

DIRECT OBSERVATION OF BORO-ALUMINOSILICATE MELT COMPOSITIONS: INSIGHTS FROM RAMAN SPECTROSCOPY OF MELT INCLUSIONS IN PEGMATITIC TOURMALINE OF THE GATUMBA-GITARAMA AREA (RWANDA)

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ABSTRACT

This study presents Raman spectroscopic analyses of melt inclusions in tourmaline from tourmaline-quartz-(muscovite) assemblages of common pegmatites of the Gatumba-Gitarama area (Rwanda). The melt inclusions show a main mineralogy composed of muscovite, α -quartz, mogánite, dickite, and minor feldspars which demonstrate, in combination with the observation of dawsonite, nahcolite, jeremejevite, and childrenite daughter minerals, a CO_2 -, H_2O -, B_2O_3 -, and P_3O_4 -enriched peraluminous boro-aluminosilicate composition for the trapped melt. The variable amount of acidic interstitial fluids inside the melt inclusions resulted mainly from heterogeneous trapping of omnipresent, exsolved aqueous fluids during melt inclusion entrapment. Aliquots of this exsolved alkali-rich aqueous fluid phase are preserved in the numerous coexisting fluid inclusions in tourmaline. The observed mineralogy and composition of the melt inclusions deviates strongly from a bulk single-phase melt crystallization model for pegmatite formation. Based on reported experimental, theoretical, and natural constraints, an alternative hypothesis can offer an explanation for the formation of the anomalous but omnipresent residual melts trapped in tourmaline: *i.e.*, the immiscibility of a hydrous fluid and a boro-aluminosilicate melt from the residual bulk aluminosilicate melt. The chemically anomalous composition of the immiscible boro-aluminosilicate melt trapped inside the melt inclusions can explain the mineralogical transition from a granitic mineral mode towards a schorl-quartz-(muscovite) assemblage within the common mineralogical zonation of the pegmatite dike.

Keywords: geochemistry, melt inclusions, mineralogy, pegmatite.

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INTRODUCTION

Granitic pegmatites are coarse-grained intrusive igneous rocks of granitic composition. This exceptional rock-type is well recognized for hosting high concentrations of diverse gems and industrial minerals (Glover *et al.* 2012, Morteani *et al.* 2012, Simmons *et al.* 2012) as well as strategic metals (Linnen *et al.* 2012; *e.g.*, Li, Be, Rb, Nb, Cs, Ta, and W). A distinctive characteristic of granitic pegmatites is mineralogical zonation, which occurs at two scales: (1) a regional zonation, manifested as increasing chemical complexity of the pegmatite bodies with distance from their granitic source, and (2) an internal zonation expressed by the mineralogical and textural changes within individual pegmatite bodies (London 2014). The development of a regional zonation is generally attributed to the continuous differentiation of the parental granitic magma, which is mainly driven by protracted fractional crystallization (Černý 1991a, Roda-Robles *et al.* 2012, Hulsbosch *et al.* 2014). During the end-stages of regional differentiation, *i.e.*, on the scale of an individual pegmatite dike, contrasting models exist regarding their internal differentiation and the formation of the conspicuous internal mineralogical zonation. London (London 1992, London 2005b, 2009, 2014) hypothesizes that an individual pegmatite body crystallizes from a hydrous and single-phase melt *via* the process of constitutional zone refining and the creation of a boundary layer melt during liquidus undercooling. In contrast, studies of melt inclusions (MI) and fluid inclusions (FI) trapped in pegmatite minerals show a supercritical pegmatite melt with extreme enrichment of fluxes (Rb, Cs, B, P, F, Cl, *etc.*) and volatiles (mostly H₂O and CO₂), to an extent that liquid (*i.e.*, melt-melt-fluid) immiscibility becomes inevitable during cooling and will proceed as an essential internal differentiation process (Webster *et al.* 1997, Thomas 2000, Thomas & Webster 2000, Peretyazhko *et al.* 2004, Veksler 2004, Thomas *et al.* 2012). Fluid exsolution in the early stages of pegmatite crystallization has been reported often (Webster *et al.* 1997, Sirbescu & Nabelek 2003b, Ackerman *et al.* 2006, Alfonso & Melgarejo 2008).

Within the controversy on the internal differentiation of pegmatites, the highly differentiated and physicochemically complex pegmatites of the rare-element class have attracted much attention in particular because of their high mining potential (Černý 1991b, Peretyazhko *et al.* 2004, Thomas *et al.* 2012, London 2014). In comparison, common pegmatites (*i.e.*, the muscovite-rare-element class), which consist entirely of ordinary igneous minerals (*i.e.*, quartz, plagioclase, K-feldspar, muscovite, bio-

tite, and tourmaline), are under-represented, especially in melt and fluid inclusion research (*e.g.*, Ackerman *et al.* 2006). These less-differentiated, common pegmatites are often regarded as intermediate members of the continuous differentiation series beginning with the granite source and ending with the most-differentiated pegmatite bodies of the rare-element class (Černý & Ercit 2005, Hulsbosch *et al.* 2014). Consequently, common pegmatites have proven to record the regional differentiation from granite to rare-element class pegmatite bodies (Černý 1991a, London 2008, Hulsbosch *et al.* 2014).

Boron saturation and tourmaline formation have been greatly studied in granitic and rare-element pegmatite systems (Pichavant 1981, Wolf & London 1997, London 1999b, Thomas *et al.* 2003, London 2008, Trumbull *et al.* 2008). Boron acts as a melt-compatible and highly effective flux element in silicate melts (Pichavant 1981, London 1999a). The solubility of tourmaline has a strong positive correlation with temperature (Wolf & London 1997). Tourmaline in lithium-cesium-tantalum (LCT) pegmatites tends to form (1) as rhythmic alternations or layers with mica-feldspar-quartz bands in the aplitic zones of the dike (London 2014); (2) along the wall zone of the pegmatite dike as inwardly flaring crystals together with quartz and plagioclase, or as branching, skeletal, or graphic intergrowths with massive quartz (London 2014); and (3) within miarolitic cavities (London 2008). Tourmaline is an ubiquitous mineral in common pegmatites of the muscovite-rare-element class of the LCT family and frequently occurs near the border and wall zone of the pegmatite dikes as graphic textures with quartz in quartz-tourmaline-(muscovite) assemblages (Wadoski *et al.* 2011, London 2014). The latter texture is often one of the sole examples of an internal zonation in the equigranular common pegmatites. Tourmaline in graphic intergrowth with quartz in granitic pegmatites has been interpreted to have formed as a primary magmatic phase (*cf.* see discussions in Grew *et al.* 2008, Wadoski *et al.* 2011). Recent stable isotope and trace element studies of tourmaline from quartz-tourmaline-(muscovite) assemblages in peraluminous granites and pegmatites indirectly indicate the role of liquid immiscibility processes by the formation of an immiscible hydrous boro-aluminosilicate melt and aqueous fluid (Tonarini *et al.* 1998, Trumbull *et al.* 2008, Drivenes *et al.* 2015, Siegel *et al.* 2016). However, direct observation and characterization of this immiscible melt batch by MI analysis is lacking. Consequently, tourmaline, as the principal borosilicate mineral and main boron sink in granitic pegmatites, forms the prime host for MI research on this immiscible boro-aluminosilicate melt. Tourmaline-hosted MI can, as such, represent a direct

source of information regarding the internal differentiation processes in pegmatites and the development of quartz-tourmaline-(muscovite) assemblages as an internal mineralogical zone.

Accordingly, this study aims to evaluate the mineralogical composition of MI in tourmaline from quartz-tourmaline-(muscovite) assemblages in common, muscovite-rare-element class pegmatites by laser Raman spectroscopy. Raman spectroscopy is a very valuable tool for research in mineralogy and geochemistry, especially in the study of FI and MI (Thomas & Davidson 2012, Li & Chou 2015). Raman spectroscopy is a sensitive technique for non-destructive, semi-quantitative chemical analysis of mineral solid-solutions (Smith 2005, Thomas *et al.* 2012).

As a result, this study will report the first compositional analyses of MI in tourmaline from quartz-tourmaline-(muscovite) assemblages in common pegmatites. Tourmaline samples have been sampled from the Gatumba-Gitarama pegmatite field in Rwanda. The Gatumba-Gitarama field is a type locality for the Mesoproterozoic (~1 Ga) pegmatite intrusions which are abundant in the African Great Lakes Region (Melcher *et al.* 2015). The Raman spectroscopic survey facilitates evaluation of the internal differentiation processes acting in common pegmatites and their role in the development of internal mineralogical zonation.

GEOLOGY OF THE GATUMBA-GITARAMA PEGMATITES, RWANDA

The rocks of the Gatumba-Gitarama area have been intruded by two main generations of granites (Tack *et al.* 2010, Dewaele *et al.* 2011). The first granite generation, G1–3, intruded the Palaeo- and Mesoproterozoic rocks at 1380 ± 10 Ma (U-Pb SHRIMP zircon age; Tack *et al.* 2010). The second generation or G4 granites were emplaced at 986 ± 10 Ma (U-Pb SHRIMP zircon age; Tack *et al.* 2010) and are attributed to post-collisional relaxation after the ~1.0 Ga main compressional event in the region (Fernandez-Alonso *et al.* 2012, Debruyne *et al.* 2015). The Gitarama-Gatumba pegmatite field is a well-developed example of a regionally zoned leucogranite-pegmatite system that culminates in Nb-Ta-Sn-mineralized pegmatites belonging to the rare-element class (Fig. 1). The pegmatites are genetically related to the post-compressional G4 granites (Varlamoff 1972, Hulsbosch *et al.* 2014). The regional pegmatite zonation comprises a sequence from leucocratic G4 granites to four successive zones of pegmatite bodies: a common biotite zone (#1), a common biotite-muscovite zone (#2), a common muscovite zone (#3), and a mineralized and most distal rare-element

class pegmatite zone (#4). The first three pegmatite zones all belong to the muscovite-rare-element class (Fig. 1). The large-scale differentiation of the four subsequent pegmatite zones and the development of the regional zonation have been characterized in terms of extensive fractional crystallization of the parental G4 granitic source magma (Hulsbosch *et al.* 2014, Muchez *et al.* 2014, Hulsbosch *et al.* 2016). The dimensions of the pegmatite dikes are rather variable, with thicknesses varying between several centimeters and 30 m and lengths ranging from tens of meters to 2400 m (Fig. 2; Hulsbosch *et al.* 2014). Based on a combined mineralogical and FI study (Hulsbosch *et al.* 2016), an immiscible medium-salinity fluid phase was observed to exsolve from the melt in the early stages of crystallization of pegmatite bodies belonging to zones #1 to #3. Aliquots of this immiscible fluid phase have been previously studied in FI (Hulsbosch *et al.* 2016) cogenetically trapped with the MI in the schorl samples studied here (Fig. 3).

Black tourmaline can occasionally occur in zone #1 to #3 pegmatites as euhedral quartz-feldspar-biotite-tourmaline assemblages. Black tourmaline occurrences are, however, generally observed in the border and wall zone of the pegmatite dikes as decimeter to several meter-sized graphic quartz-tourmaline-(muscovite) assemblages or as large euhedral prismatic tourmaline-quartz units (Fig. 2A–I) (Varlamoff 1954, Hulsbosch *et al.* 2013, 2014, Muchez *et al.* 2014). These tourmaline-rich textures are the sole examples of a faint internal zonation in the Gatumba-Gitarama zone #1 to #3 pegmatites. A mineralogical transition from an equigranular and phaneritic granitic mineral mode (*i.e.*, quartz, plagioclase, K-feldspar, muscovite, biotite, and tourmaline) to graphic quartz-tourmaline-(muscovite) assemblages can be generally observed in all pegmatite bodies of zones #1 to #3 and develops, as such, identically in all the pegmatite zones (Varlamoff 1954, Hulsbosch *et al.* 2013).

MATERIAL AND METHODS

Sample locations and wafer petrography

This study focuses on the MI content of tourmaline from common pegmatite bodies of the biotite, biotite-muscovite, and muscovite zones (#1–3) of the regional pegmatite zonation in the Gitarama-Gatumba field (Figs. 1 and 2, Table 1).

Doubly polished wafers of tourmaline crystals were prepared parallel and perpendicular to the mineralogical *c* axis with thicknesses between 300 and 650 μm . Macroscopically, the tourmaline samples have an overall black color and sub- to euhedral crystal shapes. Microscopically, most tourmaline crystals show a millimeter-scale zoning pattern defined by color

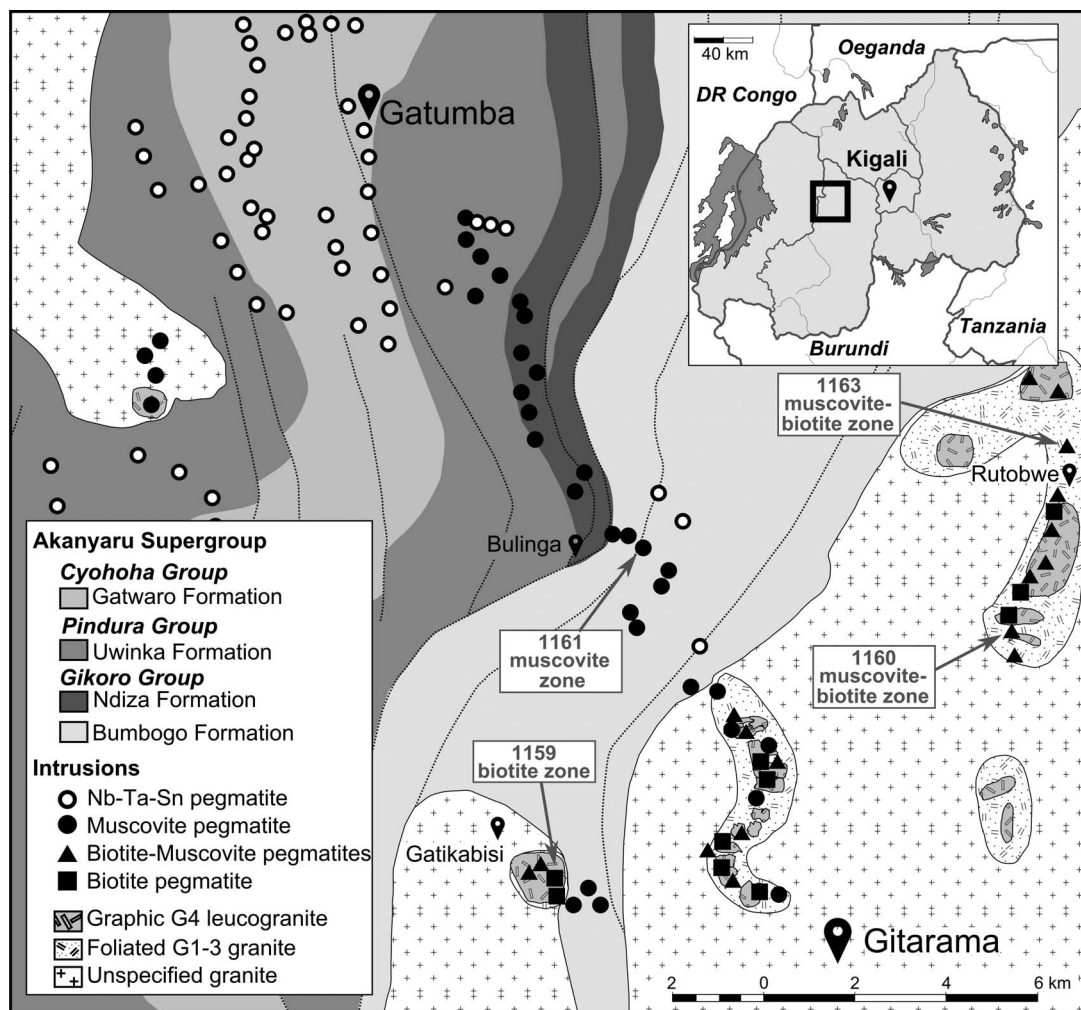


FIG. 1. Simplified geological map of Rwanda with the most important strategic metal ore deposits indicated. The location of the Gatumba–Gitarama pegmatite field is emphasized with a dotted line.

variations ranging from blackish to dark blue and from dark brown to orange-brown. Previously performed chemical analyses (Hulsbosch *et al.* 2014) were used to classify the tourmaline samples as schorl, $\text{Na}(\text{Fe}_3^{2+})\text{Al}_6(\text{Si}_6\text{O}_{18})(\text{BO}_3)_3(\text{OH})_3(\text{OH})$. Samples were microscopically studied using an Olympus BX60 microscope equipped with a Deltapix 200 camera. Melt-inclusion volume proportions have been calculated in two dimensions with Deltapix Insight software.

Laser Raman spectroscopy

Raman scattering of solid phases in the inclusions were measured with a Jobin-Yvon LabRam HR800 spectrometer at the GeoForschungsZentrum in Pots-

dam (detailed methodology in Thomas 2002). The spectrometer was equipped with an Olympus optical microscope and a long-working-distance IMPlanFI 100×/0.80 objective. A 488 nm Coherent Ar⁺ laser Model Innova 70C excitation source was used with a power of 200 mW (30 mW on the sample). Additional samples were analyzed at the Royal Belgian Institute of Natural Sciences (RBINS) in Brussels using a Senterra-Bruker laser Raman spectrometer, which was mounted on an Olympus BX50 microscope. A 532 nm green diode-pumped solid state laser type R200-532 was used as excitation source, operating at 20 mW. Both short- and long-range confocal objectives with 100× magnification were used.

Each spectrum results from the accumulation of five acquisitions of 30–50 s each. All spectra were collected with a Peltier-cooled CCD detector. The positions of the Raman bands were calibrated using the principal plasma lines in the argon laser (Coherent Ar⁺ laser) or by using the laser neon spectra (diode-pumped solid state laser). Spectra treatment was performed with the Horiba LabSpec5 software and consisted of baseline correction, spike elimination, and Gauss-Lorentzian peak searching/fitting.

Minerals included within the melt inclusions were identified by comparison of their spectral fingerprints with reference spectra (*cf.* Frezzotti *et al.* 2012). Spectra identification and verification were performed using Raman spectral databases (Frezzotti *et al.* 2012, Hurai *et al.* 2015) and the RRUFF project in combination with CrystalSleuth software (Lafuente *et al.* 2015). A summary of the minerals and vibration bands used in this study are presented in Table 2. Each entry reports the mineral name and formula, a list of the main Raman modes observed, and references. Main indicative vibrations are reported in bold. All measured spectra correspond to those reported in the literature; however, some bands are blue-shifted 2–5 cm⁻¹, which could be related to the movement of the LabRam HR800 spectrometer grating after the calibration. In addition, band blue-shifts have also been reported to be caused by a local temperature increase due to the 200 mW laser (*e.g.*, zircon; Balan *et al.* 2001). The Ag phonon for α -quartz, in particular, shows a blueshift from 464 to 459 cm⁻¹.

RESULTS

Melt inclusion typology

Crystallized MI are moderately common in the tourmaline samples (approx. 25–50 melt inclusions per cm², with diameters >15 μ m and micro-optical visible mineral phases; Figs. 4 and 5). Melt inclusions show euhedral negative-crystal, subhedral polygonal, irregular, and ellipsoid geometries, with diameters varying between ~25 and 140 μ m. Average inclusion dimensions vary between ~40 and ~65 μ m. Melt inclusions are mostly grouped in azonal three-dimensional assemblages resembling former growth surfaces (*cf.* Roedder 1979). Multiple assemblages display co-existing MI and FI (Hulsbosch *et al.* 2016). However, large (>75–90 μ m) MI are often isolated. The total population of studied inclusions shows high proportions of transparent to opaque solid phases (74–96 vol.%) in combination with a variable amount of interstitial fluid (liquid and gas; see example in Fig. 4B–E). Daughter minerals show a highly diversified mineralogy. Phyllosilicate daughter minerals can be abundantly observed as pseudohexagonal sheets. Other

TABLE 1. SAMPLE NUMBERS AND LOCALITIES WITH MINERALOGICAL DESCRIPTION OF THE TOURMALINE OCCURRENCES ANALYZED

Pegmatite dike	Zone	Mineralogy
1159	1	Euhedral schorl crystals (3–5 cm) in an equigranular quartz-microcline-schorl assemblage. The equigranular assemblage is partly surrounded by graphic quartz-schorl intergrowths.
1160	2	Schorl crystals (0.5–2 cm) in a graphic quartz-schorl-muscovite assemblage.
1163	2	Schorl crystals (1–2 cm) in a graphic quartz-schorl-muscovite assemblage.
1161	3	Schorl crystals (~1 cm) in a graphic quartz-schorl-muscovite assemblage.

common daughter minerals include colorless, low-birefringent quartz, granular translucent feldspar masses, and a highly birefringent columnar phase. The majority of the solid phases in the inclusions cannot be identified by optical techniques due to their small crystal size (<7 μ m) and were characterized by laser Raman spectroscopy.

Before presenting the mineralogy and composition of the MI and their implications for the evolution of the quartz-tourmaline-(muscovite) units in the common pegmatite zones of the Gatumba-Gitarama field, we examined the hypotheses of a primary origin of the inclusions and their representativeness for the melt system during schorl crystallization. The primary origin of the MI was evaluated by applying the criteria of Roedder (1984). All inclusions studied (1) are trapped in tourmaline, which is a chemically stable host unaffected by recrystallization phenomena; (2) are intracrystalline and occur as single or small, random three-dimensional assemblages; (3) have a large size (<30 μ m) and therefore trap, based on the available experimental and natural data (see review in Audétat & Lowenstern 2014), compositionally representative melts and no anomalous boundary-layer melt; and (4) show no occurrence as planar groups or outline healed fractures or cleavages. Moreover; the inclusions show no signs of decrepitation or rehealing and have major daughter-mineral phases that are compositionally similar. A post-entrapment process which potentially could change the composition of the MI studied is crystallization of tourmaline from the trapped melt along the wall of the host tourmaline crystal during cooling (*i.e.*, sidewall crystallization). Extensive sidewall crystallization could lead to misinterpretation of the inclusions (Kamenetsky 2006). Sidewall crystallization (*i.e.*, secondary tour-

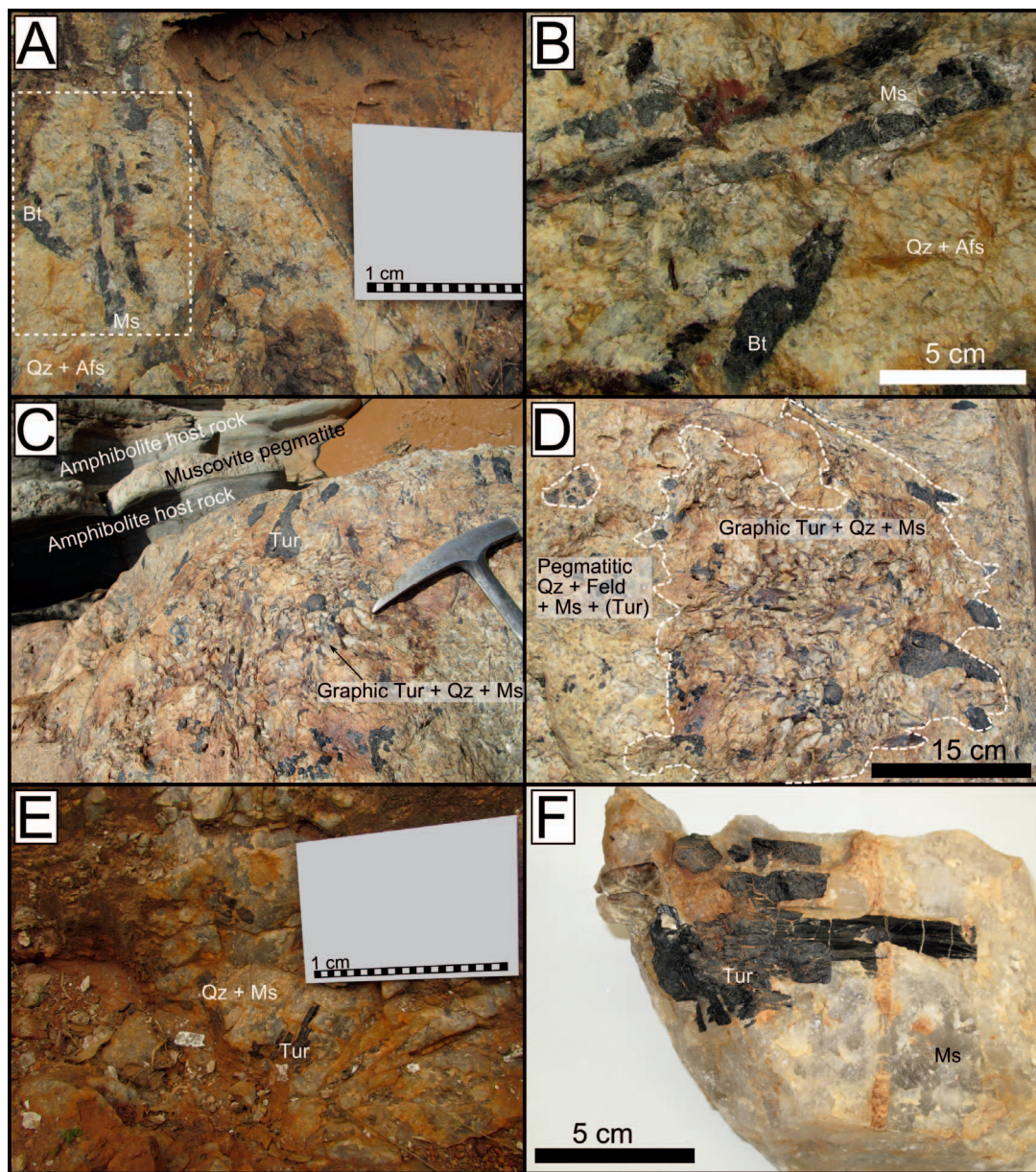


FIG. 2. Type examples of common muscovite-rare-element pegmatites with quartz-tourmaline-(muscovite) assemblages in the Gatumba-Gitarama area. (A) and close-up (B), typical granitic mineralogy of a common pegmatite belonging to the biotite-muscovite zone: K-feldspar (Afs), quartz (Qz), and the micas biotite (Bt) and muscovite (Ms). (C) and close-up (D), typical graphic quartz-tourmaline-muscovite assemblage in a pegmatitic dike of the muscovite zone: feldspar (Feld), quartz (Qz), and muscovite (Ms). (E) and close-up (F), euhedral black tourmaline (Tur) occurrence in quartz-muscovite-tourmaline assemblage (~1.5 m) in the pegmatite dike depicted in (A).

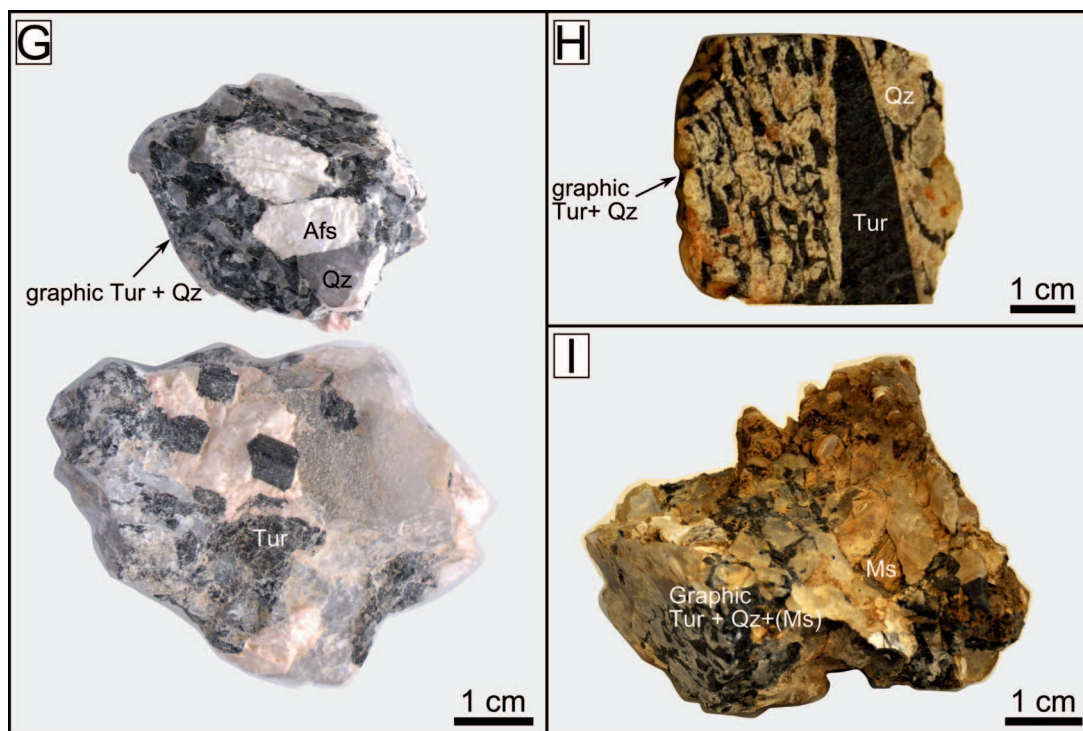


FIG. 2. (continued) (G) Hand specimen of black tourmaline in pegmatite belonging to the biotite-muscovite zone. (H) Hand specimen of black tourmaline in pegmatite belonging to the biotite zone. Quartz and tourmaline show graphic textures. (I) Hand specimen of black tourmaline in pegmatite belonging to the muscovite zone showing a typical quartz-tourmaline-muscovite assemblage.

maline crystallization) was not observed during microscopic investigation of the inclusion walls by Köhler illumination. In addition, a significant role for sidewall crystallization can be ruled out because crystallization of 1 mole of schorl on the sidewall would consume six moles of silica and three moles of

alumina from the trapped melt. This would result in a dominantly silica-poor and peralkaline MI mineralogy and composition, which is not observed for the inclusions studied (see paragraph below).

Melt inclusion mineralogical composition

Raman-active mineral, solute, and gas phases within 19 large MI were characterized by micro-Raman spectroscopy. An overview of the observed compositions of the different inclusions is provided in Table 3. A digital version of the Raman spectra, indicative for the different mineral, solute, and gas observed in the melt inclusions, can be found in the supplementary data (Table A1, available from the MAC Depository of Unpublished Data, document Boro-aluminosilicate CM55_10.3749/canmin.1600093). Raman spectroscopy indicates that the melt inclusions are composed of complex mineral assemblages (Figs. 6–8; Table 3), including muscovite $[KAl_2(AlSi_3O_{10})(OH)_2]$, α -quartz (SiO_2), dickite $[Al_2Si_2O_5(OH)_4]$, plagioclase series feldspars $[NaAlSi_3O_8-CaAl_2Si_2O_8]$, childrenite $[(Fe^{2+}, Mn^{2+})AlPO_4(OH)_2 \cdot H_2O]$, dawsonite $[NaAlCO_3(OH)_2]$, a wide variety of

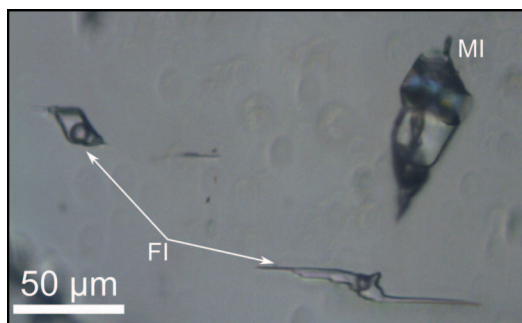


FIG. 3. Micrograph of tourmaline in a pegmatite of the muscovite zone with cogenetic occurrence of melt (MI) and fluid inclusions (FI). Reproduced from Hulsbosch *et al.* (2016). Raman analysis of MI in Figure 6.

TABLE 2. MAIN RAMAN VIBRATIONS OF THE MINERAL PHASES PRESENT IN THE MELT INCLUSIONS STUDIED

Name	Formula	Vibration Bands (cm ⁻¹)	Reference
alum-K	KAl[SO ₄] ₂ ·12H ₂ O	442, 455, 614, 974, 989 , 1104, 1130, 3072, 3396	1
alunite	KAl ₃ [SO ₄] ₂ [OH] ₆	485, 509, 654, 1026 , 1079, 1190, 3482, 3509	1
boric acid in solution	B(OH) ₃	495, 875	1
carbon dioxide gas	CO ₂	1285, 1388	2
childrenite	[Fe ²⁺ , Mn ²⁺]AlPO ₄ [OH] ₂ ·H ₂ O	208, 249, 306, 464 , 556, 597, 619, 966 , 1013, 1038	3
dawsonite	NaAlCO ₃ [OH] ₂	192 , 206, 590, 728, 1065, 1092 , 1506, 3250, 3282	1
dickite	Al ₂ (Si ₂ O ₅)(OH) ₄	121, 132, 178, 198, 245, 268, 336 , 420, 434, 463 , 744, 792, 916, 935, 1050, 1104, 3623 , 3648, 3683, 3700	1
feldspar	(Na,K)AlSi ₃ O ₈	280–290, 470–490, 504–514	4
hydrogen sulfide gas	H ₂ S	2611	2
ixiolite	[Ta,Nb,Sn,Fe,Mn] ₄ O ₈	284, 861	3
jeremejevite	Al ₆ B ₅ O ₁₅ (OH) ₃	177 , 301, 328, 372 , 417, 512, 608, 710, 749, 962 , 1067, 3624, 3672	1
K-tetraborate	K ₂ B ₄ O ₇ ·4H ₂ O	397, 456, 571 , 767, 864 , 979	1
lithium chloride	LiCl	526, 532	1
metaboric acid	HBO ₂	401, 415, 475, 595 , 809	1
Mg-hexaborate	MgB ₆ O ₁₀ ·6H ₂ O	374, 634, 638, 641, 852, 953, 964	1
mogánite	SiO ₂	129, 141, 220, 265, 317, 370, 377, 398, 432, 449, 463, 501 , 693, 792, 833, 1058, 1084, 1171, 1177	1
muscovite	KAl ₂ (Si ₃ Al)O ₁₀ (OH) ₂	98, 170, 197, 216, 261 , 385, 405, 639, 702, 753 , 907, 954, 1111, 3627	1
nahcolite	NaHCO ₃	684, 1046 , 1266, 1432	1
Na-tetraborate	Na ₂ B ₄ O ₇ ·10H ₂ O	385, 461, 576 , 756, 852, 948, 1036	1
nitrogen gas	N ₂	2331	1
qilianshanite	NaH ₄ [CO ₃][BO ₃] ₂ ·2[H ₂ O]	187, 204, 355, 498, 539, 687, 858, 880, 1012, 1028, 1038, 1159	3
sassolite	H ₃ BO ₃	187, 211, 500, 880 , 1168, 3165, 3245–3247	1
Sn-chloridepentahydrate in solution	SnCl ₄ ·5H ₂ O	154, 236, 331 , 3421, 3542	1
sodium monoborate	NaBO ₂ ·H ₂ O	741, 746, 1132 , 1276	1
α-quartz	SiO ₂	120, 128, 206, 262, 354, 402, 463 , 520, 608, 698, 807, 1066, 1161	1

1: Hurai *et al.* (2015); 2: Frezzotti *et al.* (2012); 3: RRUFF database of Lafuente *et al.* (2015); 4: Freeman *et al.* (2008)

boron species such as tourmaline [Na(Mg²⁺, Fe²⁺)₃Al₆(Si₆O₁₈)(BO₃)₃(OH)₃OH], Na-tetraborate [Na₂B₄O₇·10H₂O], K-tetraborate (K₂B₄O₇·4H₂O), Mg-hexaborate (MgB₆O₁₀·6H₂O), sassolite (H₃BO₃), and qilianshanite, [NaH₄(CO₃)(BO₃)₂·2(H₂O)], nahcolite (NaHCO₃), and traces of ixiolite [(Ta,Nb,Sn,Fe,Mn)₄O₈], alunite [KAl₃(SO₄)₂(OH)₆], and alum-K [KAl(SO₄)₂·12H₂O].

Silica mainly shows vibration bands corresponding to the α-SiO₂ polymorph. The monoclinic polymorph mogánite is, however, also observed optically by its shifting the diaphaneity of silica from transparent to

translucent and by its indicative 501 cm⁻¹ Raman band (Fig. 8A). The 501 cm⁻¹ band (in combination with the 1050 cm⁻¹ band) is the main distinctive band which differentiates mogánite from other silica species (opal, quartz, agate, chalcedony, *etc.*; Dumanska-Słowik *et al.* 2013, Schmidt *et al.* 2013). Mogánite always occurs as aggregate grains together with α-SiO₂.

Feldspar daughter mineral identification (Fig. 9) is based on the mutual correlation of the position of the three strongest feldspar Raman bands (*cf.* I_a, I_b, and II) and their systematic variation with the feldspar binary

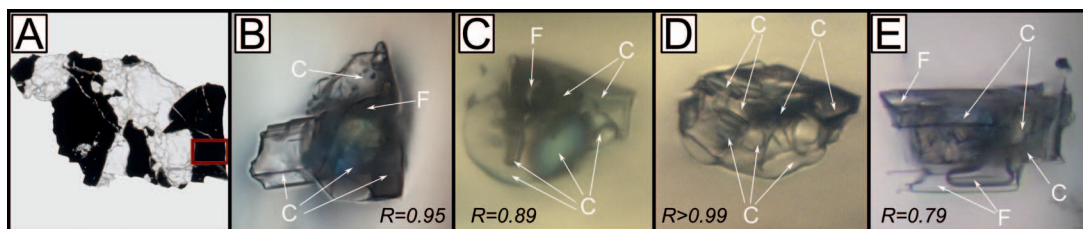


FIG. 4. Photomicrographs of representative schorl-hosted melt inclusions in sample Ga11SD59 from a biotite pegmatite. (A) Graphic quartz-schorl intergrowth with a sample length of 20 mm. The red box indicates the location of the melt inclusions depicted in (B) to (E). (B) to (E) detailed close-ups of individual melt inclusions in assemblages showing various crystal/(crystal + fluid) ratios (R): inclusions 1159_B_2B, 1159_B_4, 1159_B_6, and 1159_B_7. The boxes have a length of 50 μm . C: crystalline mineral phases, F: fluid phase.

composition (Freeman *et al.* 2008). The co-occurrence of peaks at $504\text{--}516\text{ cm}^{-1}$ (I_a), $470\text{--}490\text{ cm}^{-1}$ (I_b), and $225\text{--}295\text{ cm}^{-1}$ (II) strongly indicates feldspar species (Fig. 9B). The position of the I_a and I_b bands varies as a function of the feldspar composition (Freeman *et al.* 2008). Based on this relationship, the feldspar daughter minerals can be identified as belonging to the plagioclase series with oligoclase-andesine compositions (Fig. 9C). The presence of feldspars is often indicated in the melt inclusions by medium weak vibrations at $475\text{--}490\text{ cm}^{-1}$ and around $\sim 510\text{ cm}^{-1}$ (Fig. 8E).

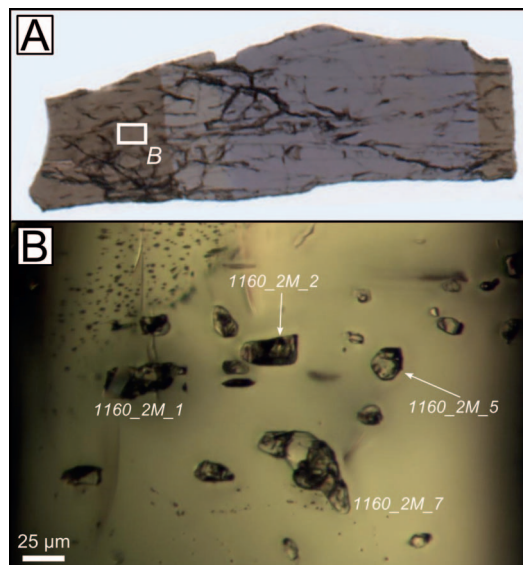


FIG. 5. Photomicrographs of representative schorl-hosted crystalline melt inclusions in sample Ga11SD60 from a two-mica pegmatite. (A) Schorl crystal with typical zonation pattern. The location of an inclusion assemblage is indicated in B. (B) Extended-focus close-up of inclusion assemblage with inclusions 1160_2M_1, 1160_2M_2, 1160_2M_5, and 1160_2M_7.

In general, muscovite, α -quartz, dickite, and minor feldspars are volumetrically the most observed daughter mineral phases. They frequently occur together as granular masses, resulting in compound spectra mixed in the $400\text{--}625\text{ cm}^{-1}$ region. Muscovite, dickite, quartz, and feldspar minerals often spatially co-occur inside the melt inclusions. In a number of inclusions, the indicative main vibrations of jeremejevite $[\text{Al}_6\text{B}_5\text{O}_{15}(\text{OH})_3]$, Na-tetraborate (borax), and the sulfates alunite $[\text{KAl}_3(\text{SO}_4)_2(\text{OH})_6]$ and alum-K $[\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}]$ have also been observed. Sodium-tetraborate (borax) was only interpreted to occur in inclusion 1163_2M_1 by allocating the 576 cm^{-1} band to a main vibration of borax (Fig. 7B). Inclusion 1163_2M_1 is dominantly composed of quartz and muscovite (with the superposition of the schorl host bands), which could mask the other bands of borax. The liquid phase, within the MI, contains chloride and boron species, such as $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ and LiCl , (meta-) boric acid, $\text{NaBO}_2 \cdot \text{H}_2\text{O}$, Na-tetraborate, and Mg-hexaborate, in combination with carbon dioxide, nitrogen, and traces of hydrogen sulfide gas within the accompanying vapor phase.

DISCUSSION

Representativity of the melt inclusions

The studied MI consist of a heterogeneous mixture of solid phases (74–99 vol.%) and interstitial fluid (26–1 vol.%) trapped with different ratios in different inclusions. This effect of heterogeneous trapping is a direct consequence of the magma being oversaturated with a fluid phase at the time of trapping (Frezzotti 2001). Aliquots of this immiscible fluid phase have been previously studied in FI, cogenetically trapped with the MI in the schorl samples studied here (*e.g.*, Fig. 2). This immiscible fluid phase has a $\text{H}_2\text{O}\text{--}\text{NaCl}\text{--}\text{KCl}\text{--}\text{MgCl}_2$ -complex salt (Rb, Cs) geochemistry, a salinity of $18.7 \pm 3.5\text{ wt.}\% \text{ NaCl}_{\text{eq}}$, and a minimal trapping temperature of $382 \pm 17^\circ\text{C}$ (Hulsbosch *et al.*

TABLE 3. OVERVIEW OF THE SELECTED MELT INCLUSIONS FOR WHICH COMPOSITIONS WERE DETERMINED BY RAMAN SPECTROSCOPY

Inclusion	Pegmatite zone	Composition by Raman spectroscopy
1159_B_2	1	alum-K, alunite, boric acid, dickite muscovite, quartz
1159_B_4	1	childrenite, feldspar, muscovite, quartz
1159_B_5	1	childrenite, dickite, feldspar, muscovite, quartz
1159_B_6	1	childrenite, dickite, feldspar, muscovite, quartz, Sn-chloridepentahydrate
1159_B_7	1	carbon dioxide gas, dickite, muscovite, nitrogen gas, quartz
1159_B_9	1	alunite, boric acid, childrenite, ixiolite, metaboric acid, muscovite, quartz
1160_2M_1	2	dawsonite, muscovite, qilianshanite, quartz
1160_2M_2	2	boric acid, carbon dioxide gas, dawsonite, dickite, muscovite, nitrogen gas, qilianshanite, quartz
1160_2M_5	2	boric acid, carbon dioxide gas, dickite, feldspar, muscovite, qilianshanite, quartz
1160_2M_7	2	alum-K, K-tetaborate, muscovite, nahcolite, quartz
1163_2M_1	2	boric acid, carbon dioxide gas, Na-tetaborate, dickite, muscovite, qilianshanite, quartz
1163_2M_8	2	alunite, boric acid, childrenite, dawsonite, dickite, K-tetaborate, lithium chloride, muscovite, quartz, sodium monoborate
1163_2M_9	2	dickite, feldspar, ixiolite, muscovite, quartz
1163_2M_13	2	childrenite, dickite, dawsonite, feldspar, jeremejevitte, moganite, muscovite, nahcolite, quartz
1161_M_1	3	alunite, carbon dioxide gas, feldspar, hydrogen sulfide gas, muscovite, nahcolite, nitrogen gas, quartz, sassolite
1161_M_2	3	dickite, metaboric acid, Mg-hexaborate, muscovite, quartz
1161_M_5	3	boric acid, carbon dioxide gas, dickite, muscovite, qilianshanite, quartz
1161_M_7	3	dickite, feldspar, muscovite, quartz
1161_M_9	3	childrenite, dickite, jeremejevitte, feldspar, muscovite, quartz, Sn-chloridepentahydrate

2016). Heterogeneous trapping of silicate melt and fluids at high temperatures has been regularly described for high-silica rocks such as pegmatites (Frezzotti 2001, and references therein). Potentially, the heterogeneous entrapment of melt-saturated major minerals could also have occurred for the inclusions studied. However, because these minerals are in equilibrium with the melt, the heterogeneous entrapment of solids should not pose any interpretative concerns for the qualitative composition and mineralogy of the inclusions. Taking the above-mentioned criteria into account, the MI studied are interpreted to be a homogenous silicate liquid with heterogeneous trapping of variable amounts of aqueous solution. The inclusions can be classified as primary and represent, therefore, a valuable source of information regarding magmatic processes during tourmaline precipitation and the formation of quartz-tourmaline-(muscovite) assemblages in the common pegmatites of the Gatumba-Gitarama area.

Boro-aluminosilicate composition of the melt inclusions

The tourmaline-hosted MI of the Gatumba-Gitarama pegmatite system show a variety of mineral phases

which predominantly consist of muscovite, α -quartz and mogánite, dickite, and minor feldspars. The mineral assemblages indicate a peraluminous composition of the melt. Moreover, dawsonite has been observed associated with the interstitial fluid phase within the inclusions, indicating a CO_2 - and H_2O -rich fluid composition (Sirbescu & Nabelek 2003a). In addition, the hydrous melt system is enriched in boron, as evidenced by the various boron species, such as tourmaline, jeremejevitte, and alkali tetra- and hexaborates, in combination with phosphate, sulfate, and chloride enrichment (*e.g.*, childrenite, alunite, and LiCl).

The mineralogical composition of the MI, as observed at room temperature, deviates from equilibria assemblages expected for hydrous boron-rich pegmatitic compositions. Natural bulk melts normally evolve towards the haplogranitic eutectic composition in the $\text{NaAlSi}_3\text{O}_8$ – KAlSi_3O_8 – SiO_2 (albite–orthoclase–quartz) system (Pichavant 1987). This emphasizes the importance of closed system, subsolidus modifications of the primary inclusion mineralogy during isochoric cooling from magmatic-hydrothermal towards ambient conditions. In particular, the strong spatial correlation of muscovite, dickite, quartz, and feldspar inside inclusions identifies hydrolytic decomposition of K-micas and feldspars as a major reaction

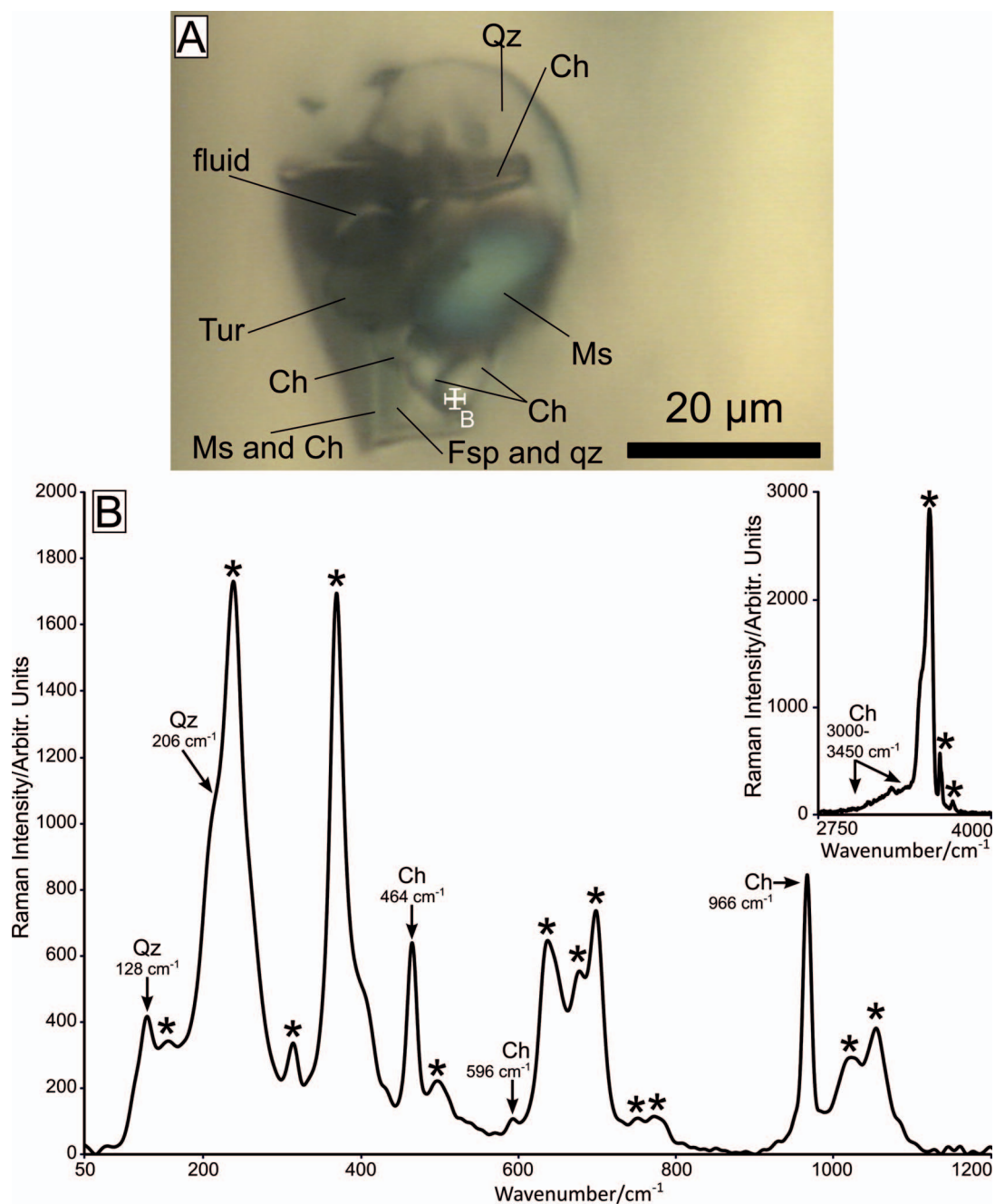


FIG. 6. (A) Daughter phase mineralogy and (B) associated Raman spectrum of representative melt inclusion 1159_B_4 in schorl from a biotite zone pegmatite. The white crosshair on the photomicrographs denotes the location corresponding to the depicted Raman spectra. The abbreviations used are Ch: childrenite, Fsp: feldspar, Ms: muscovite, Qz: quartz, Tur: tourmaline. The asterisk symbol represents the Raman bands of the host tourmaline.

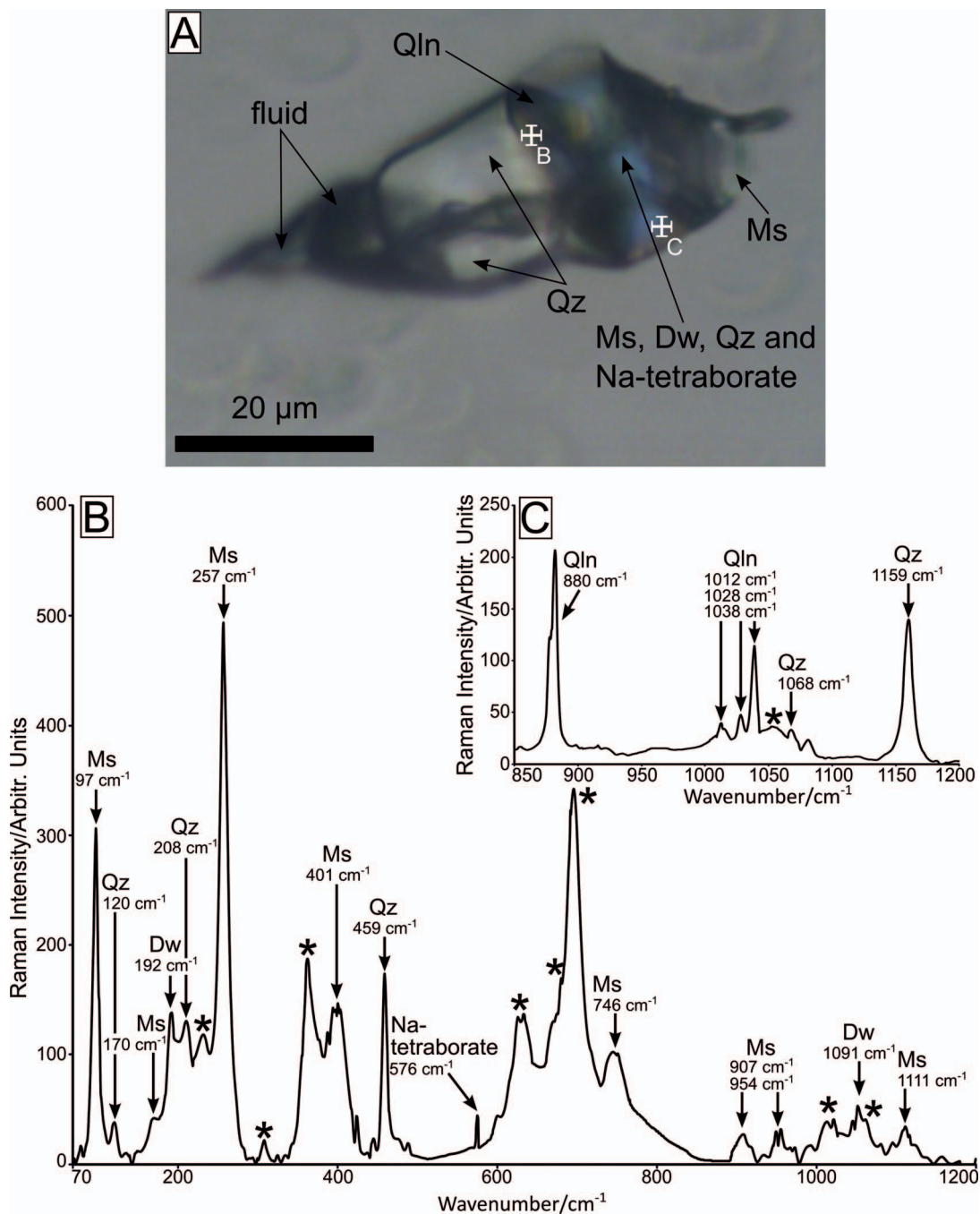
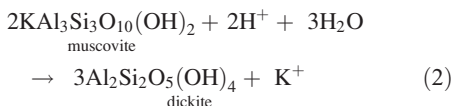
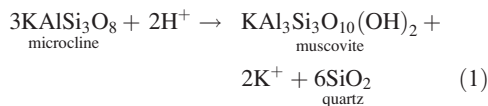
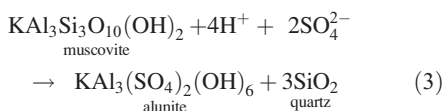


FIG. 7. (A) Daughter phase mineralogy and (B) and (C) associated Raman spectra of representative melt inclusion 1163_2M_1 in schorl from a two-mica zone pegmatite. The white crosshairs on the photomicrographs denote the analysis locations of the depicted Raman spectra. Abbreviations: Dw: dawsonite, Ms: muscovite, Qln: qilianshanite, Qz: quartz. The asterisk symbol represents the Raman bands of the host tourmaline.

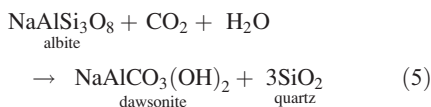
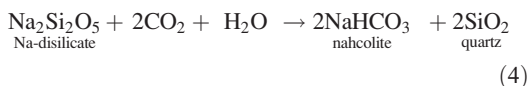
pathway during closed-system cooling inside the inclusions (Equations 1 and 2):



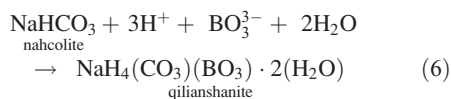
Based on Equation 1, the consumption of feldspars and H^+ during cooling increases the volumetric amount of muscovite and quartz in the inclusion. This evolution has regularly been observed in the inclusions studied (see Figs. 6–9). Moreover, traces of the sulfates alunite and K-alum, observed by Raman spectroscopy, indicate that the acidic interstitial fluid responsible for the hydrolytic decomposition was relatively oxidized, or became oxidized during cooling (Equation 3):



Kaolinite-group daughter minerals, more specifically the kaolinite polymorph, have also been observed by SEM-EDS in tourmaline-hosted MI (Sirbescu & Nabelek 2003b). The identification of the higher-temperature polymorph dickite in the Gatumba-Gitarama samples constrains the temperature conditions during subsolidus modifications of the MI mineralogy to $\sim 200\text{--}300^\circ\text{C}$ (Pirajno 2009). The presence of rare mineral species such as mogánite (monoclinic silica), dawsonite [$\text{NaAlCO}_3(\text{OH})_2$], nahcolite (NaHCO_3), and qilianshanite [$\text{NaH}_4(\text{CO}_3)(\text{BO}_3)$] can also be related to subsolidus interactions of the primary MI mineralogy with flux-rich interstitial fluids. Potential magmatic precursor phases could have been feldspars or alternatively alkali disilicate phases (Thomas *et al.* 2006). Sodium disilicate is unstable in the presence at CO_2 at room temperature (Mustart 1972) and tends to decompose to nahcolite (Equation 4). Alternatively, albite decomposition can form dawsonite (Equation 5; Zerai *et al.* 2006):



Nahcolite can, in turn, react with borate-rich interstitial waters to form qilianshanite (Equation 6):



As a result, sodium disilicate or feldspars tend not to be preserved at room temperature in MI in the presence of acidic $\text{H}_2\text{O-H}_3\text{BO}_3\text{-CO}_2$ interstitial fluids. Moreover, the formation of muscovite at the expense of feldspars (*e.g.*, microcline) is a typical evolutionary feature of peraluminous pegmatitic melts (Equation 1; *e.g.*, London 1992). Consequently, the observation of dawsonite, qilianshanite, and elevated volumetric concentrations of quartz, muscovite, and dickite are strong indications of a high peraluminosity of the trapped boro-aluminosilicate melt and of subsequent subsolidus isochoric equilibration of the magmatic mineral assemblages with acidic CO_2 -, H_2O -, and H_3BO_3 -rich interstitial fluids.

Residual melt formation

Classical experimental models for pegmatite formation demonstrated the role of immiscibility processes during pegmatite differentiation, such as the Jahns & Burnham (1969) model which invokes phase separation between a volatile-saturated aluminosilicate melt and a low-density aqueous fluid. These observations are supported by the study of a vast amount of FI and MI in natural pegmatitic minerals by Roedder (1992), who extended the immiscibility concept towards the exsolution of two fluid phases of contrasting salinity from the aluminosilicate melt during pegmatite differentiation. The role of liquid immiscibility processes in pegmatite genesis has been further elaborated by MI evidence in rare-metal pegmatites (*e.g.*, Webster *et al.* 1997, Thomas *et al.* 2012, and references therein). In contrast, the role of immiscibility processes has been questioned by experimental studies (London 1992, 2009, 2015) which attribute the development of characteristic internal mineralogical zonation within pegmatite dikes to crystallization of a super-cooled melt in a geochemically distinct layer at the crystal-melt interface (*cf.* boundary layer melt, London 2005b). This boundary layer model is characterized by disequilibrium crystallization from a single-phase granitic melt without the presence of an aqueous fluid phase. With advancing crystallization, fluxes accumulate in the boundary layer, causing the solidus to be lowered (London 2005b).

Experimental research on synthetic B-, F-, and P-rich granites suggests the formation of an unusual melt composition due to unmixing of two liquid phases (*i.e.*, a low-density hydrous fluid and a hydrosaline melt) from the residual aluminosilicate melt (Veksler &

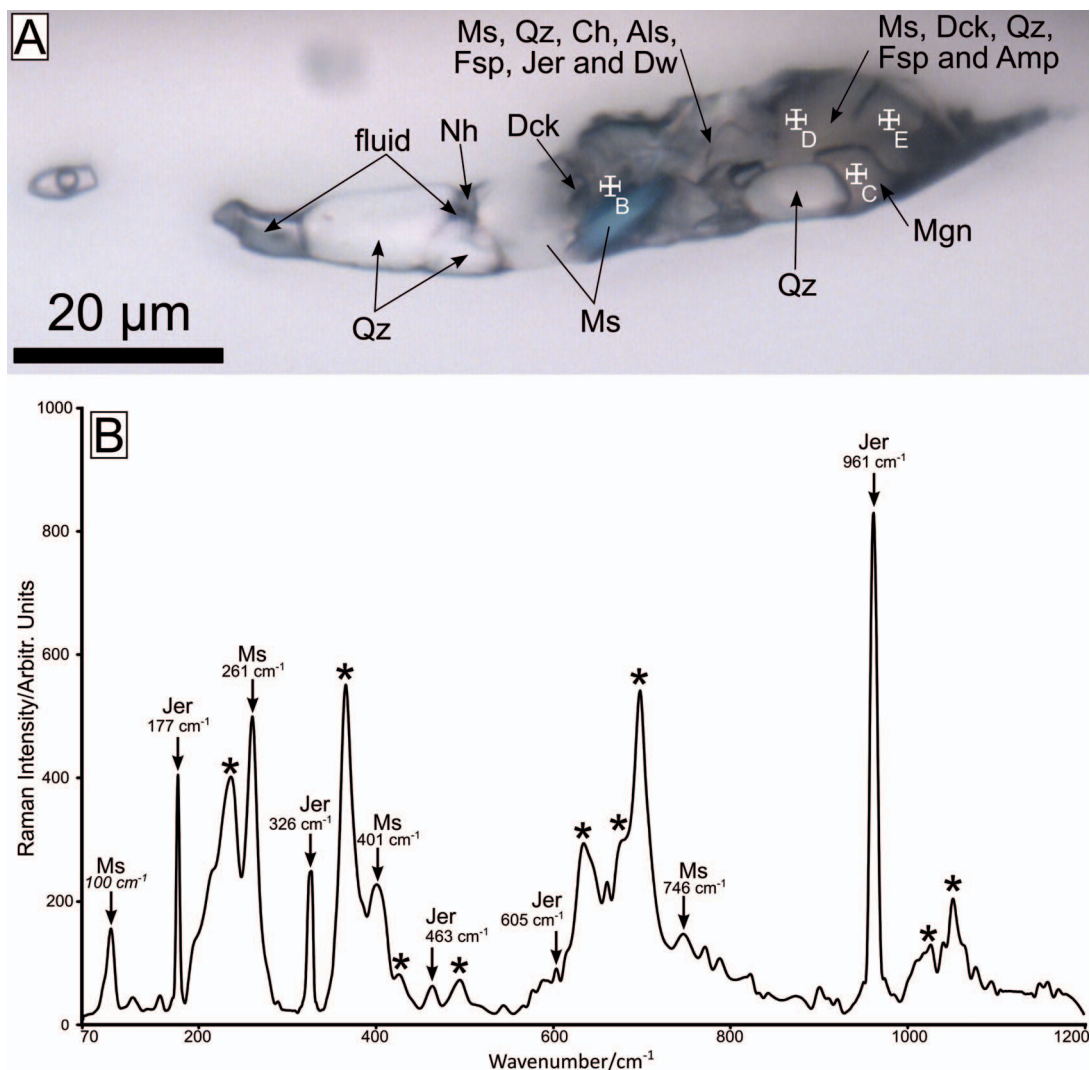


FIG. 8. (A) Daughter phase mineralogy and (B–E) associated Raman spectra of inclusion 1163_2M_13 in schorl from a two-mica zone pegmatite. The white crosshairs on the photomicrographs denote the analysis locations of the depicted Raman spectra. Abbreviations: Ch: childrenite, Dck: dickite, Fsp: feldspar, Jer: jeremejevite, Mgn: mogánite, Ms: muscovite, Nh: nahcolite, Qz: quartz. The asterisk symbol represents the Raman bands of the host tourmaline.

Thomas 2002, Veksler *et al.* 2002). These experiments, together with indications from the topology of the silicate–salt–H₂O systems (Veksler 2004), indicate the stable coexistence of three fluid phases in rare-metal granitic and pegmatitic melts at realistic geological pressure-temperature conditions. Their compositional evolution has been interpreted to include unmixing of the residual aluminosilicate melt into a dilute aqueous fluid and a hydrosaline melt (*i.e.*, a “hydrous saline boro-aluminosilicate melt”; Badanina *et al.* 2004). According to the experimental

data of Veksler *et al.* (2002) and Veksler & Thomas (2002), immiscibility of a hydrosaline melt is, moreover, favored by a moderate B₂O₃ content (~4 wt.%) and high peraluminosity. The reported chemical properties of the hydrosaline melt are: (1) a strong B-, Fe-, Mg-, and Na-compatibility; (2) a composition dominated by hydrated silicates, borates, phosphates, carbonates, and alkali chlorides; and (3) the incompatible fractionation behavior of the heavy alkalis Rb and Cs, which in turn preferentially partition towards the aluminosilicate melt (Veksler & Thomas 2002) and

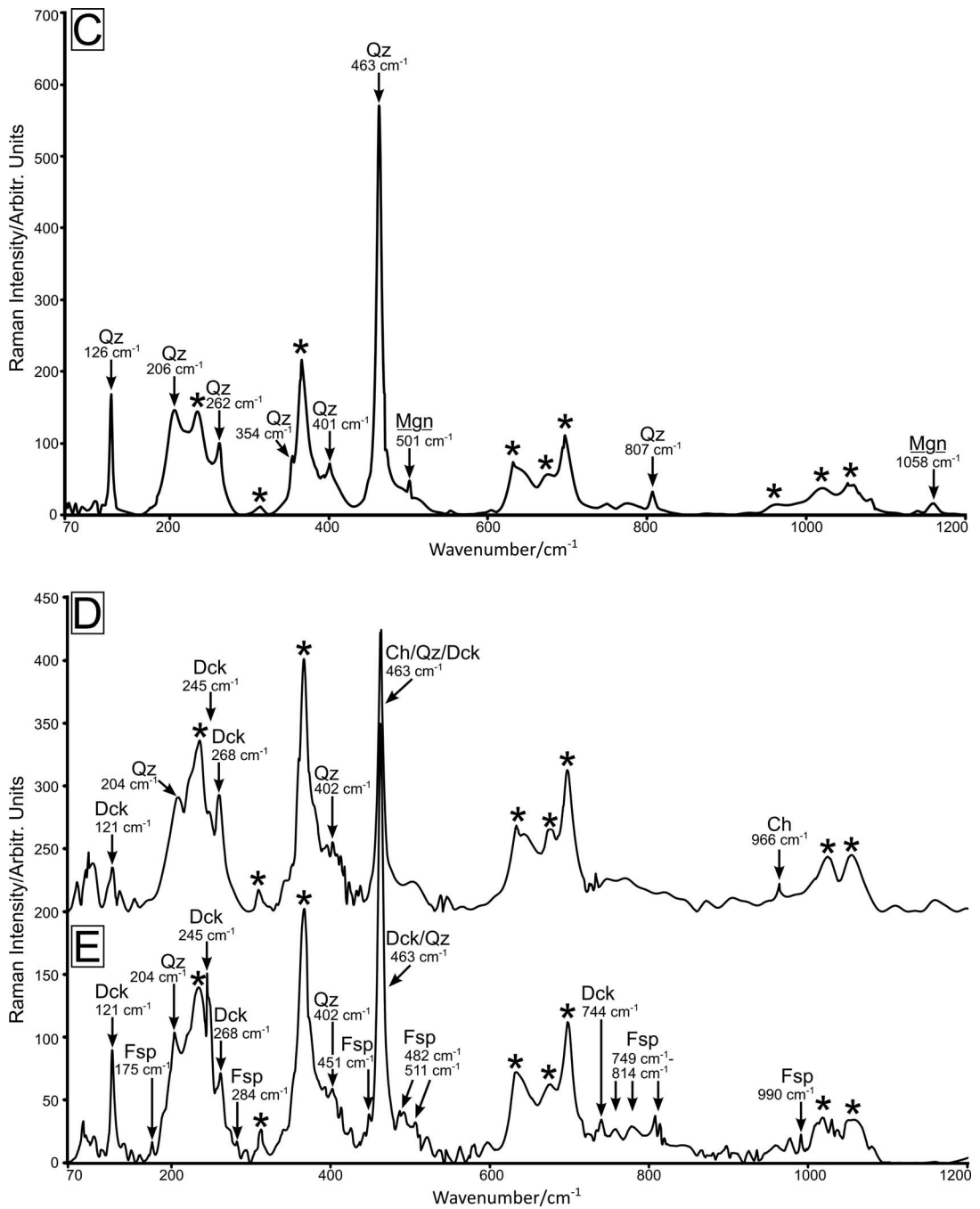


FIG. 8. (continued)

aqueous fluid phase (London 2005a). These three experimentally derived properties correspond to the compositional evolution observed in the MI within schorl from the Gatumba-Gitarama pegmatites. Al-

though fractional crystallization is surely the main mechanism by which natural pegmatitic magmas evolve and by which incompatible elements (*e.g.*, B, Rb, Cs, *etc.*) become enriched both regionally (*e.g.*,

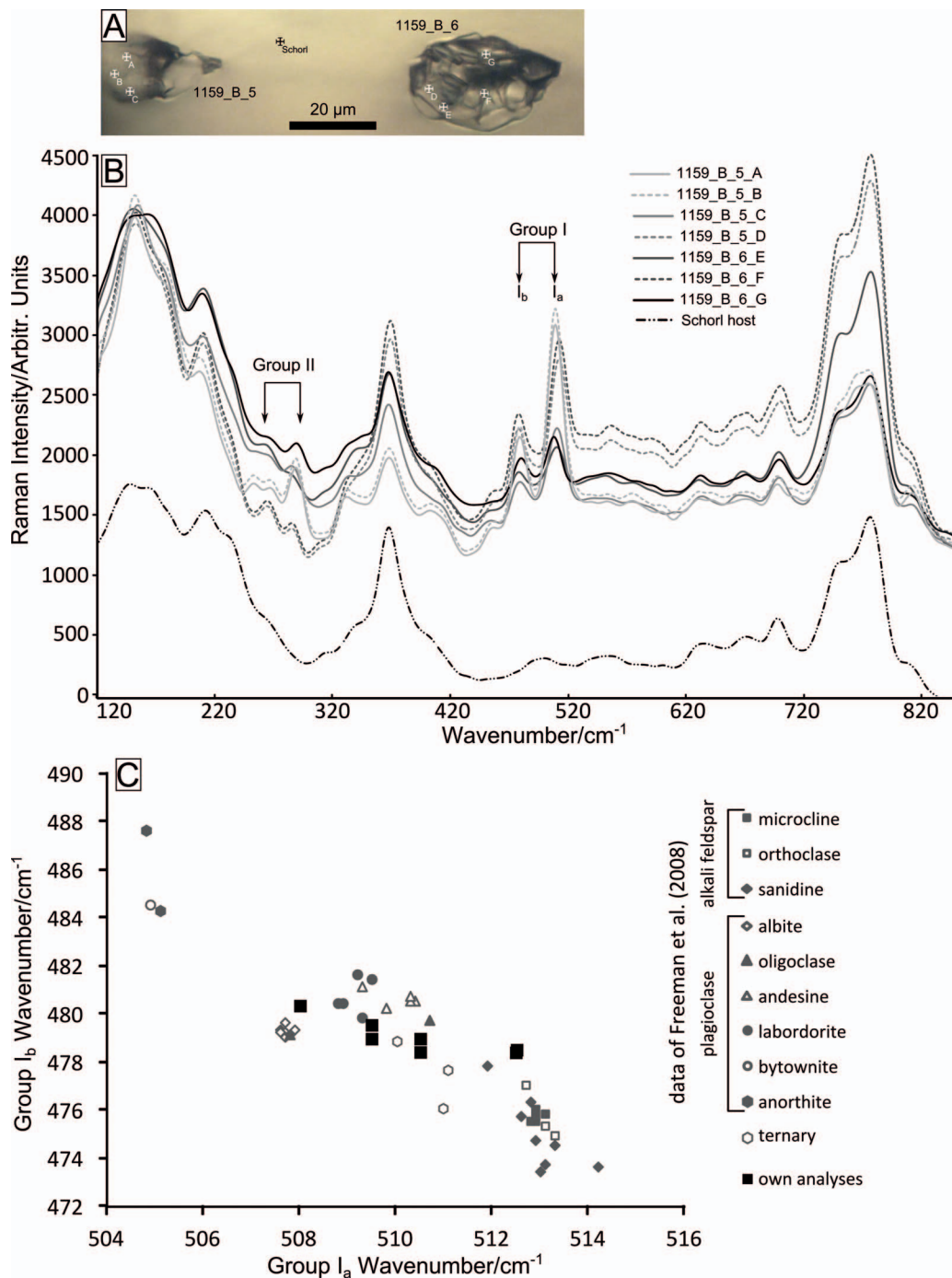


FIG. 9. (A) Feldspar daughter-phase mineral occurrences in inclusions 1159_B_5 and 1159_B_6 in schorl from a biotite-zone pegmatite. (B) Raman spectra of the feldspar daughter minerals and the locations of the principal group I peaks and group II peaks. (C) Correlation between the Raman band I_a and I_b peak positions and the feldspar binary composition (*cf.* compositional correlation of Freeman *et al.* 2008).

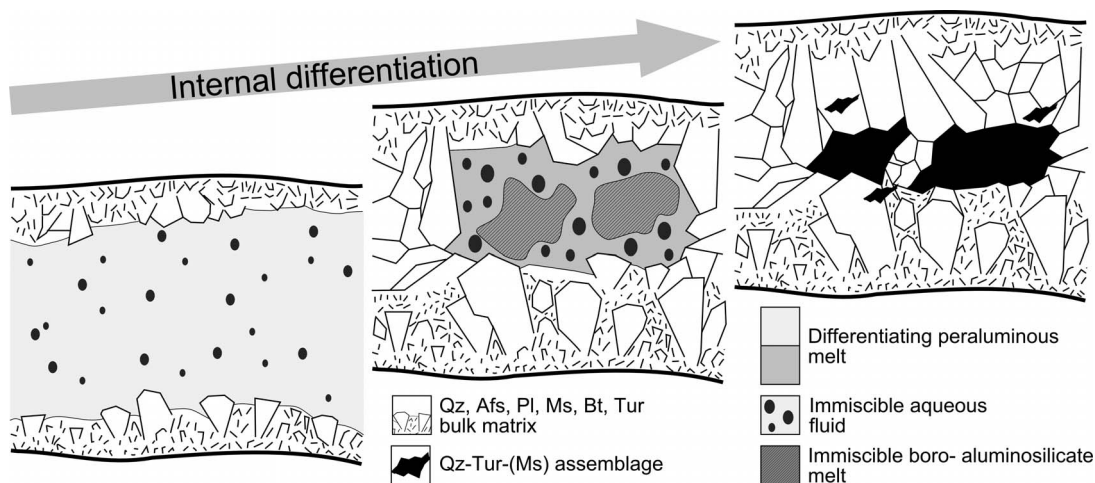


FIG. 10. Proposed internal differentiation mechanism of the common pegmatites of the biotite (#1), biotite-muscovite (#2), and muscovite (#3) zones of the Gatumba-Gitarama area. Fractional crystallization of granitic minerals (Qz: quartz, Afs: K-feldspars, Pl: plagioclase, Ms: muscovite, Bt: biotite, and Tur: Tourmaline) forms the main differentiation mechanism. Precipitation of these minerals causes the residual pegmatitic melt to become enriched in incompatible melt structure modifiers (*e.g.*, B, P, alkali metals, borates, phosphates, and H_2O), causing immiscibility processes to become increasingly important with extended mineral fractionation. Starting from the less-differentiated biotite to muscovite pegmatite melts, the boro-aluminosilicate melt and coexisting aqueous fluid exsolve from the bulk peraluminous pegmatitic melt.

Hulsbosch *et al.* 2014) and internally within pegmatite dikes (*e.g.*, London 1986), the coexistence of multiple liquid phases due to immiscibility becomes increasingly important with extended mineral fractionation and can provide an alternative explanation for the formation of chemically anomalous residual melts and associated mineral assemblages, such as quartz-tourmaline-(muscovite) pockets (Fig. 10). Moreover, the formation of quartz-tourmaline-(muscovite) assemblages in the Land's End granite (England) has also been indirectly related to the immiscibility of a hydrous boro-aluminosilicate melt produced during the late stages of magmatic differentiation, based on B isotope and trace-element geochemistry of the tourmaline (Drivenes *et al.* 2015). Our study provides the direct observation and characterization of this inferred hydrous boro-aluminosilicate residual melt phase.

Formation of quartz-tourmaline-(muscovite) assemblages

Graphic quartz-tourmaline-(muscovite) assemblages inside the zone #1 to #3 pegmatites of the Gatumba-Gitarama area have also been described by Varlamoff (1954, 1972). Graphic quartz-tourmaline-(muscovite) assemblages have also been reported from less-evolved pegmatites (Slack *et al.* 1993, Wadoski *et al.* 2011). In Figure 10, a model is presented for the formation of quartz-tourmaline-(muscovite) assem-

blages in the common pegmatites of the Gatumba-Gitarama area, based on the direct observation of the boro-aluminosilicate melt composition of the melt inclusions by Raman spectroscopy. Fractional crystallization of granitic minerals (Qz: quartz, Afs: K-feldspars, Pl: plagioclase, Ms: muscovite, Bt: biotite, and Tur: Tourmaline) is the main differentiation mechanism. Precipitation of these minerals causes the residual pegmatitic melt to become enriched in incompatible melt-structure modifiers (*e.g.*, B, P, alkali metals, borates, phosphates, and H_2O), permitting immiscibility processes to become increasingly important with extended mineral fractionation. Starting from the less-differentiated biotite to muscovite pegmatite melts, the boro-aluminosilicate melt and coexisting aqueous fluid exsolve from the bulk peraluminous pegmatitic melt. The boro-aluminosilicate melt batches crystallize as the observed quartz-tourmaline-(muscovite) assemblages and cause the observed transition in mineralogy (*e.g.*, Fig. 2C, D).

CONCLUSION

This study documents the mineralogy of primary hydrous MI trapped in schorl of quartz-tourmaline-(muscovite) assemblages within common and increasingly differentiated biotite, biotite-muscovite, and muscovite pegmatites of the Gatumba-Gitarama area. The MI show a diverse mineralogical composition

predominantly composed of muscovite, α -quartz, mogánite, dickite, and minor feldspars. The evidence suggests a peraluminous boro-aluminosilicate composition for the trapped melt in combination with a wide variety of borate species found inside the inclusions. More specifically, additional daughter minerals, such as dawsonite, nahcolite, tourmaline, jeremejevite, and childrenite, indicate a profuse CO_2 -, H_2O -, B_2O_3 -, and P_3O_4 -enrichment. However, the identification of these daughter phases at ambient conditions does not necessarily confirm their presence in the pegmatite-forming melts at magmatic conditions. Especially, the low feldspar and high quartz, muscovite, and dickite contents demonstrate the importance of closed-system equilibration of the magmatic peraluminous mineral assemblages with acidic CO_2 -, H_2O -, and H_3BO_3 -rich interstitial fluids during cooling. The amount of interstitial fluid phase inside the MI is variable and resulted mainly from heterogeneous trapping of immiscible aqueous fluids during entrapment of the MI. Exsolution of cogenetic low- to medium-saline H_2O – NaCl – KCl – MgCl_2 -complex salt fluids from the melt has previously been reported for the samples studied (Hulsbosch *et al.* 2016).

Fractional crystallization can be seen as the main mechanism by which pegmatitic magmas differentiate; however, immiscibility processes can become increasingly important with extended mineral fractionation. Based on reported experimental, theoretical, and natural constraints, an alternative unmixing hypothesis can offer an explanation for the formation of the anomalous but omnipresent residual melts trapped in schorl from schorl-quartz-(muscovite) assemblages. Moreover, it can provide a genetic link between the coexisting MI and the low- to medium-saline H_2O – NaCl – KCl – MgCl_2 -complex salt (Rb, Cs) fluid inclusions. The high nominal quartz content and strong B-affinity of the immiscible melt could also explain the observed mineralogical transition from a granitic mineral mode towards a schorl-quartz-(muscovite) assemblage within the mineralogical zonation of the common granitic pegmatite dike. Consequently, we report what is, to our knowledge, the first set of mineralogical analyses of tourmaline-hosted MI in relatively unevolved B-rich, F-poor pegmatite melts and hypothesize the significance of chemically anomalous residual melts and cogenetic aqueous fluids in the formation of quartz-tourmaline-(muscovite) assemblages in common pegmatites.

ACKNOWLEDGMENTS

We express our gratitude to Dr. Wilhelm Heinrich and Dr. Christian Schmidt (GFZ Potsdam), and to Dr. Kris Piessens (RBINS) for the hospitable

access to the Raman spectroscopic laboratories and their expertise. Dr. Michael Biryabarema and Alain Ntenge of GMD-MINIRENA are thanked for the authorization to conduct field work in Rwanda and export samples. Jean Ruzindana of Gatumba Mining Concessions is thanked for access to the Gatumba mining site. The authors also thank Dr. David Debruyne for stimulating discussions and Herman Nijs (KU Leuven) for preparing the high-quality doubly polished sections. The research of Niels Hulsbosch is funded by a Ph.D. grant from the Agency for Innovation by Science and Technology (IWT) and field work was also supported by a grant from the Dirk Vogel Fund. The research activity of Marie-Christine Boiron is supported by the French National Research Agency through the national program “Investissements d’avenir” with the reference ANR-10- LABX-21-LABEX RESSOURCES21. Philippe Muchez and Niels Hulsbosch appreciate the financial support for this project by research grant OT/11/038 of the KU Leuven Special Research Fund. This manuscript benefited from insightful and constructive reviews provided by Dr. Axel Müller and an anonymous reviewer. We are grateful to Editor Prof. Dr. Lee Groat, Managing Editor Mackenzie Parker, and Associate Editor Dr. Pietro Vignola for their comments and editorial handling.

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Received December 16, 2016. Revised manuscript accepted May 18, 2017.