

Article

Fluid and Solid Inclusions from Accessory Host Minerals of Permian Pegmatites of the Eastern Alps (Austria)—Tracing Permian Fluid, Its Entrapment Process and Its Role During Crustal Anatexis

Kurt Krenn  and Martina Husar

NAWI Graz Geocenter, Institute of Earth Sciences, University of Graz, 8010 Graz, Austria; martina.husar@gmx.at

* Correspondence: kurt.krenn@uni-graz.at

Abstract: To understand the fluid evolution of Permian pegmatites, three pegmatite fields of the Austroalpine basement units located in the Rappold Complex at St. Radegund, the Millstatt Complex, and the Polinik Complex were investigated. To achieve this goal, fluid inclusions trapped in the magmatic accessories of garnet, tourmaline, spodumene, and beryl were studied using host mineral chemistry combined with fluid inclusion microthermometry and Raman spectrometry. Taking into account the previous work by the authors on pegmatite fields in the Koralpe and Texel Mountains, Permian fluid was determined to have evolved from two stages: Stage 1 is characterized by the homogeneous entrapment of two cogenetic immiscible fluid assemblages, a $\text{CO}_2\text{-N}_2 \pm \text{CH}_4$ -rich and a low-saline H_2O -rich fluid. Both fluids are restricted to inclusions in the early-magmatic-garnet-core domains of the Koralpe Mountains. Stage 2 is linked with the $\text{CO}_2\text{-N}_2\text{-CH}_4\text{-H}_2\text{O-NaCl-CaCl}_2 \pm \text{MgCl}_2$ fluid preserved as an inclusion in all the pegmatite accessories of the KWNS. It represents the mechanical mixture of the stage 1 fluid caused by compositional changes along the solvus, which is typical for a hydrothermal vein environment process. Increasing $X_{\text{CH}_4 \pm \text{N}_2}$ proportions from the eastern toward the western pegmatite fields of the KWNS results in a tectonic model that includes magmatic redox-controlled fluid flow along deep crustal normal faults during the anatexis of metasediments in Permian asymmetric graben structures. Because of a high number of solids within the inclusions as well as their irregular shapes, post-entrapment modifications have caused density changes that have to be considered with caution. However, the conditions in the range of 6–8 kbar at $>670^\circ\text{C}$ for stage 1 and ca. 4 kbar at $<670^\circ\text{C}$ for stage 2 represent the best approximations to explain the uprise of a two-stage Permian fluid associated with accessory mineral crystallization in close relation to fractionating melt.

Keywords: fluid inclusions; heterogeneous fluid entrapment; accessory pegmatite minerals; Permian pegmatites; Eastern Alps



Academic Editors: Victoria Maneta and Mona-Liza C. Sirbescu

Received: 28 February 2025

Revised: 14 April 2025

Accepted: 16 April 2025

Published: 18 April 2025

Citation: Krenn, K.; Husar, M. Fluid and Solid Inclusions from Accessory Host Minerals of Permian Pegmatites of the Eastern Alps (Austria)—Tracing Permian Fluid, Its Entrapment Process and Its Role During Crustal Anatexis. *Minerals* **2025**, *15*, 423. <https://doi.org/10.3390/min15040423>

Copyright: © 2025 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

1. Introduction

Besides (poly-)metamorphosed rock suites, many Austroalpine basement units of the Eastern Alps contain meta-granitoids and meta-pegmatites of Permian origin (Figure 1). These rocks are associated with magmatic underplating accompanied by regional-scale continental break-up tectonics that created horst and graben structures during the Permian period [1]. Throughout this geological period, granitic melts intruded aluminous-rich metapelites and enhanced crustal anatexis from depths of approximately 25 km upward,

achieving upper-amphibolite/granulite-facies metamorphic conditions [2–4]. The resulting peraluminous granitic melts crystallized into DPA (direct products of anatexis) pegmatites of group 3, following Wise et al. [5]. Accessory magmatic/anatectic minerals, such as garnet, tourmaline, apatite, beryl, and spodumene $\pm$ staurolite, formed alongside the main pegmatoid mineral assemblage, which included orthoclase $\pm$ kyanite + albite + quartz + muscovite. Intense Cretaceous high-pressure overprints enhanced the recrystallization of the principal pegmatite-forming minerals, quartz and plagioclase, as well as retrograde reactions that produced biotite around magmatic garnet porphyroclasts. This evidence leads to the conclusion that early-anatectic Permian fluid history can only be interpreted through the inclusions of non-recrystallized pegmatite accessories that stem from a moderately fractionated melt [4,6,7]. Consequently, the textural and chemical characterizations of these host minerals, along with their inclusion content, provide valuable insights into the melts and/or fluids associated with specific stages of pegmatite evolution. For instance, analyzing the major element profiles of accessory garnet offers significant conclusions about the degree of melt fractionation during crystallization [4,7–10]. Therefore, the combination of magmatic garnet chemistry and its inclusion phases elucidates the magmatic fluid narrative and aids in assessing the conditions and processes occurring during melt crystallization stages.

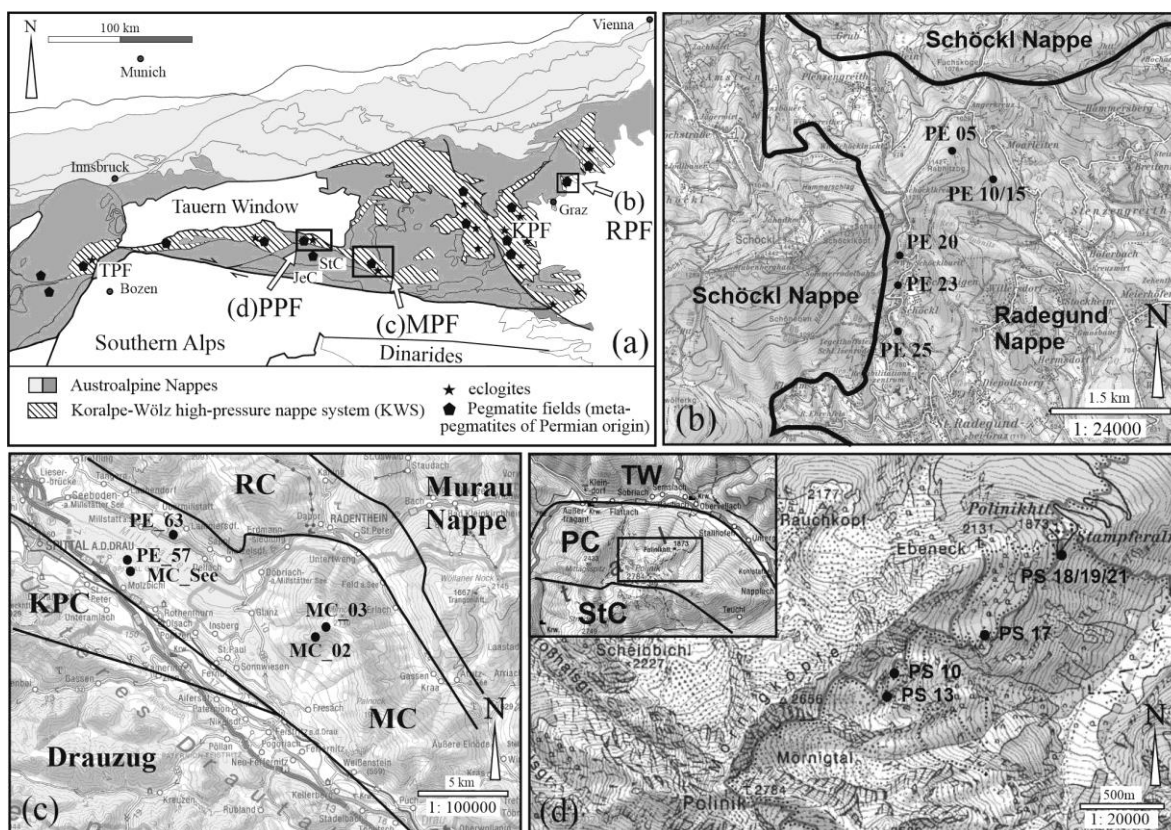


Figure 1. (a) Simplified geological map of the Eastern Alps. Investigated pegmatite field areas are outlined: RPF (St. Radegund Pegmatite Field); KPF (Koralpe Pegmatite Field); MPF (Millstatt Pegmatite Field); PPF (Polinik Pegmatite Field); TPF: (Texel Pegmatite Field); StC (Strieden Complex); JeC (Jenig Complex). (b) Sample location map of the RPF within the Radegund Nappe overlain by the Schöckl Nappe. (c) Sample location map of the MPF located within the Millstatt Complex (MC). The MC is overlain to the north by the Radenthein Complex (RC) and the Murau Nappe and to the south by the Kreuzeck–Polinik Complex (KPC) and the Drauzug. (d) Sample location map of the PPF within the Polinik Complex (PC) underlain by the Tauern Window (TW) to the north and overlain by the Strieden Complex (StC) to the south.

Combining fluid inclusion microthermometry with Raman spectrometry as an important approach to characterize the current fluid system during high-grade metamorphic stages, it is conceivable that inclusions are typically not suitable for establishing a complete and continuous record of fluid evolution during pegmatite crystallization. Therefore, the degree of fluid mixing from various sources within a hydrothermal vein environment must be considered. Furthermore, the ability of fluid inclusions to undergo post-entrapment modifications under non-isochoric PT evolution processes complicates the assessment of precursor magmatic, metamorphic, or metasomatic fluids, including their corresponding densities and chemical fluid systems [11–13]. This holds particularly true for all Permian pegmatites of the Eastern Alps, which were incorporated into subsequent overprints during the “Eoalpine” Cretaceous subduction event. These granitoid rocks were deformed into lenses of orthogneisses and meta-pegmatites during the formation of the Koralpe–Wölz Nappe System (KWNS), reaching PT conditions of up to 25 kbar and 650 °C [14,15]. Although these rocks reflect this strong overprint, a preserved Permian magmatic texture is still observed in many areas. It is evident that only fluid inclusion assemblages (FIAs) with clear indications of an earliest “primary” origin after Goldstein and Reynolds [16] and Goldstein [17], which are trapped in magmatic accessories, should be selected and studied.

Previous investigations of Permian pegmatites in the Koralpe Mountains (Koralpe Pegmatite Field: KPF) and Texel Mountains (Texel Pegmatite Field: TPF) (Figure 1) indicate a low-saline $\text{H}_2\text{O}-\text{CO}_2 \pm \text{N}_2 \pm \text{CH}_4$ -rich fluid that was trapped separately as aqueous and carbonic fluid inclusions (FIs) in accessory garnet cores, as well as in the form of immiscible aqueous–carbonic FIs in beryl and cassiterite of Permian age [4,6,7,18]. This suggests a complex fluid mixing process associated with subsequent mineral crystallization stages during crustal anatexis [7,19]. Studies on lithium pegmatites of the KWNS by Knoll et al. [20] propose a metasedimentary melt source for these pegmatites. Anatexis of staurolite-bearing metapelites, which contain significant amounts of lithium, occurred under metamorphic conditions of approximately 675 °C and 6.5 kbar, producing melt to form these large pegmatite fields. The timing of pegmatite and leucogranite emplacement, or the regional metamorphism of surrounding metapelites, clusters between 240 and 290 Ma, which corresponds to much of the Permian, along with the Early and Middle Triassic. The age distributions presented by Knoll et al. [20] show that regional metamorphism primarily occurred at the beginning of the Permian event, while the emplacement of pegmatites and leucogranites spanned the entire event. It is argued that Permian metamorphism and the emplacement of pegmatites and leucogranites were contemporaneous. In contrast to many pegmatite areas worldwide, their proposed model does not necessitate large, genetically linked parental intrusions, which are absent in the entire Austroalpine basement units.

Accordingly, the aims of this study are (1) to extend this approach to additional pegmatite field areas of the Eastern Alps; (2) to characterize the composition of fluids within these high-grade metamorphic environments; (3) to decipher the dominant fluid entrapment processes during crustal anatexis; (4) to calculate minimum pressures of host mineral formation based on the densities of representative FIs; and (5) to compare all pegmatite field areas investigated so far in the KWNS for a possible common or separate Permian fluid evolution story.

2. Geological Setting of the Investigated Pegmatite Fields

Permian pegmatites located in the KWNS predominantly occur within metasediments that have experienced up to three metamorphic imprints: a Variscan (~340 Ma) high pressure/medium temperature (HP/MT); a Permian (~260 Ma) low pressure/high temperature (LP/HT); and an “Eoalpine” Cretaceous (~100–90 Ma) high pressure/medium temperature (HP/MT) [21–23]. Areas related to these pegmatites define pegmatite fields that are located

west, south, and east of the Tauern Window (TW) and are mainly composed of staurolite and/or aluminosilicate-bearing micaschists and paragneisses (Figure 1a). The presence of andalusite but also orthoclase + kyanite intergrowth textures in pegmatites of the KPF indicate an Al-rich silicic melt that crystallized during the uprise of the fractionating anatectic melt from ca. 25 km upward [4]. The presence of magmatic staurolite in the TPF at the western end of the KWNS (Figure 1a) indicates anatexis of melt crystallization temperature conditions in the range of 650–750 °C, experimentally proven for a certain Permian pegmatite mineral assemblage [18].

Subsequent to the Permian event, Cretaceous subduction overprinted host rocks and pegmatites of the KWNS by transforming Permian solidified granitoid rocks into lenses of foliation-parallel meta-pegmatites. Peak conditions for this Eoalpine metamorphism are best constrained in the Koralpe Complex in the range of 625–730 °C at 22–28 kbar for eclogites [14] and 700 ± 68 to 600 ± 63 °C at 10–15 kbar for metapelites [15]. Ages related to this event lie between 90 and 95 Ma [14,24]. The meta-pegmatites with an Eoalpine overprint spread throughout the KWNS but also occur south of it, within units (e.g., Strieden Complex) that experienced only a weak Cretaceous metamorphism (StC in Figure 1a). *PT* conditions for the Permian metamorphism of the StC are in the range of 2.5–5 kbar at 500–750 °C [25,26]. In addition, *PT* conditions in the range of 2.4–4.2 kbar and 450–530 °C have been calculated from andalusite-bearing micaschists of the Jenig Complex (JeC in Figure 1a) further south of the Strieden Complex dated by monazite around 275 ± 25 Ma [26].

For this study, three pegmatite fields from the crystalline basement of the Eastern Alps are selected (Figure 1): the St. Radegund Pegmatite Field (RPF), the Millstatt Pegmatite Field (MPF), and the Polinik Pegmatite Field (PPF). Published data from the Koralpe Pegmatite Field (KPF) after Krenn et al. [6] and Husar and Krenn [4] as well as from the Texel Pegmatite Field (TPF in Figure 1a) after Krenn et al. [7] are added for comparison and possible genetic coherence. All pegmatite fields studied here are part of the KWNS and underwent intense Eoalpine overprint.

2.1. St. Radegund Pegmatite Field (RPF)

The RPF comprises the Radegund Nappe as part of the Rappold Complex [22] (Figure 1b). It belongs to the lowermost tectonic nappe unit of the KWNS after Schmid et al. [27] or to the Silvretta Gleinalpe Complex after Neubauer et al. [28]. Metasediments of this complex were deposited in a shelf and/or slope environment existing from the Late Cambrian up to the Carboniferous [29,30]. Based on polyphase metamorphosed garnet growth, a first metamorphic imprint of Permian age of upper amphibolite facies and partial anatexis was documented, and ranges from 275 to 255 Ma [2,31,32]. A second metamorphic overprint of Cretaceous age (Eoalpine subduction event) reached about 600 °C and 10 kbar [33,34].

The study areas are located in the western Radegund Nappe and are composed of paragneisses and micaschists with a few intercalations of amphibolite, marble, and calc-silicate rocks [35,36]. In the structural uppermost parts, staurolite-bearing garnet micaschists comprise a fine-grained matrix composed of biotite + muscovite + quartz $\pm$ plagioclase. They characterize the dominant lithology that hosts meta-pegmatites with quartz, albite (occasionally kalifeldspar), and muscovite as the major mineral assemblage [32].

The magmatic texture is still preserved, although some pegmatites are strongly affected by subsequent deformation and recrystallization by forming a foliation during Cretaceous regional metamorphism (Figure 2a). Accessories like tourmaline, garnet, spodumene, as well as apatite, zircon, rutile, and xenotime are present. Garnet shows a size up to 1 cm and tourmaline crystals reach a size up to several centimeters (Figure 2a,b). The

breakdown of Li-rich staurolite in the surrounding Al-rich metapelites is argued to be an additional source of Li in the primary anatectic melts [2,20]. Spodumene is up to several centimeters in size and shows a white up to greenish and brownish color [37]. The LiO_2 content ranges between 6.56 and 7.83 wt.% [38]. Beryl is very scarce and grayish or bluish-green up to one centimeter in length. Chemical zonation of magmatic muscovite implies a simple leucogranite source in the southern areas of the Radegund Nappe up to moderately fractionated pegmatites and spodumene pegmatites toward the northern areas, close to the overlying Schöckl Nappe of the Graz Paleozoic that is part of the Drauzug–Gurktal–Nappe System (DGNS) after Schmid et al. [27] or the Noric domain after Neubauer et al. [28] (Figure 1b). This zonation is based on the upward decrease in the K/Rb ratio along with Li and Ti increases in the rock column, which reflects an upward migration of Permian melts that are continuously fractionated [2,39].

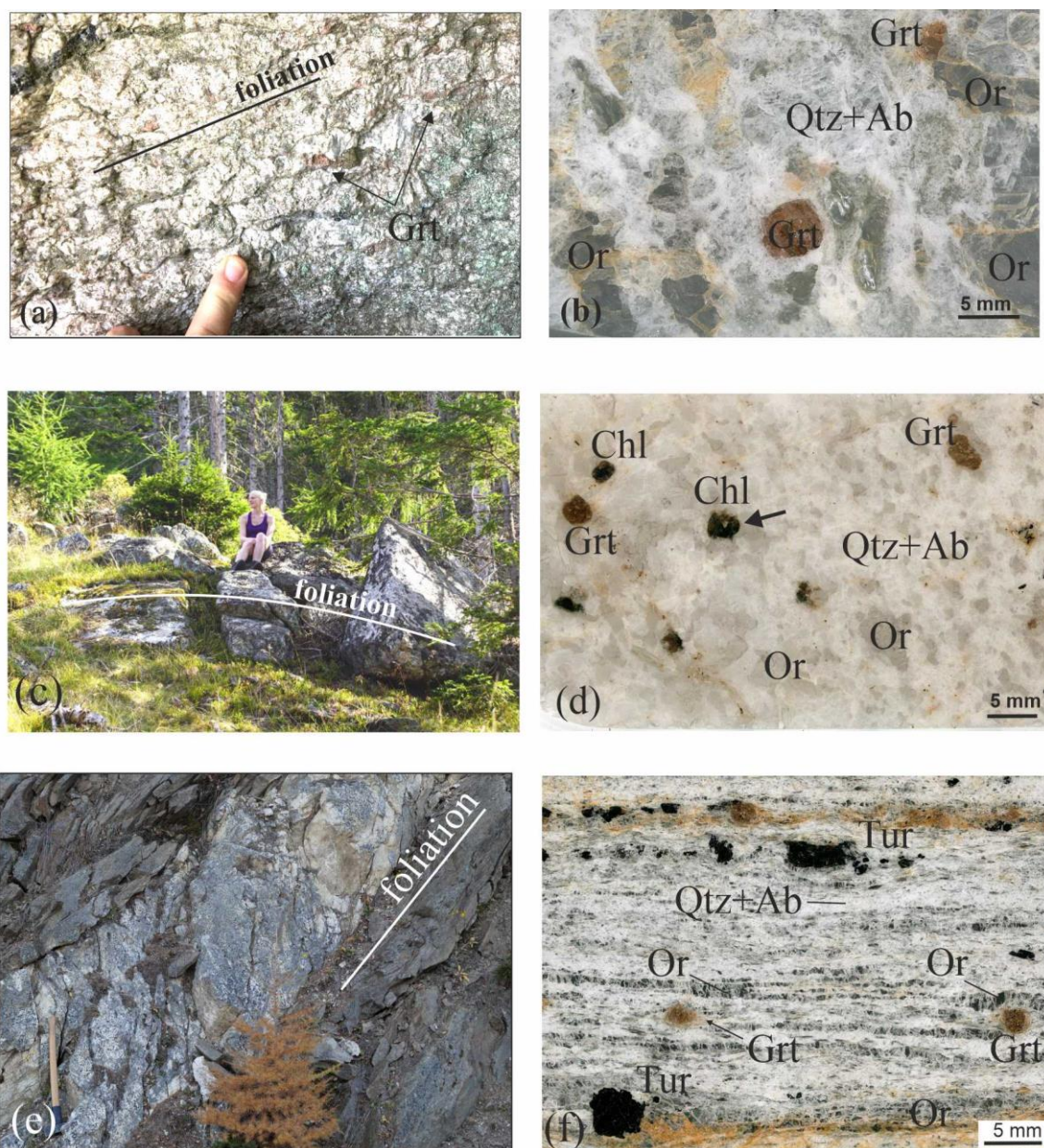


Figure 2. Outcrop situation and selected mineral assemblage of investigated pegmatite samples of the RPF (a,b), MPF (c,d), and PPF (e,f). Abbreviations: Qtz (quartz); Tur (tourmaline); Ab (albite); Or

(orthoclase); Grt (garnet); Chl (chlorite). (a) Field image of a pegmatite outcrop showing a Cretaceous post-pegmatite foliation and Permian garnets. (b) Thin section of major mineral paragenesis quartz + albite + orthoclase + garnet (sample PE05). (c) Field image of a pegmatite outcrop showing the dominant Cretaceous field foliation. (d) Pegmatite mineral assemblage quartz + albite + orthoclase + garnet (sample MC02). Garnet often shows retrogression to chlorite (arrow). (e) Field outcrop of a Cretaceous field foliation-parallel pegmatite layer hosted in metapelites. Hammer for scale. Image taken from Gotthardt [32]. (f) Foliated pegmatite sample consisting of mineral assemblage quartz + albite + orthoclase + garnet + tourmaline. Foliation consists of recrystallized quartz, albite, and orthoclase. Garnet shows dark-red cores and light recrystallized rims (sample PS 18).

Samples PE05 and PE23 were investigated for major element chemistry of garnet as well as their inclusion content (Figure 1b). PE05 comes from a fine-grained muscovite-rich pegmatite vein with a thickness between 3 and 4 m. Samples PE10 and PE15 were selected for investigating inclusions in spodumene and samples PE20 and PE25 were used for characterizing inclusions in tourmaline. No significant FIs were found in beryl host crystals. GPS sample location data are presented in Table 1.

Table 1. GPS sample location data.

RPF	MPF	PPF
PE05 47°12.62 N; 15°29.58 E	MC02 46°45.48 N; 13°41.11 E	PS10 46°54.04 N; 13°10.1 E
PE23 47°11.69 N; 15°29.02 E	MC03 46°45.58 N; 13°41.22 E	PS13 46°54.02 N; 13°10.0 E
PE10/15 47°12.42 N; 15°29.0 E	MCSee 46°46.55 N; 13°33.3 E	PS17 46°54.13 N; 13°10.36 E
PE20 47°11.90 N; 15°29.05 E	PE57 46°47.46 N; 13°31.28 E	PS18 46°54.28 N; 13°10.57 E
PE25 47°11.37 N; 15°29.02 E	PE63 46°47.50 N; 13°35.32 E	PS19/21 46°54.3 N; 13°10.58 E

2.2. Millstatt Pegmatite Field (MPF)

The MPF is located in the Millstatt Complex (MC) as part of the lowermost nappe units of the KWNS. It is bordered to the west by the Kreuzeck–Polinik Complex (KPC), to the north by the Radenthein Complex (RC), and to the east and south by the Murau Nappe and Drauzug, respectively (Figure 1c). Murau Nappe and Drauzug are part of the Drauzug–Gurktal–Nappe System after Schmid et al. [27] or part of the Upper Austroalpine units after Neubauer et al. [28]. The MC is composed of monotoneous micaschists and gneisses, quartzites, and marble, which are all intercalated by meta-pegmatites. In the southeastern MC, calcsilicates and retrogressed eclogite outcrops are documented [40]. Pegmatites are exposed as meter-sized concordant and foliated lenses within quartz-rich micaschists and of Permian age [23,41,42] (Figure 2c). Contrasting to the RPF, rocks of the MPF experienced at least three stages of metamorphism (Variscan, Permian, and Eoalpine), predating an earlier Ordovician sedimentary origin [22]. A Variscan metamorphic event is based on older garnet generation associated with kyanite and staurolite [43]. Kyanite paramorphs after Permian andalusite would indicate high-temperature metamorphism prior to a high-pressure overprint [23,44,45]. This high-pressure metamorphism reached eclogite facies conditions of >13.8 kbar and 630 ± 20 °C during the Cretaceous event [22,40]. The major pegmatite mineral assemblage comprises quartz, feldspar (albite, orthoclase), muscovite, and accessory tourmaline, garnet, monazite, zircon, and apatite. Garnet, but also tourmaline, is strongly fractured and represents porphyroclasts <10 mm in size within a fine-grained matrix composed of recrystallized quartz + albite (Figure 2d). Light-green-to-grayish spodumene phenocrysts reach an average size of ca. 4 cm. Idiomorphic to hypidiomorphic garnets are locally affected by a retrograde metamorphic overprint to chlorite.

Two garnet-bearing samples, MC02 and MC03, were selected for their inclusion content as well as calculating garnet major element chemistry (Figure 1c). Sample MC_See, used for an inclusion study in spodumene, is taken from the Lug-ins-Land area at Millstätter Seenrücken comprising monotoneous micaschists, gneisses, and quartzites with intercalated spodumene-bearing pegmatites. FIs in tourmaline have been studied in sam-

ples PE57 and PE63. PE57 was sampled near the village Edling, east of Spittal an der Drau, and PE63 along the road from Millstatt village to Dellach. GPS sample locations are presented in Table 1.

2.3. Polinik Pegmatite Field

The Prijakt–Polinik Complex, including the PPF, is located south of the southeastern Penninic Tauern Window (Figure 1a). The area is subdivided into the Polinik and Strieden Complexes, both representing the northern and southern parts, respectively (Figure 1d). The Polinik Complex (PC) is part of the KWNS whereas the Strieden Complex (SC) belongs to the Drauzug–Gurktal–Nappe System that has not experienced significant Eoalpine metamorphic overprint [21,46]. The PC and SC are grouped into the Wechsel Gneiss and Silvretta–Gleinalpe Complexes, respectively, after Neubauer et al. [28]. Similar to the MC, a comparable metamorphic evolution as well as a common Ordovician depositional age are proposed for the PC. The PC itself is composed of micaschists, quartzitic paragneisses with intercalated amphibolites, eclogites, marbles, and meta-pegmatites [43,46]. Eclogites and amphibolites derived from N-MORB basalts (tholeiitic and alkaline within-plate basalt-type metabasites) with a crystallization age around 590 Ma, while associated orthogneisses exhibited a crystallization age in the range of 460–480 Ma [47]. Th/U/Pb dating of monazite from areas south of the Tauern Window indicates a Variscan (320–340 Ma), a Permian, as well as a Cretaceous metamorphic event [47–49]. The rocks of the PC and SC record the Permian metamorphic event at 270–250 Ma with peak temperatures of ≥ 550 °C at ca. 4 kbar [23,31,50–52]. Restricted to the PC, the dominant Eoalpine overprint is constrained at ~85–110 Ma under eclogite facies conditions of at least 16 kbar and 650 °C [53].

Tourmaline–garnet–muscovite-bearing meta-pegmatites are emplaced parallel to foliated micaschists and quartzo-feldspathic gneisses (Figure 2e). In addition, spodumene crystals and occasionally beryl occur. Recrystallized quartz, albite, and alkali-feldspar usually constitute a fine-grained matrix in which garnet, beryl, and tourmaline represent porphyroclasts (Figure 2f). Muscovite forms mostly mica-fishes with a maximum size of 3 mm. Tourmaline is present as idiomorphic-to-hypidiomorphic crystals with a size of up to several centimeters. Like garnet and beryl, tourmaline appears strongly fractured. Garnet forms idiomorphic crystals with a diameter of 0.2 up to 7 mm. Note that garnet often shows small recrystallized rims (arrow in Figure 2f).

Samples PS10, PS13, PS17, PS18, PS19, and PS21 were taken along the hiking trail to the Polinikhütte (Figure 1d). They were used for inclusion studies in garnet and selectively used for studying their major element chemistry. PS10 was also prepared for studying inclusions in beryl and samples PS18 and PS21 for inclusions in tourmaline. No albite–spodumene pegmatites were found in the investigated area. All GPS sample locations are presented in Table 1.

3. Analytical Methods

3.1. Electron Microprobe

Major element compositions of selected garnet fragments were obtained with a JEOL JXA-8530F Plus field emission electron probe microanalyzer (Jeol, Freising, Germany) at the NAWI Graz Geocenter, University of Graz (Austria), and a JEOL JXA 8200 electron probe microanalyzer (Jeol, Freising, Germany) at the Universität of Leoben (Austria), both attached with EDS and WDS systems. Measurements were carried out using a 15 kV accelerating voltage and 10 nA beam current for major element garnet profiles. The following standards were used: garnet (Mg, Fe, Al, Si), rhodonite (Mn), rutile (Ti), chromite (Cr), and diopside (Ca). Element mole fractions were obtained to determine major element

zonation the profiles and major element chemistries (XFe, XMn, XMg, XCa) of garnet domains close to the studied FIs.

3.2. Fluid Inclusion Microthermometry

Microthermometric measurements of the FIs were performed using a Linkam THSMG600 (Linkam Scientific Instruments, Redhill, UK) heating and freezing stage covering a temperature range from $-196\text{ }^{\circ}\text{C}$ to $+600\text{ }^{\circ}\text{C}$ at the NAWI-Graz Geocenter. During cooling and heating, phase transitions were observed with an Olympus petrographic microscope equipped with an $80\times$ ULWD objective. The Synthetic Fluid Inclusion Reference Set (Bubbles Inc., Blacksburg, VA, USA) was used for stage calibration. Temperature measurements are reproducible to within $0.2\text{ }^{\circ}\text{C}$ at a heating rate of $0.1\text{ }^{\circ}\text{C min}^{-1}$. Calculations of fluid densities and salinities were performed with the program Bulk by using the appropriate equations of state (EOS) after Oakes [54] and Zhang and Frantz [55] for aqueous inclusions, as well as Spencer et al. [56] and Thiery et al. [57,58] for aqueous–carbonic inclusions. Isochores for representative high-dense FIs (i.e., homogenization to the liquid state) were calculated using the program Isoc. Bulk and Isoc are part of the software package FLUIDS 1 [59]. All FIs were at least initially cooled to below $-100\text{ }^{\circ}\text{C}$ ($-190\text{ }^{\circ}\text{C}$ for N_2/CH_4 -bearing FIs) and subsequently heated to determine the temperatures of phase transitions. Depending on the chemical system for any given FI, the following parameters were documented (L = liquid; V = vapor; S = solid phase): $T_e(\text{ice})$ eutectic temperature or apparent eutectic temperature of ice melting (e.g., $\text{IceV} \rightarrow \text{IceLV}$); T_e means the minimum temperature of liquid stability in a specified system associated with a unique characteristic mixture of the components. It was used to identify the aqueous fluid system after Davis et al. [60] and Goldstein and Reynolds [16]; $T_m(\text{Ice})$ final melting temperature of ice ($\text{IceLV} \rightarrow \text{LV}$); final melting temperatures of carbonic ice are presented as $T_m(\text{car})$. By using the final melting temperature of hydrohalite [$T_m(\text{HH})$] together with [$T_m(\text{Ice})$], the corresponding fluid compositions in NaCl/CaCl₂ ratios can be determined with diagrams from Oakes et al. [54] and explanations by Bodnar [61]. Partial homogenization temperatures of the carbonic vapor bubble [$T_h(\text{car})$] as well as total homogenization temperatures [$T_h(\text{tot})$ ($\text{LV} \rightarrow \text{L}$ or V)] were measured to obtain densities and minimum temperatures for the formation of homogeneously trapped FIs, respectively. A summary of the microthermometric properties of all types of FIs from the specific fluid inclusion assemblages (FIAs) is presented in Table 2.

3.3. Micro-Raman Spectrometry

To identify the fluid components and solid phases of the investigated inclusions, unpolarized Raman spectra in the confocal mode were obtained with a HORIBA JOBIN YVON LabRam-HR 800 Raman micro-spectrometer at the NAWI Graz Geocenter, University of Graz (Austria). Crystals and fluids within polished sections were excited at room temperature (RT) with a 532 nm emission line of a 50 mW Nd-YAG and 632.2 nm of a 30 mW He-Ne laser through an OLYMPUS $100\times$ objective (N.A. 0.9). The laser spot on the surface had a diameter of approximately $4\text{ }\mu\text{m}$. The light was dispersed by a holographic grating with 1800 grooves/mm. The slit width was set to $100\text{ }\mu\text{m}$. The dispersed light was collected by a 1024×256 nitrogen-cooled open-electrode CCD detector. Band shifts were calibrated by regularly adjusting the zero position of the grating and controlled by measuring the Rayleigh line of the incident laser beam. The detection range involving solid, liquid, and gas phases lay between 120 and 3800 cm^{-1} . Based on the Raman spectra, the compositions of FIs in terms of mol% of the fluid species were calculated using Equation (2) presented by Burke [62]. To compare and identify Raman spectra, the tables in Frezzotti et al.'s [63] and Hurai et al.'s [64] studies were used. Carbonate identification was performed after Dufresne et al. [65].

Table 2. Petrography and microthermometric properties of fluid inclusion assemblages.

Location	Host	Type	Sample	Fluid Chemistry	Size [μm]	car/aq Proportions	Phases at RT	T _m (CH ₄ ± N ₂)	T _h (CH ₄ ± N ₂) gL	T _m (car) [°C]	T _h (car) gL/V [°C]	T _E (ice) [°C]	T _m (HH) [°C]	T _m (ice) [°C]	T _m (Cla) [°C]	T _h (Total) gL [°C]	Salinity (Average) [Equiv.Mass%]	Density * [g/cm ³]	Solid Phases
Radegund Pegmatite Field	Grt	RG-1	PE 23	H ₂ O-NaCl-CaCl ₂ ± MgCl ₂	≤18		L _{aqu} + V _{aqu}					−53.3 to −48.9	−22.9 to −21.2	−2.2 to 0.0		286.4 to 319.9	≤3.9 (3.6)	0.70 to 0.77	n.o.
		RG-2	PE 05/23	CO ₂ ± N ₂ -H ₂ O-NaCl-CaCl ₂ ± MgCl ₂	≤25	40/60	L _{aqu} + V _{car} ± S			−58.1 to −56.6	15.6 to 21.4 (V)	−51.7 to −44.7	−25.1 to −21.2	−7.2 to 0.0	6.8 to 11.5	257.5 to 385.2	≤10.9 (6.2)	0.70 to 0.72	Rho, Cal, Ms, Xtm, Rt, Qtz
	Spd	RS-1	PE 10/15	H ₂ O-NaCl-CaCl ₂ ± MgCl ₂	≤20		L _{aqu} + V _{aqu}					−48.7 to −43.6	−24.7 to −22.4	−6.4 to −0.3		236.0 to 356.0	0.5–6.5 (5.1)	0.65 to 0.86	n.o.
		RS-2	PE 10/15	CO ₂ -H ₂ O-NaCl-CaCl ₂ ± MgCl ₂	≤20	40/60	L _{aqu} + L _{car} ± V _{car} ± S			−57.8 to −56.6	12.8 to 25.2 (V)	−47.5 to −45.1	−25.2 to −21.2	−3.9 to −0.3	4.8 to 10.5	297.2 to 346.0	0.3–6.7 (5.2)	0.70 to 0.73	Qtz, Cal, Zbl, Ms
	Tur	RT-1	PE 20/25	H ₂ O-NaCl-CaCl ₂ ± MgCl ₂	≤40		L _{aqu} + V _{aqu} ± S					−46.0	−26.9 to −21.1	−9.3 to −0.1		187.0 to 272.0	13.2 (7.1)	0.85 to 0.97	Cal
Millstatt Pegmatite Field	Grt	MG-1A	MC 02	CO ₂ -N ₂ -CH ₄ -H ₂ O-NaCl-CaCl ₂ ± MgCl ₂	≤10	90/10 to 50/50	L _{aqu} + L _{car} ± S		n.o.	−59.1 to −57.9	5.4 to 11.0 (L)	−55.4 to −47.4	−28.8 to −25.6	−7.2 to −3.7	14.7 to 18.8	272.5 to 363.6	6.5–11.1 (8.7)	0.75 to 0.90	Ap, Zrn, Ms, Cal, Rho, Qtz, Ab
		MG-1B	MC 03	CO ₂ -CH ₄ -N ₂ -H ₂ O-NaCl-CaCl ₂ ± MgCl ₂	≤8	40/60	L _{aqu} + V _{car} ± S		−99.4 to −93.7	−98.7 to −56.7	13.6 to 20.1 (V)	−53.6 to −46.6	−29.4 to −24.3	−6.2 to −3.2	16.4 to 21.0	187.7 to 280.3	5.6–10.0 (7.9)	0.70 to 0.72	
	Spd	MS	MC_See	CO ₂ -N ₂ -H ₂ O-NaCl-CaCl ₂ ± MgCl ₂	≤25	30/70 to 40/60	L _{aqu} + L _{car} ± S			−58.4 to −57.2	20.7 to 22.3 (L) 18.7 to 20.9 (V)	−55.2 to −53.5	−23.7 to −21.8	−7.8 to −5.8	11.7 to 13.8	306.9 to 350.9	9.2–11.7 (10.6)	0.82 to 0.96	Gr, Zbl, Ms, Qtz, Ap
	Tur	MT	PE 57/63	CO ₂ -N ₂ -H ₂ O-NaCl-CaCl ₂ ± MgCl ₂	<80	40/60 to 80/20	L _{aqu} + L _{car}			−59.9 to −57.3	15.9 to 18.5 (V)	−51.3 to −38.0	−25.8 to −21.2	−16.5 to −4.2	1.8 to 7.9	275.0 to 311.5	10.9–19.2 (13.6)	0.75 to 0.76	n.o.

Table 2. Cont.

Location	Host	Type	Sample	Fluid Chemistry	Size [μm]	car/aq Proportions	Phases at RT	T_m (CH ₄ ± N ₂)	T_h (CH ₄ ± N ₂) gL	T_m (car) [°C]	T_h (car) gL/V [°C]	T_E (ice) [°C]	T_m (HH) [°C]	T_m (ice) [°C]	T_m (Cla) [°C]	T_h (Total) gL [°C]	Salinity (Average) [Equiv.Mass%]	Density * [g/cm ³]	Solid Phases
Polinik Pegmatite Field	Grt	PG-1A	PS 17/19	CO ₂ -N ₂ ± CH ₄ -H ₂ O-NaCl-CaCl ₂ ± MgCl ₂	≤8	85/15	L _{aqu} + L _{car} ± S		−150.0 to −127.5	−62.3 to −61.1	−52.9 to −40.4 (L)	−55.2 to −52.5	−28.3 to −25.8	−9.1 to −0.2	19.9 to 21.5	306.7 to 341.8	0.4–13.1 (8.7)	0.86 to 0.91	Qtz, Ab, Cal, Rho, Ms, Ap, Rt, Zrn, Xen, Gr
		PG-1B	PS 10/13/18	CO ₂ -CH ₄ -N ₂ -H ₂ O-NaCl-CaCl ₂ ± MgCl ₂	≤15	40/60	L _{car} ± V _{car} + L _{aqu} ± S		−105.6 to −83.4	−65.7 to −56.6	−25.7 to 24.8 (L)	−52.0 to −45.0	−34.7 to −21.4	−8.2 to −1.6	17.2 to 22.4	178.5 to 365.7	2.7 to 13.1 (8.7)	0.86 to 0.88	
	Brl	PB	PS 10	CO ₂ -CH ₄ -N ₂ -H ₂ O-NaCl-CaCl ₂ ± MgCl ₂	≤20	80/20 to 30/70	L _{car} + L _{aqu} ± S			−66.4 to −57.7	9.1 to 10.8 (L) 9.0 to 15.8 (V)	−52.3 to −49.6	−24.9 to −21.2	−4.7 to −2.0	12.4 to 15.9	302.3 to 390.5	3.4–7.8 (6.0)	0.78 to 0.91	Qtz, Ab, Cal, Ms, ±Tpz
	Tur	PT-1	PS 18/21	CO ₂ -CH ₄ -N ₂ -H ₂ O-NaCl-CaCl ₂ ± MgCl ₂	≤50	90/10 to 20/80	L _{car} + L _{aqu}	−130.0 to −73.6	−127.0 to −85.5		−20.0 to 12.5 (L) −40.1 to 5.3 (V)	−59.0 to −30.0 °C	n.o.	−9.1 to −6.0	15.0 to 21.0	187.0 to 309.0	4.5–17.8 (12.0)	0.68 to 0.73	Qtz
		PT-2	PS 18	H ₂ O-NaCl-CaCl ₂ ± MgCl ₂	≤50		L _{aqu} + V _{aqu}					−59.0 to −46.0	−25.1 to −21.4	−8.5 to −8.3		157.0 to 188.0	12.1–12.3	0.97 to 0.99	n.o.

* densities of pressure dominated inclusions (homogenization to the liquid).

4. Results

4.1. Major Element Chemistry of Garnet Domains

All studied garnet core chemistries represent almandine–spessartine solid solutions (Figure 3a). At their outermost small rim areas, a trend to higher XCa concentrations (XGr_s) is characteristic. This is confirmed by a clear “jump” in XCa content and interpreted as rim growth during Cretaceous high-pressure metamorphism, comparable to garnet major element profiles of the Koralpe Pegmatite Field (KPF) [7,66]. Fe/Mn (molar) versus MnO (wt%) garnet compositions from the central core areas to the outermost core areas provide information about melt fractionation trends during garnet growth, which, in general, increases with increasing MnO values [8,67,68] (Figure 3b). Calculated garnet mineral chemistries are shown in Appendix A, Tables A1–A3.

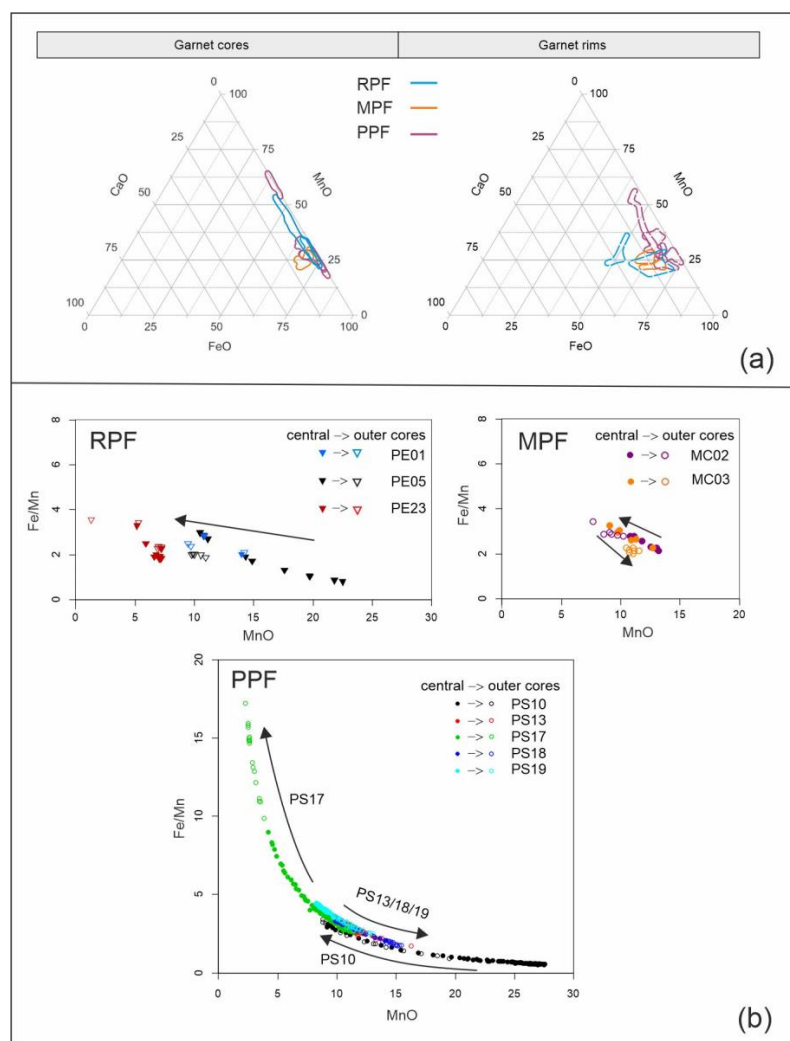


Figure 3. (a) Ternary CaO-MnO-FeO diagram of investigated garnet cores (left) and garnet rims (right) of the pegmatite fields. (b) Fe/Mn (molar) vs. MnO (wt.%) diagram of magmatic fractionation trend for garnet crystallization from central core areas toward outermost core areas (arrows). See text for data interpretation.

4.1.1. Radegund Pegmatite Field

Garnets show a trend toward increasing Fe/Mn compositions. Core areas comprise >90% of the garnet volume, however the intensity and style of profiles are different. Two representative major element profiles from garnet samples PE05 and PE23, where FIs have been investigated, are presented (Figure 4a,b). Garnet profile PE05_grt2 shows a clear con-

centric internal core zonation (oscillatory zoning) with the highest XMn concentration (Sps component) in the central core followed by a decreasing trend toward the rim zone (Figure 4a). This has also been reported for pegmatite garnets from other studies and localities of the world as an effect of the compatible property of Mn in garnet, e.g., [66,69–72].

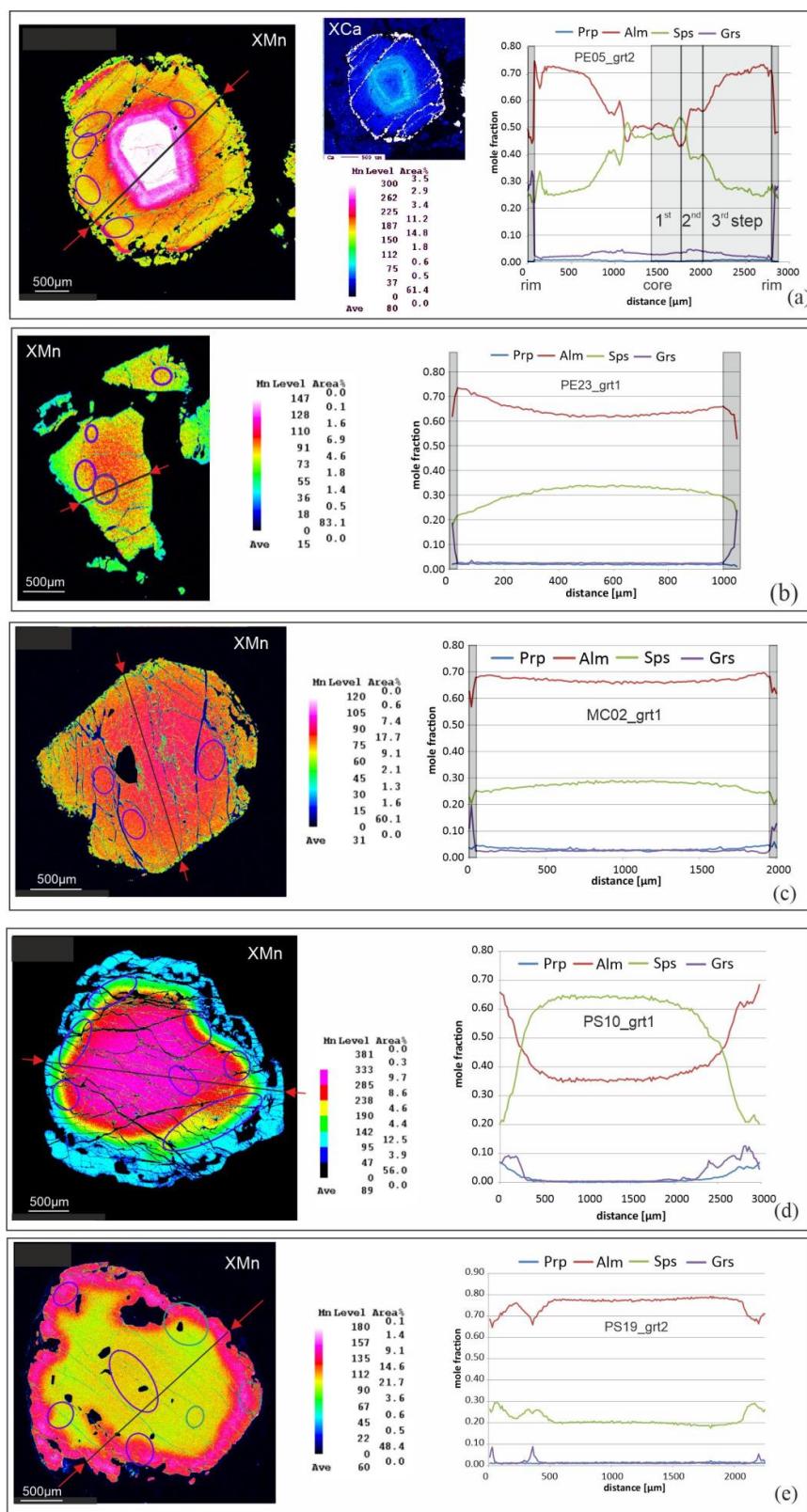


Figure 4. Selected garnet major element profiles for the RPF (a,b), MPF (c), and PPF (d,e). (a) Sample PE 05_grt2 indicates a 3-step magmatic zonation growth evolution; X-ray zonation images of major

element Mn (left side) and Ca (center) from sample PE 05_grt2. (b) X-ray zonation (left) and XMn bell-shaped profile of PE 23_grt1. (c) XMn bell-shaped profile of sample MC 02_grt1. (d) XMn bell-shaped profile of sample PS 10_grt1. (e) XMn flat-shaped profile of sample PS 19_grt2. Circles in all garnet X-ray zonation images indicate the locations of studied fluid inclusions.

The internal zonation characteristics of this garnet porphyroblast suggests a three-step magmatic growth evolution of variable increase and decrease in major element concentrations. This is typical for magmatic garnet growth by reflecting an inverse bell-shaped zonation of the spessartine component within each step of their Fe-rich and Mn-poor cores [9,10]. Decoupling between the XCa concentration (Grs component) and the XMn or XFe concentration may reflect the lower diffusion rate of XCa [73]. The small rim zone is characterized by a “jump” in XCa intensities to higher values along with a decrease in XFe (Alm component), which results from a pressure-dominant Cretaceous metamorphic overprint, confirming the interpretations by Habler et al. [66] for metamorphic garnet rim growth in pegmatites of the KPF. X-ray mapping shows also that many voids or pores are visible within the high-Ca domains equal to the rim concentrations (central image in Figure 4a). Voids represent the passage of the fluids or volatiles during the latest garnet growth stage. Therefore, the low-Ca domains (blueish areas) precipitated during the early stage of magmatic growth, whereas the high-Ca rims (white areas) formed later during the second growth stage, where the cracks were replaced and healed by Cretaceous metamorphic fluid. Investigated FIs are mainly located within third step of magmatic growth domains and show no visible connection to the cracks of high XCa content.

Contrasting to the garnets in sample PE05, sample PE23 contains garnets of continuous-flat-toward-spessartine bell-shaped profiles. Especially PE23 grt_1 exhibits a “spessartine bell-shaped” profile with higher XMn values in the center and continuously decreasing concentrations toward the outer core areas (Figure 4b). According to Dahlquist et al. [9], garnet core growth indicates growth temperatures below ~ 700 °C from very felsic magmas ($\text{SiO}_2 = 73\%–76\%$), or garnet core growth should be considered as metamorphic in origin. Due to the low XCa values of more than 90% of the garnet volume and a SiO_2 content of around 73% (72.25 for PE05 and 73.25 for PE23; see Gotthardt [32]), the first possibility of garnet growth is favored.

4.1.2. Millstatt Pegmatite Field

Garnet major element profile MC02_grt1 shows continuous core zonation characterized by XMn concentrations in the central core area that slightly decrease toward the outer core areas (Figure 4c). At the outermost rim, a clear “jump” toward a higher XCa concentration indicates Eoalpine pressure dominated metamorphic growth. Like garnet profile PE23 grt_1 from the RPF, the slightly prograde “bell-shaped” spessartine pattern indicates growth temperatures below ~ 700 °C from very felsic magmas. FIs have been studied from more outer core areas of constant XCa and slightly decreasing XMn composition.

4.1.3. Polinik Pegmatite Field

Garnet profiles show large differences ranging from Mn bell-shaped profiles over almost unzoned to inverse bell-shaped zonation patterns (Figure 4d,e). This indicates different garnet growth stages during pegmatite crystallization. However, the relatively low XCa concentrations as well as no visible jumps in XCa and XFe concentrations exclude garnet growth during the Eoalpine Cretaceous event.

Sample PS10_grt1 reflects a typical center-to-rim decrease in XMn concentration, which goes along with a systematic increase in XFe (Figure 4d). A comparable but more pronounced trend, like PE23_grt1 from RPF and MC02_grt1 from MPF, indicates growth

temperatures below ~ 700 °C from very felsic magmas. The continuous change in garnet composition from Mn-rich (core) to Fe-rich (rim) may also indicate the depletion of Mn relative to Fe in the melt during fractional crystallization [10]. A relatively flat-toward-“inverse bell-shaped” profile of garnet sample PS19_grt2 should be interpreted as clear magmatic growth after Dahlquist et al. [9] and slight peak variations can be related to late-replaced cracks and voids (Figure 4e). The same profile types apply to garnets of samples PS 13 and PS 18. In all samples, no clear “jump” in XCa as an effect of Cretaceous overprint was detected at the outermost rim domains.

4.2. Fluid Inclusion Studies

We use the term Fluid Inclusion Assemblage (FIA) after Goldstein and Reynolds [16] and Goldstein [17] for a petrographically distinguishable group of inclusions formed by a single event of fluid inclusion entrapment, independent of their liquid/vapor phase ratios and their textural characteristics of primary, secondary, or pseudo-secondary (see also Chi et al. [13] for this topic). Furthermore, fluid inclusion types and groups after Chi et al. [13] are considered here as equivalent terms.

4.2.1. Radegund Pegmatite Field

- Fluid Inclusions in Garnet (type RG)

Two separate FI types were distinguished. Type-RG-1 FIs consist of $\text{H}_2\text{O}-\text{NaCl}-\text{CaCl}_2 \pm \text{MgCl}_2$ chemistry and type-RG-2 FIs of $\text{CO}_2-\text{H}_2\text{O}-\text{NaCl}-\text{CaCl}_2 \pm \text{MgCl}_2$ chemistry. Both inclusion types characterize single or cluster FIs with a size of ≤ 25 μm and are irregular in shape (Figure 5a,b). Since both inclusion types show total homogenization to the liquid, the term of one FIA cannot be applied. It would indicate the coexistence of a CO_2 -bearing aqueous liquid (type RG-2) together with an aqueous liquid (type RG-1) that originated both from the same one-phase liquid field. It is therefore interpreted that type-RG-1 FIs originate from a different fluid that is trapped either before or after type RG-2, which would indicate a second fluid pulse. Only type RG-2 contains solids like rhodochrosite, calcite, quartz (cristobalite), muscovite $\pm$ phlogopite, rutile, and xenotime (Figure 8a,b). Solids occupy up to 40% of the inclusion volume.

Microthermometry of type RG-1 shows apparent eutectic melting of ice [$T_e(\text{ice})$] from -53.3 to -48.9 °C, which is indicative of $\text{H}_2\text{O}-\text{NaCl}-\text{CaCl}_2 \pm \text{MgCl}_2$ fluid chemistry. The last melting of hydrohalite [$T_m(\text{HH})$] between -22.9 and -21.2 °C and $T_m(\text{ice}) \geq -2.2$ °C indicates low total salinities up to 3.9 equiv. mass% with a $\text{NaCl}/(\text{NaCl} + \text{CaCl}_2)$ wt. ratio of ca. 0.9. Total homogenization [$T_h(\text{tot})$] to the liquid from 286.4 to 319.9 °C produces densities from 0.70 to 0.77 g/cm^3 (Table 2).

FIs of type RG-2 show the last melting of carbonic ice [$T_m(\text{car})$] between -58.1 and -56.6 °C indicating no significant amounts of N_2 and/or CH_4 to the CO_2 fluid component. All type-RG-2 FIs show partial homogenization [$T_h(\text{car})$] to the vapor from 15.6 to 21.4 °C. The aqueous component shows apparent eutectic melting of ice [$T_e(\text{ice})$] between -51.7 and -44.7 °C and hydrohalite melting [$T_m(\text{HH})$] from -25.1 to -21.2 °C, indicative for a range in the $\text{NaCl}/(\text{NaCl} + \text{CaCl}_2)$ wt. ratio between 0.7 and 1.0. the last melting of ice [$T_m(\text{ice})$] shows freezing-point depression down to -7.2 °C that results in total salinities up to 10.9 equiv. mass%. Clathrate melting [$T_m(\text{Cla})$] was observed between 6.8 and 11.5 °C. Total homogenization of the carbonic bubble to the liquid occurs from 257.5 to 385.2 °C and densities range from 0.70 to 0.72 g/cm^3 (Table 2).

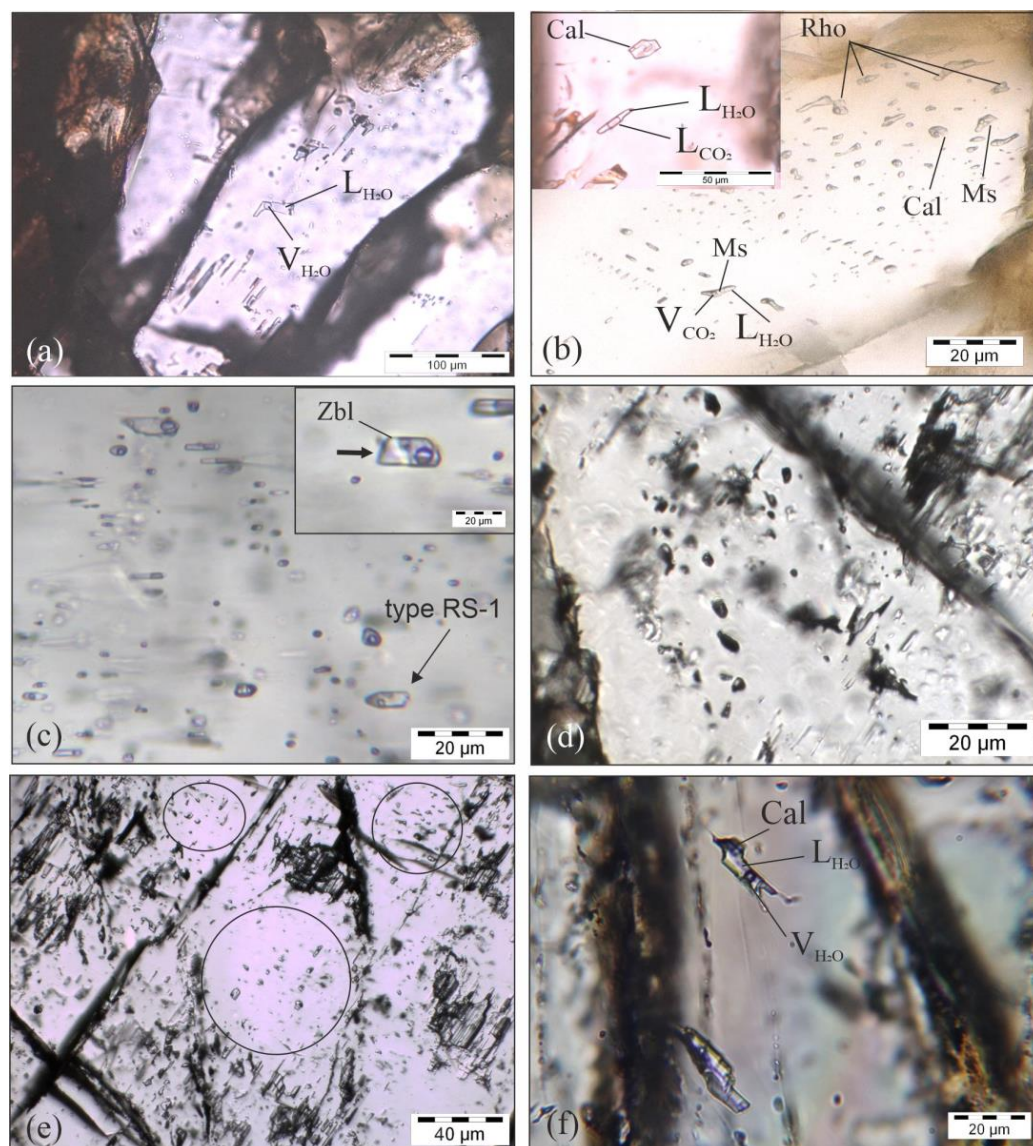


Figure 5. Fluid inclusion petrography of investigated samples of the RPF. Mineral abbreviations: Cal (calcite); Rho (rhodochrosite); Ms (muscovite); Zbl (zabuyelite). (a) Type RG-1 in garnet host of sample PE 23 and (b) type RG-2 in garnet host of sample PE 23. (c) Type-RS-1 (arrow) and type-RS-2 FIs are arranged parallel to the crystallographic cleavage. Image detail shows the shape reduction in the type RS-2 inclusion (arrow) hosting a zabuyelite solid (sample PE 10). (d) Modified dark inclusions suggest a former carbonic–aqueous fluid that underwent graphite precipitation (sample PE 25). (e) Between dark inclusion areas, 2-phase type-RT FIs occur as clusters (circles) (sample PE 25). (f) Detail of two type-RT FIs hosting calcite solids (sample PE 25).

- Fluid Inclusions in Spodumene (type RS)

Two types of FIs were distinguished in spodumene host crystals: type RS-1 of $\text{H}_2\text{O}-\text{NaCl}-\text{CaCl}_2 \pm \text{MgCl}_2$ chemistry and type RS-2 of $\text{CO}_2-\text{H}_2\text{O}-\text{NaCl}-\text{CaCl}_2 \pm \text{MgCl}_2$ chemistry. Texturally, both types occur parallel to the crystallographic cleavage and their c-axis, but are distinguished by the same arguments as shown in type-RG inclusions (Figure 5c). Both types suggest shape reductions toward negative crystals. However, only type-RS-2 FIs contain quartz, calcite, zabuyelite, and muscovite solid inclusions. They are therefore considered as being modified, which results in density and compositional changes inside the inclusions [74,75].

Microthermometry of type-RS-1 FIs shows apparent eutectic melting [$T_e(\text{ice})$] from -48.7 to -43.6 °C, which is typical for $\text{H}_2\text{O}-\text{NaCl}-\text{CaCl}_2 \pm \text{MgCl}_2$ chemistry. Hydrohalite melting [$T_m(\text{HH})$] ranging from -24.7 to -22.4 °C indicates $\text{NaCl}/(\text{CaCl}_2/\text{NaCl})$ wt. ratios around 0.8. The last melting of ice [$T_m(\text{ice})$] between -6.4 and -0.3 °C yields total salinities up to 6.5 equiv. mass%. Total homogenization to the liquid occurred between 236.0 and 356.0 °C. Because of the high range in $T_h(\text{tot})$, densities varied from 0.65 up to 0.86 g/cm³.

Type-RS-2 FIs show the last melting of carbonic ice [$T_m(\text{car})$] between -57.8 and -56.6 °C suggesting an almost pure CO_2 solution with partial homogenization to the vapor phase [$T_h(\text{car})$] from 17.0 to 25.2 °C. The aqueous component is characterized by apparent eutectic melting $T_e(\text{ice})$ from -47.5 to -45.1 °C and $T_m(\text{HH})$ from -25.2 to -21.2 °C. $T_m(\text{ice})$ ranges between -3.9 and -0.3 °C, which results in total salinities up to 6.7 equiv. mass%. $T_m(\text{Cla})$ ranges between 4.8 and 10.5 °C. Total homogenization to the liquid occurs from 297.2 to 346.0 °C and a density range between 0.70 and 0.73 g/cm³ is calculated (Table 2).

- Fluid Inclusions in Tourmaline (type RT)

Like garnet and spodumene, FIs in tourmaline can be compositionally distinguished into two different types of FIs, however they indicate both intense post-entrapment changes. Irregularly shaped FIs of a large size (up to 30 µm) suggest former inclusions of a probable aqueous–carbonic chemistry that are modified by cooling under reduced conditions along with the precipitation of graphite (Figure 5d). A second inclusion type (type RT-1) characterizes polyphase aqueous (L, V $\pm$ S) FIs of an irregular shape between 10 and 40 µm containing a vapor bubble and, in some cases, small, solid inclusions (Figure 5e,f). Liquid/vapor proportions of type RT-1 are almost constant. Solid mineral inclusions are restricted to calcite (Figure 5f).

Type-RT-1 FIs show apparent eutectic melting [$T_e(\text{ice})$] at around -46.0 °C, which indicates $\text{H}_2\text{O}-\text{NaCl}-\text{CaCl}_2 \pm \text{MgCl}_2$ fluid chemistry. Hydrohalite melting between -26.9 and -21.1 °C points to $\text{NaCl}/(\text{NaCl} + \text{CaCl}_2)$ wt. ratios in the range of 0.8 – 1.0 . $T_m(\text{ice})$ from -9.3 to -0.1 °C indicates total salinities of up to 13.2 equiv. mass%. Total homogenization to the liquid lies between 187.0 and 272.0 °C. Densities range from 0.85 to 0.97 g/cm³ (Table 2).

4.2.2. Millstatt Pegmatite Field

All FI types distinguished from the individual host minerals of the MPF characterize one fluid inclusion assemblage (FIA) of $\text{CO}_2\text{-N}_2 \pm \text{CH}_4\text{-H}_2\text{O}-\text{NaCl}-\text{CaCl}_2 \pm \text{MgCl}_2$ chemistry.

- Fluid Inclusions in Garnet (type MG)

Type-MG-1 FIs arranged as single elements or as clusters have a size ≤ 20 µm. Based on their phase presence of $L_{\text{aqu}} + L_{\text{car}} \pm S$ and $L_{\text{aqu}} + V_{\text{car}} \pm S$, they are interpreted as representing the liquid and vapor phases of an early heterogeneous fluid system that entrapped coevally into type MG-1A and type MG-1B FIs, respectively (Figure 6a,b). However, both types are trapped in different garnet samples (Table 2). In addition, type MG-1A defines FIs of various carbonic/aqueous proportions between $90/10$ and $50/50$, whereas type MG-1B characterizes almost only negative-crystal-shape inclusions by containing an evolved methane–nitrogen bubble during cooling, which homogenizes to the liquid around -95 °C (Table 2). All type-MG-1 FIs comprise solids like apatite, zircon, muscovite, calcite, rhodochrosite, quartz, and albite.

Type-MG-1 FIs always consist of $\text{CO}_2\text{-N}_2\text{-CH}_4\text{-H}_2\text{O}-\text{NaCl}-\text{CaCl}_2 \pm \text{MgCl}_2$ chemistry. The last melting of carbonic ice [$T_m(\text{car})$] occurs between -59.1 and -57.9 °C for type MG-1A and shows a large range for type-MG-1B inclusions between -98.7 and -56.7 °C. Homogenization to the liquid ranges from 5.4 to 11.0 °C (type MG-1A) and to the vapor

from 13.6 to 20.1 °C (type MG-1B). Average composition of type-MG-1A FIs comprises X_{CO_2} of 76.5 mol%, X_{N_2} of 19.7 mol%, and X_{CH_4} of 3.8 mol%, whereas type-MG-1B FIs indicate average X_{CH_4} contents around 25 mol% and around 5 mol% for X_{N_2} .

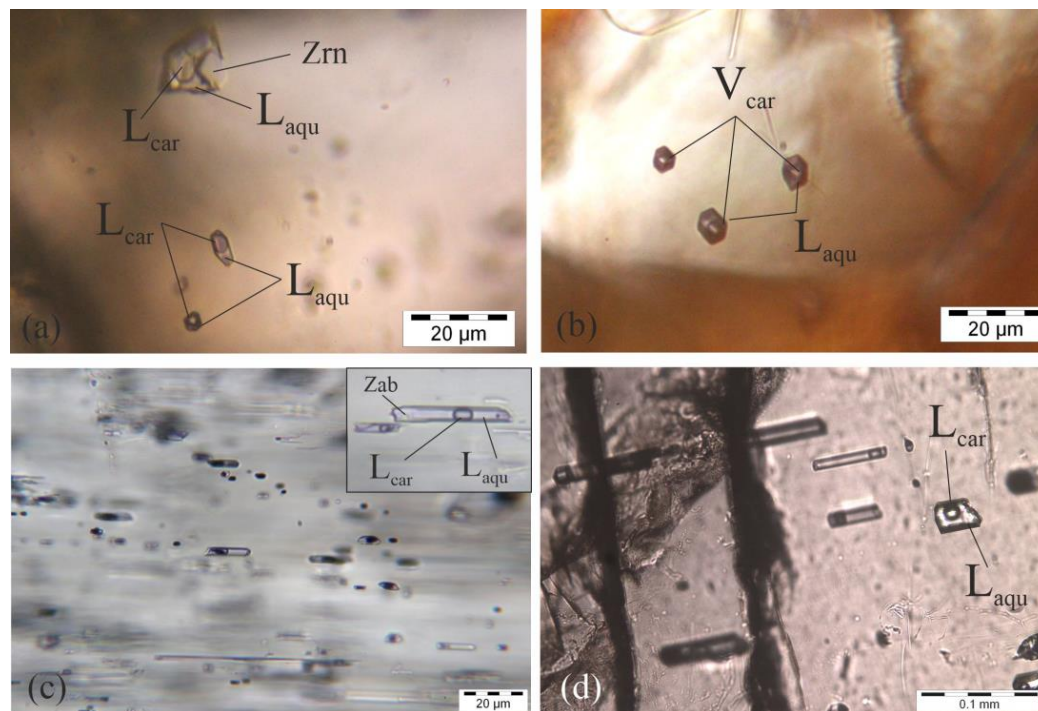


Figure 6. Fluid inclusion petrography of investigated samples of the MPF. Mineral abbreviations: Zrn (zircon); Zbl (zabuyelite). (a) Type MG-1A in garnet host of sample MC 02 and (b) type MG-1B in garnet host of sample MC 03. (c) Type MS in spodumene contains bright solids, like zabuyelite (insert), in addition to a high number of dark graphite inclusions (sample MC_See). (d) Two-phase type-MT FIs in tourmaline with a tubular shape (sample PE 57).

The aqueous component of type-MG-1 FIs is characterized by apparent eutectic melting [$T_e(\text{ice})$] between -55.4 and -46.6 °C indicating $\text{H}_2\text{O}-\text{NaCl}-\text{CaCl}_2 \pm \text{MgCl}_2$ chemistry. Hydrohalite melting [$T_m(\text{HH})$] is observed from -29.4 to -24.3 °C and the last melting of ice [$T_m(\text{ice})$] ranges between -7.2 and -3.2 °C, indicative of total salinities ranging from 5.6 to 11.1 equiv. mass% with $\text{NaCl}/\text{NaCl} + \text{CaCl}_2$ wt. ratios from 0.4 to 0.7. Clathrate melting [$T_m(\text{Cla})$] occurs between 14.7 and 21.0 °C.

Corresponding densities for type-MG-1A FIs depend on carbonic/aqueous liquid proportions ($L_{\text{car}}/L_{\text{aqu}}$) and range between 0.75 for 90/10 and 0.90 for 50/50. Type-MG-1B FIs present a narrow/close range in density from 0.70 to 0.72 g/cm³, calculated for $L_{\text{car}}/L_{\text{aqu}}$ of 40/60 (Table 2).

- Fluid Inclusions in Spodumene (type MS)

FIs in spodumene are mostly tubular (Figure 6c). They are trapped parallel to the major cleavage and consist of $\text{CO}_2\text{-N}_2\text{-H}_2\text{O}-\text{NaCl}-\text{CaCl}_2 \pm \text{MgCl}_2$ fluid chemistry. FIs show only slightly variable $L_{\text{car}}/L_{\text{aqu}}$ values between 30/70 and 40/60 and are summarized as fluid-inclusion-type MS. No methane as a fluid component is detected, however graphite is a common solid inclusion phase (Figure 6c). FIs contain additional zabuyelite, muscovite, quartz, and apatite (Figure 8c). Because of their varying phase proportions, locally reduced shape, and their solid content (i.e., zabuyelite and graphite), FIs are considered as having suffered intense post-entrapment modification processes [75].

FIs show the last melting of carbonic ice [$T_m(\text{car})$] between -58.4 and -57.2 °C, partial homogenization to the liquid from 20.7 to 22.3 °C, and to the vapor from 18.7 to

20.9 °C. The aqueous component is characterized by apparent eutectic melting from −55.2 to −53.5 °C indicating $\text{H}_2\text{O}-\text{NaCl}-\text{CaCl}_2 \pm \text{MgCl}_2$ fluid chemistry with a $T_m(\text{HH})$ range between −23.7 and −21.8 °C and $T_m(\text{ice})$ from −7.8 to −5.8 °C, reaching total salinities in the range of 9.2–11.7 equiv. mass%. Total homogenization to the liquid occurs from 306.9 to 350.9 °C. FIs have fluid densities in the range from 0.82 to 0.96 g/cm³ depending on partial homogenization to vapor and liquid, respectively. An average chemical fluid composition of X_{CO_2} of 55.0 mol% and X_{N_2} of 45 mol% was used for the calculation (Table 2).

- Fluid Inclusions in Tourmaline (type MT)

Like FIs in garnet and spodumene, FIs in tourmaline comprise $\text{CO}_2\text{-N}_2\text{-H}_2\text{O}-\text{NaCl}-\text{CaCl}_2 \pm \text{MgCl}_2$ chemistry, but without any evidence of solid inclusions (type MT). Two-phase single FIs ($L_{\text{aqu}} + L_{\text{car}}$) show rounded and tubular shapes (Figure 6d). The last melting of carbonic ice [$T_m(\text{car})$] occurs between −59.9 and −57.3 °C, indicating an additional N_2 component and, like type MS, lacks any methane composition. Partial homogenization of the carbonic bubble to the vapor ranges from 15.9 to 18.5 °C. Apparent eutectic melting [$T_e(\text{ice})$] of the aqueous liquid occurred between −51.3 and −38.0 °C, indicative of $\text{H}_2\text{O}-\text{NaCl}-\text{CaCl}_2 \pm \text{MgCl}_2$ fluid chemistry. $T_m(\text{HH})$ from −25.8 to −21.2 °C and $T_m(\text{ice})$ from −16.5 to −4.2 °C indicate the high variability of the total salinity between 10.9 and 19.2 equiv. mass% with average $\text{NaCl}/\text{NaCl}+\text{CaCl}_2$ wt. ratios of ~0.75. Clathrate melting [$T_m(\text{Cla})$] is observed from 1.8 to 7.9 °C and total homogenization [$T_h(\text{tot})$] to the liquid occurs between 275.0 and 311.5 °C. Average carbonic fluid chemistry comprises X_{CO_2} of 90 mol% and X_{N_2} of 10 mol%. Type-MT fluid densities range from 0.75 to 0.76 g/cm³ (Table 2).

4.2.3. Polinik Pegmatite Field

FIs from the PPF can be distinguished into one FIA of $\text{CO}_2\text{-N}_2\text{-CH}_4\text{-H}_2\text{O}-\text{NaCl}-\text{CaCl}_2 \pm \text{MgCl}_2$ fluid chemistry, which occurs in all studied host minerals, and into a subordinate aqueous fluid type restricted to the tourmaline host.

- Fluid Inclusion in Garnet (type PG)

Type PG-FIs in garnet have a size of $\leq 15 \mu\text{m}$ and contain up to four phases ($L_{\text{aqu}} + L_{\text{car}} \pm V_{\text{car}} \pm S$) at RT (Figure 7a,b). Solids were identified as quartz, albite, calcite, rhodochrosite, muscovite, apatite, rutile, zircon, xenotime, and graphite (Figure 8d). A representative spectrum of type-PG inclusion is presented in Figure 8e. Inclusions are arranged parallel to the grain boundaries of the garnet host and show textural coexistence with enclosed apatite solid inclusions (Figure 7a,b).

According to the lowest-measured partial homogenization temperatures, two subtypes are distinguished: type PG-1A of almost constant $L_{\text{car}}/L_{\text{aqu}}$ values around 85/15 shows partial homogenization [$T_h(\text{CH}_4 \pm \text{N}_2)$] into the liquid field between −150.0 and −127.5 °C, whereas type PG-1B with proportions of 40/60 indicates partial homogenization temperatures [$T_h(\text{CH}_4 \pm \text{N}_2)$] to the liquid between −105.6 and −83.4 °C. The last melting of carbonic ice [$T_m(\text{car})$] occurs between −62.3 and −61.1 °C for type PG-1A and between −65.7 and −56.6 °C for type PG-1B. Partial homogenization to the liquid yields a range from −52.9 to −40.4 °C for type PG-1A and from −25.7 to 24.8 °C for type PG-1B. In all FIs, high clathrate melting temperatures [$T_m(\text{Cla})$] from 17.2 to 22.4 °C support the presence of additional N_2 and CH_4 in the carbonic liquid. Calculated average fluid compositions from Raman spectra yield X_{CO_2} of 80.28 mol%, X_{N_2} of 18.59 mol%, and X_{CH_4} of 1.14 mol% for type PG-1A, and X_{CO_2} of 43.77 mol%, X_{N_2} of 21.32 mol%, and X_{CH_4} of 34.91 mol% for type PG-1B FIs. The aqueous component of both subtypes shows apparent eutectic melting of ice [$T_e(\text{ice})$] between −55.2 and −45.0 °C indicating a complex aqueous liquid of $\text{H}_2\text{O}-\text{NaCl}-\text{CaCl}_2 \pm \text{MgCl}_2$ chemistry. The last melting of hydrohalite [$T_m(\text{HH})$] and last melting

of ice [$T_m(\text{ice})$] range from -34.7 to -21.2 °C and from -9.1 to -0.2 °C, respectively. Total salinity lies between 0.4 and 13.1 equiv. mass%. Total homogenization to the aqueous liquid ranges from 178.5 to 365.7 °C. Calculated densities for type PG-1A range from 0.86 to 0.91 g/cm³ and for type PG-1B from 0.86 to 0.88 g/cm³ (Table 2).

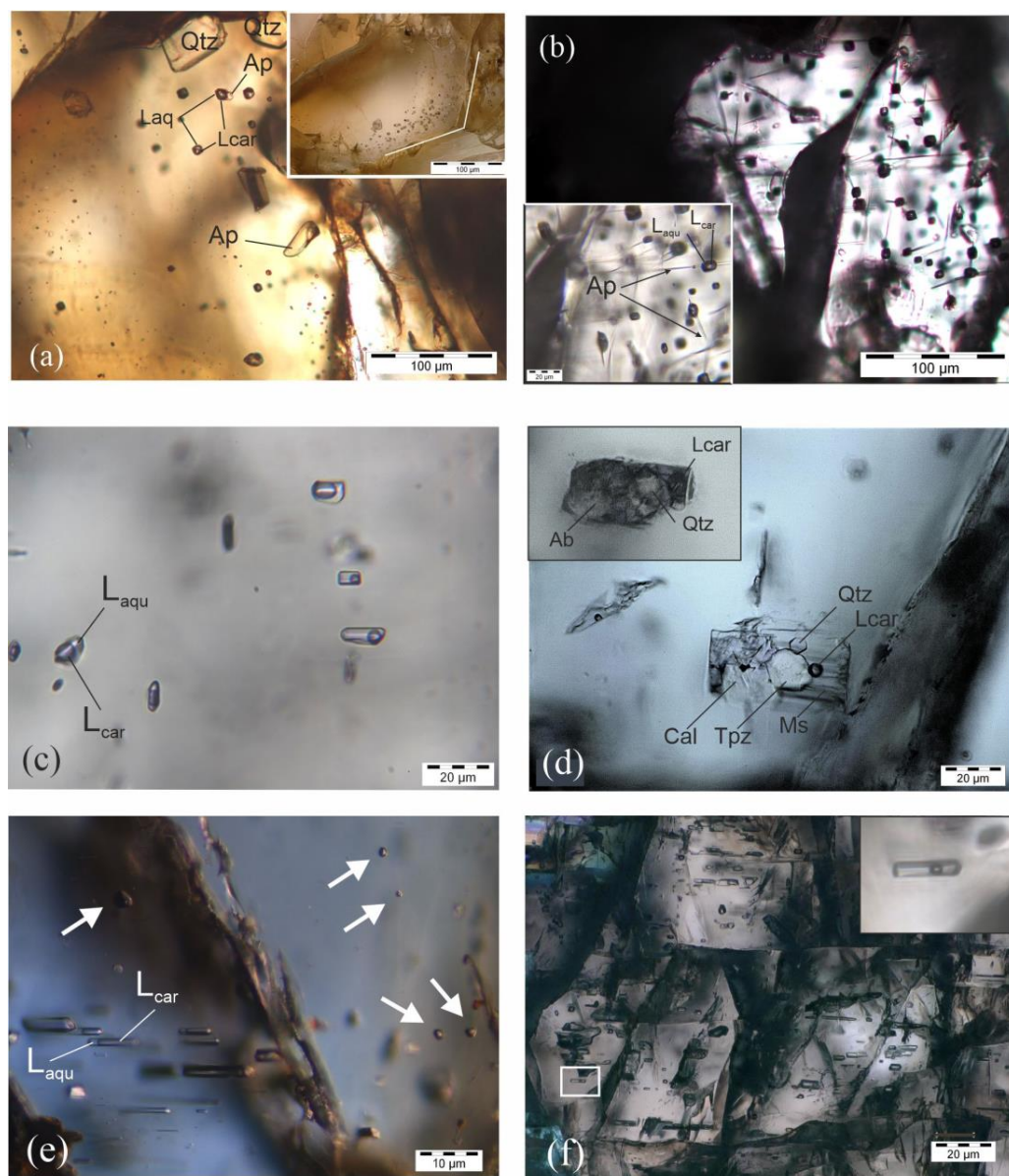


Figure 7. Fluid inclusion petrography of investigated samples of the PPF. Mineral abbreviations: Qtz (quartz); Ap (apatite); Ab (albite); Ms (muscovite); Tpz (topaz); Cal (calcite). (a) Type-PG-1A FIs in garnet close to quartz and apatite inclusions (sample PS 17). Insert suggests primary trapping characteristics. (b) Type-PG-1B FIs in garnet (sample PS 10). Insert shows a textural equivalence to apatite inclusions. (c) Two-phase solid-free type-PB inclusions of varying carb/aqu proportions in beryl host (sample PS 10). (d) Polyphase inclusions in beryl containing a high number of solids and a liquid carbonic bubble. Solids are enclosed in muscovite (center) or in albite phenocryst (insert). (e) Parallel-oriented type-PT-1 FIs of tubular (left) and rounded (right—white arrows) shapes in a tourmaline host (sample PS 21). (f) A rare aqueous type-PT-2 FI observed in tourmaline (see detail). All other FIs correspond to type PT-2 (sample PS 18).

- Fluid Inclusions in Beryl (type PB)

FIs in beryl occur as two-phase inclusions ($L_{\text{aqu}} + L_{\text{car}} \pm S$ or $L_{\text{aqu}} + V_{\text{car}} \pm S$) with a size of up to 20 μm (Figure 7c). Inclusions consist of $\text{CO}_2\text{-CH}_4\text{-N}_2\text{-H}_2\text{O-NaCl-CaCl}_2 \pm$

MgCl₂ chemistry, are arranged as single/clusters, and classified as one FIA of type-PB inclusions. Like FIs in a garnet host, they show an extended range in $L_{\text{car}}/L_{\text{aqu}}$ from 50/50 to 80/20. Solids occur in a subsidiary manner and are characterized as quartz, albite, calcite, muscovite, and topaz. Besides type-PB FIs, large-scale polyphase (melt?) inclusions occur, which comprise comparable solids together with a small vapor bubble (L_{car}) (Figure 7d). A representative spectrum of gaseous phases in type-PB inclusions is presented in Figure 8f. All solids are identified by Raman spectrometry (Figure 8g,h).

Microthermometry of type-PB FIs shows the last melting of carbonic liquid [$T_{\text{m}}(\text{car})$] between -66.4 and -57.7 °C indicative of additional N₂ and CH₄ components. During cooling, a vapor bubble appears, which homogenizes to the liquid between 9.1 and 10.8 °C and to the vapor between 9.0 and 15.8 °C. The apparent eutectic melting of the aqueous phase was in the range from -52.3 to -49.6 °C. $T_{\text{m}}(\text{HH})$ between -24.9 and -21.2 °C and $T_{\text{m}}(\text{ice})$ from -4.7 to -2.0 °C are indicative of a low-saline aqueous fluid from about 3.4 to 7.8 total equiv. mass% indicative of NaCl/(NaCl + CaCl₂) ratios between 0.7 and 1.0. Clathrate melting [$T_{\text{m}}(\text{Cla})$] occurs from 12.4 to 15.9 °C and total homogenization [$T_{\text{h}}(\text{tot})$] to the liquid lies between 302.3 and 390.5 °C. The average fluid composition calculated from Raman spectra is about 58.7 mol% X_{CO₂}, 13.9 mol% X_{N₂}, and 27.4 mol% X_{CH₄}. For the FIs that homogenize into the liquid field, the calculated densities range from 0.78 to 0.91 g/cm³ by using $L_{\text{car}}/L_{\text{aqu}}$ values of 30/70, and densities ranging from 0.33 to 0.65 g/cm³ are calculated using 80/20 (Table 2).

- Fluid Inclusions in Tourmaline (type PT)

FIs in tourmaline consist of CO₂-CH₄ ± N₂-H₂O-NaCl-CaCl₂ ± MgCl₂ and H₂O-NaCl-CaCl₂ ± MgCl₂ fluid chemistries, defining type PT-1 and type PT-2, respectively. According to the arguments presented for FIs from RPF, both FI types have not coexisted at chemical equilibrium. Type PT-1 characterizes rounded and tube-shape inclusions of variable size ranging from <5 µm up to 50 µm by containing up to three phases (L_{aqu} + L_{car} ± S) (Figure 7e). Solids inside the FIs are restricted to quartz. However, nearby investigated FIs, muscovite–calcite–quartz aggregates are frequent. Like FIs in beryl, $L_{\text{car}}/L_{\text{aqu}}$ values show a large range ranging from 90/10 to 20/80 with an average value of 80/20. Subordinately occurring two-phase (L_{aqu} + V_{aqu}) type-PT-2 FIs show a constant degree of fill of about 0.85 (insert in Figure 7f).

Observations of phase transitions during microthermometry show the development of a CH₄ ± N₂ gas bubble by cooling down from -140 °C to -190 °C. During heating, the last melting of carbonic ice [$T_{\text{m}}(\text{CH}_4 \pm \text{N}_2)$] occurs between -130.0 and -73.6 °C accompanied by the homogenization of the gas bubble between -127 and -85.5 °C [$T_{\text{h}}(\text{CH}_4 \pm \text{N}_2)$]. Partial homogenization [$T_{\text{h}}(\text{car})$] of the carbonic vapor bubble to the liquid occurs between -20.0 and 12.5 °C and to the vapor between -40.1 and 5.3 °C (Table 2). The surrounding aqueous phase shows apparent eutectic melting $T_{\text{e}}(\text{ice})$ from -59.0 to -30.0 °C. The last melting of ice is observed from -9.1 to -6.0 °C, resulting in total salinities between 4.5 and 17.8 equiv. mass%. $T_{\text{m}}(\text{Cla})$ ranges between 15.0 and 21.0 °C. Besides the presence of inclusions consisting of pure CH₄ as well as pure CO₂ bubbles surrounded by an aqueous fluid, type PT-1 holds average compositions of 60 mol% X_{CO₂}, 20 mol% X_{N₂}, and 20 mol% X_{CH₄}. Total homogenization [$T_{\text{h}}(\text{tot})$] to the liquid lies between 187.0 and 309.0 °C. Highest densities for $L_{\text{car}}/L_{\text{aqu}}$ values of 80/20 yield 0.68–0.73 g/cm³.

Type-PT-2 FIs show $T_{\text{e}}(\text{ice})$ ranging from -59.0 to -46.0 °C and indicate H₂O-NaCl-CaCl₂ ± MgCl₂ fluid chemistry. The last melting of hydrohalite [$T_{\text{m}}(\text{HH})$] ranges from -25.1 to -21.4 °C; $T_{\text{m}}(\text{ice})$ around -8.5 indicates salinities of 12.2 equiv. mass% (Table 2). Total homogenization [$T_{\text{h}}(\text{tot})$] to the liquid between 157.0 and 188.0 °C results in densities ranging from 0.97 to 0.99 g/cm³, respectively.

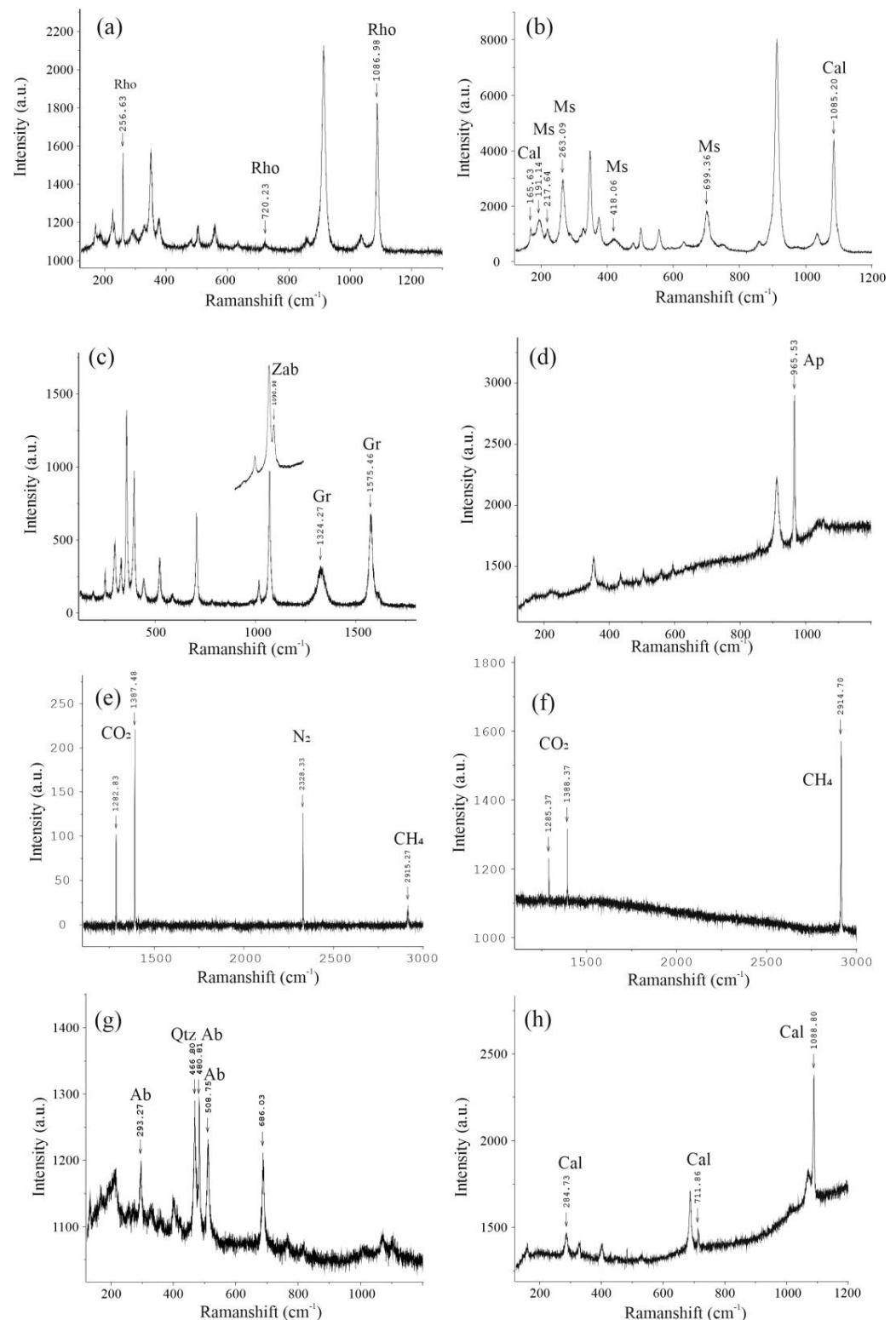


Figure 8. Representative Raman spectra of selected FIs containing solid mineral phases. Non-marked peaks are related to the host. (a) Rhodochrosite (Rho) solid in the garnet host (RPF; sample PE 05); (b) calcite (Cal) and muscovite (Ms) in the garnet host (RPF; sample PE 23); (c) graphite (Gr) and zabuyelite (Zab) in the spodumene host (sample MC_See); (d) apatite (Ap) in the garnet host (sample PS 17); (e) representative CO₂-N₂-CH₄-bearing fluid inclusion in garnet from sample PS 19; (f) representative CO₂-CH₄-bearing fluid inclusion in beryl from sample PS 10; (g) quartz (Qtz) and albite (Ab) in polyphase inclusions in the beryl host (sample PS 10); (h) calcite (Cal) in polyphase inclusions in the beryl host (sample PS 10).

5. Discussion

5.1. Compositional Variations

Chemical compositions of investigated FIs from each pegmatite field were compared, discussed, and supplemented to the results from the Koralpe Pegmatite Field (KPF) after Krenn et al. [6] and Husar and Krenn [4] (for the location area of the KPF, see Figure 1).

5.1.1. The Aqueous System

Accessory minerals of the RPF host FIs with aqueous chemistry as well as FIs with aqueous–carbonic chemistry. Considering arguments for fluid inclusion assemblages and their corresponding fluid phase equilibria, a coexistence between both types has to be excluded. Apart from rarely preserved aqueous FIs in tourmaline from the PPF, accessories of the MPF and PPF host a comparable FIA consisting of aqueous–carbonic chemistry. This is based on apparent eutectic melting $T_e(\text{ice})$ in all the investigated FIs and approximates a H_2O – NaCl – $\text{CaCl}_2 \pm \text{MgCl}_2$ system. It represents the dominant aqueous system from all the investigated pegmatite fields. Average salinities range below 13.6 equiv. mass% (Table 2). However, some peaks in total salinity up to 19 equiv. mass% exist.

In the RPF, FIs cluster in salinities of up to 10.9 equiv. mass% at $T_h(\text{tot})$ between 230 and 360 °C (Figure 9a). Highest salinities of up to 13.2 equiv. mass%, tend to lowest $T_h(\text{tot})$ below 200 °C, estimated from a group of type-RT-FIs in tourmaline, which are indicative of increased densities and salinities. Average $\text{NaCl}/(\text{NaCl} + \text{CaCl}_2)$ weight ratios cluster around 0.7 (Figure 9a).

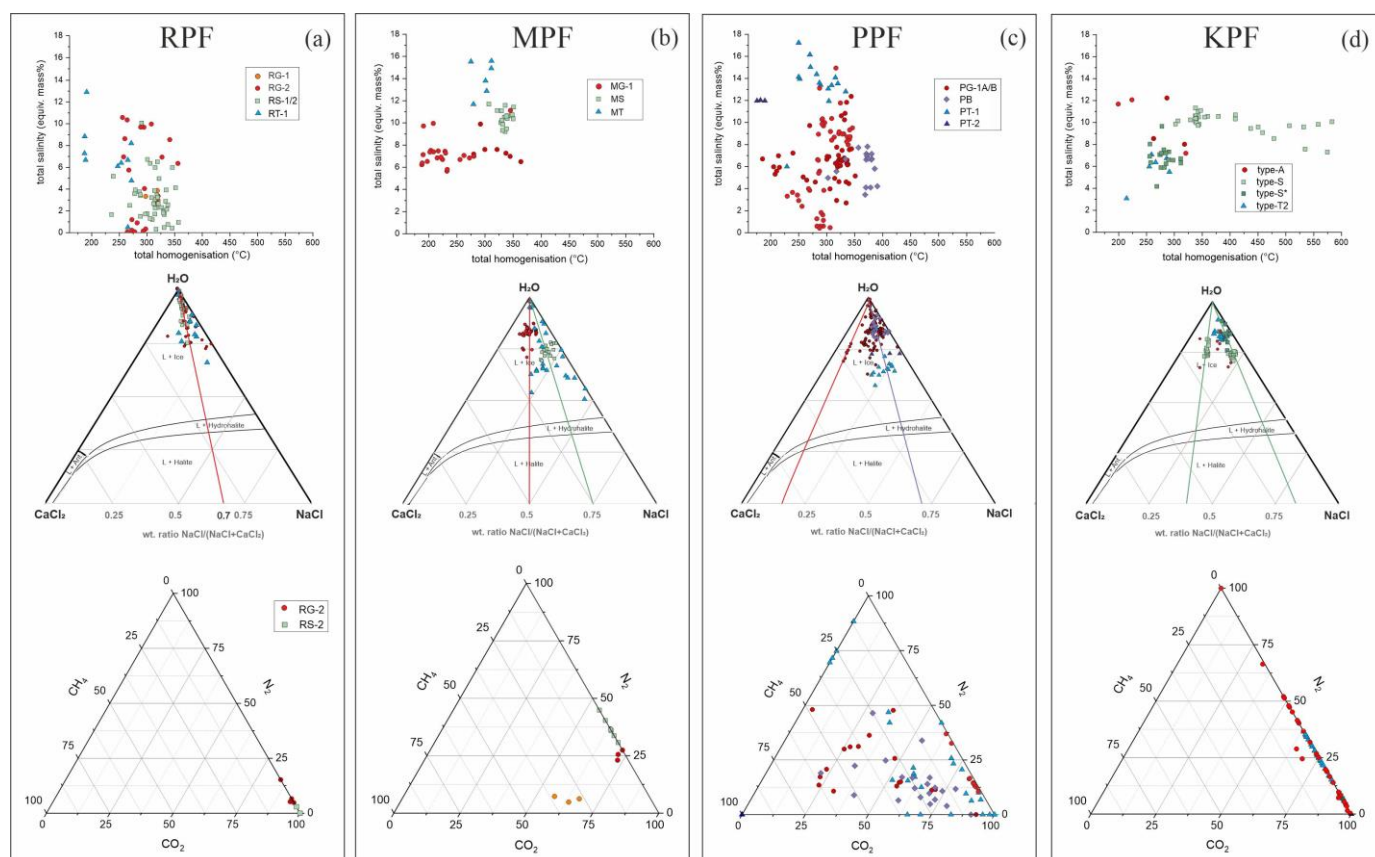


Figure 9. Fluid composition of selected FIs from the investigated pegmatite fields: RPF (a), MPF (b), PPF (c), and KPF (d). Data for KPF are taken from Krenn et al. [6]. Fluid composition is plotted as total salinity (equiv. mass%) versus total homogenization [$T_h(\text{tot})$] in °C (first row); ternary H_2O – NaCl – CaCl_2 diagram after Crawford [76] (second row); and ternary CO_2 – N_2 – CH_4 diagram (third row).

In the MPF, type-MG-1 FIs in garnet show a range in $T_h(\text{tot})$ from ≤ 200 up to ~ 370 °C at almost constant salinities between 6 and 11 equiv. mass%, whereas type-MS- and -MT-FIs tend toward increased salinities from 9 to <16 equiv. mass%, respectively (Figure 9b). This goes along with an increase in average wt. ratios of $\text{NaCl}/(\text{NaCl} + \text{CaCl}_2)$ from ~ 0.5 for garnet-hosted FIs to 0.75 for spodumene and tourmaline-hosted FIs (Figure 9b). Hence, higher saline FIs in tourmaline contain in part a dominant NaCl end-member chemistry.

In the PPF, high salinity variations from <1 up to <18 equiv. mass% at $T_h(\text{tot})$ of <200 and <400 °C are calculated (Figure 9c). FIs from the beryl host (type PB) provide the highest $T_h(\text{tot})$ values at salinities below 8 equiv. mass%, whereas FIs from the garnet host show no trend in salinities versus $T_h(\text{tot})$. This goes along with large variations in wt. ratios of $\text{NaCl}/(\text{NaCl} + \text{CaCl}_2)$ from 0.15 up to 1.0. Beryl and tourmaline reflect an average value between 0.7 and 0.75. Like FIs from tourmaline from the MPF, type PT-1 tends toward the highest salinities and differs clearly from type PB. Type PT-2 contains FIs of the highest densities (lowest $T_h(\text{tot})$ values), and salinities are around 12 equiv. mass% (Figure 9c).

For comparison, rare aqueous FIs from the Koralpe Pegmatite Field (KPF) trapped in garnet (type-A) show salinities up to 12 equiv. mass%, which are higher compared to FIs trapped in tourmaline up to 7 equiv. mass% (type T2) at almost comparable $T_h(\text{tot})$ values (Figure 9d). FIs in spodumene show a trend from higher salinities/lower densities (i.e., higher $T_h(\text{tot})$: type S) toward lower salinities/higher densities (i.e., lower $T_h(\text{tot})$: type S*) (Figure 9d). This trend goes along with $\text{NaCl}/(\text{NaCl} + \text{CaCl}_2)$ wt. ratios from 0.4 (type S) up to 1.0 (type S*). Data originate from two different spodumene-bearing localities at the KPF (Brandrücken: type S and Klementkogel: type S*). FI data are taken from Krenn et al. [6].

5.1.2. The Carbonic System

$\text{CO}_2\text{-N}_2\text{-CH}_4$ compositions of the investigated FIs differ strongly. Almost pure CO_2 with only minor N_2 is obtained from FIs of the RPF, whereas FIs of the KPF comprise CO_2 -FIs of various nitrogen compositions up to nearly pure N_2 -FIs (lower diagrams in Figure 9a,d). In the MPF and especially in the PPF, investigated FIs show high variations in additional CH_4 compositions independent of the accessory host mineral garnet, beryl, or tourmaline (Figure 9b,c). Therefore, a compositionally driven fluid flow within the early Permian crust suggests a trend in the carbonic–nitrogen–methane fluid composition during anatexis from the eastern to the western pegmatite field areas:

CO_2 (RPF) $\rightarrow$ $\text{CO}_2 \pm \text{N}_2$ (KPF) $\rightarrow$ $\text{CO}_2\text{-N}_2 \pm \text{CH}_4$ (MPF) $\rightarrow$ $\text{CO}_2\text{-N}_2\text{-CH}_4$ (PPF) $\rightarrow$ $\text{CO}_2\text{-N}_2\text{-CH}_4$ (TPF)

Studies after Krenn et al. [7] on Permian pegmatite accessories west of the Tauern Window (Texel Pegmatite Field: TPF in Figure 1a) support this trend. Higher variations in N_2/CH_4 compositions from the east to the west may be an effect of host rock composition during the anatexis of a Variscan metamorphosed basement or of a sediment stack located in post-Variscan basins. The methane and nitrogen fluid components can be interpreted as having formed in equilibrium with graphite and NH_4 -bearing micas and feldspars originating from sedimentary host rocks [77–81]. Accordingly, mica $\pm$ feldspar from metapelites as a potential source of nitrogen for N_2 -rich fluids with variable $\text{CO}_2\text{-CH}_4$ chemistries have been proven to exist and are proposed for Permian pegmatite accessories beryl and cassiterite of the TPF [7]. Mineral permeability to H_2 causes a change in hydrogen fugacity in the surrounding rocks, and CO_2 in the inclusion may react with H_2 to form methane and carbon. This would modify the CO_2/CH_4 ratios and estimated fluid densities of the investigated inclusions. Additionally, for a carbon-saturated buffered fluid, the maximum stability of graphite is restricted to temperatures ≤ 570 °C at 3 kbar [82]. At higher temperatures, CO_2 is the dominant fluid and an increase in XCO_2 goes along with

the expense of XCH_4 and water. Hence, during melting along with temperature and f_{O_2} increase, CO_2 remained as a rather immobile component in the fluid.

Furthermore, FIs from inner to outer garnet core areas reflect a general increase in nitrogen values. This increasing trend is independent of XMn zoning patterns and may be linked to a decrease in methane, realized in types PG-1A, MG-1A, and MG-1B. It is therefore argued that increasing N_2 contents from inner to outer garnet cores support a nitrogen-generated anatectic source via the progressive melting of NH_4 -bearing minerals ($\text{mica} \pm \text{feldspar}$) from the surrounding metapelitic host rocks.

5.2. P-T Conditions During Fluid Trapping and Host Mineral Crystallization

In order to determine crystallization conditions for the studied pegmatite host accessories garnet, tourmaline, spodumene, and beryl, the density isochores of selected FIs comprising high densities (i.e., homogenization to the liquid phase) were calculated (Figure 10).

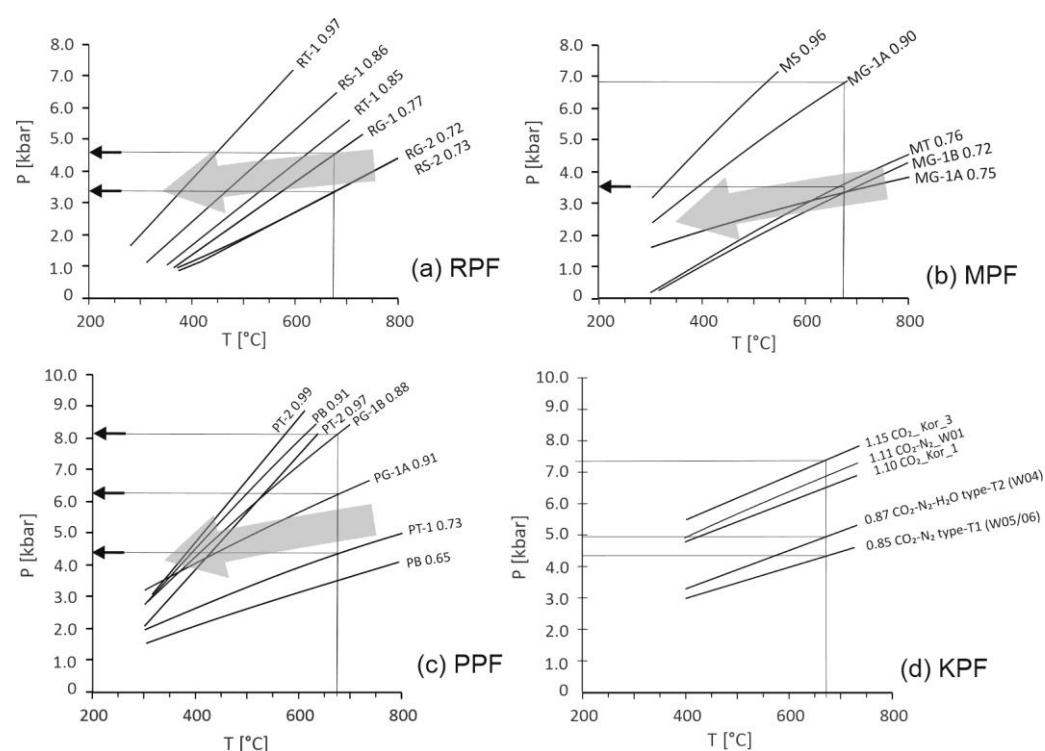


Figure 10. Calculated isochores of investigated FIs for the RPF (a); the MPF (b); the PPF (c); and the KPF (d). Data for (d) after Krenn et al. [6] and Husar and Krenn [4].

FIs in garnet and spodumene crystals contain a high number of solids. Solid inclusions in tourmaline are limited to calcite in type RT-1 and quartz in type PT-1. The nature of the solids (i.e., daughter minerals versus accidentally trapping or in situ reaction products between the fluid and the host mineral) excludes accidental trapping as the only explanation for their presence. This applies in particular to rhodochrosite in garnet and zabuyelite in spodumene, which may have evolved by in situ mineral–fluid reactions. Therefore, corresponding isochores from FIs in spodumene from the investigated areas were taken with caution due to inclusion changes in volume, shape, and composition. This would characterize FIs in spodumene as neither isochoric nor isoplethic systems (c.f. Anderson [74,75] for spodumene inclusions). Considering also processes like H_2O -leakage during recrystallization or leakage along crystal cleavage planes (e.g., Bakker and Jansen [83]), changes in density, and the fluid chemistry of the investigated FIs may have occurred, and the calculated conditions would rather present minimum estimates or re-equilibrium.

Additionally, the mechanical relaxation of the pressure difference in the inclusion and host rock minerals influences the residual fluid density. For example, garnet as the most mechanically strong mineral would be capable of maintaining excess pressure achieved through the exchange of H_2 and water with the external fluid [84,85].

Thermodynamic modeling of representative mineral assemblages proposes that the anatexis of Li-rich metapelites takes place at conditions of 675 °C and 6.45 kbar by forming melts responsible for migmatite and simple pegmatite formation (Knoll et al. [3,20] and references therein). The remaining melt enriched in its Li content enables a more fractionated stage of spodumene pegmatite formation. Accordingly, temperatures near 700 °C (690–695 °C) are close to muscovite dehydration melting and melt segregation in metapelites. The resulting pressures are always interpreted as minimum estimates.

5.2.1. Radegund Pegmatite Field

Types RG-1 (aqueous) and RG-2 (carbonic–aqueous) inclusions in garnet contain, among other solids, rhodochrosite, which suggests a modified character (Figure 5a,b). Calculated isochores with the highest fluid densities between 0.77 (type RG-1) and 0.72 g/cm³ (type RG-2) crossed at minimum temperatures of 675 °C indicate pressures of >4.5 and >3.0 kbar for garnet crystallization, respectively (Figure 10a). Because both types are not co-evally trapped, aqueous FIs are considered as resulting from a separate fluid flow, probably from an earlier stage followed by post-entrapment modification (see Figure 5e,f). Accordingly, high-dense FIs of type RT-1 as well as type RG-1 experienced modification below 675 °C and 3–4 kbar. This would also correspond to type RS-1 (density of 0.86 g/cm³). However, type RS-2 in spodumene, containing zabuyelite solids as possible solubility effects inside the inclusions, is considered with caution.

5.2.2. Millstatt Pegmatite Field

High-dense FIs in garnet show a wide range in carbonic/aqueous composition ranging from 90/10 to 50/50 for subtype MG-1A and about 40/60 for subtype MG-1B (Table 2). In general, isochore gradients steepen by increasing the aqueous fluid proportion within the inclusion. Therefore, carb/aqu proportions of 90/10 result in a “flat” carbon-dominated isochore of 0.75 g/cm³, while 50/50 proportions result in a steeper isochore of 0.90 g/cm³ (Figure 10b). Subtype MG-1B with constant proportions of 40/60 provides densities ranging from 0.70 to 0.72 g/cm³. Isochores indicate a pressure range from ca. 3.5 to >6.5 kbar at 650 °C. The frequent presence of solids, e.g., rhodochrosite, as well as some solubility effects, like negative inclusion shapes, may create those large pressure gaps. Calculated FIs from tourmaline (type MT), showing densities of 0.76 g/cm³ (carb/aqu proportions of 40/60), would support minimum pressure estimates of >3.5 kbar (Figure 10b). The highest densities up to 0.96 g/cm³ from FIs in spodumene (type MS) are linked with post-entrapment modification processes inside the inclusions and are therefore not representative of host mineral formation.

5.2.3. Polinik Pegmatite Field

Similar to the MPF, isochore gradients depend strongly on carbonic/aqueous proportions and FIs in garnet are calculated with carb/aqu proportions of 85/15 for PG-1A and 40/60 for PG-1B FIs. They reach fluid densities ranging from 0.88 g/cm³ (type PG-1B) to 0.91 g/cm³ (type PG-1A). The resulting pressure gap between >6 up to 8 kbar is comparable to type-MG FIs of the MPF, however in higher pressure conditions (Figure 10c). Type-PT-1 FIs with high variable carb/aqu proportions would also create a large pressure range. FIs of 80/20 proportions reach densities up to 0.73 g/cm³, which is indicative of pressure conditions around 4.5 kbar at 675 °C (Figure 10c). Steep isochores with the highest densities

in the range of 0.97–0.99 g/cm³ calculated from aqueous inclusions in tourmaline (type PT-2) are considered as the result of a separate fluid flow.

FIs from beryl (type PB) show variable carbonic/aqueous proportions ranging from 80/20 to 30/70 as well. Their corresponding density range from 0.65 to 0.91 g/cm³ would open a large pressure gap between 3 up to >8 kbar at 675 °C.

By comparing these data, it can be concluded that (1) FIs from garnet from the RPF reflect minimum pressures of 4.5 kbar, when assuming a temperature of 675 °C during host mineral crystallization. (2) Isochore gradients from FIs from the MPF/PPF depend strongly on the observed carbonic/aqueous proportions. (3) A trend to higher pressures of >4 kbar at 675 °C seems to be the most realistic approach for carbonic–aqueous inclusion entrapment within the MPF and PPF. (4) Isochores of aqueous FIs predominantly present in the RPF, but also in the PPF (tourmaline), suggest an early fluid pulse that underwent re-equilibration during possible isobaric cooling.

5.3. Do the Calculated Pressures from Isochores Reflect Host Mineral Crystallization?—A Heterogeneously Trapped Variable X_{CO2}-Rich Fluid in the MPF and PPF

Carbonic–aqueous fluids define a large range of immiscibility under high-grade metamorphic conditions for a wide range of compositions [55,86,87]. The solvus of the H₂O–CO₂–N₂–CH₄–NaCl(–MgCl₂–CaCl₂) fluid system at increased *PT* conditions could explain the simultaneous entrapment of two fluid systems comprising dominant CO₂–N₂–CH₄ and dominant H₂O chemistry. However, aside from aqueous FIs in the investigated host minerals of the RPF and rarely in the PPF (type PT-2), the dominant fluid inclusion assemblage is characterized as a carbonic–aqueous fluid with variable X_{CO2} composition. The high variations in carbonic/aqueous proportions result in high variations in isochoric gradients with the tendency to steepen with increasing X_{H2O}. This forms significant pressure uncertainties when crossing isochores at distinct temperatures so that pressures presented in chapter 5.2. can only be considered as rough estimates. The variable X_{CO2} proportions observed in the FIs of the investigated garnet, tourmaline, and beryl samples are interpreted as a mechanical mixture of both components caused by compositional changes along the solvus curve, typical for a hydrothermal vein environment (c.f. Diamond [87]). The dominant presence of inclusions of variable composition in all host minerals excludes the possibility that they were all caused by post-entrapment changes. Hence, the observed fluid inclusion assemblage, characterizing FIs of H₂O–CO₂–N₂–CH₄–NaCl–CaCl₂ ± MgCl₂ fluid chemistry, is entrapped heterogeneously and defines a highly varying carbonic–aqueous fluid that originates from the pegmatite parent melt, generated by crustal anatexis during the Permian metamorphic cycle. According to Diamond [85], this fluid should have been preceded by an earlier phase of homogeneous entrapment from two possible different fluid sources. Candidates for this early stage are the well-preserved high-dense clusters of CO₂–N₂ ± CH₄-rich FIs in magmatic garnet from the KPF described in Husar and Krenn [4]. These garnets originated from low-fractionated melts at lower-to-medium crustal levels between 20 and 25 km depth (>7 kbar; Figure 10d). Studies by Knoll et al. [20] show that relatively deep crustal levels comprise migmatite formation and less fractionated pegmatite melts that include magmatic garnets. Early conditions for garnet crystallization in the range of 6–7 kbar after Husar and Krenn [4] may be in line with the early migmatite stage, where staurolite breakdown was followed by muscovite dehydration melting at temperatures > 675 °C. Accordingly, melt calculations after Knoll et al. [20] reached up to 25 vol% melt escape/extraction during anatexis and would be a likely source of this CO₂–N₂ ± CH₄-rich fluid (type A in Figure 11a). Continuous breakdown reactions of alumina-rich phases (i.e., staurolite) and muscovite released H₂O and induced peritectic mineral-phase crystallization, like garnet, biotite, sillimanite, and alkali feldspar [20]. The continuous release of water by reaction staurolite + muscovite = sillimanite + biotite + H₂O triggered anatexis

wall rock reactions and can be associated with the entrapment of a separate aqueous fluid phase that is predominantly preserved in accessories of the RPF (types RG-1; RS-1; and RT), but also rarely as type PT-2 in tourmaline from the PPF (type B in Figure 11a). Given the temperature-dependent garnet zonation, exhibiting “inverse bell-shaped”, unzoned, and “bell-shaped” profiles, as well as Fe/Mg compositional melt fractionation trends during garnet crystallization (see Figure 3), garnet growth occurred not at a distinct crustal level, but continuously during the buoyant uprise of a crystallizing peraluminous melt derived from the host/surrounding metasediments. Carbonic–aqueous FIs trapped predominantly along outer garnet cores (i.e., they only rarely occur in innermost core areas; see Figure 4 for FI locations), which suggests the fluid entrapment of mixed heterogeneous fluid C from a more fractionated melting stage (type C in Figure 11a). This post-dates earlier garnet-core crystallization stages associated with the trapping of $\text{CO}_2\text{-N}_2 \pm \text{CH}_4$ -rich FIs, so far only preserved in the magmatic garnet cores of the KPF [6]. In these core domains, the presence of additional aqueous FIs is linked with initial garnet growth stages (stage 1 in Krenn et al. [6]).

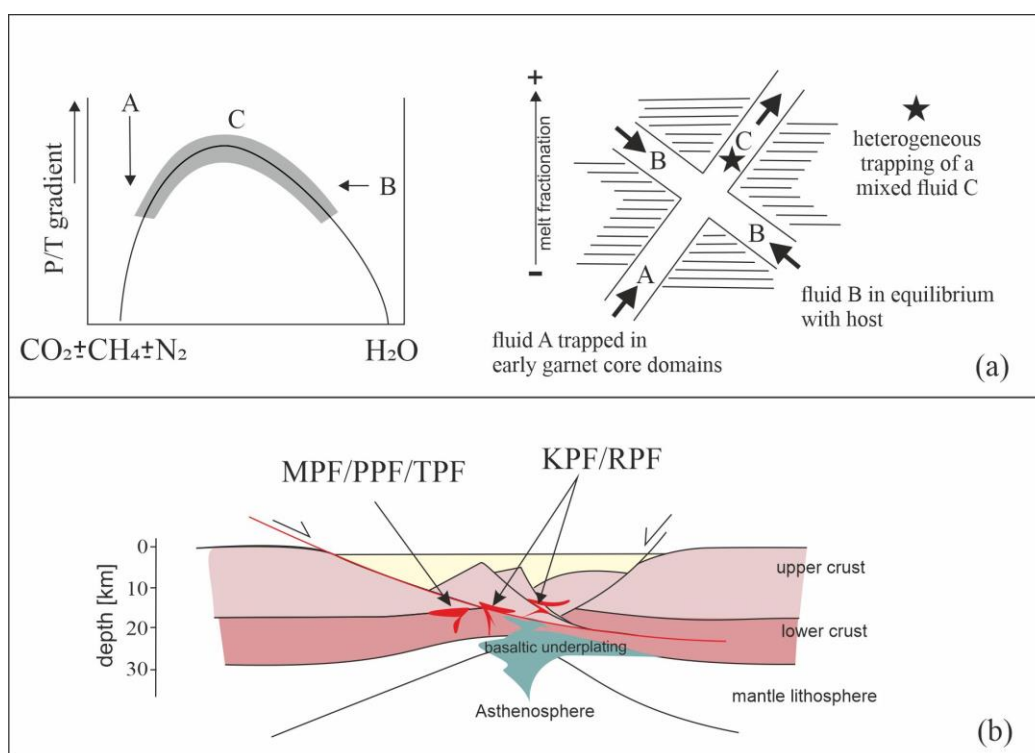


Figure 11. (a) Mixing of $\text{CO}_2 \pm \text{CH}_4 \pm \text{N}_2\text{-H}_2\text{O}$ fluids in a hydrothermal vein environment. Left: Schematic solvus diagram shows the mechanical mixing of two different fluid sources (A and B), which results in the entrapment of fluid inclusions containing fluid C with variable $X_{\text{CO}_2}/X_{\text{H}_2\text{O}}$ proportions. Besides C, separate fluids A and B are partly preserved as FIs in the early growth stages of garnet and tourmaline. Right: Fluid pathway along cracks of partially molten metapelites. (b) Permian rifting stage: a halfgraben, filled by post-Variscan sediments, evolved during asthenosphere upwelling and extensional tectonics. Fluid-rich melt associated with early pegmatite formation migrating upward particularly along faults. Possible locations of pegmatite fields at fluid-related faults (KPF/RPF) and nearby (MPF/PPF/TPF) are indicated. Red (SiO_2 -rich pegmatitic melt); green (SiO_2 -poor basaltic melt).

The more “exotic” accessory phases of beryl and spodumene formed during an evolved pegmatite stage accompanied by a remaining highly evolved Li-rich melt [20]. The presence of inclusion phases in beryl like quartz, muscovite, topaz, calcite, albite, and a liquid carbonic bubble (Figure 7c,d) supports a $\text{CO}_2\text{-H}_2\text{O}$ -rich peraluminous silicate-rich

melt. The occurrence of an H₂O–CO₂-rich fluid in all studied spodumene and beryl accessories limits the lower range for heterogeneous fluid entrapment of the carbonic/aqueous FIs in these more evolved pegmatite formation stages. However, sample PS10 shows that there is evidence for the possible coeval growth of beryl with late-stage small garnets by containing FIs of similar chemistry and N₂ content. Relevant conditions for this stage of crystallization have been calculated from a comparable fluid, the high-dense type-T2 FIs of H₂O–CO₂ chemistry in tourmaline from the KPF in the range of 4–5 kbar at <650 °C (stage 2 in Krenn et al. [6]) before albite–spodumene pegmatite crystallization, which requires a melt fractionation degree of up to 80% [20].

According to the model by Knoll et al. [20] for the Permian period, crustal collapse and mantle exhumation force the buoyant uprise of the fractionated melt that penetrates along large-scale cracks and faults within a deep-seated asymmetric graben structure (Figure 11b). The lowest *PT* conditions for pegmatite crystallization are related to the upper part of the Permian middle crust with greenschist facies imprints and are characterized by the occurrence of magmatic garnet and andalusite. A higher level of metamorphism of amphibolite facies is argued by the occurrence of andalusite after the breakdown of Variscan or Permian staurolite, as is indicative for the lower part of the Permian middle crust [23]. Deep crustal levels are proposed for areas where local anatexis at upper amphibolite/granulite facies conditions take place, e.g., at the KPF, where magmatic garnets host an early unmixed H₂O–CO₂–N₂-rich fluid [4]. Aside from the deep-stage crustal distributions of pegmatites within the Austroalpine basement units, it remains open, if the pegmatitic melts intruded in (1) a Variscan metamorphosed basement, or within (2) the sedimentary nappe stack deposited within deep graben structures. Because of the preservation of early aqueous FIs in the RPF and KPF, fluid mobility along faults related to basin tectonics can also indicate their crustal locations during anatexis (Figure 11b).

6. Summary and Conclusions

Fluid inclusion investigations in pegmatite accessories from three investigated pegmatite field areas supplemented by the results from pegmatite fields at the Koralpe (KPF) and at the Texel Mountains (TPF), provide further evidence for a common fluid evolution process of the Austroalpine basement during the Permian period. All pegmatite fields point to a complex H₂O–CO₂–N₂–CH₄–NaCl–CaCl₂-rich fluid system that operated during two major pegmatitic melt crystallization stages.

Stage 1: The simultaneous presence of two cogenetic immiscible assemblages—a CO₂ ± N₂ ± CH₄-rich fluid and a separate aqueous fluid. Both fluids coexisted during the earliest garnet core crystallization stages associated with peritectic mineral reactions under muscovite dehydration melting at temperatures > 670 °C from 6 to 8 kbar. Considering garnet major element profiles and garnet SiO₂ content, temperatures should be limited between 670 and 700 °C (after Dahlquist et al. [9]).

Stage 2: Subsequent garnet growth under a buoyant uprise of a fractionating melt is associated with continuous accessory mineral growth and heterogeneous trapping of a mechanically mixed CO₂–H₂O-rich fluid of variable X_{CO₂}/X_{H₂O} proportions. Besides late-stage garnet growth, this fluid system dominates inclusions in tourmaline, beryl, and spodumene that are considered host minerals that grew during the progressive fractional crystallization of the remaining Li-rich pegmatoid melt. Conditions for this proposed hydrothermal pegmatite vein-related process, typical for a region of fluid mixing within contact aureole zones (e.g., Ferry [88]), are linked with crystallization stages at temperatures ≤670 °C and pressures in the range of 4–5 kbar.

The X_{CO₂} composition of the heterogeneous fluid shows a trend that varies from pure CO₂ toward CO₂–N₂ up to CO₂–N₂–CH₄ from pegmatite fields in the eastern to the western

areas of the Austroalpine basement units. This may be due to possible sedimentary host rock differences during crustal anatexis controlled by the progressive melting of NH_4 -bearing minerals mica and feldspar. Fluid inclusion preservation of the earliest high-dense CO_2 - N_2 FIs and coevally trapped aqueous FIs is restricted to the eastern pegmatite fields KPF and RPF (only aqueous) that may indicate the anatexis of metapelites near possible fault zones of increased fluid mobility. Accessories in pegmatite fields MPF, PPF, and TPF host the dominant heterogeneously mixed methane-rich fluid that may originate at more reduced conditions of a less-porous metasedimentary basement.

In addition to the heterogeneous entrapment and fluid modification processes discussed above, pressure estimates derived from the studied fluid inclusion assemblages show some inconsistencies. Nonetheless, the fluid end-member compositions provide more reliable constraints on the conditions of host mineral crystallization. Additionally, the investigated pegmatite fields experienced intense overprinting during Cretaceous high-pressure metamorphism and were laterally dispersed by post-orogenic, east-directed extrusion tectonics [89]. These post-Permian events, as highlighted in this study, may also fit our pressure estimate interpretations.

Author Contributions: Conceptualization: K.K.; methodology: K.K. and M.H.; fieldwork and sample collection: K.K. and M.H.; data analysis: K.K. and M.H.; first draft preparation: K.K.; data curation: K.K. and M.H.; reviewing and editing: K.K. and M.H. All authors have read and agreed to the published version of the manuscript.

Funding: Open Access Funding by the University of Graz.

Data Availability Statement: The data presented in this study are available on request from the corresponding author.

Acknowledgments: The authors thank Anna Mikulics for her fieldwork of collecting the samples, preparation, and data analyses. C. Gotthardt is highly acknowledged for providing samples from her thesis for fluid inclusion investigations. Additionally, F. Walter (University of Graz) is thanked for the spodumene samples from Millstatt Seenrücken (sample MC_See). The authors thank three anonymous reviewers and the academic editor for their constructive review work, which improved the manuscript significantly.

Conflicts of Interest: The authors declare no conflicts of interest.

Appendix A

Garnet mineral chemistries in wt.% from the pegmatite field areas.

Table A1. Radegund Pegmatite Field.

Analysis [wt.%]	PE05				PE23a	
	Core 1	Core 2	Core 3	Rim	Core	Rim
	n	8	8	5	6	6
SiO_2	36.68 ± 0.26	36.71 ± 0.31	36.57 ± 0.43	37.76 ± 0.37	36.54 ± 0.48	37.03 ± 0.73
TiO_2	0.06 ± 0.06	0.07 ± 0.07	0.04 ± 0.04	0.02 ± 0.06	0.01 ± 0.02	0.03 ± 0.03
Al_2O_3	21.14 ± 0.14	21.31 ± 0.59	21.14 ± 0.53	21.61 ± 0.18	20.43 ± 0.21	20.65 ± 0.55
Cr_2O_3	0.02 ± 0.02	0.04 ± 0.04	0.04 ± 0.04	0.02 ± 0.06	0.01 ± 0.01	0.01 ± 0.02
FeO_{tot}	19.90 ± 1.72	24.54 ± 1.22	29.74 ± 2.04	21.60 ± 4.63	28.44 ± 3.69	28.17 ± 4.16
FeO	19.90 ± 1.72	24.54 ± 1.22	29.68 ± 1.99	21.60 ± 4.63	27.12 ± 0.92	27.38 ± 3.76
Fe_2O_3	0.00 ± 0.00	0.00 ± 0.00	0.14 ± 0.14	0.00 ± 0.00	1.79 ± 0.23	0.87 ± 0.72
MnO	20.62 ± 1.88	16.46 ± 1.15	12.40 ± 1.93	10.60 ± 0.85	13.71 ± 3.92	10.62 ± 2.76
MgO	0.08 ± 0.04	0.11 ± 0.03	0.16 ± 0.04	0.06 ± 0.03	0.52 ± 0.09	0.45 ± 0.17
CaO	1.06 ± 0.13	1.39 ± 0.18	0.81 ± 0.31	9.34 ± 4.64	0.82 ± 0.14	4.02 ± 4.43
Na_2O	0.02 ± 0.02	0.02 ± 0.02	0.01 ± 0.01	0.01 ± 0.02	0.01 ± 0.02	0.05 ± 0.05
Total	99.64 ± 0.49	100.09 ± 0.49	100.52 ± 0.74	101.02 ± 0.59	99.73 ± 0.66	101.02 ± 0.32

Table A1. Cont.

Analysis [wt.%]	PE05				PE23a	
	Core 1	Core 2	Core 3	Rim	Core	Rim
	n	8	8	5	6	6
End-members [wt.%]						
Spessartine	49.59 ± 4.05	40.35 ± 1.18	29.05 ± 4.60	24.07 ± 1.96	28.80 ± 5.98	23.86 ± 5.87
Pyrope	0.33 ± 0.14	0.44 ± 0.09	0.73 ± 0.18	0.28 ± 0.10	1.27 ± 1.25	1.12 ± 1.12
Almandine	46.97 ± 4.16	57.00 ± 2.59	68.26 ± 3.95	51.95 ± 7.92	66.72 ± 5.95	62.05 ± 7.74
Grossular	3.19 ± 0.35	4.05 ± 0.64	2.22 ± 0.83	23.58 ± 10.10	1.20 ± 0.67	12.01 ± 9.12
Andradite	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00	1.21 ± 0.66	1.29 ± 1.29
Uvarovite	0.06 ± 0.06	0.11 ± 0.11	0.13 ± 0.13	0.12 ± 0.12	0.03 ± 0.03	0.04 ± 0.04

Table A2. Millstatt Pegmatite Field.

Analysis [wt.%]	MC02		MC03	
	Core	Rim	Core	Rim
	n	7	6	6
SiO ₂	36.63 ± 0.29	36.96 ± 0.57	36.02 ± 0.55	36.46 ± 0.19
TiO ₂	0.02 ± 0.04	0.01 ± 0.04	0.01 ± 0.01	0.01 ± 0.02
Al ₂ O ₃	21.06 ± 0.18	21.48 ± 0.43	20.55 ± 0.22	20.65 ± 0.55
Cr ₂ O ₃	0.02 ± 0.04	0.02 ± 0.02	0.02 ± 0.02	0.00 ± 0.00
FeO _{tot}	29.30 ± 0.79	27.37 ± 1.93	28.73 ± 0.93	25.53 ± 0.59
FeO	29.24 ± 0.85	27.37 ± 1.95	27.12 ± 0.92	24.32 ± 0.88
Fe ₂ O ₃	0.07 ± 0.27	0.00 ± 0.01	1.79 ± 0.23	1.35 ± 0.62
MnO	11.61 ± 0.92	9.69 ± 0.69	10.77 ± 1.73	11.46 ± 0.47
MgO	0.82 ± 0.29	0.93 ± 0.13	1.04 ± 0.14	0.60 ± 0.06
CaO	0.84 ± 0.07	3.83 ± 3.02	2.39 ± 1.57	5.07 ± 0.96
Na ₂ O	0.03 ± 0.02	0.02 ± 0.02	0.03 ± 0.02	0.02 ± 0.03
Total	100.34 ± 0.64	100.31 ± 1.00	99.73 ± 0.66	99.92 ± 0.29
End-members [wt.%]				
Spessartine	27.19 ± 2.30	22.37 ± 2.22	23.95 ± 3.64	25.25 ± 1.89
Pyrope	3.55 ± 0.96	3.79 ± 0.62	4.02 ± 0.74	1.93 ± 1.30
Almandine	67.06 ± 1.55	62.52 ± 5.69	63.64 ± 3.36	56.85 ± 2.10
Grossular	2.34 ± 0.27	11.30 ± 8.32	6.68 ± 3.99	15.65 ± 3.83
Andradite	0.00 ± 0.00	0.00 ± 0.00	1.29 ± 1.29	1.84 ± 1.55
Uvarovite	0.09 ± 0.09	0.05 ± 0.05	0.06 ± 0.06	0.00 ± 0.00

Table A3. Polinik Pegmatite Field.

Analysis [wt.%]	PS10		PS13		PS17	
	Inner Core	Outer Core	Inner Core	Outer Core	Inner Core	Outer Core
	10	10	10	10	14	5
SiO ₂	35.48 ± 0.63	35.97 ± 0.26	36.39 ± 0.40	36.71 ± 0.85	36.32 ± 0.55	36.86 ± 0.30
TiO ₂	0.01 ± 0.03	0.02 ± 0.02	0.02 ± 0.04	0.01 ± 0.03	0.01 ± 0.03	0.01 ± 0.04
Al ₂ O ₃	20.23 ± 0.25	20.53 ± 0.44	20.70 ± 0.22	21.04 ± 0.33	20.55 ± 0.82	20.55 ± 0.67
Cr ₂ O ₃	0.00 ± 0.02	0.00 ± 0.02	0.02 ± 0.03	0.02 ± 0.04	0.00 ± 0.01	0.00 ± 0.01
FeO _{tot}	15.77 ± 3.28	24.79 ± 4.45	30.95 ± 2.45	27.44 ± 3.13	30.43 ± 3.59	34.6 ± 0.80
FeO	14.69 ± 3.03	24.04 ± 3.92	30.14 ± 2.36	27.05 ± 3.48	29.17 ± 4.07	33.70 ± 0.65
Fe ₂ O ₃	1.20 ± 1.20	0.83 ± 0.67	0.90 ± 0.67	0.44 ± 0.47	1.40 ± 0.75	1.10 ± 0.78
MnO	26.52 ± 3.83	13.03 ± 5.45	10.65 ± 1.58	12.47 ± 3.65	8.72 ± 3.37	2.6 ± 1.21
MgO	0.07 ± 0.29	1.09 ± 0.63	0.64 ± 0.14	0.45 ± 0.15	0.95 ± 0.25	2.54 ± 0.71
CaO	0.16 ± 0.19	2.80 ± 0.52	1.02 ± 1.06	2.49 ± 0.85	2.86 ± 0.84	2.42 ± 0.29
Na ₂ O	0.11 ± 0.10	0.06 ± 0.07	0.04 ± 0.02	0.02 ± 0.02	0.02 ± 0.03	0.01 ± 0.01
Total	98.48 ± 0.90	98.36 ± 0.38	100.51 ± 0.31	100.70 ± 1.39	100.00 ± 0.63	99.88 ± 0.58

Table A3. Cont.

Analysis [wt.%]	PS10		PS13		PS17	
	Inner Core	Outer Core	Inner Core	Outer Core	Inner Core	Outer Core
	n	10	10	10	14	5
End-members [wt.%]						
Spessartine	61.12 ± 6.06	32.30 ± 11.35	25.01 ± 3.85	32.30 ± 5.89	19.38 ± 7.65	6.27 ± 1.81
Pyrope	0.78 ± 0.78	4.80 ± 2.37	2.61 ± 0.77	1.67 ± 0.49	3.92 ± 1.36	8.40 ± 3.41
Almandine	37.37 ± 5.07	55.95 ± 8.99	69.20 ± 5.58	59.99 ± 5.85	67.18 ± 8.31	77.19 ± 1.63
Grossular	0.59 ± 0.35	8.09 ± 1.41	2.71 ± 2.64	7.30 ± 2.42	7.86 ± 2.99	6.27 ± 1.91
Andradite	0.04 ± 0.04	0.24 ± 0.24	0.44 ± 0.44	0.20 ± 0.20	1.29 ± 1.29	1.48 ± 1.48
Uvarovite	0.04 ± 0.04	0.04 ± 0.04	0.09 ± 0.09	0.09 ± 0.09	0.02 ± 0.02	0.02 ± 0.02

Table A4. Cont. Polinik Pegmatite Field.

Analysis [wt.%]	PS18a		PS19b	
	Inner Core	Outer Core	Inner Core	Outer Core
	n	11	13	6
SiO ₂	36.47 ± 0.70	36.16 ± 0.23	36.17 ± 0.27	36.34 ± 0.37
TiO ₂	0.01 ± 0.02	0.01 ± 0.01	0.03 ± 0.03	0.01 ± 0.01
Al ₂ O ₃	20.82 ± 0.38	20.56 ± 0.14	20.52 ± 0.17	20.71 ± 0.18
Cr ₂ O ₃	0.04 ± 0.05	0.02 ± 0.06	0.00 ± 0.01	0.00 ± 0.01
FeO _{tot}	28.47 ± 2.88	24.34 ± 0.96	32.14 ± 2.26	29.64 ± 1.28
FeO	28.20 ± 2.62	24.31 ± 1.00	31.77 ± 2.19	29.09 ± 1.16
Fe ₂ O ₃	0.57 ± 0.57	0.03 ± 0.08	0.82 ± 0.82	0.62 ± 0.62
MnO	12.10 ± 2.49	14.52 ± 0.83	10.36 ± 2.25	10.96 ± 0.35
MgO	0.93 ± 0.25	0.56 ± 0.11	0.32 ± 0.08	0.25 ± 0.05
CaO	0.69 ± 0.36	2.21 ± 0.89	0.53 ± 0.26	2.14 ± 0.92
Na ₂ O	0.04 ± 0.02	0.02 ± 0.02	0.05 ± 0.02	0.02 ± 0.02
Total	99.47 ± 0.46	98.39 ± 0.15	100.04 ± 0.34	100.14 ± 0.29
End-members [wt.%]				
Spessartine	28.72 ± 6.05	34.14 ± 1.93	24.21 ± 5.23	25.98 ± 1.03
Pyrope	3.85 ± 1.00	2.24 ± 0.37	1.31 ± 0.34	1.08 ± 0.17
Almandine	65.86 ± 5.66	57.42 ± 1.85	73.39 ± 5.09	67.87 ± 3.25
Grossular	1.92 ± 1.09	6.24 ± 2.33	1.04 ± 0.77	5.18 ± 3.43
Andradite	0.00 ± 0.00	0.00 ± 0.00	0.40 ± 0.40	0.52 ± 0.52
Uvarovite	0.15 ± 0.15	0.13 ± 0.13	0.02 ± 0.02	0.02 ± 0.02

References

- Schuster, R.; Stüwe, K. The Permian Metamorphic Event in the Alps. *Geology* **2008**, *36*, 603–606. [\[CrossRef\]](#)
- Schuster, R.; Knoll, T.; Mali, H.; Huet, B.; Griesmeier, G.E.U. Field trip guide: A profile from migmatites to spodumene pegmatites (Styria, Austria). *Ber. Geol. Bund.* **2019**, *134*, 1–4.
- Knoll, T.; Schuster, R.; Mali, H.; Huet, B. Die Genese der permischen Lithium-Pegmatite des Ostalpinen Kristallins. *Berg Huettenmaenn. Monatsh.* **2021**, *166*, 175–180. [\[CrossRef\]](#)
- Husar, M.; Krenn, K. High-Density Upper Amphibolite/Granulite Facies Fluid Inclusions in Magmatic Garnet from the Koralpe Mountains (Eastern Alps, Austria). *Minerals* **2022**, *12*, 873. [\[CrossRef\]](#)
- Wise, M.A.; Müller, A.; Simmons, W.B. A proposed new mineralogical classification system for granitic pegmatites. *Can. Mineral.* **2022**, *60*, 229–248. [\[CrossRef\]](#)
- Krenn, K.; Husar, M.; Mikulics, A. Fluid and Solid Inclusions in Host Minerals of Permian Pegmatites from Koralpe (Austria): Deciphering the Permian Fluid Evolution During Pegmatite Formation. *Minerals* **2021**, *11*, 638. [\[CrossRef\]](#)
- Krenn, K.; Konzett, J.; Stalder, R. Anatectic granitic pegmatites from the eastern Alps: A case of variable rare metal enrichment during high-grade regional metamorphism. III: Fluid inclusions as potential indicators for anatectic pegmatite parent melt formation. *Can. Mineral.* **2022**, *60*, 155–169. [\[CrossRef\]](#)
- Müller, A.; Kearsley, A.; Spratt, J.; Seltmann, R. Petrogenetic implications of magmatic garnet in granitic pegmatites from Southern Norway. *Can. Mineral.* **2012**, *50*, 1095–1115. [\[CrossRef\]](#)
- Dahlquist, J.A.; Galindo, C.; Pankhurst, R.J.; Rapela, C.W.; Alasino, P.H.; Saavedra, J.; Fanning, C.M. Magmatic evolution of the Peñón Rosado granite: Petrogenesis of garnet-bearing granitoids. *Lithos* **2007**, *95*, 177–207. [\[CrossRef\]](#)

10. Yu, M.; Xia, M.Q.; Zheng, Y.F.; Zhao, Z.F.; Chen, Y.X.; Chen, R.X.; Luo, X.; Li, W.C.; Xu, H. The composition of garnet in granite and pegmatite from the Gangdese orogen in southeastern Tibet: Constraints on pegmatite petrogenesis. *Am. Mineral.* **2021**, *106*, 265–281. [[CrossRef](#)]
11. Vityk, M.O.; Bodnar, R.J. Do fluid inclusions in high-grade metamorphic terranes preserve peak metamorphic density during retrograde decompression? *Am. Mineral.* **1995**, *80*, 641–644.
12. Tarantola, A.; Diamond, L.; Stünitz, H. Modification of fluid inclusions in quartz by deviatoric stress I: Experimentally induced changes in inclusion shapes and microstructures. *Contrib. Mineral. Petrol.* **2010**, *160*, 825–843. [[CrossRef](#)]
13. Chi, G.; Diamond, L.W.; Lu, H.; Lai, J.; Chu, H. Common Problems and Pitfalls in Fluid Inclusion Study: A Review and Discussion. *Minerals* **2021**, *11*, 7. [[CrossRef](#)]
14. Miller, C.; Thöni, M.; Konzett, J.; Kurz, W.; Schuster, R. Eclogites from the Koralpe and Saualpe type-localities, Eastern Alps, Austria. *Mitt. Österr. Mineral. Ges.* **2005**, *150*, 227–263.
15. Tenczer, V.; Stüwe, K. The metamorphic field gradient in the eclogite type locality Koralpe region, Eastern Alps. *J. Metam. Geol.* **2003**, *21*, 377–393. [[CrossRef](#)]
16. Goldstein, R.H.; Reynolds, T.J. Systematics of fluid inclusions in diagenetic minerals. In *SEPM Short Course*; SEPM: Tulsa, OK, USA, 1994; Volume 31, 199p.
17. Goldstein, R.H. Fluid Inclusions in sedimentary and diagenetic systems. *Lithos* **2001**, *55*, 159–193. [[CrossRef](#)]
18. Konzett, J.; Schneider, T.; Nedyalkova, L.; Hauzenberger, C.; Melcher, F.; Gerdes, A.; Whitehouse, M. Anatectic Granitic Pegmatites from the Eastern Alps: A case of variable Rare-metal enrichment during high-grade regional metamorphism—I: Mineral assemblages, geochemical characteristics, and emplacement ages. *Can. Mineral.* **2018**, *56*, 555–602. [[CrossRef](#)]
19. Konzett, J.; Hauzenberger, C.; Ludwig, T.; Stalder, R. Anatectic Granitic Pegmatites from the Eastern Alps: A case of variable Rare-metal enrichment during high-grade regional metamorphism—II: Pegmatite staurolite as an indicator of anatectic pegmatite parent melt formation—A field and experimental study. *Can. Mineral.* **2018**, *56*, 603–624. [[CrossRef](#)]
20. Knoll, T.; Huet, B.; Schuster, R.; Mali, H.; Ntaflos, T.; Hauzenberger, C. Lithium pegmatite of anatectic origin—A case study from the Austroalpine Unit Pegmatite Province (Eastern European Alps): Geological data and geochemical modeling. *Ore Geol. Rev.* **2023**, *154*, 105298. [[CrossRef](#)]
21. Hoinkes, G.; Koller, F.; Demény, A.; Schuster, R.; Miller, F.; Thöni, M.; Kurz, W.; Krenn, K.; Walter, F. Metamorphism in the Eastern Alps. *Acta Mineral. Petrogr. Field Guide Series* **2010**, *1*, 1–47.
22. Hoinkes, G.; Koller, F.; Rantitsch, G.; Dachs, E.; Hoeck, V.; Neubauer, F.; Schuster, R. Alpine metamorphism in the Eastern Alps. *Schweizer. Mineral. Petrogr. Mitt.* **1999**, *79*, 155–181.
23. Schuster, R.; Scharbert, S.; Abart, R.; Frank, W. Permo-Triassic extension and related HT/LP metamorphism in the Austroalpine—Southalpine realm. *Mitt. Ges. Geol. Bergbaustud. Österr.* **2001**, *45*, 111–141.
24. Thöni, M. Dating eclogite-facies metamorphism in the Eastern Alps—Approaches, results, interpretations: A review. *Mineral. Petrol.* **2006**, *88*, 123–148. [[CrossRef](#)]
25. Kunz, B.E.; Manzotti, P.; von Niederhäusern, B.; Engi, M.; Darling, J.R.; Giuntoli, F.; Lanari, P. Permian high-temperature metamorphism in the Western Alps (NW Italy). *Int. J. Earth Sci.* **2018**, *107*, 203–229. [[CrossRef](#)]
26. Schuster, R.; Tropper, P.; Krenn, E.; Finger, F.; Frank, W.; Philippitsch, R. Prograde Permo-Triassic metamorphic HT/LP assemblages from the Austroalpine Jenig Complex (Carinthia, Austria). *Austrian J. Earth Sci.* **2015**, *108*, 73–90. [[CrossRef](#)]
27. Schmid, S.M.; Fügenschuh, B.; Kissling, E.; Schuster, R. Tectonic map and overall architecture of the Alpine orogen. *Eclog. Geol. Helv.* **2004**, *97*, 93–117. [[CrossRef](#)]
28. Neubauer, F.; Liu, Y.; Dong, Y.; Chang, R.; Genser, J.; Yuan, S. Pre-Alpine tectonic evolution of the Eastern Alps: From Prototethys to Paleotethys. *Earth Sci. Rev.* **2022**, *226*, 103923. [[CrossRef](#)]
29. Pühr, B.; Hoinkes, G.; Proyer, A.; Schuster, R. Petrology of metacarbonate rocks of the Austroalpine basement east of the Tauern Window (Austria). *Mitt. Österr. Mineral. Ges.* **2009**, *155*, 134.
30. Frank, N.; Kurz, W.; He, D.F.; Schuster, R.; Dong, Y.P.; Hauzenberger, C. Hints on provenance and protolith age of medium to high-grade metamorphic metasediments from the Eastern Alps—based on detrital U/Pb zircon age distributions. In *Proceedings of the Arbeitstagung der Geologischen Bundesanstalt, Murau, Austria*, 24–27 June 2019; p. 211.
31. Gaidies, F.; Abart, R.; De Capitani, C.; Schuster, R.; Connolly, J.A.D.; Reusser, E. Characterization of polymetamorphism in the Austroalpine basement east of the Tauern Window using garnet isopleth thermobarometry. *J. Metam. Geol.* **2006**, *24*, 451–475. [[CrossRef](#)]
32. Gotthardt, C. Pegmatitgenese des Rappold-Komplex um St. Radegund, des Millstatt-Komplex und des Prijakt-Polinik-Komplex. Master's Thesis, Graz University of Technology, Graz, Austria, 2015; 155p.
33. Eisenberg, J.; Hauzenberger, C. Geologisch-petrologische Geländebeobachtungen des nordwestlichen Radegunder Kristallins. *Mitt. naturwiss. Ver. Steiermark* **2001**, *131*, 5–7.
34. Röggl, M. Petrographie und Petrologie des Anger Kristallins, Steiermark. Master's Thesis, Karl-Franzens University Graz, Graz, Austria, 2007; 168p.

35. Nowotny, A. Bericht 2006 über geologische Aufnahmen auf Blatt 164 Graz. *Jb. Geol. BA* **2007**, *147*, 664–665.
36. Nowotny, A. Bericht 2007 über geologische Aufnahmen auf Blatt 164 Graz. *Jb. Geol. BA* **2008**, *148*, 266–267.
37. Ahrer, S. Geowissenschaftliche und Aufbereitungstechnische Untersuchungen an Ausgewählten Pegmatiten und deren Nb-Ta-Vererzungen in den Ostalpen, Steiermark, Österreich. Master's Thesis, Montanuniversity Leoben, Leoben, Austria, 2014; 105p.
38. Koller, F.; Götzinger, M.A.; Neumayer, R.G. Beiträge zur Mineralogie und Geochemie der Pegmatite des St. Radegunder Kristallins und der Gleinalpe. *Arch. Lagerstättenforschung Geol. B.A.* **1983**, *3*, 47–65.
39. Mali, H.; Schuster, R.; Knoll, T.; Huet, B. Zoning of pegmatite fields as a key for unraveling the internal structure of basement nappes: Examples of the Eastern Alps (Austria). *Geophys. Res. Abstr.* **2019**, *21*, EGU2019-14565.
40. Teiml, X. Die Gesteine der Millstätter Serie: Petrologische und geothermobarometrische Untersuchungen. Master's Thesis, University of Graz, Graz, Austria, 1996; 199p.
41. Luecke, W.; Ucik, F.H. Die Zusammensetzung der Pegmatite von Edling und Wolfsberg bei Spittal/Drau (Kärnten) im Rahmen der Pegmatitvorkommen des Millstätter See-Rückens. *Arch. Lagerstättenforschung Geol. B.A.* **1986**, *7*, 173–187.
42. Knoll, T.; Schuster, R.; Huet, B.; Mali, H.; Onuk, P.; Horschinegg, M.; Ertl, A.; Giester, G. Spodumene Pegmatite and Related Leucogranite from the Austroalpine Unit (Eastern Alps, Central Europe): Field Relations, Petrography, Geochemistry, and Geochronology. *Can. Mineral.* **2018**, *56*, 489–528. [[CrossRef](#)]
43. Schuster, R.; Koller, F.; Hoeck, V.; Hoinkes, G.; Bousquet, R. Explanatory Notes of the Map: Metamorphic Structure of the Alps, Metamorphic Evolution of the Eastern Alps. *Mitt. Österr. Mineral. Ges.* **2004**, *149*, 175–199.
44. Walter, F. Exkursion E4 am 27.9.1998 MINPET 98 (Pörschach am Wörthersee/Kärnten) Die Pegmatite des Misstätter See-Rückens. *Mitt. Österr. Mineral. Ges.* **1998**, *143*, 437–450.
45. Walter, F. 1573) Spodumen und Holmquistit in einem Pegmatit von Lug-ins-Land. In *Neue Mineralfunde aus Österreich LVIII*; Naturwissenschaftlicher Verein für Kärnten: Klagenfurt am Wörthersee, Austria, 2009; pp. 195–196.
46. Hoke, L. The Altkristallin of the Kreuzeck Mountains, SE Tauern Window, Eastern Alps—Basement Crust in a Convergent Plate Boundary Zone. *Jb. Geol. BA* **1990**, *133*, 5–87.
47. Linner, M.; Richter, W.; Thöni, M. Frühalpidische Metamorphose- und Abkühlgeschichte der Eklogite im ostalpinen Kristallin südlich vom Tauernfenster (Schobergruppe). *Mitt. Österr. Mineral. Ges.* **1998**, *143*, 334–335.
48. Schulz, B.; Finger, F.; Krenn, E. Auflösung variskischer, permischer und alpidischer Ereignisse im polymetamorphen ostalpinen Kristallin südlich der Tauern mit EMS-Datierung von Monazit. *Arbeitstagung Geol. B.A. Österreich* **2005**, 141–153.
49. Hauke, M.; Froitzheim, N.; Nagel, T.J.; Miladinova, I.; Fassmer, K.; Fonseca, R.O.C.; Sprung, P.; Münker, C. Two high-pressure metamorphic events, Variscan and Alpine, dated by Lu–Hf in an eclogite complex of the Austroalpine nappes (Schobergruppe, Austria). *Int. J. Earth Sci.* **2019**, *108*, 1317–1331. [[CrossRef](#)]
50. Schuster, R.; Thöni, M. Permian Garnets: Indication for a regional Permian metamorphism in the southern part of the Austroalpine Basement Units. *Mitt. Österr. Mineral. Ges.* **1996**, *141*, 219–221.
51. Habler, G.; Thöni, M. Preservation of Permo ± Triassic low-pressure assemblages in the Cretaceous high-pressure metamorphic Saualpe crystalline basement (Eastern Alps, Austria). *J. Metam. Geol.* **2001**, *19*, 679–697. [[CrossRef](#)]
52. Thöni, M.; Miller, C. The “Permian event” in the Eastern European Alps: Sm–Nd and P–T data recorded by multi-stage garnet from the Plankogel unit. *Chem. Geol.* **2009**, *260*, 20–36. [[CrossRef](#)]
53. Konzett, J.; Krenn, K.; Hauzenberger, C.; Whitehouse, M.; Hoinkes, G. High-Pressure Tourmaline Formation and Fluid Activity in Fe–Ti-rich Eclogites from the Kreuzeck Mountains, Eastern Alps, Austria. *J. Petrol.* **2012**, *53*, 99–125. [[CrossRef](#)]
54. Oakes, C.S.; Bodnar, R.J.; Simonson, T.M. The system NaCl–CaCl₂–H₂O: The ice liquidus at 1 atm total pressure. *Geochim. Cosmochim. Acta* **1990**, *54*, 603–610. [[CrossRef](#)]
55. Zhang, Y.G.; Franz, J.D. Experimental determination of the compositional limits of immiscibility in the system CaCl₂–H₂O–CO₂ at high temperatures and pressures using synthetic fluid inclusions. *Chem. Geol.* **1989**, *74*, 289–308. [[CrossRef](#)]
56. Spencer, R.J.; Möller, N.; Weare, J.H. The prediction of mineral solubilities in natural waters: A chemical equilibrium model for the Na–K–Ca–Mg–Cl–SO₄–H₂O system at temperatures below 25 °C. *Geochim. Cosmochim. Acta* **1990**, *54*, 575–590. [[CrossRef](#)]
57. Thiéry, R.; van den Kerkhof, A.M.; Dubessy, J. VX properties of CH₄–CO₂ and CO₂–N₂ fluid inclusions: Modelling for T < 31 °C and P < 400 bars. *Eur. J. Mineral.* **1994**, *6*, 753–771.
58. Thiéry, R.; Vidal, J.; Dubessy, J. Phase equilibria modelling applied to fluid inclusions: Liquid-vapour equilibria and calculation of the molar volume in the CO₂–CH₄–N₂ system. *Geochim. Cosmochim. Acta* **1994**, *58*, 1073–1082. [[CrossRef](#)]
59. Bakker, R.J. Package FLUIDS 1. Computer programs for analysis of fluid inclusion data and for modelling bulk fluid properties. *Chem. Geol.* **2003**, *194*, 3–23. [[CrossRef](#)]
60. Davis, D.W.; Lowenstein, T.K.; Spencer, R.J. Melting behaviour of fluid inclusions in laboratory-grown halite crystals in the systems NaCl–H₂O, NaCl–KCl–H₂O, NaCl–MgCl₂–H₂O, and NaCl–CaCl₂–H₂O. *Geochim. Cosmochim. Acta* **1990**, *54*, 591–601. [[CrossRef](#)]

61. Bodnar, R.J. Introduction to aqueous-electrolyte fluid inclusions. In *Fluid Inclusions: Analysis and Interpretation*; Samson, I., Anderson, A., Marshall, D., Eds.; Mineralogical Association of Canada Short Course Series; Mineralogical Association of Canada: Ottawa, ON, Canada, 2003; Volume 32, pp. 81–100.
62. Burke, E.A.J. Raman microspectrometry of fluid inclusions. *Lithos* **2001**, *55*, 139–158. [\[CrossRef\]](#)
63. Frezzotti, M.L.; Tecce, F.; Casagli, A. Raman spectroscopy for fluid inclusion analysis. *J. Geochem. Expl.* **2012**, *112*, 1–20. [\[CrossRef\]](#)
64. Hurai, V.; Huraiová, M.; Slobodník, M.; Thomas, R. *Geofluids*; Elsevier: Amsterdam, The Netherlands, 2015; p. 485.
65. Dufresne, W.J.; Ruffelt, C.J.; Marshall, C.P. Raman spectroscopy of eight natural carbonate minerals of calcite structure. *J. Raman Spec.* **2018**, *49*, 1999–2007. [\[CrossRef\]](#)
66. Habler, G.; Thöni, M.; Miller, C. Major and trace element chemistry and Sm–Nd age correlation of magmatic pegmatite garnet overprinted by eclogite-facies metamorphism. *Chem. Geol.* **2007**, *241*, 4–22. [\[CrossRef\]](#)
67. Chernoff, C.B.; Carlson, W.D. Disequilibrium for Ca during growth of pelitic garnet. *J. Metam. Geol.* **1997**, *15*, 421–438. [\[CrossRef\]](#)
68. Menard, T.; Spear, F.S. Metamorphism of calcic Pelitic schists, Strafford Dome, Vermont: Compositional zoning and reaction history. *J. Petrol.* **1993**, *34*, 977–1005. [\[CrossRef\]](#)
69. Manning, D.A.C. Chemical variation in garnets from aplites and pegmatites, peninsular Thailand. *Mineral. Mag.* **1983**, *47*, 353–358. [\[CrossRef\]](#)
70. Whitworth, M.P. Petrogenetic implications of garnets associated with lithium pegmatites from SE Ireland. *Mineral. Mag.* **1992**, *56*, 75–83. [\[CrossRef\]](#)
71. Thöni, M.; Miller, C. Ordovician meta-pegmatite garnet (NW Ötztal basement, Tyrol, Eastern Alps): Preservation of magmatic garnet chemistry and Sm–Nd age during mylonitization. *Chem. Geol.* **2004**, *209*, 1–26. [\[CrossRef\]](#)
72. Gadas, P.; Novák, M.; Talla, D.; Galiová, M.V. Compositional evolution of grossular garnet from leucotonalitic pegmatite at Rudanad Moravou, Czech Republic; a complex EMPA, LA-ICP-MS, IR and CL study. *Mineral. Petrol.* **2013**, *107*, 311–326. [\[CrossRef\]](#)
73. Ganguly, J.; Cheng, W.; Chakraborty, S. Cation diffusion in aluminosilicate garnets: Experimental determination in pyrope–almandine diffusion couples. *Contrib. Mineral. Petrol.* **1998**, *131*, 171–180. [\[CrossRef\]](#)
74. Anderson, A.J. Microthermometric behavior of crystal-rich inclusions in spodumene under confining pressure. *Can. Mineral.* **2019**, *57*, 853–865. [\[CrossRef\]](#)
75. Anderson, A.J.; Clark, A.H.; Gray, S. The occurrence and origin of zabuyelite (Li_2CO_3) in spodumene-hosted fluid inclusions: Implications for the internal evolution of rare-element granitic pegmatites. *Can. Mineral.* **2001**, *39*, 1513–1527. [\[CrossRef\]](#)
76. Crawford, M.L. Phase equilibria in aqueous fluid inclusions. In *Fluid Inclusions: Applications to Petrology*; Hollister, L.S., Crawford, M.L., Eds.; Mineralogical Association of Canada Short Course Handbook: Toronto, ON, Canada, 1981; Volume 6, pp. 75–100.
77. Itihara, Y.; Honma, H. Ammonium in biotite from metamorphic and granitic rocks of Japan. *Geochim. Cosmochim. Acta* **1979**, *43*, 503–509. [\[CrossRef\]](#)
78. Thomas, A.V.; Spooner, E.T.C. Fluid inclusions in the systems H_2O – CH_4 – NaCl – CO_2 from metasomatic tourmaline within the border unit of the Tanco zoned granite pegmatite, S.E. Manitoba. *Geochim. Cosmochim. Acta* **1998**, *52*, 1065–1075. [\[CrossRef\]](#)
79. Whitworth, M.P.; Rankin, A.H. Evolution of fluid phases associated with lithium pegmatites from SE Ireland. *Mineral. Mag.* **1989**, *53*, 271–284. [\[CrossRef\]](#)
80. Linnen, R.L.; Williams-Jones, A.E. The evolution of pegmatite-hosted Sn–W mineralization at Nong Sua, Thailand: Evidence from fluid inclusions and stable isotopes. *Geochim. Cosmochim. Acta* **1994**, *58*, 735–747. [\[CrossRef\]](#)
81. Fuertes-Fuente, M.; Martín-Izard, A.; Boiron, M.C.; Viñuela, J.M. P–T path and fluid evolution in the Franqueira Granitic Pegmatite, Central Galicia, Northwestern Spain. *Can. Mineral.* **2000**, *38*, 1163–1175. [\[CrossRef\]](#)
82. Huizenga, J.M. Thermodynamic modelling of C–O–H fluids. *Lithos* **2001**, *55*, 101–114. [\[CrossRef\]](#)
83. Bakker, R.J.; Jansen, J.B.H. A mechanism for preferential H_2O leakage from fluid inclusions in quartz, based on TEM observations. *Contrib. Mineral. Petrol.* **1994**, *116*, 7–20. [\[CrossRef\]](#)
84. Wang, L.; Zhang, Y.; Essene, E.J. Diffusion of the hydrous component in pyrope. *Am. Mineral.* **1996**, *81*, 706–718. [\[CrossRef\]](#)
85. Severs, M.J.; Azbej, T.; Thomas, J.B.; Mandeville, C.W.; Bodnar, R.J. Experimental determination of H_2O loss from melt inclusions during laboratory heating: Evidence from Raman spectroscopy. *Chem. Geol.* **2007**, *237*, 358–371. [\[CrossRef\]](#)
86. Johnson, E.L. Experimentally determined limits for H_2O – CO_2 – NaCl immiscibility in granulites. *Geology* **1991**, *19*, 925–928. [\[CrossRef\]](#)
87. Diamond, L.W. Review of the systematics of CO_2 – H_2O fluid inclusions. *Lithos* **2001**, *55*, 69–99. [\[CrossRef\]](#)
88. Ferry, J.M. Dehydration and decarbonation reactions as a record of fluid infiltration. *Rev. Mineral. Geochem.* **1991**, *26*, 351–393.
89. Ratschbacher, L.; Merle, O.; Davy, P.; Cobbold, P. Lateral extrusion in the eastern Alps, Part 1: Boundary conditions and experiments scaled for gravity. *Tectonics* **1991**, *10*, 245–256. [\[CrossRef\]](#)

Disclaimer/Publisher’s Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.