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Electron microprobe petrochronology ofzite-bearing garnet micaschists in the Oetztal-Stubai Complex (Alpeiner Valley, Stubai)

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Version 21-11-2016 submitted version Crystallisation of Permo-Triassic monazite in the pre-Alpine Oetztal-Stubai Complex (Alpeiner Valley, Stubai, Eastern Alps) Bernhard SCHULZ 1)*) & Robert ZIMMERMANN 2 ¹ TU Bergakademie Freiberg, Institute of Mineralogy, Department of Economic Geology and Petrology, Brennhausgasse 14, D-09599 Freiberg/Saxony, Germany ² Helmholtz-Zentrum Dresden-Rossendorf, Helmholtz Institute Freiberg for Resource Technology, Division of Exploration, Halsbrücker Straße 34, D-09599 Freiberg/Saxony, Germany *Corresponding author: Bernhard.Schulz@mineral.tu-freiberg.de *Corresponding author: Bernhard Schulz TU Bergakademie Freiberg, Institut für Mineralogie, Professur für Lagerstättenkunde und Petrologie, Brennhausgasse 14, D-09599 Freiberg/Sachsen, Deutschland E-Mail: Bernhard.Schulz@mineral.tu-freiberg.de, Tel: +49 3731 39 2668 Keywords: monazite, garnet metapelites, amphibolites, geothermobarometry, Permian, Austroalpine basement

Abstract

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The Alpeiner amphibolite unit in the Stubai region is the eastern succession of the Central Metabasite Zone (CMBZ) in the Austroalpine Oetztal-Stubai-Complex (OSC). In the Alpeiner Valley, amphibolites and biotite-hornblende gneisses are alternating with metapelites and metapsammites. Garnet in metapelite assemblages display growth zonations with spessartine- and grossular-rich cores and pyrope-rich rims. Geothermobarometry signals a prograde metamorphism with amphibolite-facies peak conditions at \sim 12 kbar and \sim 680 °C. The post P_{max} path with a decompression to 4 kbar and 660 - 600 °C was estimated by geothermobarometry involving zoned Ca-amphiboles in retrogressed amphibolitized eclogites. This P-T evolution is similar to the Variscan P-T paths known from the central Oetztal and Sellrain regions. Electron microprobe Th-U-Pb monazite dating in the metapelites yielded two distinct maxima at ages around 270 Ma and 220 Ma. In detail, Carboniferous and Permian isochrone ages at 304 ± 26 Ma, 272 ± 16 Ma and 269 ± 13 Ma, but also Triassic isochrones at 209 ± 17 Ma can be extracted from 3 samples. Monazite corona microstructures suggest a decomposition during decreasing temperature. In contrast, clusters of small monazite within allanite signal a re-crystallization. This points to a complex retrograde evolution when the P-T path approached low pressures. No Permian pegmatites and no accompanying distinct low pressure high temperature metamorphic event have yet been reported from the Stubai region. Therefore the monazite age data in combination to the P-T path provide petrological arguments for a Permian-to-Triassic metamorphic event. The new data from the Stubai basement indicates that this event, known from other Austroalpine basement areas was not restricted to the pegmatite-bearing zones. This Permian-to-Triassic thermal evolution with monazite crystallization appears during the decompression after a Carboniferous continental collision with an eclogite to amphibolite-facies main metamorphism.

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1. Introduction

- A major part of the Eastern Alps is composed of basement units with a polymetamorphic history.
- 56 The pre-Alpine Ordovician-Silurian, Carboniferous and Permian events, and the Alpine Cretaceous
- and Tertiary metamorphism have been reported from various parts (Frey et al., 1999). The
- Austroalpine Oetztal-Stubai Complex (OSC) is located in the Central Alps (Frisch et al., 2000;

59 Egglseder and Fügenschuh, 2013). It is one of the classical areas of polymetamorphism in the 60 Alps (Purtscheller, 1978; Thöni, 1999). Various isotopic dating methods have been applied there. 61 An Ordovician high-temperature anatectic event was reported from the Winnebach, Verpeil and 62 Gaisloch migmatites (Klötzli-Chowanetz et al., 1997; Neubauer et al., 1999; Hoinkes et al., 1999; 63 Söllner, 2001; Thöny et al., 2008). Eclogite-facies conditions were locally attained during the 64 Variscan (Devonian-Carboniferous) metamorphism (Mogessi et al., 1985; Mogessi and 65 Purtscheller, 1986; Miller and Thöni, 1995; Rode et al., 2012). The Variscan metamorphic overprint 66 led to kyanite, sillimanite and andalusite mineral zones (Fig. 1) of which boundaries cut across and 67 postdate the large-scale Schlingen structures of the regional foliation (Purtscheller, 1978). Towards 68 the South, an increasing grade of the Early-Alpine (Cretaceous) overprint has been described 69 (Thöni, 1981; 1983; Hoinkes et al., 1991; 1999; Hoinkes and Thöni, 1993; Thöni, 1999). This is 70 obvious from Variscan-to-Alpine K-Ar and Rb-Sr "mixed ages" of mica, changing to Cretaceous 71 ages towards the SE. The successive occurrence of chloritoid and then staurolite towards the 72 Schneeberger Zug and the Texel Complex, accompanied by distinct growth zones in garnet 73 porphyroblasts (Frank et al., 1987; Tropper and Recheis, 2003) are also assigned to this Early 74 Alpine overprint. The Late Alpine (Tertiary) events with South Alpine indenter and lateral extrusion 75 led to faults and shear zones which reframe and dissect the OSC. The main tectonic lines are the 76 sinistral Inntal fault zone to the North, the Brenner normal fault zone to the East, the Schneeberg 77 fault zone and Vinschgau shear zone to the South, the Schlinig zone to the West and the Engadine 78 line to the Northwest (Ratschbacher et al., 1991; Frisch et al., 2000; Schmid et al., 2004). 79 80 Within this frame, Permian mica ages were formerly interpreted as Carboniferous - Cretaceous 81 "mixing ages" (Thöni, 1981). However, these days the Permian magmatic and metamorphic ages 82 which are known from various parts of the Austroalpine basement are interpreted to express a distinct geodynamic event (Schuster et al., 2001; Marotta and Spalla, 2007; Schuster and Stüwe, 83 84 2008). The Permian event has been explained by westward propagation of the Meliata ocean in 85 the course of a post-collisional extension of the Variscan orogen. Extensional fabrics and 86 decompression melting (granites and pegmatites) are discussed as indicators for this HT/LP 87 metamorphism (Schuster and Stüwe, 2008).

In this context, the OSC represents a difficult situation for the resolution of the thermal events by age dating. Dependent on metamorphic grade and P-T paths, Rb-Sr, K-Ar and Ar-Ar methods can provide at best the age of maximal pressure and further ages on the cooling history of the latest metamorphic event. Methods based on U-Pb in zircon mostly fail, as the corresponding closure temperature and formation temperatures have not been achieved during amphibolite-facies and eclogite-facies metamorphism. Other methods as Sm-Nd in metamorphic garnet are difficult in specific applications and rarely available. In this frame, the electron microprobe (EMP) Th-U-Pb monazite dating in metapelites appears as promising. Here, we report corresponding data from the Alpeiner Valley in the OSC. The monazite ages and the P-T evolution in this part of the Austroalpine basement provide a link between the domains with Variscan metamorphism and the domains where the Permian-to-Triassic event is manifested by numerous pegmatite intrusions.

2. Geological setting and petrography

In the Alpeiner Valley around the Franz-Senn-Hütte in the NE part of the OSC, a succession from metapsammites and metapelites in the southern part, to an amphibolite dominated northern part of a Wechselserie are observed. Metagranitoids occur within this sequence (Fig. 2). Previous regional petrographic and tectonic studies (Hammer, 1929; Purtscheller, 1978; Schulz, 1994; Rode et al., 2012; Egglseder and Fügenschuh, 2013) cover the NE part of the OSC, but are lacking details from the Alpeiner Valley.

The Alpeiner metabasites are mostly amphibolites and biotite hornblende gneisses and form the eastern succession of the Central Metabasite Zone (CMBZ) of the OSC. Protoliths of the CMBZ are gabbros and basalts with MORB-chemistry (Mogessie et al., 1985) and Early Cambrian ages (Miller and Thöni, 1995), emplaced in a back-arc setting. The CMBZ is subdivided from N to S into five zones (Purtscheller, 1978): (1) Roughly foliated amphibolite with layers and lenses of eclogite and rare peridotite, (2) Dark, garnet-bearing amphibolites, (3) Alumosilicate gneisses (4) Wechselserie (5) Southern eclogite zone. The Alpeiner metabasites are alternating with metapelites to metapsammites and therefore have been assigned to the Wechselserie

(Purtscheller, 1978). Lenses of retrogressed eclogites and calc-silicate-gneisses are interbedded within the succession in the northern part (Figs 2; S1).

The metapelitic and -psammitic rocks within the study area are composed of quartzites and staurolite bearing micaschists and paragneisses. In the northern part, micaschists form lenses within the "Wechselserie", often not extending more than 50 x 20 m. The mineral assemblage is quartz, plagioclase, mica, biotite, garnet, staurolite and kyanite. Accessories are tourmaline, sphene and ilmenite. Dependent on the grade of retrograde metamorphism, intense crystallisation of chlorite can be observed. Staurolites is rimmed and pseudomorphed by sericite aggregates. Plagioclase is also altered and shows deformation twins. Microstructures show asymmetric pressure shadows around the garnets and sub-grain boundary recrystallisation of quartz.

In the southern branch of the study area occur WSW striking layers of biotite-rich paragneisses. Modal mineralogy consists of quartz, plagioclase mica and biotite. Accessories are garnet, staurolite, kyanite and microcline. Chlorite and epidote occur in small scale shear zones. Snowball structures in garnet are typical of syn-deformational growth. Nests and layers of green amphiboles occur in the periphery to amphibolites. Monomineralic quartz layers up to 5 cm thickness are common. Quartz microstructures show recrystallisation by subgrain boundary rotation (SGR) and grain boundary migration (GBM). Quartz ribbons indicate a static recrystallisation during the retrograde phase.

The variety of metabasites ranges from amphibolitized eclogite, garnet-amphibolite and amphibolite to biotite-hornblende-gneiss with folded layers of calcsilicate gneiss. The unit shows in mean a smooth, zonal, anastomosing, sometimes gradational foliation. The amphibolitized eclogite can be observed in small, often altered lenses elongated several meters. Clinopyroxene and plagioclase appear exclusively in coarse-grained symplectites. Primary clinopyroxene has not been found. Garnet displays sieve-like internal structures and is often replaced by mica and feldspar.

The amphibolites and hornblende gneisses are mainly composed of green amphibole and plagioclase. Green amphibole has fringes by actinolite and chlorite. Garnet up to 2 cm in diameter overgrows the foliated main fabric, indicating a crystallisation at a late stage of microstructure formation. Plagioclase often displays saussuritisation. Epidote is characterised by core-rim-structures. Quartz with subgrain boundary rotation recrystallisation forms layers parallel to the foliation.

The calcsilicate gneiss forms folded lenses and layers within amphibolite and plagioclase-hornblende-gneisses. The SW-NE striking layers follow the main foliation and are associated to the northern rim of metabasite zone (Purtscheller, 1978). The protoliths are syn-sedimentary carbonate and marl layers. Often a fluent transition to surrounding lithology can be observed. This often goes ahead with increasing occurrence of ore minerals and gradational interbedding. Modal mineralogy is made of plagioclase, quartz, epidote, chlorite, garnet, wollastonite, Ca-amphibole and mica. Garnet is often pseudomorphed to batches composed of plagioclase, quartz, epidote and chlorite.

3. Structures and tectonic setting

The Oetztal-Stubai basement can be divided into two tectonic domains (Purtscheller, 1978; Egglseder and Fügenschuh, 2013): (1) Pre-Mesozoic large amplitude open folds in the northern part and (2) the large-scale Schlingen-structures in the southeastern part around Vent. In the studied area, these large-scale fold structures (F_3) deform a pre-Mesozoic steeply N- and S-dipping main foliation S_2 . Sub-horizontal to slightly ESE-WNW plunging non-cylindric parasitic folds F_3 are minor structures of this large-scale folds. The geometrical interpretation of the S_2 main foliation planes in the Alpeiner Valley reveals a 5 km scale gentle cylindric fold (Egglseder and Fügenschuh, 2013) with a fold axis slightly plunging to NE. The π -pole at 024/27 was calculated by an Bingham axial distribution (cylindrical best fit) with OSX Stereonet (Cardozo and Allmendinger, 2013). The additionally calculated conical best fit axis coincides with the axis from cylindrical best fit. The regional major fold pattern is South-vergent with a WNW-ENE trending fold axis (Egglseder

and Fügenschuh, 2013). Same study revealed a mixed Type 2/3 fold interference pattern (Ramsay and Huber, 1987) for pre-Alpine two-stage folding (F_2 - F_3). Measured axes of monocline second order folds result in a mean vector of L 038/39. The calculated π -pole coincides with the 95% confidence interval of the measured second order fold axes (Fig. S1). The second order folds (F_3) are outstandingly visible in the units of the Wechselserie, where they are composed of calculates or monomineralic quartz layers.

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At least, six deformation stages (e.g., Purtscheller, 1978; Egglseder and Fügenschuh, 2013) can be observed in the study area: Large amplitude isoclinal folding F₂ was originated parallel to the stretching direction during intense shearing D₁-D₂. This deformation is expressed in small scales by isoclinally folded quartz-veins and calcsilicate layers. D₂ is associated to the formation of the main foliation (S_2 and fold axes F_2) and isoclinal folds F_2 of quartz layers. The deformation stages D₁-D₂ and D₃ belong to the pre-Alpine events, because the axial traces and foliations are not observed in the Brenner Mesozoic (Egglseder and Fügenschuh, 2013). Also mineral cooling ages (Thöni, 1999) imply no Alpine (Cretaceous) metamorphic event with ductile deformation in the northern parts of the Oetztal-Stubai Complex. The subsequent Alpine deformations display an increasing brittle component (Egglseder and Fügenschuh, 2013): W to NW directed thrusts are related to a Cretaceous thrusting. This stage is not observed in the study area. A subsequent topto-SE directed shearing, appears to be related to a late Cretaceous extension. This stage is observed in the two-mica porphyroblastic gneiss in the south-eastern part of the study area. Then followed small scale NNW to SSE vergent brittle thrusts, related to thrusting of Austroalpine units upon Penninic units. The final brittle stage are NE- and NW-trending strike-slip faults, related to Miocene to Neogene lateral extrusion and exhumation of Tauern Window (Ratschbacher et al., 1991; Egger, 1997). One of these NE-SW striking faults can be observed in the western part of the Rinnengrube. Also sub-vertical NE-SW trending Mohr-fracture systems belong to this stage (Fig. S1).

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4. Analytical methods

4.1. SEM-based automated mineralogy (MLA)

Automated mineralogical methods (e.g. Fandrich et al., 2007), based on a scanning electron microscope SEM Quanta 650-FEG-MLA by FEI Company, equipped with Bruker Dual X-Flash energy dispersive spectrometers for EDX analyses were applied to complete thin sections of garnet micaschists. Electron beam conditions were set at 25 kV acceleration voltage at spotsize 5.0, which corresponds to beam current of 10 nA. A software package for mineral liberation analysis (MLA version 2.9.0.7 by FEI Company) was used for the automated steerage of the electron beam for EDX identification of mineral grains and collection of numerous EDX spectra. The following measurement routines were applied:

1) The SPL (Selected Phase Lineup) routine combines a backscattered electron (BSE) grey colour value trigger and single spot EDX-ray spectral analysis. This enables the detection of rare phases as monazite and xenotime and their surrounding minerals. One receives a catalogue of all monazite and xenotime intermineral relationships. This was used to select monazite grains for detailed EMP analysis.

2) The GXMAP routine produces a narrow grid of ~ 1600 single EDX-ray spectra per mm². Garnet and biotite were chosen as the target phases. For the classification of mineral phases and compositions in SPL and GXMAP measurements, a list of identified reference EDX-ray spectra was established by collecting spectra from matrix phases and from defined parts of several garnet porphyroblasts (core - mid - rim). Garnet reference spectra are characterized by EDX-ray single spot elemental analyses which revealed strong variations of Fe, Mg, Mn and Ca in the porphyroblasts. In a next step, the reference spectra were labelled in a generic way with the corresponding garnet Fe-Mg-Mn-Ca compositions. When the labelled spectra are arranged in a color scale, they correspond to semi-quantitative garnet zoning maps (Fig. 3a). The GXMAP measurements were classified against the reference EDX-ray spectra list with a high degree of probability of match. The GXMAP measurements allowed to select a few typical garnets out of dozens of porphyroblasts for quantitative WDS analysis with electron microprobe (EMP).

3.2. Electron microprobe (EMP) and monazite dating

The mineral-chemical analyses from metabasite and metapelite samples and were performed with a JEOL JXA-8900-RL instrument at beam conditions of 15 kV, 20 nA, 2 μ m, and with the corresponding ZAF correction procedures. The ~900 analytical points on garnet, mica, feldspar, amphibole, clinopyroxene and epidote from the metapelite and metabasite samples enclose detailed garnet zonation traverses.

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EMP-Th-U-Pb dating is based on the observation that common Pb in monazite (LREE, Th)PO₄ is negligible when compared to radiogenic Pb resulting from the decay of Th and U (Montel et al., 1996). Electron microprobe analysis of the bulk Th, U and Pb concentrations in monazite, at a constant ²³⁸U/²³⁵U, allows for the calculation of a chemical model age (CHIME) with a considerable error (Jercinovic et al., 2008; Montel et al., 1996; Pyle et al., 2005; Spear et al., 2009; Suzuki and Kato, 2008). The Mα1 lines of Th and Pb and the Mβ1 lines for U of a PETH crystal were selected for monazite analysis. Analytical errors of 2 σ at 20 kV acceleration voltage, 100 nA beam current, 5 µm beam diameter and counting times of 320 s (Pb), 80 s (U) and 40 s (Th) on peak have been considered for the calculations of ages. For Pb the error ranges typically from 0.016-0.024 wt. % for the given dwell time, based on measurement on a reference monazite (Madmon). Orthophosphates of the Smithsonian Institution were used as standards for REE analysis (Jarosewich and Boatner, 1991). Calibration of PbO was carried out on a vanadinite standard. The U was calibrated on a glass standard with 5 wt% UO₂. A reference monazite labelled as Madmon, with special ThO₂*-PbO characteristics (Schulz and Schüssler, 2013) was used for calibration and offline re-calibration of ThO₂ as well as for the control of data. Interference of YLy on the PbM α line was corrected by linear extrapolation as proposed by Montel et al. (1996). An interference of ThMy on UMβ was also corrected. The number of single analyses varies with the grain size of the monazites, e.g. 1-2 analyses in grains of <40 µm and up to 10 analyses in grains of 100 µm in diameter. Monazite chemical ages were first calculated using the methods of Montel et al. (1996). The error resulting from counting statistics was typically on the order of ±20 to ±40 Ma (1σ) for Palaeozoic ages. Weighted average ages for monazite populations calculated using Isoplot 3.0 (Ludwig, 2001) are interpreted as the time of closure for the Th-U-Pb system of monazite during

growth or recrystallisation in the course of metamorphism. Ages were further determined using the ThO_2^* –PbO isochrone method (CHIME) of Suzuki et al. (1994) and Montel et al. (1996) where ThO_2^* is the sum of the measured ThO_2 plus ThO_2 equivalent to the measured UO_2 . This is based on the slope of a regression line in ThO_2^* vs PbO coordinates forced through zero. In all analysed samples, the model ages obtained by the two different methods coincide within the error.

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5. Mineral chemistry and geothermobarometry

5.1 Metapelites

The garnet- and staurolite bearing micaschists (RZ33 and RZ42) show an overall mineral assemblage of garnet, kyanite, staurolite, biotite, muscovite, plagioclase and quartz. Sample RZ42 is an aluminous gneiss and contains all three Al₂SiO₅-phases. The aluminosilicates are not in invariant equilibrium, as andalusite statically overgrows the foliated fabric with kyanite and sillimanite, as it also has been described by Purtscheller (1978). Garnet is variable in shape and size. Crystals range from small (1 mm) isometric to several mm large subhedral to euhedral grains (Fig. 3a). Inclusions of ilmenite, titanite, mica, quartz and plagioclase can line up to an internal foliation S₁i. Asymmetric pressure shadows by quartz and mica imply a high fraction of simple shear during generation of the external foliation S₂. Garnet zonations show a core-to rim trend with decreasing spessartine (Sps 15 - 1 mole%, calculated from mole fraction*100) and grossular (Grs 20 - 10 mole%), and increasing pyrope (Prp 5 - 20 mole%) (Fig. 3a - d). Some garnets display retrogressive spessartine rich overgrowths. Such rim zones are characterised by strong decrease of the pyrope component (Fig. 3b, c). Staurolite, sometimes twinned and up to 2 mm in size, can be observed. Staurolite within the matrix is not zoned and chemically homogeneous with Fetot/(Fetot + Mg) ratio of 0.87 to 0.91 and 11.7 to 13.4 wt% FeO. Staurolite inclusions in garnet are richer in Fe exhibiting a Fe_{tot}/(Fe_{tot} + Mg) ratio of 0.65 and FeO_{tot} of 26.5 wt%. Biotite defines together with muscovite the main foliation. Single biotites are not zoned. Dependent on the sample, they display only little differences in composition with an overall range of XMg between 0.42 and 0.47 (sample RZ42), and XMg between 0.38 and 0.55 (sample RZ33). Among the microstructures, three different positions of biotite can be distinguished (Tropper and Recheis, 2003): (1) Biotites aligned

along the main foliation, (2) Biotite as inclusions in garnet with evolving Ti-contents from 0.08 to 0.10 (p.f.u.), and (3) Biotite in pressure shadows of garnets formed by the breakdown reaction of garnet = biotite + sillimanite + quartz. These biotites have highest Ti-contents (0.10 - 0.12). Matrix plagioclase shows a trend with An-rich (An₃₀) cores to albite-rich rims (An₅₋₁₀). Plagioclase grains within garnet (An₂₅₋₃₀) and in the pressure shadows (An₁₀₋₂₀) show lower An-contents. Aggregates with sericite are formed by breakdown reaction of staurolite and plagioclase during retrogression.

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The garnet zonations in the metapelite samples represent segments of a common mineralchemical trend, as can be demonstrated in the XMg-XCa coordinates (Fig. 3d). A crystallization of the garnet first at increasing temperature and pressure, then during decompression at amphibolite facies conditions, followed by decompression-cooling can be semiquantitatively derived from the zonations in the XMg-XCa coordinates (Spear, 1993). Cores of garnet and matrix plagioclase as well as relic mica and inclusion minerals in garnet should document the early stage of metamorphism. Late stage metamorphic evolution is preserved in rims of matrix plagioclase and garnet and plagioclase and large biotite in pressure shadows and microlithons. Thus, representative and distinct single analysis of garnet, plagioclase and biotite were chosen in each sample and labeled in the zonation diagrams (Fig. 3a-d, Table 1). Each single garnet zonation trend represents a segment in the overall P-T evolution. Accordingly, the garnet-biotite Fe-Mg exchange geothermometer and the garnet-plagioclase Ca-net-transfer geobarometers (Hodges and Spear, 1982) were chosen. The latter are established as linearised garnet-alumosilicateplagioclase-quartz (GASP) geobarometers. The datasets are based on internally consistent thermodynamic data given by Hodges and Spear (1982) and Spear and Kohn (1999). P-T were calculated by the program GTB OSX (Spear and Kohn, 1999). Alternatively, temperatures were estimated by the garnet-biotite geothermometers by Battacharya et al. (1992), and Holdaway (2001). Pressures were also calculated with the garnet-aluminosilicate-plagioclase-quartz (GASP) and the garnet-biotite-muscovite-plagioclase (GBMP) geobarometers, enclosing the internally consistent thermodynamic mineral data set (Holland and Powell, 1998), with the activity models for garnet and plagioclase taken from Powell and Holland (1993) and Ganguly et al. (1996), and the empirical re-calibration of the GBMP barometer by Wu (2015).

In detail and dependent on Mn bulk rock compositions, garnet cores started to crystallise at ~ 460 - 500 °C/7 - 8 kbar (Fig. 4a). Then maximal pressures at around 12 kbar were achieved at 680 °C. This was followed by a decompression to 6 kbar, accompanied by only slight cooling to 660 °C. The Mg-poor and Mn-enriched marginal zones of some garnets signal a cooling and decompression toward 590 °C/4 - 6 kbar (Fig. 4a). Geothermobarometric estimates include a minimum error of ± 35 °C and ± 1 kbar (Spear and Kohn, 1999). Thus, resulting errors of thermobarometric calculations are much higher than quantitative systematic error in thermodynamic data and microprobe analysis. If these facts are considered, the P-T path's shape and/or relative $\Delta P/\Delta T$ trends will be obtained. When applied to garnet cores and rims in the samples RZ33 and RZ42, the single P-T segments line up to a clockwise prograde-retrograde P-T path (Fig. 4a).

5.2 Metabasites

Two metabasite samples were selected for mineral chemistry analyses and related geothermobarometry. Sample RZ 24 is an amphibolitized eclogite (Purtscheller, 1978). Garnets are up to 3 mm in diameter in a matrix composed of fine-grained symplectites, green amphiboles, plagioclase, epidote and quartz. Titanite and ilmenite appear as the Ti-bearing phases. From cores to rims the garnets are zoned with decreasing spessartine (Sps 12 to 1 mole%, calculated from mole fraction*100), strongly increasing pyrope (Prp 5 - 25 mole%) at quite constant high grossular (Grs 22 - 25 mole%). This pyrope zonation trend indicates crystallization at increasing temperature. The Mg- and Ca-rich garnet rim compositions are typical of eclogites without coesite. In combination with the symplectites this indicates a former eclogitic stage for the Alpeiner amphibolite unit. Many inclusions of epidote towards the garnet rim are typical. Plagioclases are slightly zoned, sometimes with oligoclase cores, but mostly with albitic compositions at An < 10. Plagioclase is also albitic in the symplectites with secondary clinopyroxene with Jd < 10. Caamphiboles in the metabasites display considerable zonations and compositional variations which can be described best in ^{IV}Al vs. ^{VI}Al coordinates (Fig. 3e) and also in the Si vs XMg nomenclature diagram (Fig. 3f) after Leake et al. (1997). Amphibole cores in sample RZ24 have high ^{VI}Al (~ 3.8)

p.f.u.) of ferro-tschermakite and rims with lower ^{VI}AI (1.0) at similar ^{IV}AI (1.6). In sample RZ37 one observes amphibole cores with Mg-hornblende compositions at ^{VI}AI of 1.5 and ^{IV}AI of 1.2 - 1.6 (p.f.u.). In this sample, amphibole rims and also a second generation of porphyroblasts are actinolites with ^{VI}AI and ^{IV}AI below 0.4 (Fig. 3e,f).

The garnet-clinopyroxene Fe-Mg geothermometer cannot be used for sample RZ24, as the only observed clinopyroxene in the symplectites has low Na (Jd < 10) and no Na-rich clinopyroxene corresponding to the eclogitic stage remained preserved. The dependence of Si and ^{IV}Al on temperature and ^{VI}Al on pressure in Ca-amphiboles in assemblages with plagioclase, epidote, quartz, ilmenite and/or titanite can be used for P-T estimates. The amphibole-bearing assemblages in samples RZ24 and RZ match the requirements for the application of the geothermobarometer of Zenk and Schulz (2004) which involves experimental data listed by Gerya et al. (1997). Accordingly, the zoned ferro-tschermakitic to tschermakitic amphiboles in sample RZ24 crystallized during a nearly isothermal decompression from 11 to 6 kbar at 680 - 600 °C (Fig. 4b). The Mg-hornblende and actinolites in sample RZ37 crystallized at mainly decreasing temperatures from 600 to 400 °C/4 - 2 kbar (Fig. 4b). The P-T estimates from the metabasites contribute with retrograde P-T segments to the overall clockwise P-T path of the Alpeiner series.

6. Monazite ages and mineral chemistry

In the garnet micaschists the monazite appears in different grain sizes and microstructural associations (Fig. 6). Grains with an elongated shape and an average length of 200 μ m and width of 50-150 μ m allowed for up to 15 single spot analysis. The grains are parallel to S₂ foliation. Large monazite with slightly embayed grain boundaries show partly darker zones in the backscattered electron (BSE) images (Fig. 5a, b). The single ages in these large grains vary from Carboniferous to Permian (320 - 250 Ma), with Permian weighted average ages. No systematic variation of the ages with the darker core and the lighter rim zones with higher ThO₂ contents are observed. A strongly embayed large monazite gives a Triassic weighted average age due to numerous Jurassic to Cretaceous single ages apart from the Permian ages (Fig. 5c). In samples RZ31 and RZ29, one

observes Permian monazite with the double corona structure by apatite and allanite. The apatite-allanite corona structures around Permian monazite (Fig. 5d-f) are interpreted as an indicator for monazite decomposition. Monazite is progressively replaced in stages by apatite accompanied by formation of allanite surrounding apatite. The initial stage of corona formation is characterized by single tiny apatite grains which have crystallized between an allanite corona and monazite (Fig. 5d). The next stage is a continuous corona of apatite around monazite, which itself is surrounded by a mantle of allanite. The allanite mantle is composed of crystals with radial orientation (Fig. 5d-f). This can be explained by pseudomorphic partial replacement of the original monazite by apatite and allanite via a fluid-mediated coupled dissolution-precipitation process (Harlov et al., 2011; Budzyń et al., 2011). At the present stage of knowledge, such monazite corona structures are generated during decreasing pressure and temperature (Broska and Siman, 1998; Budzyń et al., 2011; Finger et al., 1998; Krenn and Finger, 2007), and retrogression (Upadhyay and Pruseth, 2012). When the weighted average ages of monazites in the corona structures are compared, a systematic shift from Permian ages in well preserved monazite cores (Fig. 5d) toward Triassic and Jurassic ages in tiny thin monazite relics in the coronas (Fig. 5f) can be stated.

Another microstructural feature are clusters composed of numerous small monazite grains with diameters of mostly < 10 µm (Fig. 5g-h). These small monazite grains are surrounded by allanite. The cluster monazite in association with allanite, plagioclase, mica display mostly Permian to Triassic ages. This arrangement of cluster monazite are distinct from the satellite monazite structure as it was described by Finger et al. (2016). The satellite monazite microstructure are small grains arranged around a larger central grain and is considered as the new crystallization of monazite in a former apatite-allanite double corona structure when monazite stability conditions are attained by re-increasing temperature after a retrogression. In contrast, the monazite clusters apparently pseudomorph large mica. Each of the small monazite grains is embedded and surrounded by allanite. However, at the present limited stage of knowledge about this structure, the Permo-Triassic monazites in the clusters represent at least a period of intense recrystallization.

The monazites in the three studied samples display a diverse mineral chemistry. In the age vs Y_2O_3 plot, monazite in sample RZ29 are mostly high in Y_2O_3 (up to 3 wt%), whereas in sample RZ42 they are mostly low in Y_2O_3 (0.2 - 1.5 wt%). In sample RZ31 the whole compositional range of Y_2O_3 contents occur (Fig. 6a). Overall, the contents of LREE, and also ThO_2 (1.5-6 wt%) and UO_2 (0.1-1.6 wt%) are within the range of metamorphic monazites (Spear and Pyle, 2002, Wing et al., 2003). In the age vs UO_2 , XHREE+Y vs XLREE and also in the $XGdPO_4$ vs $XYPO_4$ plots, overlapping trends are observed in the three samples (Fig. 6b-d). The $XYPO_4$ slightly exceed the limit of the garnet zone or garnet isograd as given by Pyle et al. (2001), but do not reach the limit between the sillimanite zone and migmatism (Fig. 6d). The XHutt is negligeable and the XCher in most monazites ranges from 0.05 to 0.15 (not shown). The dominant cheralite exchange (Th or U + Ca = 2 REE) is typical for systems with elevated Ca (Spear and Pyle, 2002). Monazites in sample RZ42 strictly follow the cheralite substitution trend in Th+U vs Ca coordinates (Fig. 6e). In contrast, the monazites in samples RZ31 and especially sample RZ29 with many Triassic ages deviate from the pure cheralite substitution trend and display almost constant Ca at increasing Th+U (Fig.6e).

In the histogram view, the distribution of single spot ages display a prominent maximum in the Permian (280 - 270 Ma) and a second and considerably lower maximum in Triassic times at 230 - 220 Ma (Fig. 6f). Only a few Carboniferous ages appear in the histogram view. Cretaceous ages are also rare. As expressed in the histogram, in the single large grains and the cluster weighted average mean ages (Fig. 5), several isochrons can be defined in the single samples. However, all these isochrones are mainly established by sorting of the data and are characterised by low values of R^2 and weak MSWD. Carboniferous isochrones at 304 ± 26 Ma (sample RZ42) and 321 ± 33 Ma (sample RZ31) are poorly defined and underlined by only a few data (Fig. 7a, b). The Permian age isochrones at 272 ± 15 Ma (RZ42) and 269 ± 13 Ma (RZ31) enclose a considerable number of single ages. For sample RZ29 the Permian isochrone at 252 ± 31 Ma is poorly defined with a few data and most monazite ages fall into the Triassic (202 ± 34 Ma, Fig. 7c). In the other samples, one can also calculateTriassic isochrones at 215 ± 59 Ma and 209 ± 17 Ma, which sometimes can be defined by monazites with lower ThO₂* (Fig. 7a, b)

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7. Discussion and Conclusions

The combination of the thermobarometric results from garnet metapelites and metabasites in the Alpeiner Valley points to a clockwise P-T path which evolved mainly in the high-pressure amphibolite-facies. The prograde P-T path started in the kyanite stability field. Maximal pressures and temperatures range around 12 kbar and 680 °C. Then the P-T path passed the sillimanite field at decreasing pressure. Zoned green amphiboles recorded conditions from 4 - 5 kbar/600 °C to 2 kbar/400 °C, indicating a retrograde P-T path which entered the andalusite stability field (Fig. 8a). This matches the observation of the three alumosilicates in sample RZ42, where and alusite overgrows the fabric at a late stage of the evolution. By a comparison to P-T data and paths from garnet metapelites in adjacent parts of the Oetztal-Stubai Complex (e.g., Schulz, 1994; Tropper and Recheis, 2001; Rode et al., 2012), it appears likely that the amphibolite-facies metamorphism in the Alpeiner Valley matches the Variscan (Carboniferous) event described from the Sellrain, Umhausen and Sölden areas (Fig. 8a). It was not possible to constrain eclogite facies P-T conditions in the Alpeiner Valley metabasites, as it has been described from the Central Metabasite Zone (CMBZ) in the Oetztal (Miller and Thöni, 1995; Rode et al., 2012). Omphacite with high jadeite contents was not preserved in the Alpeiner Valley metabasites. However, the pervasive occurrence of symplectites with low jadeite bearing clinopyroxene demonstrates that the metabasites should have experienced somewhat higher pressures as were actually recorded by the green amphiboles.

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It appears tempting to relate the pressure-dominated amphibolite-facies metamorphism in the Alpeiner Valley to the pervasive crystallisation of Permian to Triassic monazites. However, the similarity of the P-T path from the Alpeiner Valley to the Carboniferous P-T paths from the Oetztal (Fig. 8a) counts against such an interpretation. Also the monazite phase stability limits should be considered in this discussion. Studies in amphibolite-facies metapelites have identified a major pulse of monazite growth, which could be linked to the breakdown of garnet at decreasing pressure (Pyle and Spear, 1999; Pyle et al., 2001; Spear, 2010). In fact, the P-T record in the metapelite garnet ceased during decompression. This could explain the wide variety of Y in

monazite which crystallized subsequent to the garnet and which could have incorporated the Y from decomposed garnet. According to Janots et al. (2007), Spear (2010), Spear and Pyle (2010) and Goswami-Banerjee and Robyr (2015), monazite is stable under amphibolite-facies conditions. The temperature-dependent univariant allanite-monazite equilibrium with the monazite stability limit is qualitatively shifted toward lower temperature with decreasing Ca and increasing Al in the bulk rock (Fig. 8a). Within this frame, monazite should have crystallized when the actual P-T path passed the allanite-monazite stability limit at decreasing pressure (Fig. 8a). Considering XCa and XAn in garnet and plagioclase, and the occurrence of the metapelite layers within a rock suite dominated by metabasites, the Alpeiner Valley garnet micaschists should have considerably higher bulk rock Ca when compared to the aluminous micaschist samples at Umhausen, Sölden and Sellrain as reported by Rode et al. (2012). This implicates that most of the Alpeiner Valley monazite should have crystallized at comparably lower pressures and at a late stage, when the decompression P-T path passed from the sillimanite to the andalusite stability field (Fig. 8a). If this is accepted, the P-T evolution within the kyanite and sillimanite stability fields should be also Carboniferous in the Alpeiner Valley, as was similarly reported from the adjacent Sellrain, Umhausen and Sölden micaschists (Rode et al., 2012). Monazite isochrones at 324 ± 27 Ma (sample RZ31) and 304 ± 26 Ma (sample RZ42) support this interpretation. These poorly defined isochrones (Fig. 7a, b) are assembled by disperse single monazite analyses within larger grains. The bulk of monazite analyses is related to isochrones at 272 ± 15 Ma and 260 ± 12 Ma, partly with a broad cluster of the data around the regression, and a maximum in the histogram at ~270 Ma (Fig. 7b, c, 8b). One sample (RZ29) displays a Triassic isochrone (Fig. 7a), however, in the histogram view a sub-maximum of ages appears at ~220 Ma (Figs 5f, 8b). When compared to the monazite age data from the Sellrain, Umhausen and Sölden regions (Rode et al., 2012), with their unimodal age distributions around 317 ± 5 Ma, the mostly Permian Alpeiner Valley monazites apparently indicate a distinct thermal event in the histogram distribution (Fig. 8b). However, in the Alpeiner Valley on one hand large Permian monazite grains were consumed during retrogression in the double corona structures. On the other hand, the monazite cluster structures support a new

crystallization of monazite in domains of allanite. Their age pattern also differs from observations

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from the Austroalpine basement to the south of the Tauern Window, where bimodal Carboniferous and Permian monazite age distributions occur (Krenn et al., 2012). The monazite age pattern of Alpeiner Valley also differs from the Eclogite Unit of the Saualpe to the E of the Tauern Window, where Cretaceous monazite is abundant apart a Permian population (Schulz, 2016). Permian metamorphic and magmatic ages have yet been mainly reported from Austroalpine basement domains where numerous intrusions of Permian pegmatites occurred (Schuster et al., 2001; Schuster and Stüwe, 2008, and references therein). Evidently, the fluid activity associated to these intrusions enhanced the monazite crystallisation in metapelites, when low pressure and low bulk Ca compositions are given.

There are yet no own observations or reports of pegmatites and Permian pegmatites respectively from the Alpeiner Valley and the OSC nearby. As a consequence, the P-T path and the monazite ages from the Alpeiner Valley may be considered as a link between the Austroalpine domains with exclusively Carboniferous high-pressure amphibolite to eclogite facies metamorphism, and the domains with the Permian event evidently manifested by the pegmatites. The observations from the Alpeiner Valley also indicate that a distinct Permian to Triassic thermal event appeared after a precedent Carboniferous collisional crustal thickening, as proven by clockwise P-T paths.

The nature and geodynamic significance of a Permian to Triassic event in the Austroalpine and also Southalpine basement units has been increasingly discussed with the emerging new age data and the re-interpretation of existing data (Schuster et al., 2001). According to Schuster and Stüwe (2008), the Permian event can be related to (1) intrusion of Permian gabbros into the middle and lower crust, (2) granite and pegmatite intrusions at mid-crustal levels, (3) quartz-andalusite veins and (4) Permian volcanics. These Permian magmatic features are possible in an extensional tectonic cycle as outlined by Schuster and Stüwe (2008). The P-T data from the Alpeiner metamorphic rocks provide no detailed resolution of the Permian to Triassic event in terms of a reheating and then further cooling path at low pressures. However, the monazite age data at least documents a prolonged, decelerated, and possibly more complex post- Permo-Triassic history subsequent to the Carboniferous amphibolite facies stage. By comparison to P-T-t data from the

523 adjacent Oetztal, it is also evident that monazite age data not necessarily refers to the garnet 524 crystallization during the main metamorphic event in the basement, but can give witness to a 525 subsequent geodynamic evolution at lower pressures. 526 527 528 Acknowledgements 529 The electron-microprobe monazite dating and silicate analyses required long-term analytical 530 sessions with technical assistance through D. Heger, Institut für Werkstoffwissenschaft der TU 531 Freiberg. Support at the SEM studies in the Laboratory of Geometallurgy at Freiberg was provided 532 by K. Bachmann and S. Haser. R. Zimmermann thanks the team of Franz-Senn Hütte for 533 hospitality during field work in 2013. 534 535 536 References 537 Bhattacharya, A., Mohanty, L., Maji, A., Sen, S.K. and Raith, M., 1992. Non-ideal mixing in the 538 phlogopite-annite binary: constraints from experimental data on Fe-Mg partitioning and a 539 reformulation of the garnet-biotite geothermometer. Contributions to Mineralogy and Petrology, 540 111, 87–93. 541 542 Broska, I., and Siman, P., 1998. The breakdown of monazite in the West-Capathian Veporic 543 orthogneisses and Tatric granites. Geologica Carpathica, 49, 161–167. 544 545 Budzyń, B., Harlov, D.E., Williams, M.L. and Jercinovic, M.J., 2011. Experimental determination of 546 stability relations between monazite, fluorapatite, allanite, and REE-epidote as a function of 547 pressure, temperature, and fluid composition. American Mineralogist, 96, 1547–1567. 548 http://dx.doi.org/10.2138/am.2011.3741 549 550 Cardozo, N. and Allmendinger, R.W., 2013. Spherical Projections with OSXStereonet. Computers

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Figure 2: (a) Geological sketch map of the area W of Franz-Senn-Hütte in the Alpeiner Valley, Austroalpine Oetztal-Stubai basement, with sampling locations referred to in the text. See details in Fig. S1.

Figure 3: (a) Map of energy dispersive X-ray (EDX) spectra in garnet micaschist. Spectra for garnet porphyroblasts are labelled in a generic way by Fe, Mg, Mn, and Ca contents in normalised element wt%. Bt - biotite; Grt - garnet; Locations of analytical profiles and traces of foliations S₁i and S₂ are marked. Numbers are EMP analyses along profiles. (b, c) Zonations in micaschist garnet including almandine (Alm-50 %, due to scale), pyrope (Prp), grossular (Grs) and spessartine (Sps) components (in mole %). Numbers are selected garnet analyses used for geothermobarometry. The profiles are labelled from the cores (c) to the rims (r) of garnet. (d) Garnet zonations in XMg-XCa coordinates. Arrows indicate core-to-rim (c, r) zonation trends from single garnet profiles. Numbers are selected garnet analyses for geothermobarometry. The garnet XMg-XCa zonations refer to the semiquantitative pressure-temperature trends A (heating-compression), B (heating-decompression) and C (isothermal decompression), as outlined in Spear (1993). (e) Mineral chemistry and zonations of Ca-amphibole in metabasite samples, according to Leake et al. (1997). (f) Ca-amphibole zonations in ^{IV}Al vs ^{VI}Al coordinates, with relative *P-T* trend. c1, c2 - cores, r1, r2 - rims of amphiboles.

Figure 4: (a) Geothermobarometry and *P-T* estimates from garnet micaschists. Crosses mark results from garnet-biotite (Grt-Bt) thermometers and GASP and GBMP barometers (HP - Holland and Powell (1998); SK - Spear and Kohn (1999); Wu - Wu (2015). See text and Table 1 for details and combination of analyses. Arrow indicate P-T trend given by combination of data from samples RZ33 and RZ42. The aluminosilicates (And, Ky, Sill), cordierite-in (Cd+), muscovite-out (Ms-) and staurolite-in and -out (Sta+, Sta-) univariant lines are after Spear (1993). Bold cross at lower right marks a general uncertainty of ± 50 °C/1.0 kbar. (b) Geothermobarometry and P-T estimates (crosses) from amphibolitized eclogite (RZ24) and amphibolite (RZ37), by the Ca-amphibole equilibria geothermobarometer (ZS) by Zenk and Schulz (2004). Isopleths for jadeite (Jd10)

content in clinopyroxene after Holland (1980; 1983). The arrow combines the *P-T* data from garnet micaschists to data from metabasites.

Figure 5: Microstructures of monazite in backscattered electron images (BSE). Numbers are single Th-U-Pb ages in Ma. Weighted averages with 2 sigma error are calculated from several analyses within a grain. (a) Large monazite (Mnz) with slightly embayed rims and patchy darker core zones, with Permian and Triassic ages. (b) Large monazite with patchy darker core zone. (c) Embayed large monazite with darker domains and numerous Mesozoic single ages. (d) Initial stage of corona structure around a Carboniferous-to-Permian monazite with apatite (Ap) and allanite (Aln) along the margin. (e) Progressed stage of corona formation with broad apatite zones; weighted average ages are Triassic. (f) Late stage of corona formation with broad apatite and allanite rims and thin relic monazite with Triassic ages. (g) Large cluster of small monazite grains which are surrounded by allanite. (h, i) Details of monazite cluster arrangement with allanite rims around all small monazite grains. The monazite cluster is embedded in coarse-grained matrix with biotite (Bt), plagioclase (PI) and quartz (Qtz).

Figure 6: Mineral chemistry of monazite and distributions of monazite Th-U-Pb chemical ages. (a, b) Monazite mineral chemistry vs age for each sample. (c) Monazite LREE and HREE compositions in mole fractions. (d) Diagram *X*GdPO4 vs *XYPO*4, with compositions above the garnet (Grt) metamorphic mineral zone as defined by Pyle et al. (2001). Moles calculated according to Pyle et al. (2001). (e) Monazite compositions in reference to the cheralite substitution trend, note different trends in samples RZ29 and RZ31. (f) Histogram with distribution of single monazite ages to Permian (280 - 270 Ma.) and Triassic (220 - 210 Ma) populations.

Figure 7: Th-U-Pb chemical model ages of monazite (Mnz). Total ThO₂* vs PbO (wt.%) isochrons diagrams. ThO₂* is ThO₂ + UO₂ equivalents expressed as ThO₂. General minimal 2σ error on monazite PbO analysis is shown by a bar. Regression lines with the coefficient of determination R² are forced through zero (Suzuki et al., 1994; Montel et al., 1996). Weighted average ages (Ma) with MSWD and minimal error of 2σ are calculated from single analyses according to Ludwig

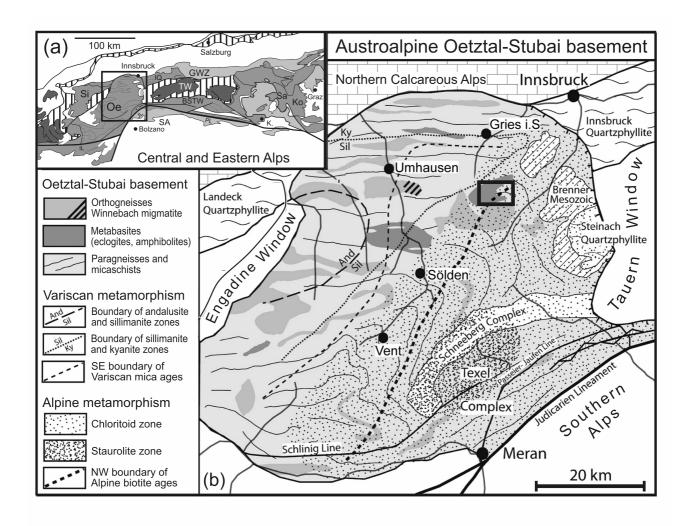
(2001). The symbols mark analyses belonging to monazite age populations and defining isochrones, falling into Carboniferous, Permian and Triassic ranges of ages.

Figure 8: (a) P-T-t evolution and monazite ages in the Stubai region (Alpeiner Valley), compared to data from the Oetztal basement to the west, given in Rode et al. (2012). Segments of the P-T path are marked with EMP monazite ages, and data from eclogites in Miller and Thöni (1995). Stability fields for kyanite (Ky), andalusite (And), sillimanite (Sil) after Spear (1993). stability fields of monazite (Mnz) and allanite (Aln) at different bulk rock contents as a function of Ca wt %, and with the xenotime (Xtm+) stability field (Janots et al., 2007; Spear, 2010).

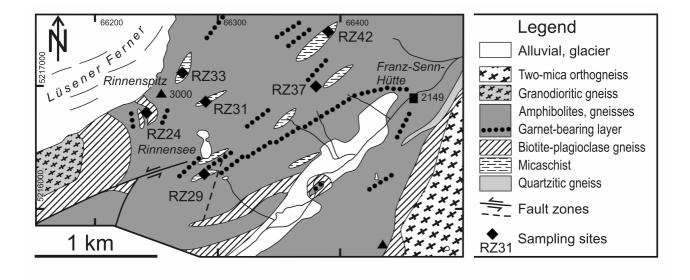
(b) Frequency distribution (recalculated to percent) of the EMP-Th-U-Pb monazite ages in Stubai (Alpeiner Valley) as reported in Fig. 5f, compared to data from the Oetztal regions to the W, as reported in Rode et al. (2012).

Table 1: Electron microprobe analyses (wt.%, p.f.u.) of garnet (Grt), biotite (Bt), muscovite (Ms) and plagioclase (PI) in micaschists and gneisses from the Austroalpine Oetztal-Stubai basement, Alpeiner Valley around Franz-Senn-Hütte, normalized to 12 oxygen (garnet), 11 oxygen (biotite, muscovite) and 8 oxygen (plagioclase). Almandine (Alm), anorthite (An), grossular (Grs), pyrope (Prp), spessartine (Sps) contents in mole %. Mineral analyses combined for geothermobarometric calculations are as follows: Sample RZ33: Grt31–Bt119–PI73; Grt4–Bt108–PI170: Sample RZ42: Grt245–Bt161–Ms187–PI171; Grt104–Bt161–Ms187–PI171; Grt84–Bt247–Ms187–PI203; Grt77–Bt247–Ms187–PI203.

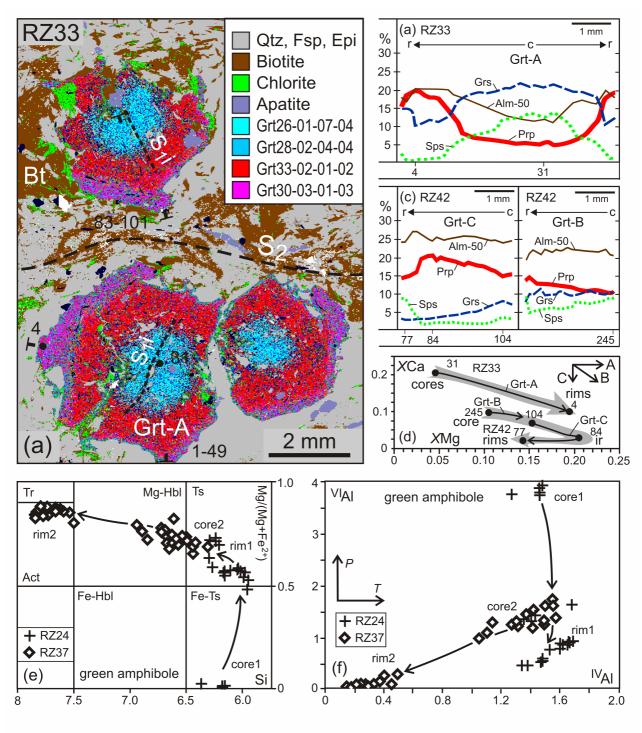
Table 2: Electron microprobe analyses of metamorphic monazite from metapelites of the Oetztal-Stubai basement in the Alpeiner Valley around Franz-Senn-Hütte. Th* is calculated from Th and U after Suzuki et al. (1994). Monazite ages from single analyses are given with 2sigma error. Mnz monazite single grain; Data from reference standard monazite Madmon (Schulz and Schüssler, 2013) is weighted average of 18 single analyses performed during the sessions on the samples.



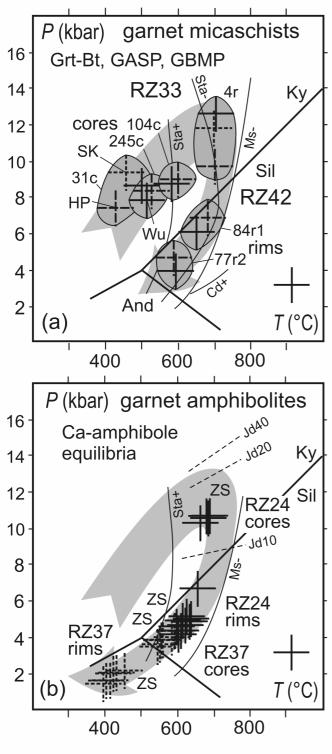
Schulz-Zimmermann-Fig 1



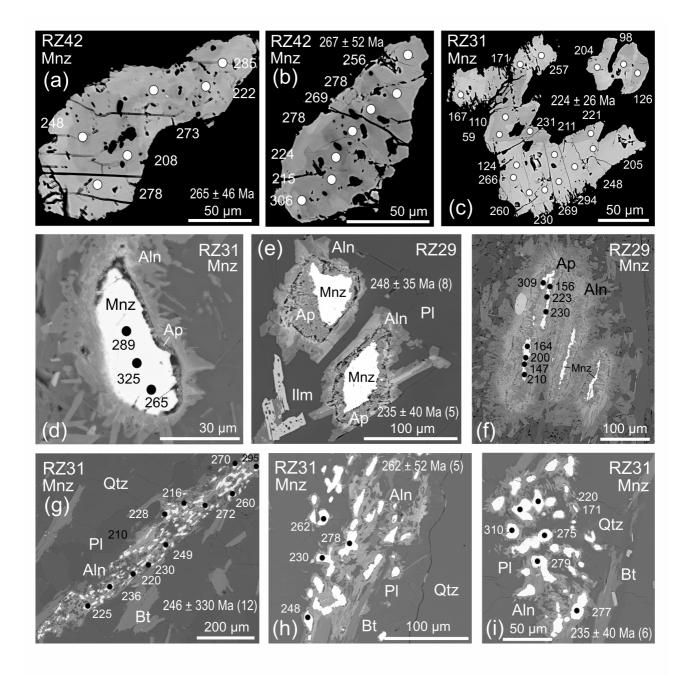
Schulz-Zimmermann-Fig 2



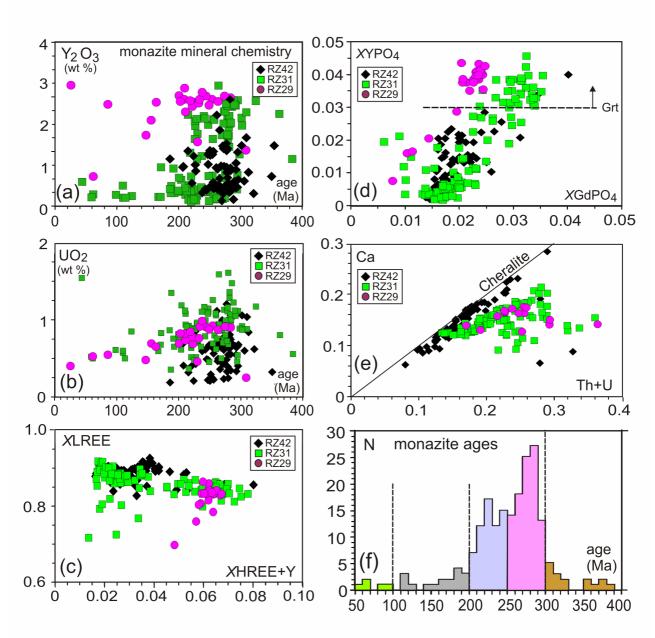
Schulz-Zimmermann-Fig 3 - online



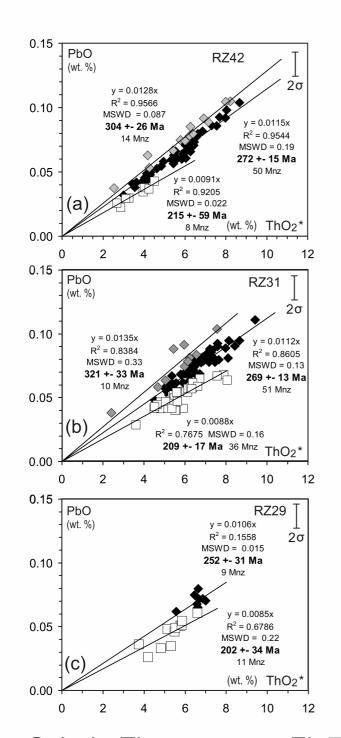
Schulz-Zimmermann-Fig 4



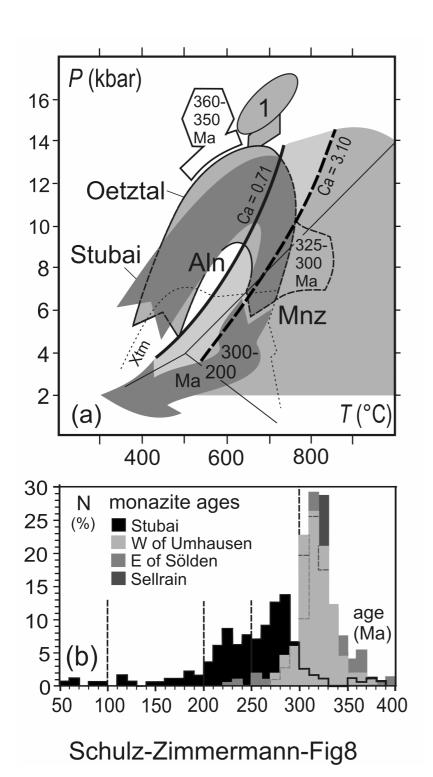
Schulz-Zimmermann-Fig5



Schulz-Zimmermann-Fig6



Schulz-Zimmermann-Fig7



974 Schulz-Zimmermann-Table 1

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Table 2																				
Sample	SiO ₂	P ₂ O ₅	CaO	Y ₂ O ₃	La ₂ O ₃	Ce ₂ O ₃	Pr ₂ O ₃	Nd ₂ O ₃	Sm ₂ O ₃	Gd ₂ O ₃	ThO ₂	UO ₂	PbO	Total	Th	U	Pb	ThO ₂ *	Age	± 2σ
RZ29-4	0.34	30.29	19.01	1.17	9.61	19.85	2.62	9.85	1.77	1.30	2.27	0.456	0.036	99.02	1.99	0.402	0.034	3.740	230	164
RZ29-8	0.15	29.50	1.75	2.16	12.87	27.76	3.52	13.75	2.60	1.89	3.14	0.816	0.051	100.56	2.76	0.720	0.047	5.770	210	106
RZ29-m2-1	0.13	29.68	1.35	1.95	12.67	27.47	3.46	13.76	2.55	1.91	3.70	0.920	0.071	100.25	3.25	0.811	0.066	6.671	254	92
RZ29-m2-10	0.16	29.51	1.51	1.89	12.99	27.39	3.41	13.54	2.47	1.78	4.15	0.762	0.065	100.25	3.64	0.672	0.060	6.607	233	93
RZ29-m2-11	0.16	29.77	1.35	1.93	12.83	27.47	3.51	13.66	2.60	1.81	3.87	0.846	0.061	100.49	3.40	0.746	0.056	6.596	219	93
RZ29-m2-9	0.20	29.68	1.29	2.01	12.61	27.34	3.53	13.94	2.65	1.87	3.51	0.911	0.075	100.28	3.09	0.803	0.069	6.462	274	95
RZ31-m1-12	0.21	29.61	1.33	1.68	12.58	28.04	3.19	12.72	2.61	2.30	3.35	0.802	0.091	99.15	2.94	0.707	0.085	5.963	363	103
RZ31-m1-13	0.69	29.42	2.48	1.62	12.60	27.06	3.03	12.23	2.40	2.10	3.59	0.915	0.084	98.81	3.15	0.806	0.078	6.554	302	94
RZ31-m1-4	0.15	28.48	1.66	0.34	12.74	29.07	3.24	12.96	2.40	1.57	3.42	0.888	0.059	97.60	3.01	0.783	0.054	6.287	221	98
RZ31-m1-5	0.13	29.69	0.92	0.54	13.33	30.01	3.49	13.92	2.78	1.80	2.75	0.635	0.044	100.68	2.42	0.560	0.041	4.803	220	128
RZ31-m1-6	0.17	29.43	1.12	1.17	12.98	28.42	3.22	12.95	2.73	2.29	3.57	0.684	0.068	99.46	3.14	0.603	0.064	5.788	280	106
RZ31-m1-7	0.15	29.43	1.32	1.44	12.71	28.13	3.11	12.74	2.80	2.26	3.81	0.998	0.083	99.72	3.34	0.879	0.078	7.037	281	87
RZ31-m1-8	0.17	29.34	1.43	1.49	12.45	27.43	3.14	12.70	2.77	2.38	3.94	1.146	0.080	99.27	3.46	1.011	0.074	7.644	248	80
RZ31-m10-12	0.34	29.31	1.12	0.85	13.82	29.17	3.47	13.31	2.45	1.55	3.28	0.961	0.062	100.33	2.88	0.847	0.057	6.380	230	96
RZ31-m10-13	0.34	29.17	0.89	0.09	14.52	30.67	3.52	14.10	2.40	1.33	2.85	0.514	0.042	100.89	2.50	0.453	0.039	4.503	220	136
RZ31-m12-4	0.13	29.61	1.23	1.72	12.87	28.40	3.41	13.53	2.51	1.90	3.36	0.881	0.081	100.23	2.95	0.777	0.076	6.219	310	99
RZ31-m12-6	0.27	29.66	1.24	1.31	12.81	28.54	3.44	13.77	2.58	1.88	3.32	1.163	0.083	100.73				7.087	279	87
RZ31-m14-1	0.13	29.71	1.34	1.48	13.47	28.70	3.41	12.87	2.29	1.86	3.32	0.871	0.078	100.14	2.92	0.767	0.073	6.146	303	100
RZ31-m4-19	0.19	29.38	1.54	0.21	13.53	29.44	3.39	13.03	2.42	1.41	4.22	0.915	0.078	100.37	3.71	0.806	0.072	7.181	257	85
RZ31-m5-4	0.26	29.92	1.49	1.85	12.51	27.45	3.25	12.76	2.60	2.27	3.31	1.068	0.081	99.54	2.91	0.941	0.075	6.774	284	91
RZ31-m9-2	0.20	29.40	1.47	1.59	12.74	27.92	3.40	13.66	2.81	2.39	2.67	0.919	0.054	99.98	2.35	0.810	0.051	5.636	229	109
RZ42-m1-1	0.21	29.50	1.05	0.46	14.18	29.25	3.63	14.38	2.58	1.54	3.94	0.660	0.075	101.46	3.46	0.582	6.077	0.069	291	101
RZ42-m1-2	0.20	29.32	0.88	1.02	14.27	29.45	3.73	14.15	2.54	1.58	3.46	0.210	0.044	100.85	3.04	0.185	4.136	0.041	251	148
RZ42-m10-3	0.17	29.40	1.11	0.65	14.00	28.93	3.48	14.32	2.62	1.65	4.22	0.553	0.072	101.17	2.47	0.408	4.309	0.044	284	102
RZ42-m10-4	0.28	29.14	1.43	0.25	14.17	29.17	3.57	14.09	2.61	1.44	4.13	0.593	0.061	100.93	5.30	0.345	7.304	0.080	238	102
RZ42-m12-4	0.18	29.24	0.84	1.01	14.22	28.65	3.52	13.81	2.94	2.45	2.18	1.202	0.071	100.32	2.97	0.199	4.112	0.041	278	101
RZ42-m13-11	0.22	29.11	0.91	0.38	14.44	29.72	3.64	14.14	2.51	1.35	3.56	0.640	0.060	100.67	3.62	0.605	6.346	0.071	255	109
RZ42-m13-12	0.27	29.31	1.04	0.23	14.38	29.23	3.64	14.26	2.60	1.41	4.26	0.619	0.085	101.33	3.71	0.488	6.009	0.067	322	98
RZ42-m13-8	0.13	29.29	1.20	0.62	14.00	28.73	3.59	13.98	2.47	1.46	4.20	0.837	0.092	100.62	3.63	0.523	6.043	0.056	313	88
RZ42-m14ig2	0.25	29.27	1.36	1.11	12.92	27.70	3.48	13.57	2.65	2.08	4.79	1.056	0.105	100.34	1.15	0.375	2.687	0.024	302	75
RZ42-m15-3	0.18	29.39	1.34	0.12	14.24	29.20	3.53	13.69	2.39	1.09	4.62	1.054	0.098	100.96	1.92	1.060	6.072	0.066	289	76
RZ42-m4-4		29.38	0.83	0.68	14.74	30.06	3.65	14.20	2.65	1.56	2.81	0.462	0.048	101.19	3.13	0.564	5.628	0.056	263	142
RZ42-m5-1	0.26	29.18	1.46	0.52	13.68	28.46	3.55	13.49	2.43	1.24	6.04	0.391	0.086	100.79	3.74	0.545	6.271	0.079	279	84
RZ42-m6-1	0.26	29.17	0.97	0.46	15.08	29.62	3.61	13.67	2.39	1.38	3.85	0.599	0.075	101.13	3.70	0.738	6.924	0.085	306	106
RZ42-m7-1	0.26	29.10	1.03	0.36	14.49	29.25	3.62	13.91	2.54	1.40	4.12	0.687	0.077	100.83	4.06	0.929	8.039	0.091	287	97
Madmon-18	3.15	25.07	0.14	0.98	7.91	25.20	4.01	15.96	4.64	2.24	10.92	0.383	0.262	100.98	9.59	0.344	0.242	12.195	504	15

