberian Zone (CIZ).

GEOLOGICAL BACKGROUND

The Central Iberian Zone consists of Proterozoic to lower Paleozoic metasedimentary rocks and orthogneisses, intruded by numerous syn- or late-kinematic Variscan granitoids (Martínez Catalán et al. 2004). It includes two domains (Fig. 1): (1) the narrow Ollo de Sapo Domain to the north, where an abundance of Cambro-Ordovician metavolcanics and metagranites crop out (Bea et al. 2006) and (2) the broad Schist-Graywacke-Complex (SGC) Domain to the south, characterized by a large Upper Proterozoic-Lower Cambrian metasedimentary sequence (Díaz Montes et al. 2004). A conspicuous feature of the northern part of this domain is a set of small bodies of pre-Variscan gneissose granites that form part of the Alamo Complex. These are located to the south of the Ollo de Sapo Domain and constitute a discontinuous belt that extends from west to east about 150 km (Fig. 1). In this belt, structural-metamorphic domes, which are made up of pelitic and psammitic schists, gneisses, migmatites, aplo-pegmatites, and leucogranites, occur within a low-grade metasedimentary sequence of Upper Proterozoic to Lower Cambrian age. Subordinate amounts of amphibolites and calc-silicate

rocks are also observed. Tourmaline is relatively abundant and widespread throughout the metamorphic domes.

The tectonic evolution of Central Iberia is complex (see Abalos et al. 2002 for an overview). The first phase of Variscan deformation (D_1) is related to crustal shortening that gave rise to thickening of the crust to ~50 km (Ferreira et al. 1987; Serrano Pinto et al. 1987). Based on differences in the geometry of D₁ folds, Díez Balda et al. (1990) distinguished two structural domains within the CIZ: (1) the domain of recumbent folds in the northern part of the CIZ, and (2) the domain of vertical folds that occupies most of the central and southern part of the CIZ. The age of the D_1 event, not yet well known, has been estimated from Late Devonian to Early Carboniferous. The second deformation phase (D2), notably diachronous and variably intense, was related to the protracted extensional collapse of the orogen. In the Alamo Complex, the effects of D_1 are significantly masked by D₂ whose structural features are closely related to the metamorphic zonation. This second deformation caused isoclinal to sheath folds with a strong, locally mylonitic, subhorizontal foliation (Díez Balda 1986). The age of D₂ for this area can be estimated from the synkinematic Cespedosa granite, neighboring the Alamo gneisses, which has a Rb-Sr age of 344 ± 5 Ma (Bea et al. 1999). The third Variscan deformation phase (D_3) is characterized by major folds, which define a set of subvertical antiforms and synforms that fold the extensional D₂ shear zones, and localized subvertical shear zones. During



FIGURE 1. Simplified geological map (after Martínez-Catalán et al. 2004) showing the location of the Alamo Complex including the tectonometamorphic domes: (1) Pereruela; (2) Martinamor; (3) Alamo; (4) Castellanos; (5) Gallegos de Sobrinos; and (6) Sierra de las Yemas.

D₁, the rocks recorded a clockwise *P*-*T* path that reached pressures of ~4.5 kbar at temperatures of ~600–700 °C, followed by a nearly isothermal decompression during D₂ leading to low pressure conditions (~2 kbar) that account for the stabilization of andalusite. More details about the structural and metamorphic evolution of this region can be found in Díez Balda (1986) and Díez Balda et al. (1995).

The igneous rocks from the Alamo Complex crop out in several areas and include two main groups. The first group consists of small bodies of metavolcanic rocks and metagranitoids, considered to be Cambro-Ordovician in age (Bea et al. 2006, 2007), which are now augen-gneisses interlayered with psammo-pelitic schists. They were strongly deformed during the Variscan and are composed of quartz + plagioclase + alkali feldspar + biotite + muscovite + apatite \pm tourmaline. The second group consists of syn- to late-kinematic, tourmaline-bearing leucogranitic and pegmatitic bodies that alternate with metamorphic rocks and are parallel to S₂.

ANALYTICAL METHODS

Tourmaline compositions for representative samples from tourmaline-rich rocks, orthogneisses, granites, and veins were determined at the Granada University with a Cameca SX50 electron microprobe. Operating conditions included an acceleration potential of 20 kV, a 30 nA beam current, a beam diameter of 2 μ m, and 20–30 s count times on peaks and backgrounds. Natural and synthetic standards were used for tourmaline analyses including: natural fluorite (F), natural sanidine (K), synthetic MnTiO₃ (Ti, Mn), natural diopside (Ca), synthetic Fe₂O₃ (Fe), natural albite (Na), natural periclase (Mg), synthetic SiO₂ (Si), synthetic Cr₂O₃ (Cr), and synthetic Al₂O₃ (Al). To better characterize the tourmaline composition for the selected samples, EPMA data were supplemented by Li (LCP-MS) and Fe³⁺ (Mössbauer spectroscopy). The operating conditions were identical to those described in Pesquera et al. (2005). The results reveal that Li and Fe³⁺ are present in insignificant quantities, lower than 190 ppm and 0.01 apfu, respectively. Accordingly, structural formulae were calculated on the basis of 15 (T + Z + Y) cations, assuming all Fe as Fe²⁺ and that boron has a stoichiometric value of 3 apfu.

Six rock types were selected for ⁴⁰Ar/³⁹Ar analysis of tourmaline: orthogneiss, mylonitized tourmalinite, folded tourmalinite, fine-layered tourmalinite, tourmaline-rich psammo-pelitic schist, and a tourmaline-bearing leucogranite. Biotite grains from the orthogneiss were also analyzed. Tourmaline and biotite separates were prepared using magnetic separation. Single tourmaline and biotite crystals from 0.15-0.25 mm in size were optically examined with a binocular stereoscopic microscope. In all cases, individual tourmaline and biotite grains were hand-picked to greater than 99% purity. Tourmaline samples were analyzed by IR-laser stepwise heating techniques. Argon isotope ratios were measured on a 5400 Ar mass spectrometer at the Guangzhou Institute of Geochemistry. Tourmaline samples and a monitor standard DRA1 (sanidine with an age of 25.26 ± 0.07 Ma; Wijbrans et al. 1995) were irradiated at the 49-2 reactor in Beijing for 55 h. Correction factors for interfering argon isotopes derived from Ca and K are (39Ar/37Ar) $Ca = 8.984 \times 10^{-4}$, $({}^{36}Ar/{}^{37}Ar)Ca = 2.673 \times 10^{-4}$, and $({}^{40}Ar/{}^{39}Ar)K = 5.97 \times 10^{-3}$. To obtain J-values for the samples, the monitor DRA1 was packed between every five samples in quartz sample tubes, each tube containing 10 to 15 packets of DRA1. From each packet containing DRA1, five splits were used to measure the J-values, and the weighted mean was taken as the J-value. DRA1 is very homogeneous and replication is usually excellent (Wijbrans et al. 1995). Based on the J-values and the positions of DRA1 in the sample tube, a regression line for each sample tube was obtained, and the J-values of the samples were calculated by interpolation from the regression line. The J-value uncertainty of 0.15% (1 σ) was propagated into the age calculations. Prior to analysis, blanks were reduced by heating the whole apparatus to 150 °C using heating tape and the sample chamber was placed under an infrared lamp for ca. 24 h. The blanks are ³⁶Ar (0.002-0.004) mV, ³⁷Ar (0.0002-0.0006) mV, 38Ar (0.0004-0.0015) mV, 39Ar (0.0025-0.0051) mV, and 40Ar (0.51-1.3) mV. The sample/blank ratios of ³⁹Ar range from 33 to 910. The samples were heated by the MIR10-50W CO2 laser, which is operated using the software of the New Wave Research Laser Ablation System version 1.8.13.0. The released gases were purified by two SorbAC NP10 pumps (made by the SAES Advanced Technologies). One was operated at ca. 400 °C and the other at room temperature.

The purification time was 5 min for biotite and 10 min for tourmaline. The purified gas was then analyzed for argon isotopes in the 5400 Ar mass spectrometer using the Noble Gas Software version 2.93. The analytical data was calculated using the ArArCalc software (Koppers 2002). More details on the analytical methods can be found in Qiu and Jiang (2007).

PETROGRAPHY AND TOURMALINE COMPOSITION

Tourmaline is relatively abundant in the Alamo Complex. In addition to being the principal ferromagnesian silicate mineral of tourmalinite (>15–20% tourmaline by volume), it occurs in clastic metasedimentary rocks, pre-Variscan orthogneisses, Variscan leucogranites, aplo-pegmatites, and veins.

Tourmalinites are conspicuous minor lithologies throughout the antiforms, which occur as discontinuous stratiform bodies within metasediments from the SGC. Most of the tourmalinites are fine grained (usually <1 mm), dark brown to black rocks, with variable amounts of tourmaline (up to ~90%), and with a massive to layered appearance. The layering is commonly defined by the alternation of fine-scale tourmaline-rich laminae with quartz-rich laminae (Fig. 2a). Oval nodules (up to 20 cm in length), composed of quartz and tourmaline, occur locally within the schists. Quartz with variable amounts of plagioclase, muscovite, and biotite are the most abundant minerals that coexist with tourmaline in the tourmalinites; apatite and rutile are the main accessory minerals.

At several localities tourmalinites are deformed and recrystallized as a result of Variscan deformation and metamorphism. In thin section, these tourmalinites show two geometrically defined foliations, S1 and S2, with tourmaline grains aligned parallel to both foliations. This suggests a syn-tectonic mineral crystallization with respect to D_1 and D_2 (Fig. 2b). S-C structures, transposition, σ - and δ -type tourmaline porphyroclasts, and more complex forms are characteristic features that have resulted from mylonitization (Fig. 2c). The porphyroclasts are made up of numerous very small tourmaline crystals coexisting with interstitial quartz \pm plagioclase \pm rutile ± pyrite. They are commonly linked to long tails, extending mainly along S₂ surfaces where fine-grained tourmaline and quartz have been incorporated into the mylonitic matrix (Figs. 2c and 3a). Boudinage affecting tourmaline layers and crystals is often associated with mylonitization. In some cases, the boudinage is accompanied by tourmaline overgrowths that tend to heal the separated boudins (Fig. 3b). Locally, the S₂ foliation is overprinted by a discrete crenulation cleavage (S₃) in tourmalinites, defined by the concentration of tourmaline crystals and tourmaline-bearing dark seams with wriggly to smooth appearance. In addition to discontinuous deformation, crystal-bending and sweeping extinction with development of subgrains and granoblastic textures are relatively common (Figs. 3a and 3c). There are also tourmaline-rich rocks (Fig. 2d) in contact with granitic and pegmatitic bodies that are largely unaffected by the deformation, and are thought to reflect later tourmalinization events. Textural and geochemical data are consistent with a psammo-pelitic protolith of the tourmalinites (Pesquera et al. 2005).

Most of the tourmaline crystals from the tourmaline-rich rocks are weakly zoned, perhaps reflecting annealing during deformation and metamorphism, with non-systematic gradational changes in color from reddish brown cores to yellowish brown or green rims. Back-scattered electron (BSE) images reveal the presence of embayed interiors truncated by external zones as well as cellular textures. Overall, tourmaline compositions fall within the alkali field with low Ca contents, Mg/(Mg+Fe) = 0.608-0.723 and X/(X+Na) = 0.176-0.43, where X represents X-site vacancy. K₂O ranges from 0.02 to 0.23 wt% (Table 1). The patterns of chemical zoning are complex, commonly involving significant fluctuations in Al, Fe, Mg, Ti, Na, and F. However, it is worth emphasizing that in some samples from the Alamo Complex, tourmalines show a general trend in which cores tend to be richer in Al and poorer in Ti than the rims (Pesquera et al. 2005).

Tourmaline from the orthogneiss samples is an accessory or minor mineral (<2 vol%). It occurs as very fine- to medium-grained, subhedral to anhedral, pale-green to green-colored crystals, and as irregularly shaped clusters associated with quartz and feldspar. Tourmaline porphyroclasts (usually <5 mm) surrounded by a foliation defined by micas are commonly present (Fig. 2e). Small euhedral tourmaline crystals (<100 μ m) included in feldspar megacrysts have been also observed. The compositional range of orthogneiss tourmaline is narrower than that of the tourmalinites, with Mg/(Mg+Fe) = 0.59–0.624, X/(X+Na) = 0.258–0.283, and K₂O contents ranging from 0.04 to 0.08 wt% (Table 1). Irregularly shaped tourmaline grains coexisting with cordierite and sillimanite locally occur in migmatitic gneisses. Kawakami (2001) described a similar association in rocks of the tourmaline-out isograd in the Ryoke metamorphic belt.

Two distinct tourmaline-bearing granitic rocks are found in the Alamo Complex: (1) two-mica leucogranites, with biotite + muscovite + plagioclase + K-feldspar + quartz + apatite \pm tourmaline \pm Al silicates \pm ilmenite, and (2)



FIGURE 2. Photomicrographs, 40 Ar/ 39 Ar apparent age and K/Ca apparent spectra, and 36 Ar/ 40 Ar vs. 39 Ar/ 40 Ar isochron plots. (a) Fine-layered quartz (light gray)-tourmaline (dark gray) tourmalinite. (b) Crenulation cleavage (S₂) in quartz-tourmaline tourmalinite with asymmetric microfolds. The foliation is defined by cleavage domains and microlithons (fold hinge areas). (c) Mylonitic tourmalinite in a section perpendicular to foliation and parallel to stretching lineation. Notice the tourmaline porphyroclasts (dark gray) as "pull-aparts" coexisting with σ - and δ -type porphyroclasts that are wrapped by the mylonitic foliation. There is a sinistral shear sense. The light layers are made up of quartz ± plagioclase. (d) Post-tectonic tourmaline-rich micaschist. (e) Tourmaline-bearing orthogneiss. The foliation (running from top right to bottom left) wraps around the tourmaline (Tur) and plagioclase (PI) megacrysts. (f) Tourmaline-rich leucogranite.



FIGURE 2.—CONTINUED

tourmaline leucogranites (Fig. 2f), with the assemblage muscovite + tourmaline + albite + K-feldspar + quartz + apatite \pm garnet. Tourmaline occurs as black, fine- to medium-grained crystals generally disseminated throughout the granite, but is also concentrated in ovoid or lenticular clots (usually <1 cm). In thin section, tourmaline crystals are usually unzoned or weakly zoned with euhedral to anhedral shapes, and are typically embayed by quartz \pm feldspar. Pleochroism varies from

pale or bluish-green to green. Small euhedral tourmaline grains may be enclosed by muscovite and garnet. Tourmaline compositions plot in the schorl field with Mg/(Mg+Fe) and X/(X+Na) ratios of 0.249–0.486 and 0.254–0.351, respectively, and K₂O contents ranging from 0.04 to 0.07 (Table 1).

Sub-millimeter to meter scale veining is extensive throughout the antiforms in the Alamo Complex. Tourmalinite layers show abundant pre-, syn-, and post-



FIGURE 3. (a) Mylonitic tourmalinite showing a "tadpole" porphyroclast made up by numerous small crystals of tourmaline with interstitial quartz, rutile, and pyrite. The light layers consist of quartz + plagioclase. (b) Micro-boudinage of tourmaline in psammitic schist. Notice the tourmaline fibers that tend to mend the separated boudins. (c) Recrystallized syntaxial quartz-tourmaline vein in tourmalinite displaying a granoblastic texture. (d) Partially resorbed tourmaline in a gneiss from the migmatite zone, associated with quartz (Qtz), biotite (Bt), sillimanite (black). Irregularly shaped embayments indicate that tourmaline was unstable in the rock prior to anatexis.

TABLE 1. Representative compositions (wt%) of tourmalines from different associations in the Alamo Complex

Occurrence	Tourmalinites					Tourmaline-rich schists			Orthogneisses			Granites			Veins			
SiO ₂	36.07	36.54	36.01	36.61	36.41	36.31	36.88	36.46	36.10	35.60	35.48	35.76	36.14	35.25	35.17	36.01	36.81	36.06
TiO ₂	0.47	0.31	0.37	0.51	0.67	0.87	0.81	1.19	0.97	0.84	1.06	1.10	0.47	0.45	0.51	0.75	0.82	1.17
AI_2O_3	33.43	34.67	33.94	32.63	33.47	31.22	32.91	31.07	33.63	34.10	33.99	34.05	34.33	33.47	33.57	33.83	34.22	31.97
Cr ₂ O ₃	0.02	0.06	0.04	0.02	0.05	0.04	0.06	0.03	0.03	0.04	0.04	0.01	b.d.	b.d.	b.d.	b.d.	0.02	b.d.
FeOt	6.58	6.37	6.90	5.97	6.95	6.20	5.13	5.80	6.73	6.73	6.55	7.02	8.88	12.42	11.83	8.77	5.74	11.08
MnO	0.05	0.05	0.03	0.05	0.04	0.08	0.03	0.02	0.06	0.07	0.05	0.05	0.05	0.13	0.12	0.03	0.04	0.06
MgO	6.72	6.26	6.00	7.25	6.16	7.51	7.53	7.90	6.21	6.20	6.09	5.68	4.25	2.31	2.72	4.65	6.32	3.61
CaO	0.27	0.17	0.26	0.05	0.35	1.04	0.60	1.19	0.48	0.55	0.47	0.53	0.22	0.16	0.10	0.30	0.41	0.06
Na₂O	1.97	1.71	2.03	2.60	2.15	2.06	2.00	1.80	2.07	2.06	2.13	2.04	1.95	2.00	2.16	2.17	1.97	2.09
K₂O	0.23	0.15	0.10	0.03	0.02	0.03	0.02	0.02	0.05	0.08	0.05	0.04	0.04	0.05	0.05	0.07	0.01	0.05
F	0.28	0.16	0.26	1.01	0.30	0.59	0.27	0.39	0.33	0.31	0.27	0.21	0.26	0.32	0.42	0.21	0.11	0.60
O=F	0.12	0.07	0.11	0.43	0.13	0.25	0.11	0.17	0.14	0.13	0.11	0.09	0.11	0.14	0.18	0.09	0.05	0.25
H ₂ O*	3.55	3.64	3.55	3.23	3.55	3.38	3.59	3.48	3.54	3.55	3.55	3.59	3.55	3.44	3.41	3.57	3.67	3.34
$B_2O_3^*$	10.67	10.77	10.65	10.77	10.72	10.62	10.77	10.64	10.73	10.71	10.67	10.69	10.65	10.42	10.46	10.64	10.80	10.52
Total*	100.20	100.79	100.04	100.31	100.72	99.70	100.51	99.82	100.80	100.71	100.30	100.69	100.68	100.30	100.34	100.92	100.88	100.36
Si	5.918	5.933	5.931	6.014	5.973	6.034	6.021	6.033	5.922	5.842	5.849	5.887	5.973	5.942	5.916	5.952	5.999	6.056
AI(IV)	0.082	0.067	0.069	0.000	0.027	0.000	0.000	0.000	0.078	0.158	0.151	0.113	0.027	0.058	0.084	0.048	0.001	0.000
В	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3
AI(Z)	6.000	6.000	6.000	6.000	6.000	6.000	6.000	5.984	6.000	6.000	6.000	6.000	6.000	6.000	6.000	6.000	6.000	6.000
AI(Y)	0.385	0.569	0.522	0.318	0.447	0.118	0.334	0.078	0.426	0.440	0.455	0.496	0.661	0.594	0.572	0.545	0.574	0.329
Ti	0.058	0.038	0.046	0.063	0.083	0.108	0.099	0.148	0.120	0.104	0.132	0.137	0.058	0.058	0.065	0.093	0.100	0.147
Cr ³⁺	0.003	0.007	0.006	0.003	0.006	0.005	0.008	0.005	0.003	0.006	0.006	0.001	-	-	-	-	0.002	-
Fe ²⁺	0.903	0.865	0.950	0.821	0.953	0.862	0.701	0.802	0.924	0.924	0.904	0.967	1.228	1.750	1.664	1.212	0.782	1.556
Mn	0.007	0.006	0.004	0.007	0.005	0.012	0.005	0.003	0.009	0.010	0.007	0.007	0.007	0.018	0.017	0.004	0.006	0.008
Mg	1.644	1.514	1.473	1.774	1.505	1.861	1.832	1.948	1.518	1.516	1.497	1.393	1.046	0.579	0.682	1.145	1.536	0.903
ΣΥ	3.000	3.000	3.000	2.986	3.000	2.966	2.979	2.983	3.000	3.000	3.000	3.000	3.000	3.000	3.000	3.000	3.000	2.944
Ca	0.047	0.030	0.046	0.008	0.061	0.182	0.104	0.208	0.084	0.096	0.082	0.093	0.039	0.028	0.018	0.053	0.070	0.011
Na	0.621	0.536	0.642	0.813	0.676	0.653	0.627	0.569	0.649	0.648	0.673	0.644	0.619	0.654	0.704	0.695	0.616	0.671
К	0.049	0.031	0.020	0.005	0.003	0.007	0.003	0.004	0.011	0.016	0.011	0.009	0.008	0.012	0.011	0.015	0.001	0.011
ΣX	0.717	0.596	0.708	0.827	0.740	0.842	0.735	0.781	0.744	0.760	0.766	0.746	0.666	0.694	0.733	0.763	0.688	0.693
F	0.143	0.081	0.136	0.517	0.154	0.304	0.139	0.204	0.168	0.157	0.139	0.108	0.133	0.172	0.223	0.110	0.056	0.313
OH*	3.857	3.919	3.864	3.483	3.846	3.696	3.861	3.796	3.832	3.843	3.861	3.892	3.867	3.828	3.777	3.890	0.000	3.687
Mg/(Mg+Fe)	0.645	0.636	0.608	0.684	0.612	0.683	0.723	0.708	0.622	0.621	0.624	0.590	0.460	0.249	0.291	0.486	0.663	0.367
(X)/(X+Na)	0.313	0.430	0.312	0.176	0.278	0.195	0.297	0.277	0.283	0.270	0.258	0.283	0.351	0.319	0.275	0.254	0.336	0.314
Note: b.d. = b	elow de	tection l	mit.															

* Calculated using stoichiometric constraints.

tectonic veins. Some veins occur within the necks of boudinaged layers or elongate crystals. Multiple stages of tourmaline formation at vein scale are supported by the occurrence of fibrous and elongate blocky veins that show inclusion bands, consistent with a crack-seal mechanism (Ramsay 1980) (Fig. 3c). Whereas some fibrous veins clearly formed by a crack-seal mechanism, in most cases it is difficult to assess the mechanism responsible for vein formation due to the recrystallization processes. The tourmaline compositions from the veins straddle the fields of the schorl and dravite, with Mg/(Mg+Fe) and X/(X+Na) ratios of 0.367–0.663 and 0.314–0.336, respectively. Amounts of K₂O vary between 0.01 to 0.05 wt% (Table

1). A detailed description about the field relationships, petrography, and composition of tourmaline-rich rocks occurring in the Martinamor antiform can be found in Pesquera et al. (2005).

40AR/39AR RESULTS

⁴⁰Ar/³⁹Ar data for tourmaline analyses are summarized in Table 2. Plateau ages and mean square weighted deviations (MSWD) were calculated based on general criteria, i.e., sections of age spectra with at least three consecutive steps carrying >50% of the total ³⁹Ar released, whose ages overlap, and they do not differ at the 95% confidence level (see McDougall and Harrison 1999; Baksi 2006). Errors are reported at the 2σ level. The significance level was calculated with a χ^2 test for N – 1 degrees of freedom, where N is the number of steps and χ^2 = MSWD*(N – 1). Low- to high-temperature gas fractions display very small fluctuations in apparent K/Ca ratios, suggesting that the release of ³⁹Ar_K occurred from compositionally uniform sites. The high apparent age shown by some samples within the first few percent of gas released may be due to the effect of ³⁹Ar recoil during irradiation as well as possible excess ⁴⁰Ar.

Tourmaline from laminated tourmalinites yielded a welldefined plateau age of 317 ± 2 Ma (MSWD = 0.61) (Fig. 2a), in which approximately 75% of the total amount of ³⁹Ar was released. High-temperature discordance is matched with low K/Ca ratios for high-temperature steps, which may be due to argon derived from compositionally distinct sites. The isochron analysis is not significantly different, yielding an apparent concordant age of 321.23 ± 6.82 Ma and MSWD = 0.46 (Fig. 2a).

Tourmaline from folded tourmalinites is characterized by anomalous steps at low to moderate temperatures, which prohibits estimation of a plateau age. However, a pseudo-plateau age of 342 ± 7 Ma (MSWD = 17.29) was obtained from relatively concordant steps between moderate and high temperatures (Fig. 2b). A total fusion age gives 367.47 ± 2.10 Ma. The inverse isochron age (341.54 ± 12.0 Ma, MSWD = 19.57) is consistent with the pseudo-plateau age, with a composition of initial Ar statistically indistinguishable from atmospheric Ar (Fig. 2b).

Tournaline from the mylonitized tournalinite shows a disturbed spectrum (Fig. 2c), with a series of discordant steps ranging in age from ~320 to 380 Ma, which is unsuitable for precise age determination. A pseudo-plateau age of 355 ± 11 Ma (MSWD = 13.75) was obtained from this tournaline, but if we consider just the central steps accounting for ~40% of Ar release, the mean age is 347 ± 9 Ma (MSWD = 3.98). The spectrum of this sample suggests a non-uniform Ar distribution, which may account for (1) incorporation of excess of Ar through intragranular diffusion and (2) coexisting distinct tournaline populations. The isochron analysis yields a geologically meaningless age of 326.57 ± 38.70 Ma with MSWD = 12.10 (Fig. 2c).

Tourmaline from the tourmaline-rich psammo-pelitic schists yields a well-defined plateau age of 315 ± 2 Ma (MSWD = 0.49) (Fig. 2d). The ³⁶Ar/⁴⁰Ar ratios are relatively constant over most of the gas released, indicating little intrasample compositional variation. Small intrasample variations in apparent K/Ca ratios suggest that ³⁹Ar_K was released from compositionally similar sites. The isochron age of 312.85 ± 3.78 Ma (MSWD = 0.17), and ³⁶Ar/⁴⁰Ar intercept indistinguishable from atmospheric Ar (Fig. 2d), is similarly concordant.

Tourmaline from the orthogneiss yields a pseudo-plateau age of 370 ± 4 Ma (MSWD = 3.62) for the intermediate- and hightemperature steps (Fig. 2e). The total fusion age for the sample is 360.98 ± 2.21 Ma. The apparent K/Ca (0.102 ± 0.003) is low and nearly constant. The inverse isochron defines an age of 373.49 ± 16.37 Ma (MSWD = 5.15) that is concordant with the plateau age, and 36 Ar/ 40 Ar intercept statistically indistinguishable from the atmospheric ratio (1/295.5) (Fig. 2e). Biotite coexisting with tourmaline in the orthogneiss shows, nevertheless, a "steppingup" spectrum with a mean age of 305 ± 1 Ma (MSWD = 3.4) that reflects loss of argon (Fig. 2e). It records younger ³⁶Ar/⁴⁰Ar ages than tourmaline, perhaps by re-heating of the biotites above their closure temperatures between ~370 and 305 Ma. The ³⁶Ar/⁴⁰Ar vs. ³⁹Ar/⁴⁰Ar isochron plot shows that the composition of initial Ar in biotite differs from atmospheric (Fig. 2e), with an age of 305.71 ± 1.29 Ma (MSWD = 2.75).

Tourmaline from leucogranites exhibits a saddle-shaped apparent age spectrum defined by relatively old initial and final steps that flank a set of intermediate steps with an integrated age of 310 ± 4 Ma (MSWD = 7.4), but without statistical significance (Fig. 2f). The inverse isochron defines an apparently concordant age of 307.13 ± 7.57 Ma with a MSWD = 7.33. It is likely to contain excess ⁴⁰Ar, as evidenced by its saddle-like shape and badly fitted isochron (Lanphere and Dalrymple 1976), so that the real age of this tourmaline might be approached with a minimum age of ~ 307 ± 8 Ma.

DISCUSSION

The occurrence of tourmaline concentrations in association with various metamorphic, hydrothermal, and magmatic rocks denotes an important mobilization of boron in the continental crust of the Iberian massif. The behavior and source of boron, nonetheless, is difficult to assess with the available information. A precursor exhalative or evaporitic sedimentary source as suggested for other regions in which tourmaline-rich rocks occur (e.g., Broken Hill district, Sullivan deposit; Slack 1996; Slack et al. 2000), is unlikely judging from geological and geochemical data of the Neoproterozoic-Lower Cambrian sedimentary sequence (e.g., Valladares et al. 2002; Rodriguez-Alonso et al. 2004). A model involving tourmaline formation as a result of the circulation of late-diagenetic and metamorphic B-bearing aqueous fluids derived from thousands of meters of thickness of the SGC sedimentary sequence can potentially account for regional boron metasomatism. In clastic metasediments, boron is hosted by muscovite and tourmaline, the latter containing ~ 3 wt% B. At high grades, sillimanite can also incorporate significant amounts of boron (Grew and Hinthorne 1983; Pereira and Shaw 1996). With progressive metamorphism, the proportion of boron residing in micas decreases, whereas the proportion sequestered in tourmaline increases significantly (Sperlich et al. 1996; Nakano and Nakamura 2001). Prograde metamorphism and devolatilization may lead to significant depletion of boron in higher grade metasediments (Moran et al. 1992). Boron must be concentrated by geochemical processes, such as pervasive or channelized fluid flow during prograde metamorphism, to form tourmaline wherever the physical and chemical conditions are favorable. If this is the case, it would require high fluid/rock ratios to yield important concentrations of tourmaline, such as in the Alamo Complex. However, geochemical data suggest that tourmalinites formed under relatively low fluid/rock conditions (Pesquera et al. 2005). In the studied tourmaline-rich rocks, the modal proportion of tourmaline is equivalent to more than 4000 µg/g B. Such a quantity of boron is highly unlikely to be inherited from any pelitic protolith (Leeman and Sisson 1996), which argues in favor of an external source of boron (Henry and Dutrow 1996; Dutrow et al. 1999).

Sten	Laser now (W)		36Ar.	³⁷ Arc.	³⁸ Ar _{c1}	³⁹ Ar ₂	⁴⁰ Ar*	Ane +	2σ (Ma)	⁴⁰ Ar* (%)	³⁹ Ar ₄ (%)	
				AI Ca	AIC		AI	Age ± i	20 (1114)	AI (70)	AIK (70)	
J = 0.011	118, w = 0.0402 g											
1	7.0	+	0.00001	0.00149	0.00001	0.00050	0.00878	323.03	± 5,59	68.58	8.40	
2	9.0	+	0.00001	0.00141	0.00000	0.00062	0.01001	299.88	± 5,90	79.10	10.38	
3	11.0	+	0.00001	0.00091	0.00000	0.00037	0.00594	296.12	+6.48	76 59	6.25	
4	13.0	+	0.00001	0.00063	0.00000	0.00026	0.00424	300.78	+ 11 51	72.82	4 38	
	15.0	+	0.00001	0.00005	0.00000	0.00020	0.00727	200.10	+ 16 26	07.02	2.10	
5	15.0	T	0.00000	0.00045	0.00000	0.00019	0.00303	300.18	± 16,36	87.84	3.13	
6	19.0	+	0.00000	0.00072	0.00000	0.00030	0.00504	311.38	± 8,26	93.10	5.02	
7	25.0	+	0.00000	0.00057	0.00000	0.00024	0.00400	311.53	± 10,24	83.98	3.98	
8	35.0	+	0.00000	0.00110	0.00000	0.00045	0.00758	309.62	± 6,07	84.77	7.59	
9	42.0	+	0.00001	0.00272	0 00000	0.00110	0.01839	307 14	+ 3 04	89 36	18 58	
10	12.0	+	0.00000	0.00205	0.00000	0.00174	0.02005	211 14	+ 2 00	04.55	20.97	
10	40.0		0.00000	0.00303	0.00000	0.00124	0.02095	210.06	± 5,09	94.33	20.87	
11	54.0	Т	0.00000	0.00112	0.00000	0.00044	0.00762	318.96	± 5,39	83.90	7.39	
12	100.0	+	0.00000	0.00059	0.00000	0.00024	0.00425	325.77	± 9,87	85.75	4.03	
Fine-laye	ered tourmalinite											
J = 0.0111	138, w = 0.0436 a											
1	70	+	0 00004	0.00286	0.00003	0.00390	0.06759	318 78	+ 3.08	85 95	48 26	
2	2.0	+	0.00001	0.00200	0.00000	0.00051	0.0000	210.07	± 172	00.00	6 27	
2	0.0		0.00001	0.00077	0.00000	0.00051	0.00890	516.07	± 4,75	00.22	0.57	
3	9.5	Ť	0.00001	0.00063	0.00000	0.00049	0.00829	314.19	± 4,28	80.08	6.02	
4	12.0	+	0.00001	0.00071	0.00000	0.00051	0.00881	317.89	± 5,51	80.57	6.31	
5	15.0	+	0.00000	0.00058	0.00000	0.00037	0.00639	317.42	± 5,67	86.28	4.58	
6	20.0	+	0.00001	0.00055	0,00000	0.00030	0.00522	316.40	+10.01	77.02	3 76	
7	20.0	+	0.00001	0.00055	0.00000	0.000000	0.00322	212 54	11,01	60.07	2.74	
/	20.0	1	0.00001	0.00051	0.00000	0.00022	0.00576	515.54	± 11,29	00.07	2.74	
8	35.0		0.00000	0.00129	0.00000	0.00030	0.00613	368.02	± 8,20	83.53	3.74	
9	42.0		0.00002	0.00277	0.00000	0.00090	0.01732	351.10	± 5,23	77.83	11.12	
10	48.0		0.00001	0.00194	0.00000	0.00057	0.01389	431.19	± 5.65	90.21	7.10	
Myloniti	r tourmalinite								_ =,==			
1 - 0.0111	$155 m = 0.0252 \alpha$											
J = 0.011	155, W = 0.0555 g					0 00047		4500 50		67 00		
1	5.0		0.00004	0.00159	0.00002	0.00017	0.02200	1589.50	± 16,22	67.88	5.05	
2	6.0	+	0.00001	0.00070	0.00000	0.00027	0.00565	381.53	± 13,97	60.19	7.79	
3	8.0	+	0.00001	0.00098	0.00000	0.00047	0.01000	381.46	± 13,50	70.83	13.79	
4	10.0	+	0.00001	0 00064	0 00000	0.00032	0.00617	356 68	+ 11 12	69 34	917	
5	14.0	+	0.00001	0,00000	0.00000	0.00046	0.00880	3/8 60	+ 6.42	60.02	13 53	
5	17.0	1	0.00001	0.00090	0.00000	0.00040	0.00009	222.72	1551	(2.52	5.55	
6	17.0	Т	0.00001	0.00033	0.00000	0.00018	0.00333	333./2	± 15,51	03.52	5.32	
7	22.0	+	0.00000	0.00025	0.00000	0.00015	0.00305	362.10	± 12,51	69.43	4.46	
8	28.0	+	0.00000	0.00018	0.00000	0.00011	0.00212	345.51	± 22,46	79.88	3.26	
9	35.0	+	0.00001	0.00047	0.00000	0.00028	0.00521	335.59	+8.89	77.00	8.28	
10	40.0	+	0.00001	0.00105	0.00000	0.00060	0.01254	375.07	+ 6.46	80.81	17 58	
10	40.0		0.00001	0.00105	0.00000	0.00000	0.01234	373.97	± 0,40	74.20	17.56	
11	45.0	Т	0.00001	0.00050	0.00000	0.00029	0.00535	336.07	± 8,60	74.30	8.48	
12	45.0	+	0.00000	0.00025	0.00000	0.00011	0.00196	318.51	± 19,62	81.88	3.29	
Tourmali	ne-bearing schist											
J = 0.0111	170. w = 0.0372 a											
1	50		0.00003	0.00068	0 00000	0.00010	0.00426	696 51	+ 33 34	31 34	2 1 1	
2	5.0	+	0.00003	0.00000	0.00000	0.00010	0.00720	215.25	± 55,54	51.54	2.11	
2	7.0		0.00001	0.00592	0.00000	0.00045	0.00775	515.55	± 0,95	00.00	9.40	
3	9.0	Ť	0.00001	0.00411	0.00000	0.00046	0.00787	315.37	± 8,35	67.03	9.63	
4	12.0	+	0.00002	0.00368	0.00000	0.00043	0.00735	318.09	± 9,25	58.45	8.91	
5	16.0	+	0.00000	0.00300	0.00000	0.00035	0.00595	313.78	± 9.50	86.04	7.32	
6	22.0	+	0.00001	0.00267	0,00000	0.00031	0.00542	318 20	+ 19.06	68 24	6.57	
7	20.0	+	0.00001	0.00207	0.00000	0.00031	0.000 12	210.20	10,00	74.06	15.60	
/	29.0		0.00002	0.00069	0.00000	0.00075	0.01295	516.50	± 0,20	74.00	15.09	
8	34.0	†	0.00003	0.00717	0.00000	0.00083	0.01427	317.26	± 6,74	65.09	17.34	
9	42.0	+	0.00000	0.00881	0.00000	0.00096	0.01632	313.09	± 3,39	94.23	20.12	
10	50.0		0.00000	0.00111	0.00000	0.00014	0.00247	334.66	± 14,72	75.95	2.84	
Folded to	ourmalinite											
I = 0.011	104 w = 0.0402 a											
1	194, W – 0.0402 g		0.00000	0.00022	0 00000	0.00010	0.01026	1200.24	+ 20.02	65.22	1 70	
1	5.0		0.00002	0.00025	0.00000	0.00010	0.01050	1309.54	1 20,05	05.22	1./0	
2	7.0	Ť	0.00001	0.00073	0.00000	0.00057	0.01091	349.65	± 5,//	/5.61	10.18	
3	9.0	+	0.00000	0.00060	0.00000	0.00046	0.00900	355.54	± 5,73	92.78	8.25	
4	12.0	+	0.00001	0.00047	0.00000	0.00035	0.00690	361.13	± 9,17	80.88	6.22	
5	15.0	+	0.00000	0.00036	0.00000	0.00027	0.00517	352.52	+10.09	96 97	4 79	
6	20.0		0,00000	0.00025	0.00000	0.00010	0.00307	303.40	+ 13 70	96 79	3 35	
7	20.0		0.00000	0.00023	0.00000	0.00019	0.00307	226.04	1 13,79	30.79	3.33	
/	27.0	т	0.00000	0.00027	0.00000	0.00022	0.00400	336.04	± 9,94	/5.45	3.90	
8	33.0	+	0.00000	0.00104	0.00000	0.00081	0.01578	356.84	± 4,30	91.52	14.40	
9	37.0	+	0.00000	0.00138	0.00000	0.00100	0.01843	337.18	± 3,44	93.45	17.90	
10	40.0	+	0.00001	0.00163	0.00000	0.00108	0.01969	336.15	± 2,81	88.31	19.19	
11	110	+	0.00001	0.00064	0.00000	0.00040	0.00000	222.12	+ 7 20	76.60	8 50	
11	44.0	ľ	0.00001	0.00064	0.00000	0.00048	0.00832	522.02	± 7,30	70.08	0.50	
12	50.0	t	0.00001	0.00009	0.00000	0.00009	0.00153	326.09	± 36,60	37.33	1.54	
Tourmali	ne-bearing orthog	neiss										
J = 0.0111	102, w = 0.0358 a											
1	10.0		0.00000	0.00130	0.00000	0.00038	0.00857	400.19	+ 7.69	88 16	4 51	
2	10.5	+	0 00003	0.00281	0.00000	0 00007	0.01864	349 57	+ 9 65	64 55	11 22	
∠ 2	10.5	1	0.00003	0.00201	0.00000	0.00097	0.01004	222.27	- 10.00	70.05	7.50	
3	11.0	Т	0.00002	0.00201	0.00000	0.00065	0.01187	332.81	± 10,60	70.26	7.65	
4	11.5	+	0.00001	0.00133	0.00000	0.00037	0.00679	334.90	± 12,17	74.09	4.35	
5	12.5	+	0.00000	0.00111	0.00000	0.00030	0.00540	333.24	± 14,30	78.62	3.48	
6	14.0	+	0.00000	0.00099	0.00000	0.00027	0.00504	342.29	± 10.52	80.27	3.15	
7	16.0	+	0,00000	0 00080	0.00000	0.00024	0.00456	347 00	+ 8 00	77 40	2 80	
, o	10.0	+	0.00000	0.00009	0.00000	0.00024	0.00-00	247.20	<u>.</u> 0,90	77.TU	2.00	
0	∠0.0	ť	0.00000	0.00107	0.00000	0.00028	0.00537	547.64	± 0,94	ŏ2.92	3.30	

 TABLE 2.
 Summary of ⁴⁰Ar/³⁹Ar dating results

30.0

9

t

0.00000

0.00079

0.00000

0.00019

0.00353

344.61

± 10,37

continued on next page

2.19

81.89

TABLE 2.—CONTINUED

Step	Laser pow. (W)		³⁶ Ar _A	³⁷ Ar _{Ca}	³⁸ Ar _{Cl}	³⁹ Ar _K	⁴⁰ Ar*	Age ±	Age ± 2σ (Ma)		³⁹ Ar _K (%)
Tourmali	ne-bearing ortho	ogneiss	5								
J = 0.0111	02, w = 0.0358 g										
10	40.0		0.00001	0.00369	0.00000	0.00089	0.01852	376.81	± 4,55	90.01	10.41
11	60.0		0.00002	0.01155	0.00000	0.00283	0.05805	369.61	± 2,19	90.23	33.34
12	80.0		0.00001	0.00335	0.00000	0.00080	0.01634	369.28	± 5,08	84.28	9.40
13	100.0		0.00000	0.00151	0.00000	0.00034	0.00693	364.72	± 7,65	83.63	4.04
Tourmali	ne-bearing ortho	ogneiss	5								
J = 0.0111	02, w = 0.0358 g										
1	10.0		0.00000	0.00130	0.00000	0.00038	0.00857	400.19	± 7,69	88.16	4.51
2	10.5		0.00003	0.00281	0.00000	0.00097	0.01864	349.57	± 9,65	64.55	11.38
3	11.0		0.00002	0.00201	0.00000	0.00065	0.01187	332.81	± 10,60	70.26	7.65
4	11.5		0.00001	0.00133	0.00000	0.00037	0.00679	334.90	± 12,17	74.09	4.35
5	12.5		0.00000	0.00111	0.00000	0.00030	0.00540	333.24	± 14,30	78.62	3.48
6	14.0		0.00000	0.00099	0.00000	0.00027	0.00504	342.29	± 10,52	80.27	3.15
7	16.0		0.00000	0.00089	0.00000	0.00024	0.00456	347.90	± 8,90	77.40	2.80
8	20.0		0.00000	0.00107	0.00000	0.00028	0.00537	347.64	± 6,94	82.92	3.30
9	30.0		0.00000	0.00079	0.00000	0.00019	0.00353	344.61	± 10,37	81.89	2.19
10	40.0	+	0.00001	0.00369	0.00000	0.00089	0.01852	376.81	± 4,55	90.01	10.41
11	60.0	+	0.00002	0.01155	0.00000	0.00283	0.05805	369.61	± 2,19	90.23	33.34
12	80.0	+	0.00001	0.00335	0.00000	0.00080	0.01634	369.28	± 5,08	84.28	9.40
13	100.0	+	0.00000	0.00151	0.00000	0.00034	0.00693	364.72	± 7,65	83.63	4.04
Biotite o	rthogneiss										
J = 0.0110)75, w = 0.0370 g										
1	3.00		0.00025	0.00014	0.00000	0.02363	0.36974	288.30	± 1.46	83.06	7.13
2	3.50		0.00010	0.00011	0.00000	0.02486	0.40355	298.27	± 1.18	93.13	7.50
3	4.00		0.00009	0.00012	0.00000	0.03443	0.56541	301.46	± 1.17	95.54	10.39
4	4.50	+	0.00005	0.00010	0.00000	0.03166	0.52281	303.03	± 1.19	97.02	9.56
5	5.00	+	0.00003	0.00009	0.00000	0.02545	0.42273	304.64	± 1.20	97.98	7.68
6	5.30	+	0.00002	0.00007	0.00000	0.01761	0.29101	303.18	± 1.20	98.38	5.32
7	5.60	+	0.00001	0.00004	0.00000	0.01283	0.21431	306.29	± 1.41	98.97	3.87
8	5.90	+	0.00001	0.00005	0.00000	0.01439	0.23943	305.17	± 1.45	98.98	4.34
9	6.20	+	0.00001	0.00004	0.00000	0.01115	0.18519	304.65	± 1.31	98.86	3.37
10	6.60	+	0.00001	0.00004	0.00000	0.01512	0.25085	304.41	± 1.19	98.79	4.56
11	7.00	+	0.00001	0.00005	0.00000	0.01618	0.26855	304.36	± 1.26	99.25	4.89
12	7.40	+	0.00001	0.00004	0.00000	0.01311	0.21833	305.34	± 1.48	99.27	3.96
13	7.80	+	0.00000	0.00005	0.00000	0.01530	0.25368	304.22	± 1.25	99.48	4.62
14	8.20	+	0.00000	0.00012	0.00000	0.01094	0.18175	304.60	± 1.27	99.53	3.30
15	8.60	+	0.00000	0.00010	0.00000	0.01583	0.26314	304.92	± 1.29	99.44	4.78
16	9.00	+	0.00000	0.00003	0.00000	0.00851	0.14244	306.77	± 1.34	99.32	2.57
17	9.80	+	0.00000	0.00003	0.00000	0.01016	0.16979	306.48	± 1.51	99.40	3.07
18	10.60	+	0.00000	0.00001	0.00000	0.00715	0.11807	303.16	± 1.60	99.44	2.16
19	15.00	+	0.00001	0.00004	0.00000	0.02111	0.35314	306.61	± 1.16	99.24	6.37
20	20.20		0.00000	0.00000	0.00000	0.00189	0.03268	316.72	± 5.46	98.17	0.57
+ Samples	s included in the is	sochror	ane calculatio	ากร							

An early boron metasomatic event driven by boron-rich aqueous fluids related to Cambro-Ordovician magmatism is tenable for several reasons. (1) Tourmaline-bearing Cambro-Ordovician orthogneisses show feldspar and tourmaline megacrysts with similar textural characteristics (Fig. 2e). The occurrence of very fine, euhedral crystals of tourmaline included in feldspar megacrysts imply that tourmaline began to crystallize earlier, or at the same time, as their host feldspar. (2) Deformed tourmalinites are spatially related to Cambro-Ordovician orthogneisses. At greater distances from the orthogneiss bodies, tourmaline is an accessory mineral in the metasedimentary rocks. Tourmaline-bearing aureoles associated with many igneous intrusions are obvious evidence for B-rich fluid infiltration from a magmatic source (Leeman and Sisson 1996; Dutrow et al. 1999). Aqueous fluids exsolved from solidifying igneous bodies can constitute an efficient transport medium for highly soluble elements such as boron (London et al. 1988; Schatz et al. 2004). (3) The orthogneiss yields the oldest tourmaline age (~370 Ma) that is consistent with the age of the first Variscan deformation phase in other regions of Iberia (Quesada and Dallmeyer 1994; Rodríguez et al. 2003). Tourmalines from mylonitized and folded tourmalinites, which show disturbed spectra with pseudo-plateau ages of ~340-350

Ma, may have geological significance by considering the age of muscovites associated to S₂ (ca. 343 Ma; Dallmeyer et al. 1997) (Figs. 2b and 2c). These tourmalinites, nevertheless, were deformed under medium- to high-grade metamorphic conditions at temperatures higher than ~520 °C (see Pesquera et al. 2005). Assuming a closure temperature for Ar in tourmaline to be similar to that of hornblende (~500-550 °C; McDougall and Harrison 1999), tourmaline may have undergone changes in its chemistry, grain size, and density of defects and dislocations during deformation and metamorphism. All these changes are considered to influence argon diffusivity and retentivity of the minerals (Goodwin and Renne 1991; Dahl 1996; Villa 1998; Mulch et al. 2002). Ar-isotope diffusion in tourmaline appears to become significant at ~525 °C (De Jong 1991). Consequently, the ages of \sim 370–340 Ma may be indicative that tourmaline has been unable to retain its radiogenic argon during the Variscan deformation and metamorphism. (4) Tourmaline-bearing leucogranites are common in the Alamo Complex. Boron-rich leucogranites that contain tourmaline, a typical association in continental collision regions, appear to require unusual degrees of B enrichment in their source areas (Leeman and Sisson 1996).

Furthermore, the occurrence of irregularly shaped tourmaline

associated with sillimanite + cordierite in migmatitic zones (Fig. 3d), suggests that tourmaline broke down according to the reaction tourmaline \pm albite \pm K-feldspar \pm quartz = sillimanite + cordierite + boron-bearing melt (Kawakami 2001). Fluids could also contribute to destabilize tourmaline. Boron concentrated in anatectic melts may result in the crystallization of tourmaline in leucosomes, pegmatite veins, and leucogranites. However, as Barbey et al. (1996) argued, the fact that the tourmaline content in gneisses is lower than in leucogranitic bodies may be indicative of anatexis driven by B-bearing fluid percolation. Boron-rich fluids derived from local remobilization of pre-Variscan tourmaline-rich rocks by deformational and metamorphic processes during the Variscan orogeny are believed to be responsible for the formation of multiple syntectonic tourmaline \pm quartz veins, and may have influenced anatexis. Boron is considered a fluxing agent that not only lowers solidus and liquidus temperatures for silicate systems, but also reduces the viscosity of melts (Dingwell et al. 1996). In north-central Portugal, Reavy (1989) claimed that the presence of B-rich fluids may have promoted anatexis in a transpressional environment. Tourmaline-rich rocks with welldefined plateau ages of ~315-317 Ma (Figs. 2a and 2d) would represent an additional metasomatic event concomitant with anatexis and generation of boron-bearing granites, pegmatites, and hydrothermal fluids.

Although there is no compelling evidence for metasomatic events driven by Cambro-Ordovician boron-rich magmatic fluids, the observations in this study suggest this may be possible. Further investigation is necessary to assess the boron source and the precise timing of tourmalinization. The ⁴⁰Ar/³⁹Ar results must be used with caution, but they suggest considerable potential for using tourmaline to record the age of tourmalinization, metamorphism, and magmatism. The lack of data relative to the closure temperature, uncertainty of Ar diffusion parameters in tourmaline, effective diffusion length scales, and cooling rates in tourmaline stand make this line of research a challenge.

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