Incipient wolframite deposition at Panasqueira (Portugal): W-rutile and tourmaline compositions as proxies for the early fluid composition

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Abstract

The main event responsible for the deposition of tungsten at Panasqueira was closely associated with strong tourmalinization of the wall rocks. Tourmaline is coeval with a W-rich rutile (up to 8-10 wt% W) and both minerals record an early introduction of W in the system, just before the main W deposition. Uranium-Pb dating of the rutile by LA-ICP-MS yielded an age of 305.2±5.7 Ma, which is 6-10 Ma older than the K-Ar age of 296.3±1.2 Ma obtained on muscovite, which was therefore not coeval of wolframite. Major and trace element concentration variations in tourmaline record fluid mixing between two end-members, both considered to be of metamorphic derivation on the basis of REE profiles. We report evidence for a fluid enriched in Co, Cu, Pb, Sc, Sr, V, Cr, Nb, Ta, Sn, interpreted to be of “local” origin, e.g., well-equilibrated with the host formations, and a fluid rich in Li, F, Fe, Mn, W inferred to be of deep origin and related to biotite dehydration. The second fluid carried the metals (in particular Fe and Mn) necessary for wolframite deposition, which were not necessarily inherited from the wall rocks through fluid-rock interaction. Micrometer scale variations in tourmaline and rutile crystal-chemistry are indicative of pulsatory fluid input during tourmalinization.

Introduction
Tungsten (W) in western Europe, was mainly concentrated during the Variscan orogeny. The total endowment is estimated to be 1.1 Mt W. The Central Iberian Zone (CIZ), which contains 210 kt W, is one of the main provinces. Others include the Erzgebirge (270 kt W) and Cornwall (≥425 kt W) (Marignac and Cuney, 2013). The Panasqueira mine in the CIZ, which has been active for more than 130 years, exploits one of the largest W deposits in western Europe, with a total production of 76 kt W since 1934 and estimated total resources of ~38 kt W (Almonty, 2016; Vigne et al., 2018), i.e., an ab initio endowment of at least 115 kt W.

Since the 1970s, numerous mineralogical, geochemical and fluid inclusion studies have discussed the genesis of the Panasqueira deposit (e.g., Kelly and Rye, 1979; Bussink, 1984; Snee et al., 1988; Polya, 1989; Noronha et al., 1992; Lüders, 1996; Foxford et al., 2000; Polya et al., 2000; Lecumberri-Sanchez et al., 2017; Codeço et al., 2017; Launay et al., 2018). The deposit, which is hosted by the Beira schists, and overlies an inferred contact with a granite pluton (inferred from the presence of a greisenized cupola), is characterized by thousands of sub-horizontal veins filled by wolframite and quartz. Following Kelly and Rye (1979), most studies have concluded that the granite intrusion played a major role in controlling a unique hydrothermal megacycle. Snee et al. (1988) dated muscovite at 296.3±1.2 Ma (2σ), using the ⁴⁰Ar/³⁹Ar age step-heating method, and considered this age to represent the approximate timing of the main W depositional stage, assuming coeval crystallization of wolframite and muscovite.

Recent investigations carried out on the scale of the whole deposit reported observations of mineral sequences synchronous with the incipient opening of the W veins. The fluid inclusion record of the event in which wolframite was deposited (the OSS stage of Polya et al., 2000) was lost due to decrepitation and/or deformation after wolframite crystallization (Cathelineau et al., 2017; 2018; Carocci, 2019), a fact which unfortunately was overlooked by all previous studies. As a result, there is no reliable record of the fluids responsible for wolframite crystallization. A potential way to constrain the composition of these early fluids is to study the crystal-chemistry and trace element concentrations in minerals coeval with incipient wolframite deposition. Here, we demonstrate that tourmaline in the wall rock, and associated rutile, were indeed coeval with wolframite deposition. Both minerals display chemical zoning, taken as proxy for the evolution of the fluid chemistry during their growth. Tourmaline is known to be highly stable under a wide range of physico-chemical conditions (van Hinsberg et al., 2011). Its complex structure inhibits significant element diffusion on available timescales (Hawthorne and Dirlam, 2011) and records changes in fluid chemistry at all stages of crystal growth (Marschall and Jiang, 2011; Sluck and Trumbull, 2011; van Hinsberg et al., 2011). Although several studies of the Panasqueira tourmaline have examined the major element and boron isotope composition (Neiva et al., 2007; Codeço et al.,...
2017; Launay et al., 2018), none have investigated the trace element chemistry and the possibility that it could record the evolution of the fluid or change(s) in the fluid source(s).

The main objective of this study was therefore a comprehensive analysis of tourmaline and rutile chemistry in order to constrain the nature of the ore forming fluids. This resulted in a modified conceptual model of the early hydrothermal system at Panasqueira. A subordinate objective was to date the rutile using the in situ U-Pb method, in order to constrain the onset of hydrothermal activity and provide a comparison to the published $^{40}$Ar muscovite age.

Regional background

Panasqueira is located in the Iberian Massif, which is the southern branch of the so-called Iberian-Armorican Arc (IAA), at the western termination of the Variscan belt. The IAA is an orocline formed in about 10 Ma at the end of the Carboniferous (Weil et al., 2013). The Iberian Massif is subdivided into a number of tectonostratigraphic units (or Zones) (Julivert et al., 1972) delimited by tectonic boundaries (Fig. 1). Most of these terranes are Gondwanian in origin. The Central Iberian Zone (CIZ) is the main unit of a series of autochthonous terranes derived from the Paleozoic Gondwanian passive margin. They were covered by a unique nappe stack (Galicia-Tras-os-Montes Zone and Ossa Morena Zone) (Pérez-Caceres et al., 2017). The CIZ comprises a thick sequence of late Ediacarian-Cambrian metasedimentary rocks (the Schist-Greywacke Complex, or Beira Group) overlain unconformably by the Early Ordovician Armorican Quartzite (Diez-Fernandez et al., 2013).

The tectono-thermal Variscan history of the CIZ, which begins in the Early Carboniferous and ends in the Early Permian, is subdivided into five events, D1 to D5 (Diez-Fernandez et al., 2016, and references therein; Diez-Fernandez and Pereira, 2017). The first event, D1 crustal thickening and stacking of the allochthon, was dated at c. 354-347 Ma (e.g., Rubio Pascual et al., 2013). The subsequent D2-D5 evolution was characterized by large-scale crustal melting, resulting from a combination of mid-crustal post-thickening heating and mantle-derived heat input at the base of the continental crust (Pereira et al., 2017). The D2 (c. 327-316 Ma) event recorded the first episode of heat input and mid-crustal melting, with the development of migmatite domes (Fig. 1) (e.g., Llana-Fúnez and Marcos, 2007; Diez Fernandez et al., 2012; Rubio-Pascual et al., 2013; Pereira et al., 2017). Associated mafic syn-migmatitic sills and sheet-like bodies of late-kinematic monzogranite and granodiorite (319-316 Ma) are widespread (e.g., Castro et al., 2003; Pereira et al., 2017). The D3 to D5 evolution corresponds to a protracted sequence of episodic intra-crustal transcurrent deformation, initiated at ca. 315-310 Ma by the development of km- to 10 km-sized NW-SE to N-S
Figure 1. Geologic map of the Iberian Massif, with Panasqueira location. The map is adapted and simplified from Diez Fernandez et al. (2016), with complementary data from Alcock et al. (2015), Llana-Furez and Marcos (2007), Rubio Pascual et al. (2013) and Rubio-Pascual et al. (2016). BTolP: basal thrust of the Iberian Paraautochthon; ET: Espina thrust; JPSCZ: D4 Jusbado-Perralva do Castelo shear zone; LPSZ: Los Pedroches shear zone; OF: Onza fault; PGCVD: Puente Genave-Castelo Vide detachment fault; PRSZ: Palas de Rei shear zone; PTSZ: Porto-Tomar D5 shear zone; SISZ: South Iberian shear zone; VF: Viveiro fault
upright F3 folds, with a S3 axial-plane schistosity, followed by D4 (c. 309-305 Ma) left-lateral and D5 (c. 304-295 Ma) dextral faulting (Diez Fernandez and Pereira, 2017; and references therein). Crustal melting and concomitant mantle-derived heat input continued through D3 to D5, with the pervasive emplacement of syn- to post-kinematic granite plutons, in three pulses roughly coincident with the D3 to D5 events (e.g., Dias et al., 1998; Mateus and Noronha, 2010; Sant'Ovaia et al., 2010; Fernandez-Suarez et al., 2011). Water-absent dehydration melting (incongruent biotite melting) produced cordierite-bearing diatexites in the cores of D2 migmatitic domes (Pereira Gomez et al., 2000). Permian mafic dikes (290-265 Ma) testify to a mantle influence until the very end of the collision (Orejana et al., 2009; Scarrow et al., 2011).

Numerous mineralized systems were active in the CIZ in close association with Late Carboniferous tectonics and granitoid emplacement giving rise to more than 150 peri- and intra-granitic rare metal (Nb-Ta, Li, W, Sn) and shear-zone hosted (Au-Ag-As-Sb-Pb-Zn-Cu) deposits (Tornos et al., 2000; Neiva, 2002; Mateus and Noronha, 2010; Noronha, 2017).

**Geological setting and previous work**

The Panasqueira W-Cu (Ag)-Sn deposit in central Portugal lies within the Central Iberian Zone (CIZ) (Fig.1), in the core of a late Carboniferous anticlinorium bordered by narrow synclines of Ordovician Armorican Quartzite (Fig. 2-A). The deposit consists of a dense network of sub-horizontal mineralized quartz veins crosscutting the subvertical foliation of the greenschist facies mica-schists of the Beira Schists (Fig. 2-B). These veins crosscut numerous pods and vein-like masses of barren quartz locally named “seixo-bravo” which are probably late kinematic and cover an area of over six km²; their vertical extent is several hundred meters (Polya, 1989).

A granite body concealed beneath the deposit (Fig. 2-B) was responsible for a 6x3 km metamorphic contact aureole of schists, marked by cordierite-biotite spots and cordierite-andalusite assemblages. These mineral assemblages constrain the pressure to have been less than 300 MPa at the time of emplacement of the Panasqueira granite (Pattison, 2001; Kuhn, 2018). A greisenized cupola at the top of the granite is still observed in some of the galleries. This cupola was described by Kelly and Rye (1979) as having being overlain by a quartz cap, although this has not been corroborated. The greisenized cupola sits atop a sheet-like body of evolved granites that are mainly evident in a few drill holes (Bussink, 1984; De Amorin, 2017), but have been encountered locally in some of the deepest galleries of the mine (LB level, Barroca Grande sector: Lourenço, 2002). The cupola sent out several sill-like apophyses, and towards its base, a matrix-supported breccia formed with large (up to 2 m) joint-bounded hornfels clasts (Kelly and Rye, 1979). The greisenized cupola...
Figure 2. Panasqueira geological setting. A. Geologic map of the Panasqueira area (redrawn from Ribeiro, 2017), with location of the cross section in B. Note the tight synform roots picked out by Ordovician quartzites. B. Cross section of the Panasqueira deposit (adapted from Bussink, 1984 and De Amorin, 2017)

is cut by the quartz-wolframite veins. The evolved granites are typical of the peraluminous rare metal granite (RMG) family (Linnen and Cuney, 2005), and are albite-rich, displaying typical “snowball” quartz textures. They contain (rare) cassiterite and columbo-tantalite as accessory minerals (Lourenço, 2002; De Amorin, 2017). A porphyritic (K-feldspar megacrysts) biotite-(muscovite) granite (Bussink, 1984) is likely representative of the main granite body responsible for the metamorphic aureole and could be related to the late D3 granites from the nearby Serra de Estrela (Sant’Ovaia et al., 2010) and Serra de Gardunha (Fig. 2-A). According to recent gravimetric data (Ribeiro, 2017), the main Panasqueira granite has the shape of a laccolith, with a flattened top, a NNE striking elongated trend (~6.3×3.8 km) and an average thickness of 1 km, but with a 2 km thick keel. The evolved granites have been dated at c. 290 Ma, by whole-rock K-Ar (Clark, 1970) or Rb-Sr (Priem and Den Tex, 1984) methods. Close to the deposit, the Fundão granodiorite (Garcia,
2004) and the small Argemela RMG intrusion (Michaud et al., 2020) are associated with a quartz-
cassiterite vein system (Inverno et al., 2009).

The Panasqueira deposit first attracted research attention in the second half of the 20th century
(Kelly and Rye, 1979; Polya et al., 2000, and references therein; Lourenço, 2002; Burnard and
Polya, 2004) and continues to be the subject of considerable interest. Jaques and Pascal (2017) and
Jacques et al. (2018) addressed the tectonic and fluid pressure conditions required for the creation
and opening of the quartz vein system. Lecumberri-Sanchez et al. (2017), using LA-ICP-MS
analyses of fluid inclusions, and Codeço et al. (2017), using B-isotope data from tourmaline,
addressed the origin of the fluids. Launay et al. (2018) used tourmaline growth features to interpret
the direction and velocity of flow of the fluids.

**Samples and methods**

Our work is based on analyses of >250 samples collected in the late 1970s on levels 0 and 1, in
the historical centre of the mine, and in 2015-2016 on levels 0 to 3, to the south-west of the
historical zones. Following petrographic examination with an OLYMPUS BX51 (transmitted and
reflected light) optical microscope and a VHX-200 KEYENCE numeric microscope, selected
samples were studied with a Schottky-FEG (Field Emission Gun) JEOL J7600F scanning electron
microscope (SEM) equipped with an SDD-type EDS spectrometer at the GeoRessources Laboratory
(Nancy, France). Backscattered electron (BSE) images were obtained after setting the acceleration
voltage at 15 kV.

Major-element mineral compositions were determined for tourmaline and rutile using a
CAMECA SX100 Electron microprobe (EPMA) equipped with a wavelength dispersive
spectrometer (WDS) and a Schottky-FEG (Field Emission Gun) JEOL J7600F scanning electron
microscope (SEM) equipped with a SDD-type EDS spectrometer at the GeoRessources Laboratory
(Nancy, France). The analytical conditions were a 12 nA current and an accelerating voltage of 15
kV for the EPMA, and a 1 nA current and an acceleration voltage of 15 kV for the SEM, with a
counting time of 10 s. The same natural and synthetic oxides and silicate standards were used for
the two types of analyses. For tourmaline analysis, these standards were topaz (F), albite (Na),
olivine (Mg), orthoclase (Si, K), wollastonite (Ca), MnTiO3 (Ti, Mn) and hematite (Fe). For rutile
analysis, the standards were TiO2 (Ti), Cr2O3 (Cr), vanadinite (V), hematite (Fe), LiNbO3 (Nb),
LiTaO3 (Ta), cassiterite (Sn) and scheelite (W).

Trace and rare earth elements in tourmaline were analyzed at the GeoRessources Laboratory,
using a 193 nm GeoLas Pro ArF Excimer laser at 5 Hz laser frequency, the aerosols being analyzed
with an Agilent 7500c Quadrupole ICP-MS. The analytical settings for laser ablation are detailed in Leisen et al. (2012) and Lach et al. (2013). Laser ablations were performed with a constant fluence of 10 mJ.cm\(^{-2}\) and a constant repetition rate of 5 Hz. Helium was used as a carrier gas to transport the laser generated aerosols from the ablation cell to the ICP-MS. Before entering the ICP torch, Helium was mixed with Argon at a typical flow rate of 0.5 l.min\(^{-1}\). The hole produced by the laser was 24 µm in diameter, except for REE measurements, for which it was 120 µm in diameter. A peak hopping ablation mode was initiated ~ 20 s after the beginning of signal acquisition, in order to sample the background signal before ablation (used for data reduction), and was stopped after 200 pulses. The return of the background signal to its initial value was checked before ablating a new zone. The NIST reference glasses 610/612 were used as external standards; Si, previously analysed by EPMA, was used as an internal reference. The data were processed using the Iolite software (Paton et al., 2011).

Rutile U-Pb geochronology was conducted by in-situ laser ablation ICP-MS at Géosciences Rennes using an ESI NWR193UC Excimer laser coupled to a quadrupole Agilent 7700x ICP-MS equipped with a dual pumping system to enhance sensitivity (Paquette et al., 2014). The instrumental conditions are reported in Appendix A1, Table A1. The ablated material was carried into helium, and mixed with nitrogen and argon, before injection into the plasma source. The instrument was aligned and calibrated for mass before each analytical session using the NIST SRM 612 reference glass, by inspecting the \(^{238}\text{U}\) signal and minimizing the ThO+/Th+ ratio (<0.5%). During the course of an analysis, signals for \(^{204}\text{Pb} (\text{Hg})\), \(^{206}\text{Pb}, \ ^{207}\text{Pb}, \ ^{208}\text{Pb}, \ ^{232}\text{Th}\) and \(^{238}\text{U}\) masses were acquired.

Single analyses consisted of 20 s of background integration followed by 60 s of sample integration with the laser firing and then a minimum delay of 10 s to wash out the previous sample. Ablation spot diameters of 45 µm with repetition rates of 5 Hz were used for all the analyses. For each analytical session, we used the following standard bracketing procedure. Two analyses of the R10 rutile standard (Luvizotto et al., 2009) were used as the primary rutile reference, and one analysis of the R19 rutile standard (489.5 ± 0.9 Ma, Zack et al., 2011) was used for quality control, followed by six analyses of the rutile grains. This sequence was repeated three times with an analysis of the R19 standard and two analyses of the R10 standard at the end of the session.

The data were corrected for U–Pb fractionation and for mass bias by repeated measurements of the R10 rutile standard. The R19 rutile standard measurements, treated as unknowns, were used to control the reproducibility and accuracy of the corrections. These standards yielded an age of 490 ± 3 Ma (MSWD = 1.11; n=13) during the April 2016 session and 493 ± 12 Ma (MSWD=2; n=12) during the December 2017 session. The data reduction was carried out with the data reduction
scheme, VizualAge_UcomPbine, a set of Iolite procedures that work with Igor Pro (Chew et al. 2014). All the data were plotted at 2 sigma on Tera-Wasserburg Concordia diagrams using the Isoplot 3.75 software (Ludwig, 2012).

Analyses of $^{40}$Ar/$^{39}$Ar were performed at the University of Manitoba (Canada) using a multi-collector Thermo Fisher Scientific ARGUS VI mass spectrometer linked to a stainless steel Thermo Fisher Scientific extraction/purification line, a Photon Machines (55 W) Fusions 10.6 CO$_2$ laser, and a Photon Machines (Analyte Excite) 193 nm laser. Isotope abundances were corrected for extraction-line blanks, which were determined before every sample analysis. Line blanks in both the Excimer and CO$_2$ system averaged ~3 fA for mass 40 and ~0.013 fA for mass 36. Mass discrimination was monitored by online analysis of air pipettes based on a power law relationship (Renne et al., 2009), which gave $D = 1.0081 \pm 0.0002$ per amu, based on 71 aliquots interspersed with the unknowns. A value of 295.5 was used for the atmospheric $^{40}$Ar/$^{36}$Ar ratio (Steiger and Jäger, 1977) for the purpose of routine measurement of mass spectrometer discrimination using air aliquots, and correction for atmospheric argon in the $^{40}$Ar/$^{39}$Ar age calculation. Corrections were made for neutron-induced $^{40}$Ar from potassium, $^{39}$Ar and $^{36}$Ar from calcium, and $^{36}$Ar from chlorine (Roddick, 1983; Renne et al., 1998; Renne and Norman, 2001). The data were plotted using DensityPlotter (Vermeesch, 2012). Complementary information is given in Appendix A2.

**Results**

**Petrography of the tourmalinized wall rocks**

Tourmaline is a common mineral in the wall rocks to the W-veins in the Panasqueira deposit, but may also be observed far from the deposit, bordering either barren quartz veins or even “dry” joints. The tourmaline-bearing rocks extend from the vein/joint boundaries for distances varying from a few cm ($\leq 10$) to 1 m, or roughly 25 cm on average.

As first noted by Bussink (1984), and later by Foxford et al. (1991), thin quartz veinlets (1-5 mm in average) are common in the tourmaline-bearing wall rocks adjacent to the main veins, and in many cases define the vein margins. They display clear evidence for a crack-seal mechanism of opening, and are labelled Qcs hereafter (Fig. 3-A).

There is a clear organization of the tourmaline in layers parallel to $S_0$, preserving the protolith fabric, as pointed out by Codeço et al. (2017). The tourmalinized wall rocks generally contain more than 50 vol.% tourmaline and tourmaline abundance is locally high enough to classify the rock as tourmalinite. Tourmaline is invariably associated with quartz, and with muscovite in the most pelitic protoliths, where the mica defines the schistosity. It is accompanied by abundant rutile (see...
Figure 3. A. Typical tourmalinized wall-rock, with Qcs quartz veinlets. Sn, regional schistosity. Note the numerous overprinting arsenopyrite (Apy) crystals. Sample PAN-III-8-c1 (NL). B. Poorly zoned tourmaline 1 seen in natural light. Sample PAN-II-8. C. Typical zoning of tourmaline 1(BSE), showing the three Tur0, Tur1a and Tur1b zones. Sample PAN-I-3-1.

below), zircon and fluor-apatite and sporadic monazite or xenotime crystals, usually no more than 10-20 µm, and commonly only a few µm in diameter. Aggregates of micrometer-scale crystals of zircon and xenotime or zircon and monazite are common. In addition to these ubiquitous accessories to the tourmaline, a number of other hydrothermal minerals were later involved in the alteration of the Panasqueira wall rocks, and include quartz (silicification), topaz, muscovite, sulfides (pyrrhotite, sphalerite, chalcopyrite, arsenopyrite), apatite and siderite.

Tourmaline textures

Tourmaline habit and zoning: The tourmaline habit may be either acicular, with lengths between 500 µm and 1 mm and diameters of 20-50 µm, or, more commonly, stocky prismatic, with lengths between 50 and 150 µm and diameters of 10-20 µm (Fig. 4-A, B). The prisms are mostly sub-parallel to the schistosity of the Beira schists (Fig. 4-A), but they may be perpendicular to it. Contact metamorphic cordierite was replaced by tourmaline (Bloot and de Wolf, 1953).

The tourmaline crystals are brown and weakly zoned in thin section (Fig. 3-B), but display well-characterized growth zoning in SEM images (Fig.3-C and 4-C, D) expressed as nearly homogenous
Figure 4. A. Typical early assemblage in the tourmalinized wall-rock, with Tur1 elongated along (erased) schistosity and disseminated rutile. Sample PAN-III-8-c1 (SEM). B. Acicular tourmaline in a silicified wall-rock. Sample PAN-VII-6-b1 (NL). C-D. Evidence for coeval growth of Tur1b and early wolframite: C. Wolframite growth inhibited the development of Tur1b zones; D. Wolframite growth progressively inhibited first Tur1a, then Tur1b growth. Sample PAN-VII-6-b1 (SEM). E-F. Evidence for coeval growth of Tur1b and the W-rich rutile in a Qcs veinlet. Sample PAN-III-8-c1 (SEM).
zones of variable grey intensity, with sharp boundaries. A dark irregularly shaped core is commonly present, although not systematically, but there is no evidence for sector zoning. These cores are interpreted to be relicts of the early tourmaline and are labelled Tur0 hereafter. The outer parts of the tourmaline prisms comprise a medium grey zone, labelled Tur1a and a clearer rim, labelled Tur1b. In rare cases, there is an outermost rim characterized by the recurrence of a darker hue.

**Figure 5.** Synthesis of the stage Ia tourmalinization. A. Initialization of alteration (Tur0) in relation to simple “dry” joints. B. Main tourmaline development (Tur1a) and first increments of opening in Qcs veinlets. C. Growth of Tur1b tourmaline relative to increments of Qcs opening and coeval rutile growth. D. Local variant with early wolframite growing in the wall-rock coevally with Tur1b. E. Transition to the main wolframite deposition stage

Some changes in the relative proportions of the different zones may be observed in relation to the distance from the vein boundaries. Distal to veins, the proportion of Tur0 zones is higher, on
average these zones are wider, locally the crystals display regular (prismatic) shapes and the
development of Tur1b rims is less pronounced. Furthest from the veins, the Tur1b rim may even be
absent. Close to the veins, there is a greater development of the Tur1b zone, and the Tur0 cores are
less common, corroded, and tend to represent a comparatively smaller proportion of the crystal
volume. On the basis of a limited number of examples, it would appear that this tendency is roughly
correlated with the presence of abundant wolframite in the nearby vein. Indeed, in the wall rocks of
barren quartz veins, either in outcrop, or in the deeper levels of the mine (L3), Tur1b is usually
absent.

Micro-inclusions are common in the tourmaline, although not systematically distributed. In order
of importance, they are: zircon, rutile, quartz, and rare monazite, pyrite, and apatite. Most
commonly, the inclusions “overprint” the zone boundaries, and in most cases, the proportion of
inclusions is the same in the Tur1a or Tur1b zones. The Tur0 cores are relatively free of inclusions,
extcept for those of quartz. The zircon may be zoned in respect to their U-Th content. In addition,
microanalysis revealed the probable presence of concealed micro-inclusions (see below).

**Tourmaline and Qcs quartz veinlets:** Tourmaline prisms are systematically present at the walls
of the Qcs veinlets, displaying both Tur1a and Tur1b zones, the latter usually developed to a far
higher extent than in the wall rocks (Fig.4-E, F). Thus, as pointed out by Foxford et al. (1991), the
development of both the main Tur1a tourmaline prisms and the Tur1b rims was coeval with the first
increments of vein opening evident by the Qcs veinlets. This is pictured schematically in Fig. 5. The
very existence of Tur0, which is typically absent from the Qcs veinlets, nonetheless demonstrates
that the onset of tourmalinization was earlier than these veinlets (stage A in Fig. 5).

**Tourmaline and other alteration minerals:** Irrespective of the nature and the number of
hydrothermal minerals in the wall rocks, the tourmaline crystals invariably display the same
sequence of Tur0-Tur1a-Tur1b crystallization. Other alteration minerals are typically later. For
example, the occurrence of topaz and/or muscovite is accompanied by a distinct overgrowth on
Tur1b rims. In the same way, the development of apatite-bearing vugs in the tourmalinized wall
rocks was accompanied by distinct overgrowths on the undissolved tourmaline crystals. As sulfides
(chalcopyrite, sphalerite, pyrrhotite) and siderite are mainly present as stringers in the wall rocks, it
is easy to recognize that these stringers overprint tourmaline 1 prisms and their characteristic
zoning.

Small euhedral arsenopyrite crystals, a few 100 µm in diameter, are frequently disseminated in
the wall rocks (Fig. 3-A), locally (but not commonly) with inclusions of zoned tourmaline prisms.
Nevertheless, arsenopyrite grew after the Tur0-Tur1a-Tur1b sequence, because: (i) arsenopyrite
mostly replaced tourmaline prisms, and (ii) arsenopyrite overprinted Qcs veinlets (Fig. 3-A).
Tourmaline and wolframite: Wolframite from the mineralized veins is not, as a rule, associated with tourmaline but developed as large crystals along the walls of the open fractures. There are rare occurrences of the development of wolframite crystals in the wall rock, close to the mineralized veins (Fig. 4-B). These crystals include zoned tourmaline, and detailed observations show that wolframite growth was either coeval with Tur1b rim development or slightly later (Fig. 4-C, D). This wolframite was, in turn, reworked in relation to the main opening and deposition of the main wolframite, which is consistently devoid of any tourmaline inclusions (stages E and F in Fig. 5).

Rutile textures

Rutile is systematically associated with tourmaline, being present both in the wall rocks, as small (from 10 µm to 80-100 µm) crystals, scattered or densely disseminated, or as large (up to 500 µm or more) isolated crystals in the Qcs veinlets, where they were clearly coeval with Tur1b growth (Fig. 4-E, F). Micro- to nano-inclusions (from about 1 µm, to <100 nm) of wolframite are common. They are usually located at crystallographic boundaries (e.g., faces intersections, twin planes, quartz inclusion boundaries) showing that they were coeval with the host rutile (Fig. 6-A). Their compositions, estimated from SEM-EDS measurements, are ferberitic, with Fe/Fe+Mn ratios between 0.67 and 0.83.

Figure 6. Panasqueira rutile. A, B, C: Back-scattered SEM images of Panasqueira rutile. A. Crystal aggregate from the wall-rock of a wolframite-bearing vein. Note the primary wolframite nano-inclusions (Wfm). B. Crystal in the wall rock of a barren vein from the deep L3 level. Note the ilmenite lamellae (Ilm) and the late apatite (Ap), overprinting the rutile crystal. C. Large isometric crystal from a Qcs vein in the wall-rock of a wolframite-bearing vein. Note the superimposition of sector zoning (SZ) on the compositional (oscillatory) zoning. Square: location of images D to G. D to G: false-color X-ray (EPMA) images, showing the differential effect of SZ on the minor element concentrations, and the anti-correlation of W and Nb in the OZ.
In the barren wall rocks, rutile crystals are less abundant and are characterized by the presence of inclusions of ilmenite lamellae (Fig. 6-B).

Tourmaline chemical composition

**Major element crystal chemistry:** For reasons made explicit in Appendix A0, most analyses were performed using SEM-EDS. A total of 86 crystals from 19 representative samples was analyzed (Appendix A3: Table A3). No systematic variation in the compositions of the different zones was evident, however, either as a function of the distance to the vein boundary, or among tourmaline crystals from different settings (wall rock, Qcs veinlet, inclusions in early wolframite).

The structural formulae were calculated by normalizing to 26.5 (O, OH, F), which (with the assumption of stoichiometric boron) allowed us to take into consideration the fluorine content and not assume the filling of the Y site, which may contain Li, and possibly vacancies (Bosi, 2018). The generalized structural formula of the tourmaline super-group is $\text{XY}_3\text{Z}_6(\text{T}_8\text{O}_{18})(\text{BO}_3)_3\text{V}_3\text{W}$ (Bosi, 2018). The T site is occupied primarily by Si, which may be replaced by minor Ti, Al or B. The nine-coordinated site X may be occupied by Na$^+$ and Ca$^{2+}$, or minor K$^+$, and vacancies ($X^{\cdot}$) may be present. This defines the main chemical groups of tourmaline: alkali, calcic and alkali-deficient groups (Henry et al. 2011). The V, or (O)3, site is occupied mainly by OH (and possibly O), whereas the W, or (O)1, site is occupied by OH, F or O, defining the hydroxy, fluor, and oxy groups, depending on the dominant anion in the site. The six-coordinated Z site is mainly occupied by trivalent cations (mainly, Al$^{3+}$, but also Fe$^{3+}$, Cr$^{3+}$), but may contain divalent cations, mainly Mg (Bosi, 2018). The six-coordinated Y site is occupied by mono- (Li$^+$), bi- (Mg$^{2+}$, Fe$^{2+}$, Mn$^{2+}$) and trivalent (mainly Al$^{3+}$, and possibly Fe$^{3+}$, Cr$^{3+}$) cations, but vacancies ($Y^{\cdot}$) may also be present (Bosi, 2018). Following the criteria of Henry and Dutrow (2011), calculated tourmaline formula were rejected if Si was > 6.15 atoms per formula unit (apfu), the sum of the Y + Z + T cations was >15.5 apfu, or the sum of the X-site cations exceeded 1.1 apfu. For reasons given in Appendix A0, all analyses yielding Si apfu values > 6.12 were rejected. Using the empirical formula of Bosi (2018), the $Z$Al apfu content of the Z site was found to be relatively constant, ~5.23 apfu, irrespective of the zone, and, whereas there was sufficient Mg to fill this site in Tur0 and Tur1a, a small complementary content of $Z$Fe was necessary in Tur1b (Table A3, Appendix A3).

Based on the classification diagram of Henry et al. (2011), which compares the normalized X-vacancy to the Mg# (Mg/Mg+Fe) ratio, the tourmaline classifies mainly as schorl (Fig. 7-A). There is a systematic shift from Mg-rich (ferro-dra prize) to Fe-rich compositions for the sequence Tur0 to Tur1a to Tur1b, and a tendency towards foitite compositions. Indeed, as shown in Figure 7-B, the X-site vacancy is between ~0.2 and ~0.6 pfu (and thus, the Panasqueira tourmaline trends toward
Figure 7. Crystal chemistry of the Panasqueira tourmaline, illustrating the characteristics of the Tur0, Tur1a and Tur1b zones. Note in all the diagrams the continuity of composition variations among the three zones. A. Classification diagram. B. Al vs. X-site lacune diagram, demonstrating the presence of a foitite component. C. Fe vs. Mg diagram, illustrating the presence of an oxy-schorl component, together with the classical schorl-dravite exchange vector. D. Linear relationships between F and the X-site charge; the forbidden zone and references are from Henry and Dutrow (2011): grey domain, worldwide tourmaline (~8,900 values); light blue line: Cruzeiro gold mine fibrous tourmaline; dashed blue line: McCombe pegmatite tourmaline (magmatic trend). E. Na + R2+ vs. Al+X-site lacune diagram, illustrating the deviation from the schorl (dravite)-foitite (Mg-foitite) exchange line due to a combination of the oxy-schorl (dravite) exchange vector and a vector responsible for the creation of Y-site vacancy. F. Fe vs. Al diagram, showing the combination of all exchange vectors involved in the Panasqueira tourmaline.

alkali-deficient species) corresponding to the operation of the Al_{1+1}^{+1}Na_{+1}R_{2+1} vector, which leads to a solid solution between schorl-dravite and foitite-Mg-foitite. From Figure 7-C, E and G, it is evident that other vectors combined to displace the observed trends from the preceding trend. The Al_{+1}O_{1+1}(OH)_{1+1}(Mg, Fe)_{-1} vector seems to have been particularly important, implying an oxy-schorl...
(or oxy-dravite) component, but the intervention of another exchange vector $^\text{Y}_1\text{Al}_2\text{R}^{2+}$, responsible for an Y-site vacancy (Bosi, 2011), seems to have been equally important. Indeed, a Y-site vacancy is observed in our analyses, commonly larger than 0.1 apfu, and also those of Codeço et al. (2017) and Launay et al. (2018) (Table 3, Appendix 3). This vacancy cannot be due to ignored Li, because the LA-ICP-MS results (see below) show that the Li content is negligible, being at most of ~330 ppm and averaging ~170 ppm (Tur1a) or ~290 ppm (Tur1b); these contents would be reflected by an amount of no more than 0.05 apfu Li and more commonly 0.02-0.04 apfu.

Figure 8. A. AFM diagram for the Panasqueira tourmaline, with location of the main tourmaline end-members. (1)-(8) reference fields from Henry and Guidotti (1985): (1) Li-rich granitoids, (2) Li-poor granitoids, (3) Fe$^{3+}$-rich quartz-tourmaline rocks (hydrothermally altered granites), (4) Al-buffered metapelites, (5) not Al-buffered metapelites, (6) Fe$^{3+}$-rich quartz-tourmaline rocks, calc-silicate rocks, and metapelites, (7) low-Ca meta-ultramafics and Cr,V-rich metasediments, and (8) metacarbonates and meta-pyroxenites. Compositions of CIZ schists from Oosterom et al. (1984) and De Amorin (2017). The grey arrow emphasizes the global increase in Fe/Fe+Mg ratio from Tur0 to Tur1b. B. Enlargement of A, illustrating the sequence Tur0-Tur1a-Tur1b: (a) individual paths, (b) synthesis. Note that, if there is a jump from a zone to another, the starting and final compositions differ for each individual crystal.

In contrast to Tur0, which appears to be essentially free of fluorine, there is a distinct and similar fluorine enrichment (up to ~1% F) of Tur1a and Tur1B, and a trend of increasing F apfu with X-site charge (Fig.7-D). The latter is due to the high X-site Na content; Tur1a and Tur1b are Ca-poor, whereas Tur0 is enriched in Ca, which, in turn, explains the higher X-site charge of Tur0 in Figure 7-D.

The complex covariations between aluminum, iron and magnesium that are depicted in Figure 7 are conveniently summarized in the AFM diagram of Figure 8-A, in which it is also possible to identify the most common compositional paths from Tur0 to Tur1a and then Tur1b at the crystal
Figure 9. Profile of the Fe# ratio (Fe/Fe+Mg) along an acicular prism of tourmaline 1 (EPMA analyses), compared to the false color X-image of the same crystal (sample PAN-VII-6-b2). The height of the elliptical symbol corresponds to the estimated error on Fe#. Of the three zones (Tur0, Tur1a, Tur1b) seen on the X-image, only the two latter are documented in the profile. At the rim of Tur1b zone, a recurrence of low Fe# is observed. Note the second and third order modulations of the Fe# ratio along the profile. c: microcrack filled by Tur1b.

scale (Fig. 8-B). This figure illustrates an apparently continuous variation of the Fe to Fe+Mg ratio (Fe#) from Tur0 to Tur1b, although detailed profiles show that there were small-scale modulations of the Fe# during crystal growth (Fig. 9).

Trace element contents: As LA-ICP-MS analyses produce laser pits with a diameter of at least 24 µm, analysis to the desired detection limits was possible only for the largest Tur1 zones in a limited number of crystals. Moreover, the tourmaline cores (Tur0) were too small for them to be reliably analyzed, so analyses were restricted to the two external rims, Tur1a and Tur1b. A total of 77 spots, in 47 crystals from 7 samples were analyzed for their trace element concentrations. The REE concentrations were also analyzed, but to obtain the required signal, a laser beam diameter of 120 µm was necessary, and therefore only two crystals, from two samples, could be analyzed for the REE. This yielded an average composition of Tur1a and Tur1b zones from the two crystals. The results are summarized in Table 1 and detailed in Appendix A4 (Table A4).

For some elements, several LA-ICP-MS spectra displayed anomalous peaks (anomalous values in Table A4), interpreted as recording the presence of concealed micro- to nano-inclusions. Thus, a Mn outlier at 2,600 ppm was likely due to siderite, and a Zn outlier at 8,500 ppm is interpreted to be due to sphalerite. Several W anomalies record the presence of W-bearing minerals: W-bearing rutile, where correlated with both Ti and Nb-Ta-Sn anomalies; cuprotungstite, where correlated
Table 1. Summary of LA-ICP-MS trace element analyses for the Panasqueira tourmalines. All contents in ppm.

For the purpose of average calculations, the bdl (below detection level) in Table A4 were taken at half the detection level values (i.e., the without bias best estimates) when needed (italics). As a result, the averages for Nb (0.2 ppm) and Ta (0.2 ppm) are not provided in the table.

with a Cu anomaly (a rare occurrence); and wolframite, where no correlation was observed with either Ti or Cu. Most of these W anomalies were found in the Tur1b zones.

The results of the trace element analyses are illustrated in Figure 10-A (trace elements except REE) and Figure 11 (REE profiles). As seen in Figure 10-A, Ti, (530 to 4,360 ppm), Zn (160 to 930 ppm) and Mn (135 to 600 ppm) are the most abundant trace elements, followed by Li (40 to 330 ppm), V (10 to 740 ppm) and Cr (10 to 1,000 ppm). Strontium (7 to 285 ppm) and Sn (4 to 160 ppm), are present in lower concentrations, followed by Sc (5 to 30 ppm), Be (3 to 20 ppm), and Pb (1 to 18 ppm). Concentrations of other elements were commonly below the detection level (bdl), e.g., Ni (up to 56 ppm), Co (up to 13 ppm) and Y (up to 7 ppm). Most measured tungsten concentrations were between 0.4 and 30 ppm, but for ~25 % of analyses of Tur1a and 50 % of Tur1b, the W concentration was below the detection level of 0.4 ppm. The measured concentrations for Nb are between 0.1 and 3.2 ppm, but for ~ 75% of the analyses, they were below the detection level of 0.3 ppm; the few measured Ta values were between 0.3 and 1.6 ppm; the overwhelming majority of analyses yielded values below the detection level of 0.3 ppm. From the limited REE data, the $\sum$REE concentration is low (between 1.2 and 12 ppm), and the REE profiles are
characterized by high La\textsubscript{N} to Yb\textsubscript{N} ratios of 6.37 to 6.77, and slightly negative Eu\textsubscript{N}/Eu\textsuperscript{*}\textsubscript{N} anomalies (0.65 to 0.83) (Fig. 11).

Figure 10. Trace-element patterns in Panasqueira tourmaline 1. A. Box plots of LA-ICP-MS results for tourmaline 1a and 1b. The full box represents the lower quartile to upper quartile interval. The whiskers represent the 5%-95% interval. Black circle: average value, black vertical line: median value. Open circle: outlier value, comprised in the 5% lowest or highest data. Inset: normalization of average values of Tur1a to the Tur1b reference. B. Comparison of trace-element distribution (average values) between Panasqueira tourmaline 1a and Beira schists. The elements are arranged from left to right in accordance with their increasing concentration in tourmaline 1a. Data for Beira schists are from De Amorin (2017), Bussink (1984), Oosterom et al. (1984), Pinto (2014) and Valladares et al. (2002).

From Figure 10-A, it can be seen that Tur1a and Tur1b compositions are quite similar, although there are minor but significant differences between them with most of the trace elements being
Figure 11. Chondrite-normalized REE profile for the Panasqueira tourmaline (samples PAN-I-3-c2 and PAN-III-8-c1) compared to the profiles for the Panasqueira metasediments (1: De Amorin, 2017), the fluids associated to the Sarekoubu orogenic gold deposit (2: Xu et al., 2008), the Yellowstone spring water (3: Lewis et al., 1997) and magmatic-derived fluids (4: Banks et al., 1994; 5: Poitrasson et al., 1995) (explanations in the text).

Depleted in Tur1b relative to Tur1a. The notable exceptions to this are Li, Mn and Zn, which are depleted in Tur 1a. This is also evident from the differences in the average values (Table 1, and insert in Figure 10-A), and from the shift between the full boxes (lower quartile to upper quartile interval) in the box plot of Figure 10-A.

A principal component analysis was performed on the trace element data (using the JM Pro software), the results of which are presented in Figure 12. Three axes (PC1-3) explain 52.7% of the
PCA analysis of the trace element composition of the Panasqueira tourmaline, allowing the definition of several groups of trace elements, namely: Mn-Zn-Li, Cr-V-Sc, Co-Ni-Sr-Y-Sn, Be-Pb, and Nb-Ta (explanations in the text).

The first axis (PC1) clearly distinguishes Tur 1a and 1b, as well as two groups of elements: a group A (Li-Mn-Zn) and a group B (nearly all other elements) reproduce, as expected, the relationship observed in Figure 10. The PC2 and PC3 axes display correlations within group B, providing evidence of several subgroups, namely: Co-Ni-Sr-Y-Sn, Cr-V-Sc, Nb-Ta and Pb-Be. Copper, Ti, and W behave independently, and W appears uncorrelated to Nb-Ta.

In binary plots, elements of group A display rough linear trends expressing positive correlations (when outliers are excluded), as seen for example in Figures 13-A to C, and predicted by the principal component analysis. Similarly, elements of group A display negative correlations with elements of group B, as seen, for example, in Figures 13-D to H. Less expected were the linear...
Figure 13. Binary plots of selected trace elements from Panasqueira tourmaline, showing contrasting behaviour, including positive, negative and null correlations, depending on the elements (explanation in the text).
relationships between elements from the various B subgroups, as seen for example in Figures 13-I to K. The rare metals (W, Nb, Ta) behave differently. Whereas Nb-Ta show a very loose negative correlation with Li (Fig.13-L), there is no correlation between W and Li (Fig. 13-M), nor between W and Nb-Ta (Fig. 13-N). Finally, Sn is not correlated with Nb-Ta (Fig. 13-O) or with W (Fig. 13-P).

Rutile composition:
The composition and zoning of the Panasqueira rutile have been described in detail in Carocci et al. (2019) and only a summary is given here. This rutile contains variable proportions of: Fe from 0.18 to 2.95 wt%, V from <1000 ppm to 3.48 wt%, Cr from <1000 ppm to 2.41 wt%, Nb from <1000 ppm to 1.64 wt%, Ta from <1000 ppm to 2.17 wt%, and W from 0.20 to 10.7 wt%. Despite locally high values, Nb and Ta concentrations are usually low; the Nb+Ta content is usually < 0.5 wt% and the Nb/Nb+Ta ratio varies from 0.05 to 0.97 (on average 0.6).

The crystals display marked sector zoning, exhibited mostly by W and Fe and, to a lesser extent, by Nb and Ta; Sn, V (and Cr), and display less evidence of zoning (Fig. 6- C to G). The maximum W concentration varies from 1.12 to 10.7 wt.% in the metal-rich sectors, depending on the sample; W concentrations in the metal-poor sectors vary between 0.26 to 1.40 wt %. As metal-rich sectors reach their highest W contents in wall rocks adjacent to veins in which wolframite is abundant, whereas in barren wall rocks the metal-rich sectors are less endowed in W (no more than 3.5 wt% W), it would appear that the W enrichment in rutile is related to the wolframite endowment in the nearby veins. Association of a very W-rich rutile with wolframite was also observed in the Puy-les-Vignes breccia-pipe tungsten deposit in the French Massif Central (Harlaux, 2016).

The sector zoning is superimposed on a conspicuous compositional zoning, expressed from the crystal scale down to the 10 µm to µm scale of the doublets characteristic of oscillatory zoning (Fig. 6-C). The zoning, however, is qualitatively and quantitatively the same irrespective of the rutile setting. All the minor elements, W, Nb(Ta), Fe, V, Cr and Sn, are involved in the compositional zoning. At all scales, W and Nb(Ta) are inversely-correlated, whereas Sn and V display inconsistent behavior, being either correlated with Nb(Ta) and inversely-correlated with W or the opposite.

The bulk evolution during crystal growth was variable from one crystal to the next, even at the sample scale. In some crystals, there is continuous evolution from a Nb-rich and W-poor core to a Nb-poor and W-rich rim, whereas the opposite is observed in others. Most commonly, however, the zoning displays moderate deviations from the average W content.

Age determinations
Figure 14. Results of U-Pb age determinations of wall-rock Panasqueira rutile (Tera-Wasserburg Concordia diagrams). Note the highly discordant behaviour of the rutile. A. All data, showing the importance of lead loss in the rutile crystals. B. Data remaining after elimination of analyses more affected by lead loss. C. Idem, with data constrained to be consistent with the common lead value of Stacey and Kramers (1975) at c. 300 Ma. Explanations in the text.

Rutile: Petrographic examination suggests that rutile from both the tourmalinized wall rocks and the Qcs veinlets were coeval with the early tourmaline and the earliest wolframite deposition. Unfortunately, the number of rutile crystals suitable for U-Pb dating was limited by the size of the laser spot (45 µm). Some crystals from Qcs crack-seal veins are large enough to be analyzed, but
very few crystals in the wall rocks reach 50 µm in diameter. Thus, only 22 crystals from 5 samples could be analyzed for their U-Pb isotopic compositions.

The analyzed crystals have variable concentrations of common lead, and low radiogenic Pb contents (Appendix 6, Table A6). On a Tera-Wasserburg diagram they plot in a discordant to a very discordant position, except for one sample (PAN-III-8-c1), which plots close to the Concordia curve. Figure 14 illustrates three regression lines: (i) using all the data, the regression line results in a discordia with a lower intercept at 302.7 ±8.9 Ma (2σ, MSWD =5.3) (Fig. 14-A), the poor quality of this age determination being due to large lead losses, (ii) a discordia in which data corresponding to the greater lead losses were ignored (Fig. 14-B), passes through the concordant data and yields a lower intercept at 305.2 ± 5.7 Ma (2σ, MSWD = 1.9), the upper intercept yielding a common lead 207Pb/206Pb ratio of 0.906, which is slightly higher than the 0.855 value predicted by the Stacey and Kramers (1975) model for the same age; and (iii) a discordia, anchored to the Stacey and Kramers composition at 305 Ma, yielding a lower intercept at 303.7 ± 6.6 Ma (2σ, MSWD = 3.9) (Fig. 14-C). A similar date of 303.7 ± 6.6 Ma, with a slightly higher MSWD value of 3.9 is obtained by constraining the regression to fit the Stacey and Kramers (1975) common lead composition. A critical issue is the 207Pb/206Pb value of the common lead in the CIZ at c 305 Ma. At c. 320 Ma, the 207Pb/206Pb ratio of the Ediacaran and Tremadocian metasediments was between 0.885 and 0.96 (calculated from Nägler et al. 1993, 1995 data). It thus evident that the 0.906 value for the common lead in the Panasqueira rutile is in accordance with the regional values, and, consequently, the date of 305.2 ± 5.7 Ma is interpreted as the best estimate for the crystallization age of the rutile. As Poly et al. (2000) demonstrated that the Qcs veins immediately preceded the main opening of the quartz vein system and wolframite deposition, the age of c. 305 Ma is also interpreted to be the age of the main wolframite deposition.

Figure 15. Synthesis of radiometric ages for the Panasqueira deposit, comparing results of the present work with those of Snee et al. (1988). Explanation in the text.

Complementary dating: To complement the U-Pb age determinations, a muscovite selvage (sample PAN-XIV-181-1) was dated using the 39Ar/40Ar method at the University of Manitoba.
(Canada) and yielded a good plateau age of 296±2 (1σ) Ma, which is indiscernible within the limits of error (Appendix A7-Table A7) from the preceding $^{39}$Ar/$^{40}$Ar age of 296.3±0.6 Ma (1σ) obtained by Snee et al. (1988) on muscovite selvages. Until now, this age was considered to be the age of the main mineralization (OSS stage of Polya et al., 2000), assuming that this muscovite preceded wolframite deposition. The new results show, however, that the muscovite selvages are at least 2 Ma younger.

Discussion

Tourmalinization: one or two fluids?

Tourmaline as a fluid proxy

According to von Goerne et al. (2001), van Hinsberg (2011), Berryman et al. (2016) and Vereshchagin et al. (2018), the trace element partition coefficients between tourmaline and the medium from which it crystallizes are close to unity. Thus, the relative proportions of the trace elements in tourmaline reflect the relative proportions of trace elements in the fluid from which it crystallized. Fluorine concentration is subject to crystallographic constraints, because of its dependence on the X-charge in the structural formula (Henry and Dutrow, 2011). Within these constraints, the incorporation of F into the tourmaline structure is controlled by external factors, in particular, the F availability, and thus tourmaline may also be considered a F proxy.

In the absence of measurable fluid inclusions (FI) in the tourmalinized wall rocks at Panasqueira, information on the nature of the fluids responsible for the tourmalinization can be obtained indirectly, using the tourmaline composition. The major and trace element concentrations differ from Tur1a to Tur1b, pointing to a change in the fluid composition. Consideration of Figure 8-A and 10-A shows a shift from a Co, (Cu), Pb, Sc, Sr, V, Cr, Sn, Nb, Ta package in Tur1a, towards a Li, Fe, Mn, Zn, W rich package in Tur1b. The correlations shown in Figure 13 are clear evidence of a continuous evolution. This evolution could, however, have resulted from either the differentiation of a single fluid or the mixing between two fluid end-members.

Discussion of single fluid models

Single fluid models for the Panasqueira system have been favored by previous workers (Bussink, 1984; Lecumberri-Sanchez et al., 2017; Codeço et al., 2017). Codeço et al. (2017) assumed that the Fe# increase was the result of a decrease in the temperature of a single fluid, from ~480°-460°C during alteration of the wall rocks to 360°-230°C in the mineralized quartz veins. The former temperature was estimated using the Ti-in-quartz thermometer (Codeço et al., 2017), whereas the latter come from earlier fluid inclusion studies (e.g., Kelly and Rye, 1979). Recent fluid inclusion
studies (Dejean, 2017; Cathelineau et al., 2017; 2018; Carocci, 2019) have concluded, however, that the temperature of the main quartz-wolframite deposition stage was $450^\circ\pm50^\circ$C. Therefore, a strong temperature decrease cannot be the explanation for the change in Fe#.

Lecumberri-Sanchez et al. (2017) related the wolframite deposition to wall rock alteration. They concluded that the muscovitized parts, which commonly (but not systematically) fringe the mineralized quartz veins were coeval with the more distal tourmalinized zone, and that wolframite deposited due to the interaction of a Fe-poor, but W-bearing fluid, with the schists as a result of the release of Fe from the latter during muscovitization. This model is unsupported because: (1) muscovitization at the vein borders post-dated tourmalinization (see above), (2) the muscovitized fringes formed synchronously with the muscovite selvages of the mineralized quartz veins, and (3) the geochronological data reported in this study show that muscovite formed later than the wall-rock tourmalinization.

A fractional crystallization model could explain the Fe# increase from Tur1a to Tur1b but would require that the system was closed, which is inconsistent with the crack-seal textures of the Qcs veinlets associated with fluid influx into the wall rocks. It is difficult to reconcile this model with the differential behavior of the trace elements between Tur1a and Tur1b, some having been enriched, and others impoverished, something which cannot be explained by the effect of differences between partition coefficients. This model also explains the significant overlap of the trace element compositions of Tur1a and Tur1b (Fig. 13).

A final single fluid model that could be considered is one in which the system evolved continuously from wall rock-controlled (Tur0) to fluid-controlled (Tur1b stage) conditions during the course of fluid-rock interaction. High water-rock ratios are indicated by the absence of compositional differences in either the Tur1a or Tur1b zones, with respect to the position of tourmaline in the system, irrespective of whether the tourmaline is in Qcs veinlets or part of the tourmalinized wall rock, proximal or distal to the veinlets. Furthermore, the widespread evidence of corrosion of the Tur0 cores points to sudden changes in the ambient fluid composition, which is difficult to reconcile with the single fluid model. During such fluid-rock interaction, the Tur0 composition would reflect the host-rock composition prior to the alteration, masking the characteristics of the incoming fluid. Petrographic observations indicate that tourmaline grew at the expense of earlier ferro-magnesian minerals (biotite, cordierite). Thus, the Fe# in the Tur0 cores would be expected to reflect the Fe# of the Beira schist, which is not the case (Fig. 8A). In addition, the lack of F in Tur0 is in strong contrast with the high F content of the Beira schists (570 ppm in average: Oosterom et al., 1984). Also, despite the high Ti content (0.6 to 1.0 wt% TiO$_2$) of the Beira schists (Bussink, 1984), the tourmaline is Ti-poor, which may, however, be due, at least in part, to...
competition with the coeval rutile. The Tur1a and Tur1b trace element package is, in order of decreasing abundance (Figure 10-A): Ti-Zn-Mn-(V, Cr)-(Sr,Li)-Sn-(Sc,Ni)-Be-Pb-W-(Cu,Co)-Y-Nb-Ta. A compilation of local data (Figure 10-B) reveals that in the Beira schists, these elements are in a significantly distinct order of decreasing abundance: Ti-Mn-(Zn,V,Li)-(Cr,Sr)-Ni-Cu-(Co,Y,Sc)-Nb-Pb-(W,Sn)-Be-Ta. Therefore, concentrations in Tur0 and Tur1a are not strictly mimetic of the Beira schist composition.

In conclusion, no single fluid evolution model is able to fully explain all the data, and a two-fluid model must be seriously considered.

A two-fluid mixing model

We propose a fluid-mixing model involving two end-members, the first of which (F1) was associated with the formation of Tur0, and the second (F2) of which mixed with F1 to form Tur1a and then Tur1b. The F1 fluid end-member composition, like Tur1a, was enriched in Co, (Cu), Pb, Sc, Sr, V, Cr, Sn, Nb, Ta, depleted in F and more magnesian than F2. The F2 fluid end-member composition, like Tur1b, was enriched in Li, Mn, Zn, Fe and F (Fig. 7-D). As tungsten concentration does not correlate with that of Nb, Ta and Sn (Fig. 12 and 13), we propose that it was enriched in the F2 fluid, despite the fact that Tur1b is generally depleted in W relative to Tur1a (Fig. 10-A) and attribute this apparent contradiction to competition for tungsten between Tur1b and the coeval W-rich rutile. This proposal is supported by the abundance of W-bearing nano-inclusions in Tur1b (as inferred from tungsten anomalies in the LA-ICP-MS record, see above) and the occurrence of the coeval W-rich rutile.

The fluid-mixing model explains the inter-element correlations and anti-correlations displayed in Figure 13. The corrosion exhibited by the Tur0 core may mark the arrival of F2 into the system and the onset of the mixing process. The evidence for a continuous process and the conflicting evidence of a sharp transition between Tur1a and Tur1b, could indicate a sudden increase in the F2 to F1 fluid ratio. This increase could have been related to an interruption in deposition due to a temporary closure of the vein system. Local corrosion, or overprinting (Fig. 9), of Tur1a by Tur1b is a further evidence for this explanation. The small scale oscillations of Fe# during crystal growth, as well as the recurrence of low Fe# at the end of the Tur1b growth, could reflect also temporary variations in the F2 to F1 fluid ratio, explaining the overlap between Tur1a and Tur1b trace element compositions in Figure 13.

The fluid source

Magmatic or metamorphic source: boron and REE constraints
**Boron:** the boron in tungsten deposits is usually considered to be of magmatic origin (e.g., London, 2011), and this interpretation has been adopted for Panasqueira in the recent works of Lecumberri-Sanchez et al. (2017), Codeço et al. (2018) and Launay et al. (2018). According to these studies, fluids released from the Panasqueira granite, and in particular, from the greisenized cupola, provided the boron required for tourmalinization. Codeço et al. (2017) reported that the δ11B values of the Panasqueira tourmaline are between -4‰ and -13‰ (with 90% of the data between -7‰ and -11‰) and display a Gaussian distribution. These values are consistent with either a magmatic or a metasedimentary source for the boron.

Tourmaline replaced the contact metamorphic aureole minerals related to the emplacement of the main Panasqueira granite, and is therefore later than this magmatic stage. Consequently, tourmalinization is unlikely have been caused by magmatic fluids issued from this large body by itself. In fact, the cupola, as well as the sheet-like body of rare metal granite (RMG) type, at the top of the main granite body (De Amorin, 2017), may have been emplaced later, and, consequently may have been a source of boron, and the fluid to transport it. A mass balance calculation (details presented in Appendix A8) shows that the cupola could not by itself have supplied the quantity of boron needed for wall rock tourmalinization, at the deposit scale. By the same calculation, the subjacent sheet-like RMG body could, however, have supplied a significant part of this boron, although certainly not all that was required. The calculations were done under the assumption of a tourmaline-saturated melt. Yet, tourmaline is typically absent from the cupola or the subjacent RMG, and observation of the cupola/schist contact did not reveal evidence for tourmalinization of the wall rock. The calculated B deliveries are therefore greatly overestimated. Another problem is the volume of fluid that was needed for tourmalinization. The Panasqueira RMG sheet-like body could only have supplied an order of magnitude less than the required volume of fluids (Appendix A8). Another source of boron (and fluids) is clearly required.

Concentrations of boron are around 0.5 to 1%, at tourmaline saturation in aqueous fluids buffered in respect to aluminium silicate at temperatures between 500 and 600°C, according to experimental data (Weisbrod et al., 1986; London, 2011). Consequently, metamorphic fluids may have the capacity to extract and transport boron. The Beira schists contain on average ~ 100 ppm B (Oosterom et al., 1984). Mass balance calculations (Appendix A8) show that the 410 to 810 kt of boron required to account for the observed tourmaline, and the 2.2 to 4.3 km3 of fluid, necessary to dissolve, transport and deposit this amount of boron, may be produced by the devolatilization of no more than 20 km³ to 40 km³ of Beira schists.

**Rare earth elements:** the REE profiles of Tur1 are very similar to those of the Beira schists (Fig. 11), suggesting that the fluids responsible for tourmalinization were of metamorphic origin or
equilibrated with metasedimentary rocks at high temperature. Similar REE profiles are observed in tourmaline from deposits for which a metamorphic origin of the fluid is accepted, as for example the orogenic gold deposit of Sarekoubu (Xu et al., 2008) (Fig. 9). In contrast, magmatic-hydrothermal fluids, as well as fluids that equilibrated with granite at a high subsolidus temperature, display a pronounced negative europium anomaly (e.g., Banks et al., 1994; Poitrasson et al., 1995), which is absent from the REE patterns of Panasqueira tourmaline (Fig. 11). A significant magmatic contribution to the tourmalinizing fluids is therefore unlikely.

**Distinguishing F1-F2 fluids: trace elements constraints**

The characteristic Ti, V, Cr, Sr, Sn, Sc, Pb, Ni, Be, Co, Cu, Y, Nb, Ta trace element package deduced for the F1 end-member in a preceding section is consistent with F1 having been equilibrated with a metasedimentary sequence like the Beira Schists. Indeed, it is known that metamorphic fluid compositions reflect those of the related metamorphic rocks (e.g., Tang and Liu, 2002).

The F2 composition characterized by the Fe, F, Mn, Li, Zn, W package could suggest equilibrium with a granitic magma. Magmatic fluids issued from RMG melts (e.g., Harlaux et al., 2017) rich in F, Li, Fe and Mn, however, are richer in Sn than W, contain similar W and Nb-Ta contents, and are depleted in Zn. These significant differences with the F2 package consequently do not support a magmatic origin for the F2 fluid.

This apparent paradox may be resolved in the context of the processes occurring in the CIZ middle crust at the end of the Carboniferous. Dehydration-melting in migmatite domains involving biotite breakdown and the formation of granitic melts (Pereira Gomez et al., 2000) likely took place at the end of the Carboniferous, as in equivalent domains of the Variscan belt at this time (e.g., Guttierez-Alonso et al., 2011; Barbey et al., 2015). It is known that biotite from the high-grade (unmelted) Beira schists contains significant proportions of F, Li, as well as Fe, Mn, Zn and W (Acosta-Vigil et al., 2011). Biotite breakdown is therefore a potential source for Li, Fe, Mn, Zn, and rare metals. The dehydration-melting anatectic domains are also potential sources of large fluid volumes (larger than those released by most granite plutons), produced only through the biotite incongruent melting. During crystallization of the haplogranitic leucosome melt, the unmixed migmatitic fluid would therefore bear the biotite signature in trace elements. This signature, which differs from that of metamorphic fluids issued from unmelted areas, is consistent with the F2 trace element package. Final melting of tourmaline in the anatectic domains delivered boron (Acosta-Vigil et al., 2011), and thus F2 may have contained the boron required for the Tur1b crystallization.
Proposed conceptual model

In order to integrate the preceding results into a workable model for the tourmalinization at Panasqueira, a starting point is to consider the upward transfer of the boron-rich F2 fluid from the inferred source at depth to the deposit level. Here, the concept of a mid-crustal channelized fluid flow (Connolly, 1989) may be called for. According to the modelling by Connolly (1989), deep fluids issued from biotite dehydration gather into a collection zone, and are then focused and channelled into a mid-crustal fault zone, ascending at high rates up to a dispersion region in cooler rocks. The half-width of the collection and dispersion zones is typically in the 3-5 km range, and the height of the system is on the order of 10 to 15 km. The flow results in upward heat advection on a \( \sim 10^4 \) yr time-scale, inducing a temperature increase of several 10s °C at the 100 kyr time-scale in the dispersion region (Connolly, 1989).
Figure 16. Conceptual model of the crustal scale hydrothermal system at the onset of the main wolframite stage at Panasqueira. A geothermal gradient of ~ 40°C.km⁻¹ is assumed (Cathelineau et al., 2018). The model involves two sources of metamorphic fluids at different structural levels (F1 and F2), and their mixing in the Panasqueira vein system. Explanations in the text.

Applied to the Panasqueira system, the collection domain of this model could have been located at depths of 15-20 km, where F2 fluids could have been generated by incongruent melting of biotite. With a total width of 10 km, such a collection domain would have been large enough to provide both the required mass of boron and the fluid volume for tourmalinization. The fault zone necessary for the channelling is thought to have been related to the emplacement of the main
Panasqueira granite. Owing to the NNW-SSE elongation of the body (Ribeiro, 2017), this postulated fault should have a similar direction. In addition, fluid ascent was facilitated by the vertical permeability (S0 and schistosity) in the core of the Panasqueira anticline.

At a level corresponding roughly to the bottom of the dispersion level of Connolly (1989), the ascending F2 fluid encountered the Panasqueira granite body and was forced around it, as a consequence of the thermal boundary layer hindering penetration of the flowing fluids into the granite body (this implies that the initiation of the hydrothermal system immediately succeeded granite emplacement). Thereafter, it was driven towards the main permeability channel (the system of joints that guided the future vein system), where it met the resident fluid. As seen in Figure 16, at c. 305 Ma, a continuous cap of thick impermeable Ordovician quartzite (Armorican Quartzite) covered the Beira schists, defining a reservoir for the metamorphic fluids released by either the first LP-HT event in the CIZ at c. 320-317 Ma or by the contact metamorphism of the main Panasqueira granite or both. These fluids are interpreted to represent the F1 end-member. The continuous transfer of heat by the F2 fluid and the resulting heating of the dispersion zone (Connolly, 1989), is thought to have driven convective flow of F1 in the Panasqueira reservoir, promoting the mixing of F1 with F2 fluids in the high permeability domain, which resulted in tourmaline deposition (Fig. 16). Cooling of the Panasqueira granite pluton, could have contributed to the thermal anomaly.

Launay et al. (2018) described an outwardly flow pattern in the close vicinity of the “greisen cupola”, which they interpreted as the radial flow of magmatic fluids out from the cupola. As suggested in Figure 16, this remarkable pattern could as well have resulted from the limited penetration of the F2 fluid in the uppermost granite layers (F2’ pattern in Figure 16). Because the F2 input may have varied with time, the model in Figure 16 is consistent with the short-term variations in the F1 to F2 ratios that are inferred from the rutile zoning and tourmaline profiling.

Conclusions

1. The earliest hydrothermal event in the Panasqueira system was wall rock tourmalinization. Zoned tourmaline replaced ferro-magnesian minerals in the protolith in a Tur0-Tur1a,b sequence. This event coincided with the first fluid-overpressure-induced opening of crack-seal fractures (Qcs veinlets).

2. The early Tur1 tourmaline, and in particular, the development of Tur1b rims, was coeval with the formation of W-bearing rutile (which is among the richest in W anywhere) and the first appearance of wolframite.
3. On the basis of a limited number of observations, it seems that there is a correlation between the presence/abundance of wolframite in quartz veins and the relative importance in the adjacent altered wall rock of Tur1b rims, and a high content of tungsten in rutile. The poor development of the Tur1b rim, and limited W enrichment in the rutile, together with the presence of ilmenite lamellae, are indicators of barren veins. This is of potential interest for evaluating exploration drill holes from a resource and mine development perspective.

4. The early rutile crystallized at 305.2 ± 5.7 Ma and coincided with early tourmalinization and the first appearance of wolframite. This new age is greater than the currently accepted age of c. 296 Ma, which was obtained on muscovite selvages that post-dated wolframite deposition.

5. The Panasqueira hydrothermal system was active for more than 6-8 Ma and was the product of a much deeper crustal system than proposed in previous studies, in which the W mineralizing fluids were released by a single granite intrusion.

6. Two fluids, both of metamorphic origin, were involved in tourmaline growth. The first, rich in Ti, V, Cr, Sr, Sn, Sc, Pb, Ni, Co, Cu, Y, Nb, Ta, and of “local” derivation, was replaced progressively by a second fluid, rich in Li, F, Fe, Mn, W, of deeper origin (biotite dehydration). This second fluid carried the metals necessary for wolframite deposition and in particular Fe and Mn, which were not inherited from the host rocks.

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Appendix A0. Comparaison of SEM-EDS and EPMA analyses of Panasqueira tourmaline

1. Problems in measuring Tur compositions by EPMA

The Pnq tourmaline crystals from the tourmalinized wall rocks are very small and therefore so are the different zones in the crystals. Owing to the rather low contrasting capacity of back scatter imaging by EPMA in our laboratory, it is usually challenging to assure that a given spot is really located in the desired zone: this is particularly true for the Tur 0 residual cores, that are usually not seen with EPMA. What is more, it is not so easy to retrieve under EPMA the crystals imaged by SEM - given that we ordinary explore the sections at random to find the best crystals.

For all these reasons, it was desirable to make measurements while identifying the zoning features, i.e., to mainly use SEM-EDS. To ensure compatibility of the two approaches, EPMA and SEM measurement were both performed on chosen crystals. Comparison between the results of the two kinds of measurement was thus made possible, and is effected in the following sections.

2. Reality and extent of a Si apfu bias in SEM-EDS analyses

As shown in Fig. A0-1, statistics of Si apfu from SEM-EDS analyses (calculated on an O, OH, F basis) display a shift towards values higher than 6.00, contrasting with the average 6.00 obtained from EPMA analyses.

![Figure A1. Comparative statistics of Si apfu measurements by EPMa or SEM-EDS.](image)

More precisely, the distribution is plurimodal, and ~ 35 % are comprised between 6.0 and 6.06 (averaging 6.04), ~ 45 % are comprised between 6.06 and 6.12 (averaging 6.10) and only ~20 % are higher; the latter are named “outliers” in the following. It may also be noted that there is a consistent overlap between the EPMA distribution and the first mode of the SEM-EDS distribution: in fact, EPMA distribution could be interpreted as bimodal, with the second mode nearly coincident with the first SEM-EDS mode.

It results that ~ 80 % of the SEM-EDS analyses yield lower than 6.12 Si apfu values, and it may be expected that this will cause only small shifts (if any) from the EPMA reference in the various crystal chemistry diagrams: this will be addressed in the following section.

Considering the outliers, it appears that most of them (~ 60 %) come from the Tur0 relict cores. A possible explanation of such deviant analyses could be the presence in the cores of nano-inclusions of quartz crystals: as mentioned in the main text, many tourmaline crystals of the tourmalinized wall-rocks are clouded of quartz inclusions, often concentrated in the core zones. If so, the formula calculation should not affect too much the elemental ratios, and it may be expected that plotting of the analyses in the various diagrams will reveal the same trends as the “cleaner” analyses. This will be examined in a following section.

3. SEM-EPMA comparison
For the comparison, the more suitable crystals, of sufficiently large size, appear to belong to a second generation of tourmaline (Tur2), not addressed in the manuscript, of which two sets of crystals were available, in samples PAN XIX-16-a2-b1 and PAN-III-8-c1/2; in the latter, however, sufficiently contrasted zoned crystals of the first generation (Tur1) found in crack-seal quartz veinlets (see Figure 4 in main text) could also be measured by the two method, as well as late (Tur3) overgrowths on Tur2.

**Figure A2**. Comparison of EPMA and SEM-EDS measurements on selected sets of tourmaline crystals in two samples (see text).

Comparison is made in a series of diagrams in Fig. A0-2, and results are the following:

- the diagram characteristics (range of values, distribution of Tur types) are basically the same for the two sets of analyses;
- very limited shifts affect the trends in the Al vs [] and Na+R2+ vs Al+[+] diagrams for SEM-EDS analyses relative to EPMA ones: nevertheless, the SEM-EDS trends remain included in the dispersion field of EPMA analyses;
- the Al/Fe/Mg ratios seem in particular identical in the two sets of results; this is confirmed by examination of the AFM diagrams in Fig. A0-3. It is noteworthy that the dispersion of the Al/Fe+Mg ratios is similar whatever the analysis method, thus certifying that this dispersion is real.

It may thus be concluded that use of SEM-EDS analyses in place of EPMA ones for the considered crystals did not affect the restitution of crystal chemistry properties.
1232 these mode 1 analyses may thus be in turn used as reference for the other sets of analyses.

1235 Figure A. Comparison of EPMA and SEM-EDS analyses in AFM diagrams. A: Tur2 (samples PAN-XIX-16-a2-b1
1236 and PAN-III-8-c2) and Tur3 (PAN-III-8-c2; B: Tur 0 and Tur 1 (sample PAN-III-8-c1, excepted Tur0-EPMA, taken
1237 from other samples).

1238 4. Internal consistency of SEM-EDS analyses

1239 Separating the analyses in three sets corresponding to the three modes in Fig. A0-1 (mode 1 =
1240 “low” Si, mode 2 = “high” Si, mode 3 = “outliers”) is done in the diagrams of Fig. A0-4 and

1241 Figure A0-4. Checking the internal consistency of SEM-EDS analyses using classical crystal chemistry diagrams. The
1242 domain boundaries are those corresponding to mode 1 in all diagrams. The red lines correspond to EPMA reference.

1243 A0-5.

1244 (i) A first result is that in the Al vs [ ] and Na+R$^{2+}$ vs Al$^{+}$ diagrams, the whole of the mode 1
1245 values behave as the ones in sample III-8-c, as indeed expected. The crystal chemistry diagrams of
1246 these mode 1 analyses may thus be in turn used as reference for the other sets of analyses.
(ii) In all the diagrams, the mode 2 values yield basically the same relations, and in particular, the boundaries between “Tur0”, “Tur1a” and “Tur1b” fields are very consistent in the three Fe vs. Al, Fe vs Mg and []# vs. Mg# diagrams in Fig. A0-4, and in the AFM diagrams in Fig. A0-5.

(iii) As expected, the “outlier” values are shifted in the Al vs [] and Na+R\(^{2+}\) vs Al+[] diagrams, displaying nevertheless the same characteristics. They however are highly compatible with the preceding sets of values in the other diagrams. This is particularly significant for the Tur0 values.

**Figure A0-5.** Checking the internal consistency of SEM-EDS analyses in the AFM triangle. A: mode 1 ("low Si"); B: mode 2 ("high" Si); C: mode 3 ("outliers"). The domain boundaries are those corresponding to mode 1 in all three diagrams.

5. The case for F

It is known that, in tourmaline, there may be a rough linear relationships between F content and the ionic charge associated with the site X infilling. Consideration of Fig. A0-6 shows that this is indeed the case and that:

- (i) there is no significant differences between the SEM-EDS analyses corresponding to either mode 1, or mode 2 or mode 3 of the Si distribution (Fig. A0-6A to C)

- (ii) the scarcity of EPMA measurements in Tur 1 prevents a comparison zone by zone, although the rare Tur0 measurements by EPMA confirm that F content in Tur0 is generally low (Fig. A0-6A)

- (iii) if therefore EPMA and SEM-EDS analyses are considered as a whole (Fig. A0-6D and E), both sets of analyses display a large dispersion and a very rough linear relationship, with a slight difference between the two sets which nevertheless does not introduce a significant difference for the data interpretation.
Figure A0-6. Relationships between F and the X-site charge: comparison of EPMA and SEM-EDS results. A to C: comparison zone by zone (A: Tur0; B: Tur 1a; C: Tur 1b); D-E: bulk comparison. Contours in E: from D.

6. Conclusion

It results from the preceding that the SEM-EDS analyses may be safely used for the crystal chemistry characterization of the Panasqueira tourmaline, provided that analyses from mode 3 group be discarded.

Finally, 117 spots in 19 samples are taken into consideration in the main text.
## Appendix A1-Table A1: Operating conditions for the LA-ICP-MS equipment

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<tr>
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</tr>
<tr>
<td>Sample preparation</td>
<td>Rutile grains in context in thin-sections</td>
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### Laser ablation system

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<tr>
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### ICP-MS Instrument

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<td>Extraction lenses</td>
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<tr>
<td>Data acquisition protocol</td>
<td>Time-resolved analysis</td>
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<td>Scanning mode</td>
<td>Peak hopping, one point per peak</td>
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<tr>
<td>Detector mode</td>
<td>Pulse counting, dead time correction applied, and analog mode when signal intensity (&gt; \sim 10^6) cps</td>
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<td>Masses measured</td>
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<td>Dwell time per isotope</td>
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</table>

### Data Processing

| Gas blank                         | 20 seconds on-peak |
| Calibration strategy              | R10 Rutile used as primary reference material, R19 rutile used as secondary reference material (quality control) |
| Reference Material info           | R10 (Luvizotto et al., 2009) |
|                                   | R19 (Zack et al., 2011) |
| Data processing package used      | Iolite (Paton et al., 2010), VizualAge_UcomPbine (Chew et al., 2014) |
| Quality control / Validation      | R19: Apr 2016: 490 ± 3.4 Ma (MSWD=1.11; N=13) |
|                                   | Dec 2017 : 493 ± 12 Ma (MSWD=2; N=12) |
Appendix A2: Ar-Ar dating of muscovite (methodology)

Argon isotopes (from mass 40 to 37) were measured using Faraday detectors with low noise $1 \times 10^{12} \Omega$ resistors and mass 36 was measured using a compact discrete dynode (CDD) detector. The sensitivity for argon measurements is $\sim 6.312 \times 10^{17}$ moles/fA as determined from measured aliquots of Fish Canyon Sanidine (Dazé et al., 2003; Kuiper et al., 2008). Standards and sample were placed in 2 mm deep wells in 18 mm diameter aluminium disks, with standards placed strategically so that the lateral neutron flux gradients across the disk could be evaluated. Planar regressions were fit to the standard data, and the $^{40}\text{Ar}/^{39}\text{Ar}$ neutron fluence parameter ($J$) interpolated for the unknowns. Uncertainties in $J$ are estimated at 0.1 - 0.2% (1σ), based on Monte Carlo error analysis of the planar regressions (Best et al., 1995). All specimens were irradiated in the Cadmium-lined, in-core CLICIT facility of the TRIGA reactor at the Oregon State University (USA). The duration of irradiation was 17 hours and using the Fish Canyon sanidine (Kuiper et al., 2008) and GA1550 biotite (Spell and McDougall, 2003) standards. Standards for $^{40}\text{Ar}/^{39}\text{Ar}$ measurements were placed in a Cu sample tray, with a KBr cover slip, in a stainless steel chamber with a differentially pumped ZnS viewport attached to a Thermo Fisher Scientific extraction/purification line and baked with an infrared lamp for 24 hours. Single crystals were fused using the CO$_2$ laser. The sample selected for the $^{40}\text{Ar}/^{39}\text{Ar}$ dating has been previously investigated by optical microscopy and SEM in order to spot homogeneous areas devoid of alteration, micro-inclusions or internal zoning. Discs of 5 mm in diameter and ~150 µm thick were cut from the same polished thick section (150 - 200 µm thick). The discs were mounted using a ceramic adhesive (PELCO) on a quartz slide placed in a stainless steel chamber with a sapphire viewport attached to the same stainless steel high vacuum extraction system as the CO$_2$ laser, and baked with an infrared lamp for 48 hours. For this study, a raster size of about 100 x 100 µm was used and ablation pits were excavated to an estimated depth of 50 µm. Reactive gases were removed for both the standard and unknown, after 3 minutes, by three GP-50 SAES getters (two at room temperature and one at 450 °C) prior to being admitted to an ARGUS VI mass spectrometer by expansion. Five argon isotopes were measured simultaneously over a period of 6 minutes.

References cited


Appendix A8: Mass balance calculations

Boron mass balance calculations

Boron endowment in the granites: It must be emphasized that the greisenized cupola and the subjacent granites layer are typically devoid of tourmaline, meaning that the original melts were not tourmaline saturated. This raises the question of these granites being a boron source for the Panasqueira system. In any case, these granites being of the RMG family, and their solidus temperature being accordingly in the c. 600°-650°C range (Aksyuk and Konyshev, 2011), their boron content could not have been higher than the equilibrium B content in equilibrium with tourmaline in the melt at these temperatures, i.e., no more than 0.5 wt% B$_2$O$_3$ (London, 2011; and references therein). The volume of the cupola itself (approximated by a cone, high 150 m, diameter 250 m) being of $\sim 2.5.10^6$ m$^3$, it could not contain more than $\sim 9$ kt B (with a melt density of 2.3 t.m$^{-3}$: Dingwell et al., 1993). The subjacent RMG sheet-like body, made of several separate intrusions (De Amorin, 2017), may be approximated as a 100 m thick body with about 1 km$^2$ surface (Fig. 2), yielding a $\sim 10^8$ m$^3$ volume and a maximal content of 360 kt B. Thus, the total possible boron yield by the evolved granites could not have exceeded 370 kt B.

Boron required for the wall-rock tourmalinization: These values must be compared with the B content in the tourmalinized wall-rock. (i) At the single vein scale, we consider an average vein system based onto the description by Foxford et al. (2000, their Fig.8): an elliptical area (minor axis $\sim 100$ m, major axis $\sim 300$ m), a total width of the tourmalinized margins of 0.45 m (i.e., 15 cm on one side of the vein and 30 cm on the other) and an averaged 50 volume % of tourmaline in the altered zones. This yields a unitary volume of the altered zone of $\sim 1.1.10^4$ m$^3$. Adopting an average density of 3.1 t.m$^{-3}$, and a boron content of 3.3% for the tourmaline, this unitary volume contains $\sim 540$ t B. (ii) The number of elementary veins may be estimated using the published values for the total volume of the vein system, between 3 and 6.10$^3$ km$^3$ (Polya, 1989), and assuming an average vein thickness of 0.2 m (Foxford et al., 2000). This yields an estimated number of elementary veins comprised between 750 and 1500. (iii) Finally, the total B content of the tourmalinized wall rocks may be bracketed between 410 and 810 kt. These values are clearly higher than the maximum boron tonnage possibly delivered by the Panasqueira RMG.

Volume of magmatic water required for boron transportation

At the elementary vein scale, and at any time of the tourmalinization process, the effective volume of fluid present in the $V_0$ volume of altered rocks (estimated at 1.2.10$^4$ m$^3$, see above) is controlled by rock porosity. If $\phi$ is the porosity, this effective volume is only $\phi.V_0$. The porosity of
metamorphic rocks is generally considered to be in the \(10^1\) to \(10^2\) range (Bickle and McKenzie 1987), and was for instance estimated at 0.08 in the Tinos schists (Breeding et al., 2003). Here, we take \(\phi = 0.1\). The effective \(\phi V_0\) volume contains a boron mass \(m_0 = \phi V_0 \rho_w X\), with \(\rho_w\) the fluid density and \(X\) the boron content in the fluid. For a magmatic fluid equilibrated with tourmaline at the solidus temperature, the boron content \(X\) will be close to 1 wt % \(B_2O_3\) (Weisbrod et al., 1986) and the fluid density will be in the 0.62-0.68 t.m\(^{-3}\) range, depending on salinity between \(\sim 10\) and \(\sim 20\) wt% NaCl (Sakuma and Ichiki, 2016); taking an average 0.65 yields \(m_0 = 2\) t B. Therefore, to attain the 540 t B accumulated in the tourmalinized wall rock, the \(\phi V_0\) volume must be renewed 540/2=270 times, i.e., a total flow of \(270 \phi V_0 = 2.9 \times 10^6\) m\(^3\) of fluid must be channelled through the transforming schist. At the deposit scale, this in turn means that a volume of fluid comprised between \(2.2 \times 10^9\) and \(4.3 \times 10^9\) m\(^3\) was required for the tourmalinization to be effective.

Possible water yield by the granite system

The water content of a RMG melt is \(\sim 5\) wt%. Thus, the Panasqueira RMG sheet-like body, with a volume of \(10^8\) m\(^3\) and a melt density of 2.3 t.m\(^{-3}\), contained about 1.2 \times 10^7\) t water, i.e. (with a water density of 0.65 t.m\(^{-3}\)) could have expelled \(\sim 1.8 \times 10^7\) m\(^3\) of fluid. This is clearly two orders of magnitude below the required fluid quantity. It must be noted that it is the same for the main wolframite deposition stage, as already stated by Polya (1989), who estimated a several 100 km\(^3\) (up to 1000) flow to produce the deposit. This was however based on a 0.2 ppm W content in the fluid, which was clearly underestimated: owing to the data of Wood and Vlassopoulos (1989), a content of \(\sim 500\) ppm W is more realistic, and would demand a volume of \(\sim 5.10^8\) m\(^3\) to yield the c. 150 kt of W of the deposit, one order of magnitude larger than the granite water endowment.

Metasediments as a source of boron and fluid

The Beira schists contain in average \(\sim 100\) ppm B (Oosterom et al., 1984). With this content, and assuming a density for the schist of 2.77 t.m\(-3\) (Ribeiro, 2017), a schist volume of 1.7 km\(^3\) to 3.4 km\(^3\) is required, admitting a 100% efficient extraction, which is not so likely. However, the few data available for the high grade Beira schists (Peña Negra migmatitic complex, Acosta-Vigil et al., 2011) suggest that boron extraction may have reached 70% efficiency. With this value, the needed volumes become comprised between \(2,8\) km\(^3\) and \(4,8\) km\(^3\). On the other hand, to yield the volume of fluid required by the boron transportation and deposition (see above), assuming a water productivity of about 3 wt % (Fyfe et al., 1978), between 20 km\(^3\) and 40 km\(^3\) of schist are necessary. The source of boron and fluids for the tourmalinization at Panasqueira could therefore have been the Beira schists.
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