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| 1  | New evidence for the prograde and retrograde PT-path of high-pressure granulites,  |
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| 2  | Moldanubian Zone, Lower Austria, by Zr-in-rutile thermometry and garnet diffusion  |
| 3  | modelling  |
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#### **ABSTRACT**

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Compositional zoning in garnet, mineral inclusions and the application of the Zr-in-rutile thermometry on rutile inclusions in garnet in combination with conventional geothermobarometry and thermodynamic modelling allows a reconstruction of the prograde pressure-temperature evolution in felsic and mafic high-pressure granulites from the Moldanubian Zone, Bohemian Massif, Lower Austria. Most garnets in these rocks show homogeneous core compositions with high grossular contents (~30 mol.%), while their rim zones have a markedly reduced grossular content. Rutile inclusions in the grossular rich garnet cores have low Zr concentrations (400 to 1300 ppm) indicating a formation temperature of ~810–820 °C which implies that the garnet host grew at these temperature conditions as well. Based on numerous polycrystalline melt inclusions, high Tibiotite relics and a generally high Ti concentration in garnet cores, the peritectic biotite breakdown reaction is considered to be responsible for a first garnet growth, now observed as high-grossular garnet cores. The corresponding pressure is estimated to be in the range of 1.6 to 2.5 GPa, based on experimentally determined biotite breakdown reactions, thermodynamic modelling and the occurrence of high-Ti biotite in garnet cores. Rutile inclusions in low-Ca garnet rims contain significantly higher Zr concentrations (1700 to 5800 ppm) resulting in ultrahigh temperatures of ~1030 °C. Similar temperature as well as corresponding pressure estimates of 1000  $\pm$  50 °C and  $1.60 \pm 0.10$  GPa were obtained by geothermobarometry and thermodynamic modelling using garnet rim and re-integrated ternary feldspar compositions. These high pressure and ultrahigh temperature conditions are well known from literature for these granulites. The proposed two-phase garnet growth is not only seen in different temperatures obtained from rutile inclusions in garnet core and rim areas, but also in discontinuous trace (Cr, Ga, P, Ti, V, Zr) and heavy rare earth element profiles across garnet porphyroblasts, implying a different reaction mechanism for garnet rim growth. This second phase of garnet growth must have occurred during near isobaric heating to the ultrahigh temperature peak, most likely even at slightly lower pressures compared to the garnet core growth.

By applying a binary Fe-Mg diffusion model to strongly zoned garnet grains a maximum timescale of 5-6 million years was estimated for the exhumation and cooling process, assuming a linear cooling path from 1000 °C at 1.6 GPa to 760 °C at 0.8 GPa. This short-lived ultrahigh temperature event corresponds to cooling and exhumation rates of 40–50 °C Ma<sup>-1</sup> and 5.3–6.6 mm y<sup>-1</sup>, respectively. Keywords: Bohemian Massif; Moldanubian granulite; prograde metamorphic evolution; Zr-in-rutile thermometry; rapid exhumation/cooling 

#### 1. INTRODUCTION

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Ultrahigh-temperature (UHT) metamorphism is defined as a sub-division of the granulite facies (700–1000 °C and 0.3–1.5 GPa) where rocks are subjected to extreme temperatures of more than 900 °C (Harley, 1998). More than forty occurrences of UHT rocks have been documented so far, for instance in the Highland Complex in Sri Lanka (e.g. Osanai et al., 2006), the Oygarden Complex in Antarctica (Kelly and Harley, 2004), the Labwor Hills in Uganda (Sandiford et al., 1987), the Lewisian Complex in Scotland (Baba, 2003), the Gruf Complex in Italy (Droop and Bucher-Nurminen, 1984), the Peekskill, New York, USA (Caporuscio and Morse, 1978), the Saxonian Granulite Massif (Rötzler and Romer, 2001; O'Brien and Rötzler, 2003) and the Moldanubian Zone of the Bohemian Massif in Austria and the Czech Republic (Carswell and O'Brien, 1993; Kotková and Harley, 1999; Cooke, 2000; Cooke et al. 2000; Janousek et al., 2004; Vrána et al., 2005). Studying the petrogenesis and the geological (tectonic) evolution of UHT rocks is a challenge, due to the fact that high peak temperatures erase nearly all traces of the incipient metamorphic PT path (e.g. Carswell and O'Brien, 1993; Hauzenberger et al., 2005; Jedlička et al., 2015). The rapid reaction kinetics at high temperatures causes most pre-UHT mineral phases to decompose and even stable minerals like garnet re-equilibrate by solid state diffusion where chemical zoning pattern as a consequence of prograde growth is erased. Only in case of a short residence time at high peak conditions, and in a fluid/melt poor environment, there is a chance that minerals from the prograde metamorphic stage survive. For instance, Cooke et al. (2000) documented the preservation of early, prograde high-Ca garnet cores surrounded by high-Mg garnet mantle and Zack et al. (2004) and Usuki et al. (2017) showed that Zr-in-rutile thermometry gives meaningful results for prograde rutile relics in garnet. The focus of this study are felsic to mafic UHT granulites from the Austrian part of the Bohemian Massif. The high-grade metamorphic nature of these rocks was recognized many years

ago (Scharbert and Kurat, 1974). Later work by Carswell and O'Brien (1993), Cooke et al. (2000) and Cooke (2000) has highlighted a very complex polyphase PTt (pressure-temperature-time) evolution of these rocks, involving a HP-HT (high-pressure and high-temperature) granulite facies stage (~1000 °C and ~1.6 GPa), subsequent near isothermal decompression to intermediate granulite facies conditions (900 °C, 1.0 GPa), and final cooling to amphibolite facies conditions with significantly lower exhumations rates.

More recently Faryad et al. (2010) postulated that granulites in the Bohemian Massif experienced an eclogite facies PT-path prior to the HP-HT granulite facies stage. Based on coesite and microdiamond inclusions in garnets, Perraki and Faryad (2014) reported UHP metamorphic conditions of about 3.2–4.0 GPa (at 700 °C) for granulites in the Czech part of the Bohemian Massif. Whether the granulites in the Austrian part of the Moldanubian Zone experienced a similar eclogite facies prograde metamorphic evolution, is controversially debated. Carswell and O'Brien (1993) argued that an eclogite facies imprint on these rocks is unlikely due to the lack of clear eclogite facies textures and mineral assemblages in metabasic rocks directly enclosed within these granulites.

In this study, we present new evidence for the prograde evolution of the Moldanubian granulites from the Pöchlarn-Wieselburg, Dunkelsteinerwald and Zöbing areas, Lower Austria, based on major and trace element zoning patterns of garnets, and by investigating the inclusions preserved in the garnets, with particular emphasis on Zr-in-rutile thermometry. In addition, we model the retrograde Fe-Mg diffusive re-equilibration of garnet based on detailed microprobe profiles to quantify the fast exhumation and cooling segment of the retrograde path.

#### 2. REGIONAL GEOLOGY

The Variscan orogenic belt is exposed in several large-scale basement blocks which outcrop across western and central Europe (Fig. 1a). The Bohemian Massif is the easternmost of these

| 114 | Variscan basement blocks. The Austrian sector of the Bohemian Massif exposes mainly the                               |
|-----|---|
| 115 | Moldanubian Zone, which is considered to represent the exhumed core of the Variscan orogeny.                          |
| 116 | Regionally, the Moldanubian Zone is subdivided into three tectonic units, the hangingwall Gföhl                       |
| 117 | Unit, the underlying Drosendorf Unit (Variegated Series) and the Ostrong Unit (Monotonous Series)                     |
| 118 | at the bottom (e.g. Fuchs and Matura, 1968). The UHT granulites are part of the Gföhl Unit, and                       |
| 119 | occur in contact to large masses of migmatic gneiss termed the Gföhl gneiss. There is wide                            |
| 120 | agreement that the Gföhl Unit underwent Variscan continental collision and, subsequently, fast                        |
| 121 | exhumation to mid-crustal levels (Finger et al. 2007).  |
| 122 | The Moldanubian granulites in Lower Austria show significant similarities in terms of                                 |
| 123 | lithology and metamorphism to their counterparts in the Czech Republic, which have been more                          |
| 124 | intensively studied in the recent past (e.g. Faryad, 2009; Faryad et al., 2010; Jedlička et al., 2015;                |
| 125 | Usuki et al., 2017). Almost all Moldanubian granulite bodies contain both felsic and mafic types,                     |
| 126 | with estimated peak metamorphic conditions ranging between $850-1100~^{\circ}\text{C}$ and $1.6-2.0~\text{GPa}$ (e.g. |
| 127 | Carswell and O'Brien, 1993; Petrakakis 1997; O'Brien et al., 1997; Kotková and Harley, 1999;                          |
| 128 | Cooke, 2000; Cooke et al., 2000; Cooke and O'Brien, 2001; Štípská and Powell, 2005; Tajčmanová,                       |
| 129 | et al., 2006; Kotková and Harley, 2010).  |
| 130 | U-Pb zircon and Rb-Sr whole rock dating show two distinct age clusters at 490-430 Ma and                              |
| 131 | c. 340 Ma (Arnold and Scharbert, 1973; Frank et al., 1990; Kröner et al., 2000; Friedl et al., 2004,                  |
| 132 | 2011). The Ordovician ages are generally interpreted as the time of protolith formation, the early                    |
| 133 | Carboniferous dates as the age of the UHT stage of metamorphism. A number of ages of around 370                       |
| 134 | Ma, obtained by Sm-Nd garnet geochronology in various granulites and peridotites (Carswell and                        |
| 135 | Jamtveit, 1990; Brückner et al., 1991; Prince et al., 2000) are interpreted to reflect a Devonian HP-                 |
| 136 | UHP event.  |
| 137 |   |
| 138 | 3. METHODS  |

Quantitative mineral analyses were performed on carbon coated thin sections using a JEOL JSM 6310 scanning electron microscope (SEM) at the NAWI Graz Geocenter-Department of Petrology and Geochemistry, University of Graz, Austria equipped with a LINK ISIS energy dispersive system and a MICROSPEC wavelength dispersive system. Additional analyses and chemical maps were obtained using a JEOL JXA-8200 electron probe microanalyzer (EPMA) at the Eugen F. Stumpfl Electron Microprobe Laboratory, UZAG, University of Leoben, University of Graz, Graz University of Technology. BSE images of submicron mineral inclusions were obtained with a JEOL JXA-8530F Plus EPMA at the NAWI Graz Geocenter. Measurement conditions of the SEM and EPMA were 15kV acceleration voltage, 10 nA beam current and ~1 µm beam diameter with 20s counting time on peak and 10s on each background.

To ensure that the garnets selected in thin section for compositional profiles have actually been cut through their true cores, we measured the average garnet grain size as seen in the related hand specimen and then chose equivalent sized garnets in the thin section for analysis.

Detailed systematic investigation of mineral inclusions in garnet, zircon and kyanite was conducted using polished thin sections of whole rocks and separated grains embedded in epoxy.

More than 700 garnet, zircon and kyanite grains from different granulite samples were investigated. In order to obtain central cuts through the separated garnet, kyanite and zircon grains only the largest were selected and ground down until their predetermined maximum diameter was reached.

Concentration of Zr-in-rutile was determined using the EPMA with operating conditions of 15kV, 120nA beam current, ~1 µm beam diameter and count times of 60s on peak and 30s on each background. So as to enhance the detection limit, three spectrometers equipped with TAP and PETJ analyzer crystals were chosen to measure the Zr-La ratio. For the trace element Zr-in-rutile thermometer we used the empirically calibration of Zack et al. (2004) as well as the experimentally calibration of Ferry and Watson (2007) and Tomkins et al. (2007).

The original composition of the early, peak hypersolvus ternary feldspar was determined by the re-integration technique of Raase (1998). Following this procedure the host and exsolution

feldspar were analyzed by a slightly defocused microprobe beam to avoid Na loss. The volume percentage of the exsolved phase was determined by computer image analysis of back-scattered-electron (BSE) images and then transformed into weight percentages. The bulk composition of the early, peak hypersolvus ternary feldspar was obtained by combining the weight percentages of both the host and exsolution feldspar phases.

Whole rock compositions were determined by X-ray fluorescence (XRF) on glassy discs using a Bruker Pioneer S4 under standard conditions at the NAWI Graz Geocentre.

Trace elements and REE contents in garnet, apatite and perthitic alkali-feldspar were obtained from polished thin sections using an LA ICP MS (laser ablation inductively coupled plasma mass spectrometer) system at the NAWI Graz Central Lab for Water, Minerals and Rocks, with an ESI New Wave 193 Excimer Laser (193nm wavelength) coupled to an quadrupole Agilent 7500 CX mass spectrometer. The settings for the element analyses were a beam size of 35–50 µm, with a fluence energy of ~4–5 J/cm², helium flow of 0.7 l/min, 30 ms gas blank followed by 60 s of ablation and a dwell time of 30 s for each mass were used for the element analyses. We used NIST SRM 612 glass for standardization. As internal calibration Si and Ca were used for garnet, perthitic alkali-feldspar and apatite, repsectively. The USGS reference glass BCR-2G was analyzed as a monitor standard that could be reproduced within errors. Values of 0.1–0.5 ppm were quantified fairly accurate. For data reduction, the software "GLITTER" was used and the values for NIST SRM 612 were taken from Jochum et al. (2011).

186 (2010).

# 4. PETROGRAPHY AND MINERAL CHEMISTRY

For this study, 225 granulite samples were collected from 62 localities within three granulite bodies in the south-easternmost Moldanubian Zone in Lower Austria. All three granulite bodies

Mineral abbreviations used in subsequent sections of this paper are after Whitney and Evans

formed a coherent granulite occurrence, which is now displaced by the Diendorf Fault system. (21 samples from Zöbing, 101 samples from Dunkelsteinerwald and 103 samples from Pöchlarn-Wieselburg). The sample localities are shown in Figure 1b, with geographical coordinates, lithologies etc. provided in Table A of the supplementary material.

The detailed petrography and textural relations of the Moldanubian granulites in Lower Austria, have been discussed in Carswell and O'Brien (1993), Cooke et al. (2000) and Cooke (2000). Two varieties of granulites are present. The most abundant type is a middle to fine-grained, leucocratic granulite. With the exception of the small granulite body near Zöbing, these felsic granulites are accompanied by subordinate, massive, mafic granulites. Both rock types are acidic in terms of their SiO<sub>2</sub> content but differ in their absolute concentrations. Whilst felsic granulites show 70–77 wt.% SiO<sub>2</sub>, mafic granulites are lower with 63–70 wt.%. In addition, mafic granulites are enriched in CaO, FeO, MgO and depleted in K<sub>2</sub>O resulting in a different HP mineral assemblage (e.g. Fiala et al. 1987; Carswell and O'Brien, 1993).

# 4.1 Felsic granulites

The retained HP granulite facies mineral assemblage in felsic granulites is represented by garnet + kyanite + perthitic alkali-feldspar + quartz, along with accessory rutile, apatite and zircon. This equilibrium assemblage is best preserved in least deformed, very light-coloured samples with partly preserved granoblastic fabrics (Fig. 2a). Red garnet, deep-blue kyanite and perthitic alkalifeldspar, reaching up to 3 mm in size, appear as disseminated coarser grained porphyroblasts enclosed in a strongly recrystallized quartzo-feldspatic matrix (Fig. 2b).

Retrogression accompanied by strong deformation has led to the formation of secondary biotite, sillimanite, ilmenite and recrystallization of the early single-phase perthitic alkali-feldspar into separate K-feldspar and plagioclase. In addition, fine-grained plagioclase (100–300  $\mu$ m in size) within the matrix appear to have formed due to the recrystallization of the early feldspar. Retrograde

biotite predominately occurs within distinct slightly darker bands developed within the very light-coloured felsic granulite (Fig. 2c). Within these bands, fine-grained sillimanite interpenetrates the flaky biotite and rare ilmenite to form elongated masses oriented parallel to foliation, which is mainly defined by quartz ribbons (Fig. 2d, e). The formation of sillimanite and biotite is the result of the continuous reaction garnet + K-feldspar +  $H_2O$  = biotite + sillimanite + quartz. Locally, some sillimanite seems to have been formed by direct replacement of earlier kyanite.

# Garnets

Light red, subhedral garnet porphyroblasts show two different patterns of chemical zoning. Garnet zoning profile type I (Fig. 3a, b and c) appears in felsic granulites with a whole rock composition slightly elevated in CaO (1.80–3.60 wt.%). Their core regions (up to c. 800 μm wide) are homogeneous with a compositional of Alm<sub>41–48</sub>, Pyp<sub>22–27</sub>, Grs<sub>24–36</sub> and Sps<sub>1</sub> (Table 1). In contrary, their rims (up to c. 500 μm wide) with Alm<sub>46–57</sub>, Pyp<sub>24–34</sub>, Grs<sub>7–28</sub> Sps<sub>1</sub> show a marked chemical zonation, where grossular content decreases substantially, matched by an increase in almandine and pyrope as well as an increase in X<sub>Mg</sub>. The spessartine content remains constant along the whole profile. A similar garnet zoning pattern has been reported from leucocratic granulites in the Blanský les Massif, Czech Republic (Kotková and Harley, 2010).

Garnet zoning profile type II (Fig. 3d and e) usually occurs in felsic granulites with slightly lower amounts of CaO 0.60–1.20 wt.% in their whole rock geochemistry. The garnet has a composition in the range of Alm<sub>78–46</sub>, Pyp<sub>44–16</sub>, Grs<sub>4–14</sub> and Sps<sub>1–2</sub> (Table 1) and is characterized by the absence of a wide, homogeneous core. The zonation is also less pronounced with grossular content decreasing gradually from core to the rims, while almandine and pyrope contents increase progressively from core towards the rims. Spessartine content is low throughout the garnet with no obvious zoning.

Small garnet grains in biotite and sillimanite rich domains (Fig. 2d, e) have a general composition of Alm<sub>77</sub>, Pyp<sub>17</sub>, Grs<sub>4</sub> and Sps<sub>1</sub> (Table 1).

Feldspars

Carswell and O'Brien (1993) and O'Brien and Rötzler (2003) documented the occurrence of perthitic alkali-feldspar instead of an early peak ternary feldspar in felsic granulites in the Moldanubian Zone. This perthitic alkali-feldspar recrystallized into K-feldspar and plagioclase during retrogression. Compositional re-integration of the millimeter-sized, perthitic alkali-feldspar porphyroblasts reveals a composition in the range of An<sub>5-11</sub> Ab<sub>17-25</sub> Or<sub>78-64</sub> in our samples (Table 3). Significantly finer-grained plagioclase (100 to 300 μm in size) within the quartz-rich

granoblastic matrix is also interpreted to be the result of recrystallization of the early single-phase feldspar. It has a compositional range between  $An_{17}$   $Ab_{80}$  to  $An_{24}$   $Ab_{75}$  (Table 4).

#### **Biotites**

Biotite, up to 1.5 mm in length, is especially abundant within the slightly darker bands, which pervade the leucocratic granulites (Fig. 2c, d). These biotite flakes have a significant fluorine content, with a maximum of 5.40 wt.% (1.265 apfu) (Table 2). Rare biotites outside the slightly darker bands also show elevated F contents, typically higher than 0.5 wt.%, as reported from similar rocks by Tropper and Hauzenberger (2015).

### 4.2 Mafic granulites

Mafic granulites (Fig. 2f) are not as common as the felsic type. In some places a sharp boundary between both granulites is observed, in other cases gradual changes are noticed (e.g. road outcrop between Aggsbach-Dorf and Wolfstein, E15.423122, N48.292625). The HP granulite facies mineral assemblage is represented by the coexistence of garnet + clinopyroxene + ternary feldspar + quartz, together with accessory rutile, apatite and zircon (Fig. 2g). However, clinopyroxene is not observed as stable phase in the matrix anymore and is only found as inclusion in garnet. Red garnet and antiperthitic plagioclase form homogeneously distributed coarser grains of up to 1.5 mm size,

which are embedded within a recrystallized fine-grained quartzo-feldspathic matrix. Almost all samples of mafic granulites display an intensive retrogression accompanied with the growth of abundant orthopyroxene (Fig. 2g). These orthopyroxene grains were formed during decompression subsequent to the HP granulite facies peak (Cooke, 2000).

In some samples the retrogression and rehydration cause the growth of late stage biotite and amphibole which are locally intergrown with orthopyroxene, small ilmenite and garnet grains (Fig. 2i, j). The formation of these amphibole and biotite grains is due to a garnet and/or orthopyroxene consuming reaction. As a consequence of retrogression, the former single high-temperature feldspar phase recrystallized into antiperthitic plagioclase with irregular intergrowths between plagioclase host (80–74 vol.%) and K-feldspar patches. Fine-grained plagioclase and minor K-feldspar within the matrix are also thought to be formed by recrystallization of the early single-phase peak feldspar and are considered to be part of the retrograde metamorphic assemblage.

283 Garnets

Large garnet porphyroblasts in mafic granulites (Fig. 3f) display a garnet zonation pattern similar to the garnet zonation profile type I seen in felsic granulites. The zonation is characterized by a uniform central high grossular portion (up to 1 mm wide) with a narrow compositional range of Alm<sub>43–46</sub> Pyp<sub>14–16</sub> Grs<sub>39–41</sub> Sps<sub>1</sub> (Table 1). In contrast, their rims (up to 200 μm wide) are strongly zoned with a grossular decrease and pyrope and almandine increase. Their composition is Alm<sub>44–59</sub> Pyp<sub>19–28</sub> Grs<sub>10–36</sub> Sps<sub>1–2</sub>. In some garnets, an increase of X<sub>Mg</sub> at the rim zone is also present. Within the mafic granulites there is always a slight increase in the spessartine content towards the rims of garnets, typical for resorption and back diffusion (Müller et al., 2015). Small garnet grains associated with amphibole, biotite and ilmenite rich patches in some mafic granulites are Alm<sub>63</sub> Pyp<sub>19</sub> Grs<sub>16</sub> Sps<sub>2</sub> (Table 1).

#### **Feldspars**

Coarse grained porphyroblasts (up to 1.5 mm size) of antiperthitic plagioclase occur in a strongly recrystallized, granoblastic matrix. They show an irregular, patchy-like intergrowth between host and exsolution lamellae, with a calculated re-integrated composition of  $An_{39}$   $Ab_{35}$   $Or_{26}$  (Table 3). Recrystallized fine-grained matrix plagioclase and K-feldspar (200 to 300  $\mu$ m in size), coexisting with the retrograde mineral assemblage of amphibole + biotite + ilmenite, show compositions about  $An_{27}$   $Ab_{71}$  and  $Or_{89}$   $Ab_{10}$  (Table 3 and 4), respectively.

# Orthopyroxenes

Numerous small orthopyroxene grains belonging to the retrograded mineral assemblage occur throughout the rock matrix in mafic granulites (Fig. 2i). Orthopyroxene is rich in ferrosilite component ( $X_{Mg}$  0.43–0.22), with  $Al_2O_3$  content of about 0.44–1.19 wt.% (Table 2).

# **Amphiboles**

Light to dark green secondary amphiboles, up to  $600 \, \mu m$  in size, occur primarily in biotite and ilmenite rich mafic granulites, which are strongly affected by retrogression. They are Ferro-Tschermakites, with low fluorine and chlorine contents ( $\sim 0.05 \, \text{wt.\%}$ , Cl  $\sim 0.35 \, \text{wt.\%}$ , respectively) and  $X_{Mg}$  values ranging between  $0.41 \, \text{and} \, 0.44 \, \text{(Table 2)}$ .

# **Biotites**

Retrograde biotites (up to 500  $\mu$ m in size) are especially abundant within amphibole and ilmenite rich domains (Fig. 2j). They have TiO<sub>2</sub> contents of ~4.34 wt.%, X<sub>Mg</sub> values of 0.44 and, compared with biotites in felsic granulites, have low fluorine contents (<0.50 wt.% / <0.116 apfu) (Table 2).

# 5. MINERAL INCLUSIONS

Red garnet pophyroblasts from both, felsic and mafic granulites commonly enclose a variety of different mineral phases. The most common inclusions are quartz, perthitic alkali-feldspar, antiperthitic plagioclase, kyanite, apatite and rutile. However, white mica relics, clinopyroxene, high-Ti biotite, and polyphase mineral inclusions composed of quartz + K-feldspar + plagioclase or kaolinite + K-feldspar + quartz are also present in some garnet grains. Deep blue kyanite porpyhroblasts in felsic granulites contain perthitic alkali-feldpsar. K-feldspar, quartz, monazite and pyrite grains have been observed within zircon grains.

We distinguish two different varieties of rutile inclusions within garnets. The first type forms thin, euhedral needles, with greater abundance in garnet cores compared to their rims. This needle-like rutile clearly indicates exsolution along crystallographic planes from a former high titanium garnet during retrogression. The second type of rutile inclusions form rounded, anhedral grains, up to 300 µm in size (Fig. 4a) which are very common in both, the cores and rims of garnet.

Apatite is a common inclusion within garnets of both felsic and mafic granulites. It appears as a prismatic subhedral single phase up to 300  $\mu m$  in size and is present in the core as well as the rim of the garnet.

Euhedral biotite inclusions, up to 40 μm in size, are only found in the grossular-rich cores of garnet from felsic granulites, in some cases associated with tiny rutile and quartz (Fig. 4b). These biotites have very high TiO<sub>2</sub> content (6.1 wt.%) and elevated fluorine content (2.32 wt. %) (Table 2).

Perthitic alkali-feldspar, up to a maximum size of  $\sim$ 400  $\mu$ m, are commonly included within both garnets and kyanites of the felsic granulites (Fig. 4c). The perthitic texture is laminar, with plagioclase exsolution occupying 30–35 vol.% of the K-feldspar host. The reintegrated compositions are similar to those of matrix perthite grains, approximately An<sub>6</sub> Ab<sub>26</sub> Or<sub>68</sub> (Table 3). In contrast, garnets of mafic granulites contain antiperthitic plagioclase inclusions.

Clinopyroxene inclusions, up to 80  $\mu$ m in size, are found in the medium to low Ca garnet zone in mafic granulites (Fig. 4d). It has a diopsidic composition with  $X_{Mg} = 0.55-0.61$ ,  $X_{Na} =$ 

Na/(Na+Ca) = 0.04–0.05 and Al<sup>IV</sup> = 0.015–0.024 (Table 1). The complete lack of clinopyroxene in the matrix and the abundant occurrence of orthopyroxene indicates that the decompression driven reaction grt + cpx + qz = opx + pl took place.

White mica occurs in polyphase inclusions within the high-grossular garnet cores, intergrown with biotite, quartz and locally also with apatite and rutile (Fig. 4e). Although these inclusions show some signs of late alteration, analyses of white mica reveal a phengitic composition with MgO contents of 0.90–1.44 wt.%, and FeO of 1.68–2.47 wt.%, and a Si content of up to 3.164 apfu (Table 2). Biotite in such inclusions has an unusual low TiO<sub>2</sub> content of about 0.30 wt.%.

Intergrowths of anhedral kaolinite, K-feldspar and quartz were found in the central parts of Ca-rich garnets from felsic granulites (Fig. 4f). These inclusions reach up to a maximum of 300  $\mu$ m in size and frequently contain kyanite, tiny rutile and small flakes of strongly decomposed white mica.

Small euhedral-shaped, former melt inclusions in crack-free garnet domains (Fig. 4g–i) consist of quartz, K-feldspar, biotite,  $\pm$  rutile,  $\pm$  plagioclase,  $\pm$  ilmenite and  $\pm$  apatite. This type of inclusion is commonly found in felsic and mafic granulites within the garnet core and rim.

#### 6. GARNET TRACE ELEMENT ZONING

The garnet from felsic granulite sample WG336 was selected to compare major and trace element zoning (Fig. 3a and 5). In this particular garnet the zoning pattern of trace elements is correlated to changes in grossular, almandine and pyrope contents. However, the decrease or increase in trace elements occurs over a shorter distance compared to the major elements.

Therefore, the slower diffusing trace elements such as Ti, Zr, Y and Er are better suitable to define the original core-rim interface (Fig. 5). For detailed LA-ICP-MS mineral chemical data see Table B in the supplementary material. The selected garnet shows a general homogeneous core composition, rich in phosphorous, titanium and zirconium, with a marked and sharp decrease of these elements at

the outer rims. The distribution of vanadium, chromium and gallium follows the opposite trend, with low concentrations in the core and high concentrations at the rims (Fig. 5). Yttrium, as well as heavy REE (HREE: erbium, ytterbium) show a relatively uniform concentration in the garnet core, with a marked depletion at the outermost rim. Light REE (LREE: neodymium, europium) concentrations are generally low with flat profiles in the core and strong depletion towards the rims. In a chondrite normalized spider plot (Fig. 5q), using chondrite REE compositions from Nakamura (1974), this particular garnet shows HREE-enriched and steep LREE-depleted pattern for the core as well as for the rim. Furthermore, the rim composition is even more depleted in REE compared to the core. It also has a negative europium anomaly as a whole, which is more pronounced for rim composition.

#### 7. APATITE TRACE ELEMENT COMPOSITION

Fourteen single apatite grains with different textural appearance have been analysed for trace elements from the same felsic granulite sample WG336. LA-ICP-MS mineral chemical data are given in Table C in the supplementary material. Interestingly, apatite crystals cannot only be differentiated based on their textural appearance but also on their varying Y concentrations. Apatite within the high-grossular core of garnet shows by far the lowest Y concentrations (310–530 ppm, mean=425, n=4). In contrast, apatite within the garnet rim (967–1003 ppm, mean=985, n=2) and matrix (649–862 ppm, mean= 765, n=8) are significantly higher in Y. Based on the chondrite normalized spider plot in Fig. 6a, all analysed apatite crystals show a steep HREE depleted and LREE-enriched pattern with a marked negative Eu anomaly. Apatite within the garnet core is more depleted in HREE compared to those in the matrix and garnet rim area.

### 8. PERTHITIC ALKALI-FELDSPAR TRACE ELEMENT COMPOSITION

Nine spot analyses by LA-ICP-MS on large perthitic alkali-feldspar porphyroblasts were obtained from the felsic granulite sample WG336. In a chondrite normalized spider plot (Fig. 6b), the analysed perthitic alkali-feldspar exhibits enrichments in LREE and depletions in HREE as well as a marked positive Eu anomaly. For detailed LA-ICP-MS mineral chemical data see Table D in the supplementary material.

### 9. PRESSURE – TEMPERATURE ESTIMATION

In order to constrain the prograde evolution from the onset of garnet core growth in felsic and mafic granulites up to UHT granulite facies peak we applied the Zr-in-rutile thermometry to single rutile grains, enclosed in garnet cores and rims displaying zoning profile type I. For evaluating the full PT path, we additionally estimated PT conditions of the metamorphic peak mineral assemblage and retrograde mineral assemblage by using an approach that consisted of robust net-transfer reactions, feldspar solvus thermometry and Zr-in-rutile thermometry of matrix grains, combined with phase equilibrium modelling (pseudosections). Estimates of these peak and retrograde PT conditions are consistent with results from literature (Carswell and O'Brien, 1993; Kotková and Harley, 1999; Cooke, 2000; Cooke et al., 2000; Cooke and O'Brien, 2001; Štípská and Powell, 2005; Tajčmanová, et al., 2006; Kotková and Harley, 2010).

# 9.1 Zr-in-rutile thermometry on rutile inclusions within garnets

Both, garnet cores and rims commonly enclose grains of quartz, zircon and anhedral rounded rutile of up to 300 µm in size (Fig. 4a). Based on this observation we conclude that the Zr-content in rutile inclusions is buffered with respect to SiO<sub>2</sub> and ZrO<sub>2</sub> activities by the coexisting quartz and zircon. The rutile inclusions in the high-grossular garnet cores formed during the early prograde metamorphic evolution, whereas those in low-grossular garnet rims are considered to have

recrystallized during the high pressure - ultrahigh temperature granulite facies peak. Corresponding  $X_{Grs}$  values of the garnet host mineral were calculated as mean values from three separate analyses 5–10  $\mu$ m around the rutile inclusion to ensure sufficient spatial resolution. For a detailed summary of rutile analyses, including measured Zr-contents, calculated temperatures following the calibrations of Zack et al. (2004), Ferry and Watson (2007) and Tomkins et al (2007) and corresponding  $X_{Grs}$  values see Table F in the supplementary material. Presented temperature estimates in the text are related to the pressure independent calibration of Zack et al. (2004) and the pressure dependent calibration of Tomkins et al. (2007) for an assumed pressure of 1.6 GPa. In the following these two calibrations are referenced as (Z04) and (T07), respectively.

Rutile inclusions in garnet cores of felsic granulites (0.285 <  $X_{Grs}$  > 0.313) have rather low Zr-contents, ranging from 444 to 814 ppm. Zr-in-rutile thermometry applied to these rutile grains yields an average temperature of ~810 °C (Z04, Fig. 7a) and ~740 °C (T07, Fig. 7b) for this early stage of garnet growth. Rutile grains enclosed within garnet rims of these felsic granulites, which have considerably lower  $X_{Grs}$  (0.030 <  $X_{Grs}$  > 0.143), yield significantly higher Zr-contents, in the range of 1651 to 5774 ppm. The average temperature estimate obtained from these high Zr-rutile grains is ~1030 °C (Z04) and ~930 °C (T07). This higher temperature is in accordance with the PT conditions of c. 1000 °C at 1.6 GPa reported from the literature.

Rutile inclusions within garnet cores and rims from mafic granulites show a similar correlation between calculated temperature and corresponding position in garnet. Rutile grains enclosed in high-grossular garnet cores (0.354 <  $X_{Grs}$  > 0.370) have low Zr-concentrations (385–1184 ppm) resulting in an average temperature estimate of ~ 820 °C (Z04, Fig. 7c) and ~750 °C (T07, Fig. 7d). In contrast, rutile grains in low-grossular garnet rims (0.081 <  $X_{Grs}$  > 0.166) have higher Zr contents ranging from 1851 to 5774 ppm yielding significantly higher average temperature estimates of ~1025 °C (Z04) and ~920 °C (T07).

# 9.2 Peak mineral assemblage

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# **9.2.1** Conventional geothermobarometry

To obtain robust estimates for pressures and temperatures of the granulite facies peak mineral assemblages the GASP barometer and the one and two feldspar thermometry are applicable. The GASP reaction was evaluated using the TWEEQU software of Berman (1991, version winTWQ 2.3, updated 1996) with the internally consistent thermodynamic data set of Berman (1988, 1990), as well as with the calibration from Koziol (1989). For the one and two feldspar thermometry, originally established by Fuhrman and Lindsley (1988), we used the ternary feldsparmixing model after Benisek et al. (2010). Additionally, we applied the trace element Zr-in-rutile thermometer to matrix rutile by using the empirically calibration of Zack et al. (2004) as well as the experimentally calibration of Ferry and Watson (2007) and Tomkins et al. (2007). Carswell and O'Brein (1993), Cooke et al. (2000), Cooke (2000) and Kotková and Harley (2010) pointed out that the application of geothermobarometers to granulites are problematic as the stable mineral assemblage at the peak conditions change their compositions due to diffusional modifications, re-equilibration and/or re-crystallization. In the case of our granulite samples this uncertainty addresses the garnet composition coexisting with a ternary feldspar composition. This ternary feldspar is now represented by perthitic alkali-feldspar which must be reintegrated before being used for estimating peak temperature by the feldspar solvus thermometry. Although this approach is well established, the intensive mylonitisation of our granulite samples leading to a pervasive recrystallization of the feldspar bedevilled our attempt to obtain the original ternary feldspar composition. Consequently, we restricted our geothermobarometric applications by only selecting the very coarsest grained, undeformed perthitic alkali-feldspar porphyroblasts from felsic granulites that display regular exsolution lamellae right up to their grain boundaries. It should be noted that any calculated temperatures for hypothetical coexisting feldspar pairs will give only a minimum temperature, since, at peak granulite facies conditions obviously only one hypersolvus ternary feldspar existed. In this study we have applied the feldspar thermometry method after Kroll

et al. (1993) and feldspar activity models of Benisek et al. (2010) at an assumed pressure of 1.60 GPa. Further we assumed that the hypothetical recovered compositions of the feldspar pairs lie on the same solvus in the ternary feldspar diagram. The one-feldspar thermometric approach on non-equilibrated reintegrated perthitic alkali-feldspar (An<sub>5-11</sub> Ab<sub>17-26</sub> Or<sub>78-64</sub>) and the two-feldspar thermometry applied to the same feldspar composition and secondary matrix plagioclase (An<sub>17-24</sub> Ab<sub>80-75</sub>), provides approximately similar temperature conditions, ranging from 960 up to 1090 °C. We note, however, the occurrence of rare feldspar pairs that gave higher temperature estimates of up to 1150 °C. A comparison of the results of the one- and two-feldspar thermometry is shown on a ternary plot An-Ab-Or in Figure 8.

The preserved garnet zoning in felsic granulites aggravates a clear identification of the actual granulite facies peak garnet composition. As discussed in previous sections garnet rim zones of zoning profile I in very light-coloured, biotite and sillimanite poor felsic granulites (Fig. 3a), display a strong decrease in grossular component at the rim. The decreasing grossular content is matched with an increase in  $X_{Mg}$  and is therefore interpreted to reflect prograde garnet growth during temperature increase. Thus, utilizing the composition of garnet rim and the reintegrated perthitic alkali-feldspar composition, the GASP barometer yields peak pressures ranging between  $\sim$  1.45 and  $\sim$  1.70 GPa, at a temperature of 1000 °C. For representative mineral analyses see Table 1 and 3. The combined results of the GASP barometry and the feldspar thermometry indicate PT conditions of 1.60  $\pm$  0.10 GPa and 1000  $\pm$  50 °C for the formation of the peak equilibrium mineral assemblage comprising garnet  $\pm$  kyanite  $\pm$  ternary feldspar  $\pm$  quartz.

The granulite facies peak mineral assemblage includes matrix rutile coexisting with quartz and zircon in both felsic and mafic granulites. Consequently, Zr-in-rutile thermometry can be applied in addition to feldspar thermometry (see also Kotková and Harley, 2010). Details of the compositional analyses of all rutile grains, with corresponding Zr-content and calculated temperatures are shown in Table E of the supplementary material. The Zr concentrations of the 51

matrix rutile grains analysed are in the range of 1747–5256 ppm, providing temperature estimates of about 940–1090 °C (Z04, Fig. 7e) and 850–990 °C at 1.6 GPa (T07, Fig. 7f).

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# 9.2.2 Phase equilibrium modelling

Phase equilibrium modelling calculations were performed over the PT range of 0.6–3.0 GPa and 400–1100 °C, for the ten-component system Mn-NCKFMATSH. We utilised the Gibbs free energy minimization software Theriak/Domino (de Capitani and Brown, 1987; De Capitani, 1994; de Capitani and Petrakakis, 2010, see also: http://titan.minpet.unibas.ch/minpet/theriak/theruser.html), employing the thermodynamic dataset from Holland and Powell (1998) and subsequent updates. The following mixing models were used: Benisek et al. (2010) for feldspar, Coggon and Holland (2002) for white mica, Tajčmanová et al. (2009) for biotite, Holland and Powell (1998) for garnet, Powell and Holland (1999) for orthopyroxene and Holland and Powell (1996) for clinopyroxene. The model utilised for the melt phase was that initially introduced by Holland and Powell (2001) and adapted from White et al. (2001).For meaningful peak PT estimates, a pseudosection was calculated for a weakly deformed, felsic granulite sample with partly preserved granoblastic fabrics, as it represents the dominant high-grade assemblage rock type in investigated granulite bodies. The selected sample is poor in secondary biotite and sillimanite but rich in kyanite, perthitic alkali-feldspar and contains garnet with zoning profile type I (Fig. 3a). It is very siliceous, with a normalized whole rock composition (in weight %) of SiO<sub>2</sub> 71.10, TiO<sub>2</sub> 0.48, Al<sub>2</sub>O<sub>3</sub> 14.64, FeO 2.71, MnO 0.039, MgO 0.85, CaO 1.56, Na<sub>2</sub>O 2.82, K<sub>2</sub>O 4.80, H<sub>2</sub>O 1.00. As the sample selected is a very fresh felsic granulite, we assume that it has a very low water content due to metamorphic dehydration reactions. Therefore, for our calculations we have assumed that during the high temperature imprint the water content was 1.00 wt.%. In order to evaluate sensitivity, we constructed additional pseudosections using 0.5 % and 1.5 % water contents, noting that there were no significant changes in their geometry. As the

granulite selected contains only small amounts of garnet and biotite, we concluded that ferric iron was not likely to be an important component in this system. This assumption was supported by a redox-titration analysis, following Yokoyama and Nakamura (2002), which found that the proportion of ferric iron was close to zero. It was recognised that sequestration of chemical components into garnet cores during their growth (Stüwe, 1997) may have altered the effective bulk composition of the rock. Even though we ensured that the selected sample had a low garnet content, we double checked by constructing a pseudosection using a bulk composition calculated by subtracting chemical components incorporated into garnet cores from the whole rock composition. This variation in bulk chemistry had negligible effect to the pseudosection geometry.

The resulting pseudosection is shown in Figure 9. The peak metamorphic assemblage observed in thin section comprises garnet + ternary feldspar + kyanite + rutile (+ liquid) + quartz, which is stable at pressures and temperatures higher than 1.40 GPa and 850 °C, respectively. Based on computed isopleths, the grossular content (7 mol.%) at the outer rims of zoning profile type I garnets (Fig. 3a), which are considered to represent equilibrium composition at peak temperatures, and the anorthite content (11 mol.%) of the re-integrated perthitic alkali-feldspar, equilibrium conditions were reached at about 1.70 GPa and 1030 °C (field 1 in Fig. 9a and b). This estimate fits well with PT conditions derived from conventional geothermobarometry (field 2).

# 9.3 Retrograde mineral assemblage

#### **9.3.1** Conventional geothermobarometry

Reasonable temperature estimates of the retrograde assemblage using Fe-Mg exchange thermometry are hampered by continuous diffusional resetting of Fe-Mg ratios during cooling, resulting in temperature underestimation and strong scattering. In contrast, metamorphic conditions calculated from net-transfer reactions are less affected by such retrogressive diffusion processes.

Therefore, we applied the amphibole-plagioclase thermometer after Holland and Blundy (1994) to

mafic granulites, where petrographic evidence indicated that these minerals had obviously recrystallised during late deformation and are stable phases within the retrograde assemblage together with biotite and ilmenite. These results were combined with calculated pressures by the GASP barometry applied to garnet in biotite-rich domains (Fig. 2d, e) and newly crystallized sillimanite in felsic granulites (TWQ 2.3, Berman, 2007). Undoubtedly garnet in these domains grew under prograde granulite facies conditions. However, they show direct contact with biotite, sillimanite and ilmenite and are thought to have experienced substantial elemental diffusion to have chemically re-equilibrated with the retrograde metamorphic assemblage. Using the composition of these garnet grains and finely grained recrystallized matrix plagioclase, combined with sillimanite, the GASP barometer provides pressure estimates in a narrow range of 0.80–0.85 GPa (assuming a temperature of 760 °C). For detailed mineral chemical analyses used for the calculation see Table 1 and 4.

The amphibole-plagioclase thermometry applied to mafic granulites, utilizing homogeneous compositions of amphibole and fine-grained recrystallized plagioclase (Table 2 and 4), gives temperature estimates in the narrow range of 740–765 °C (assuming a pressure of 0.80 GPa).

Results from felsic and mafic granulites clearly indicate a recrystallization event at about  $0.85 \pm 0.1$  GPa and  $760 \pm 50$ °C. This metamorphic overprint was accompanied by deformation and mylonitization (Figs. 2d,e, i).

9.3.2 Phase equilibrium modelling

Additional constraints on the PT conditions of the retrograde mineral assemblage were obtained by constructing a PT pseudosection in the range of 700–850 °C and 0.6–1.1 GPa for the ten-component system Mn-NCKFMATSH (Fig. 10) for a biotite rich domain of a felsic granulite (Fig. 2c), which contains besides biotite the retrograde minerals sillimanite and ilmenite. The normalized whole rock composition (in weight %) is SiO<sub>2</sub> 76.75, TiO<sub>2</sub> 0.12, Al<sub>2</sub>O<sub>3</sub> 12.46, FeO 1.49, MnO 0.028, MgO 0.17, CaO 0.40, Na<sub>2</sub>O 2.81, K<sub>2</sub>O 4.77, H<sub>2</sub>O 1.00. As for previous samples

discussed above, a check on the validity of this pseudosection was performed by calculating an alternative pseudosection using an alternative bulk rock composition by subtracting garnet cores from the whole rock XRF analysis. Again, there are no significant differences between the geometries of the two pseudosections generated.

The computed pseudosection (Fig. 10) shows that the retrograde assemblage sillimanite, biotite, plagioclase and ilmenite can only be stable in the presence of both garnet and melt at maximum PT conditions of 770 °C and 0.90 GPa. In this respect, the compositional garnet isopleths of grossular (4 mol.%) in garnet grains from biotite and sillimanite rich domains, suggest that equilibrium for this particular retrograde mineral assemblage was obtained at conditions of approximately 770 °C and 0.8 GPa (field 1 in Fig. 10a and b). These estimates are in good agreement with estimated PT conditions using conventional geothermobarometry (field 2).

# 10. FE-MG DIFFUSION CHRONOMETRY MODELLING

Diffusion chronometry has been shown to be a powerful tool to extract timescales of cooling and exhumation processes in metamorphic rocks (Müller et al. 2010). We developed a 1-D numerical model to simulate multicomponent diffusion in garnet (Loomis, 1978) to determine the timescales of retrograde re-equilibration processes. Three compositional profiles have been chosen (WG1, WG94, and WG336), that have been identified to be close to central sections and represent type 1 and type 2 profiles. Diffusive element transport in garnet depends on composition, temperature and pressure. Following mineralogical arguments provided by Borinski et al (2012), we limit our model to PT dependent Fe-Mg inter-diffusion and ignore the role of the grossular component. Diffusion coefficients are updated for each timestep and calculated for each node following the data of Borinski et al (2012) and the activation volume of Chakraborty and Ganguly (1992). Müller et al. (2015) has presented convincing evidence that garnet compositions are effectively homogenised independent of the cooling rate above 1000°C. Thus, we model a linear

cooling path from 1000 to 750 °C accompanying linear decompression from 1.6 to 0.8 GPa. The initial concentration profile is assumed to have a homogeneous core with an overgrowth rim that is equally homogeneous in composition (dashed lines in Figure 11) assuming fast overgrowth of an existing garnet core of homogeneous composition. Although, this is a substantial simplification, the combination of observed compositional zoning patterns and Zr-in-rutile thermometry data justify the choice of a simple kink-step profile as starting condition. For each individual garnet, the core and boundary compositions have been adjusted to the measured values for each garnet simulation (Fig. 11). The modelled profiles were chosen as being closest to a central section. Inspection of Figure 11, however, reveals that measured profiles are not perfectly symmetric. Nevertheless, modelled profiles still match the data satisfactorily. It is important to bear in mind that any section that is off the central cut will produce a geometrical artefact that will increase the "virtual" diffusion profile and thus result in longer timescales. Hence, the extracted timescales need to be regarded as maximum timescales. The rim thickness was determined to be half of the observed distance between the flat core composition and the garnet interface. We note, that this ignores possible retrograde garnet resorption and thus the profile might have been shortened to some extent. Similarly, modelled timescales of diffusive re-equilibration must be regarded as maximum estimates. Model simulations have been fitted to measured Fe and Mg concentration profiles by varying the run duration. Modelling results of all three garnet profiles representing central sections (including type 1 and type 2) yield timescales for the exhumation and cooling history of 5–6 Ma (Fig. 11). This translates into exhumation rates of 5.3–6.6 mm y<sup>-1</sup>, and cooling rates of 40–50 °C Ma<sup>-1</sup>, respectively.

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#### 11. DISCUSSION

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# 11.1. A key issue: the prograde evolution of the Moldanubian granulites

| There is wide agreement today that the Moldanubian granulites are high pressure - ultra high       |  |  |
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| temperature rocks which experienced conditions of ca. 1000 °C and 1.6-1.8 GPa during the           |  |  |
| Variscan orogeny. There is also consensus that the rocks then underwent a strong recrystallization |  |  |
| during their rapid exhumation to intermediate granulite facies conditions and their subsequent     |  |  |
| cooling to amphibolite facies conditions (e.g. Vrána, 1992; Kotková and Harley, 1999, 2010;        |  |  |
| Carswell and O'Brien, 1993; Cooke, 2000; Cooke et al. 2000; Kotkova, 2007; Tajčmanová et al.,      |  |  |
| 2009; Jedlička et al., 2015). However, many uncertainties exist with reference to the prograde PT  |  |  |
| evolution of the Moldanubian granulites.   |  |  |
|  |  |  |

For some granulite bodies in the Czech Republic (Kutná Hora and Blanský les), Faryad et al. (2010) showed an incipient phase of eclogite facies metamorphism preceding the granulite facies stage (see also Perraki and Faryad, 2014 and Jedlička et al., 2015). On the other hand, based on an occasionally preserved prograde zoning in garnet and prograde corona reaction textures, Carswell and O'Brien (1993) and Cooke et al. (2000) proposed a prograde PT evolution for the Lower Austrian granulite bodies under amphibolite-facies to granulite facies conditions. These authors excluded that the Lower Austrian granulites did ever experience a typical plagioclase-free eclogite facies imprint, arguing that any eclogite facies assemblages in metabasic rocks intercalated with granulites are completely missing. Only few mantle-derived garnet bearing peridotite lenses tectonically emplaced within the granulite bodies show signs of UHP metamorphism (Carswell and O'Brien, 1993). Available data from the literature is summarized in Figure 12.

The question whether or not the Moldanubian granulites (and which of them) have experienced an eclogite facies precursor stage, is important and absolutely crucial for the tectonic interpretation of this part of the Variscan orogen (see e.g. Schulmann et al. 2009, Finger et al. 2007, Faryad 2009, Faryad et al. 2010). Based on our new petrological observations we discuss this issue below.

#### 11.2. Significance of mineral inclusions in garnet

Preserved primary mineral inclusions in garnet provide the chance to constrain the pre-UHT metamorphic evolution of the granulites. We could not find any eclogite facies mineral relics in the garnets, despite of a careful search. The most abundant primary inclusions in the garnets are: crystallized melt inclusions, Ti-rich biotite, rutile, and composite kaolinite-K-feldspar-quartz inclusions replacing primary muscovite.

Trapped melt inclusions: garnet cores in both felsic and mafic granulites commonly bear small composite inclusions of quartz + K-feldspar + biotite + rutile ± plagioclase ± ilmenite ± apatite (Fig. 4g–i), which can be interpreted as trapped melt. Their high abundance implies a rapid growth rate of the garnet cores, most probably in the course of peritectic garnet producing reactions. Such possible melt and garnet producing reactions are listed below. Reaction (1) is driven by increasing pressure whilst reactions (2), (3), (4), and (5) are overstepped with increasing temperature (Vielzeuf and Holloway, 1988; Patiño Douce, 2005).

$$bt + als + qz = phe + grt + melt$$
 (1)

$$bt + phe + qz = grt + kfs + melt$$
 (2)

phe + 
$$qz = grt + kfs + als + melt$$
 (3)

$$bt + als + qz = grt + kfs + melt$$
 (4)

**Biotite:** Inclusions of unaltered biotite within the high-grossular garnet cores of felsic granulites (Fig. 4b) have significantly elevated Ti-contents compared to biotites in the matrix. These inclusions are completely surrounded by crack-free hosting garnet and thus belong to the stable mineral assemblage at this stage. Similar biotite inclusions in garnet cores were reported in felsic granulites by Carswell and O'Brien (1993). The solubility of Ti in biotite is mainly a function of temperature, pressure and chemical composition of a biotite grain (Henry et al., 2005 and references therein). Experimental work by Robert (1976) demonstrated that the Ti solubility in biotite is

relatively low at 0.1 GPa and 600 °C (0.07 Ti apfu). It increases to 0.20 Ti apfu at 800 °C and to 0.70 Ti apfu at 1000 °C. Thus, we conclude that the Ti-rich biotite inclusions in the garnets (with 0.333 Ti apfu) were in equilibrium with garnet cores at a temperature of about 800–850 °C.

Composite kaolinite-K-feldspar-quartz inclusions: The presence of polyphase inclusions of kaolinite (interpreted as hydrated kyanite) + K-feldspar + quartz within garnet cores (Fig. 4f) indicates initial garnet growth in the presence of white mica, which probably subsequently decomposed by the melt producing reaction: muscovite + quartz = K-feldspar + kyanite + melt. In rare cases we have found relics of white mica in the same core regions of garnets.

Rutile inclusions and Zr-in-rutile thermometry: Rutile inclusions in high-grossular garnet cores show significantly lower Zr-contents compared to those in the low-grossular garnet rims. As rutile grains enclosed in garnet should be largely shielded by diffusive re-equilibration during cooling (Zack et al., 2004) the compositional variability of rutile inclusions from core to rim can be used to determine the temperature evolution during the growth of the garnets and importantly, allow us to define the formation temperature of the early garnet and the subsequent granulite facies peak garnet growth. However, the Zr-in-rutile temperature estimates vary depending on the used calibration. In Figure 7, the empirical calibration of Zack et al. (2004) results in temperatures which are ~80–100 °C higher compared to results from the experimentally calibrated equation of Tomkins et al. (2007) at a pressure of 1.6 GPa. Although the calibration of Zack et al. (2004) does not include a pressure dependent term we use this version of the Zr-in-rutile thermometer due to its consistent results with feldspar solvus thermometry and pseudosection modelling.

The Zr-contents of rutile enclosed in the garnet cores from both the felsic and mafic granulites indicate that the majority of garnet cores grew at ~810–820 °C (Fig. 7a). Slightly lower temperatures of 700–800 °C were reported for incipient garnet growth in garnet-clinopyroxene bearing granulites from the St. Leonhard granulite body (Cooke et al., 2000). These temperatures were obtained from the Fe-Mg exchange garnet-clinopyroxene thermometer. As correctly indicated by the authors, these clinopyroxene is only in equilibrium with the HP granulite facies mineral

assemblage and therefore temperature estimates for the early garnet core growth are uncertain. Comparable temperatures (~830 °C) were recently reported from Zr-in-rutile thermometry of rutile inclusions in high-grossular garnets from the Blanský les granulites (Usuki et al. 2017). Considering our results as well as from literature, the garnet cores in the granulites started to nucleate at unusual high T conditions, considerably above the hypothetical equilibrium grt-in reaction as expected for a typical prograde metamorphic evolution of metagranitoids (see Spear, 2017).

The higher Zr content in rutile enclosed in garnet rims of both felsic and mafic granulites give a temperature estimate of ~1030 °C. This result is in good agreement with temperatures of matrix rutile and feldspar solvus thermometry obtained by this study and previous studies (e.g. Kotková and Harley, 2010) and is proof of the garnet rim growth during the HP-UHT granulite facies stage.

# 11.3. Garnet growth history revealed by trace element zoning

Both, major and trace elements show a nearly flat zoning profile over a broad core region but change sharply at the rim. The changes in trace elements at the rim occurs over a shorter distance compared to major elements, reflecting their lower susceptibility to diffusion within the garnet structure and makes them more likely to record earlier evolutionary stages (e.g. Spear and Kohn, 1996). The homogeneous and flat zoning of trace elements (P, Ti, Zr, Y, V, Cr, Ga and REE) in the broad garnet core region implies that this part of the garnet formed during a single garnet forming reaction at a narrow PT range. Considering the relatively high Ti-content of about 900 ppm in the garnet core, we interpret that a Ti-rich reactant mineral was involved in the garnet forming reaction. Since high-Ti biotite is a common inclusion it is likely that the garnet cores grew at the expense of biotite. Based on the Zr-in-rutile temperature estimate of 810–820 °C for the garnet core growth, reaction (1) bt + als + qz = phe + grt + melt is considered to be responsible for garnet core growth during pressure increase.

The sharp decrease of Ti within the garnet rim region as well as sharp changes in other trace elements suggest that the UHT rims formed by different garnet producing reactions. We speculate that the UHT garnet rims formed by incongruent melting reactions involving phengitic white mica (±clinopyroxene), for instance by reactions (3) or (5). The kyanite consuming reaction (4) is less likely since kyanite is part of the granulite facies peak mineral assemblage. Also, reaction (2), which requires biotite, was probably not involved, as indicated by the low Ti-content in the garnet rims. The significant drop of Zr within the garnet rims may be explained by enhanced crystallisation of rutile which incorporates high amounts of Zr at UHT conditions. The increase in V, Cr, and Ga at the outermost garnet rim is interpreted as the result of white mica decomposition en route to peak granulite facies conditions. The elevated contents of P, Y and LREE in the garnet core and the pronounced drop of these elements at the rim indicate that garnet core grew prior to significant ternary feldspar and apatite crystallization. Similar observations has been reported from leucocratic granulites in the Blanský les Massif (Kotková and Harley, 2010).

### 11.4. Possible geological scenario

The new data presented and discussed above strongly suggest that the prograde PT evolution of the granulite bodies in the southeastern Moldanubian Zone involved two separate stages: (1) the UHT stage of ~ 1000 °C and 1.6 GPa, which has been documented in a number of earlier studies as well (see Kotková, 2007 for review), and (2) a preceding lower-T metamorphic stage which is represented by the garnet cores and their inclusions. This stage occurred at temperatures of ~810–820 °C. Unfortunately, we do not have precise constraints on the pressure conditions of this stage. Rutile inclusions in the garnet cores define a lower pressure limit of ~1.2 GPa (Fig. 13). If the garnet cores formed by overstepping of the biotite consuming peritectic reaction (1), what we consider most likely, then the pressure should have been at around 1.6 GPa. Experimental data by Hermann (2002) showed that Ti-rich biotite can be stable up to ~2.5 GPa at ~810–820 °C, setting the upper pressure limit for the early garnet core formation. Assuming a geothermal gradient of ~10

°C/km, which is observed in subduction settings with fast plate motion, pressures of 2.0–2.5 GPa could be reached at a temperature of ~810–820 °C. At a higher geothermal gradient of ~20 °C/km, the peritectic reaction (1) is overstepped at significantly lower pressure (~1.5–2.0 GPa).

Depending on the geometry of the prograde path (Fig. 13), the subsequent granulite facies event was either (a) caused by isobaric heating (likely in case of a geothermal gradient of 20 °C/km), or (b) by decompression and contemporaneous heating or (c) isothermal decompression followed by heating (likely in case of a thermal gradient of 10 °C/km). The ultimate cause for the UHT metamorphism was most likely the introduction of mantle heat, either provided by slab breakoff (Finger et al., 2007), mantle delamination (Massone, 2006) or slab roll back (Sizova et al., 2018). As a result, the superheated, partially molten crustal material becomes highly mobile and "flows" upward into a mid-crustal position where it re-equilibrates (Schulmann et al. 2009).

# 11.5. Exhumation and cooling history of the Lower Austrian granulites

Previous studies concluded that the exhumation and cooling rates of the Moldanubian granulites were in a range of. 2.9–3.5 mm year<sup>-1</sup> and 7–20 °C myr<sup>-1</sup>, respectively (Svojtka et al., 2002; Tajčmanová et al., 2006). These numbers are based on either an extrusion model or a combination of petrographic observations and zircon dating in multiple rock units. In this study we use a combination of methods (geothermobarometry, pseudosections and diffusion chronometry) on individual rock specimens. In all cases, we determined a minimum uplift of 5.3–6.6 mm year<sup>-1</sup> and cooling rates of 40–50 °C myr<sup>-1</sup>. Thus, our results indicate a much faster exhumation compared to previous results for Moldanubian granulites. We note, however, that these estimates are still about an order of magnitude lower than those simulated for the uplift of mantle xenoliths further north in the Granulite Massif (Müller et al., 2015). Hence, we interpret our rates which are based on a holistic approach to be realistic and provide estimates of the steep exhumation and cooling history from peak HP granulite facies conditions to lower granulite/amphibolite facies conditions.

The proposed PT evolution for granulites from this study area differs from the PT path of granulites from the northern and central part of the Moldanubian Zone (Blanský les and Kutná Hora granulite). In the latter, an eclogite facies evolution at about 700 °C at 3.2–4.0 GPa was reported based mainly on ultra-high pressure phases included in garnet (Faryad et al., 2010; Perraki and Faryad, 2014). Our study does not provide any evidence for such an UHP imprint for the large granulite bodies in the southeastern part of the Moldanubian Zone. Nevertheless, we do not necessarily rule out a PT path up to coesite or diamond stability (Fig. 13), since relics of this UHP evolution are likely to be of limited extent and extremely rare in these granulites.

# 12. Conclusions

- 1. Rutile inclusions in garnet and application of the Zr-in-rutile thermometry provides a tool to improve our understanding of the prograde metamorphic evolution of granulites from the Moldanubian Zone. Garnet cores with high grossular content formed at a temperature of ~810–820 °C contemporaneous with extensive melting recorded in abundant polycrystalline melt inclusions throughout these cores. The presence of high-Ti biotite inclusions within the garnet cores constrains confining pressures between 1.6 and 2.5 GPa.
- 2. Rutile inclusions in low-grossular rims of the same garnets record UHT conditions at  $\sim 1030$  °C. This temperature is within errors to T estimates of  $1000 \pm 50$  °C based on conventional geothermobarometry and pseudosection phase diagrams. Pressure was estimated with  $1.60 \pm 0.10$  GPa for the garnet rim growth.
- 3. High-grossular garnet cores from felsic granulites do not show significant compositional changes in trace elements indicating a single reaction (peritectic biotite breakdown reaction) for the garnet core crystallization. In contrast, the sharp changes in trace element contents within the rim of garnets implies different garnet forming reaction(s). The low-grossular garnet rim was most likely formed by incongruent phengitic white mica consuming and melt

- producing reactions. Also white mica is not observed as a matrix mineral phase, inclusions in garnet confirm the presence of white mica during the prograde PT path.
- 4. The pronounced zoning of major elements at the garnet rim despite UHT conditions points to an extremely short lived metamorphic episode. Otherwise diffusion would have homogenised the garnet right through to its core. Therefore, the garnet rim must have formed rapidly, probably due to a certain overstepping of the garnet rim forming reactions.
- Binary Fe-Mg diffusion chronometry on garnet profiles indicates that the Moldanubian granulites in the southeastern Bohemian Massif underwent rapid exhumation and cooling (~4.4–5.3 mm y<sup>-1</sup> and ~40–50 °C Myr<sup>-1</sup>) subsequent to granulite facies peak conditions.

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# References

Arnold, A., Scharbert, H.G., 1973. Rb-Sr Altersbestimmungen an Granuliten der südlichen
 Böhmischen Masse in Österreich. Schweizerische mineralogische und petrografische Mitteilungen
 53, 61–78.

838 Baba, S., 2003. Two stages of sapphirine formation during prograde and retrograde metamorphism 839 in the Palaeoproterozoic Lewisian complex in South Harris, NW Scotland. Journal of Petrology 44, 840 329–354. 841 842 Benisek, A., Dachs, E., Kroll, H., 2010. A ternary feldspar-mixing model based on calorimetric 843 data: development and application. Contributions to Mineralogy and Petrology 160, 327–337. 844 845 Berman, R.G., 1988. Internally-consistent thermodynamic data for minerals in the system Na2O-846 K2O-CaO-MgO-FeO-Fe2O3-Al2O3-SiO2-TiO2-H2O-CO2. Journal of Petrology 29, 445–522. 847 848 Berman, R.G., 1990. Mixing properties of Ca-Mg-Fe-Mn garnets. American Mineralogist 75, 328-849 344. 850 851 Berman, R.G., 1991. Thermobarometry using multi-equilibrium calculations: a new technique, with 852 petrological applications. The Canadian Mineralogist 29, 833–855. 853 854 Berman, R.G., 2007. WinTWQ (version 2.3): A software package for performing internally-855 consistent thermobarometric calculations. Geological Survey of Canada Open File 5462, pp. 1–41. 856 857 Borinski, S.A., Hoppe, U., Chakraborty, S., Ganguly, J., Bhowmik, S.K. (2012). Multicomponent 858 diffusion in garnets I: general theoretical considerations and experimental data for Fe-Mg systems. 859 Contributions to Mineralogy and Petrology, 164, 571–586. 860 861 Brückner, H.K., Medaris, L.G., Bakun-Czubarow, N., 1991. Nd and Sr age and isotope patterns from Variscan eclogites of the eastern Bohemian Massif. Neues Jahrbuch für Mineralogie, 862

863

Abhandlungen 163, 169–196.

| 864 |  |
|-----|--|
| 865 | Caporuscio, F.A., Morse, S.A., 1978. Occurrence of sapphirine plus quartz at Peekskill, New York.  |
| 866 | American Journal of Science 278, 1334–1342.  |
| 867 |  |
| 868 | Carswell, D.A., Jamtveit, B., 1990. Variscan Sm-Nd ages for the high-pressure metamorphism in      |
| 869 | the Moldanubian Zone of the Bohemian Massif, Lower Austria. Neues Jahrbuch für Mineralogie,        |
| 870 | Abhandlungen 162, 69–78.   |
| 871 |  |
| 872 | Carswell, D.A., O'Brien, P.J., 1993. Thermobarometry and geotectonic significance of high          |
| 873 | pressure granulites: examples from the Moldanubian Zone of the Bohemian Massif in Lower            |
| 874 | Austria. Journal of Petrology 34, 427–459.   |
| 875 |  |
| 876 | Chakraborty, S., Ganguly, J., 1992. Cation diffusion in aluminosilicate garnets: experimental      |
| 877 | determination in spessartine-almandine diffusion couples, evaluation of effective binary diffusion |
| 878 | coefficients, and applications. Contributions to Mineralogy and Petrology 111, 74–86.              |
| 879 |  |
| 880 | Coggon, R., Holland, T.J.B., 2002. Mixing properties of phengitic micas and revised garnet-        |
| 881 | phengite thermobarometers. Journal of Metamorphic Geology 20, 683-696.                             |
| 882 |  |
| 883 | Cooke, R.A., 2000. High-pressure/temperature metamorphism in the St. Leonhard Granulite Massif,    |
| 884 | Austria: evidence from intermediate pyroxene-bearing granulites. International Journal of Earth    |
| 885 | Sciences 89, 631–651.  |
| 886 |  |
| 887 | Cooke, R.A., O'Brien, P.J., Carswell, D.A., 2000. Garnet zoning and the identification of          |
| 888 | equilibrium mineral compositions in high-pressure-temperature granulite from the Moldanubian       |
| 889 | Zone, Austria, Journal of metamorphic Geology 18, 551–569.   |

915 Faryad, S.W., Nahodilová, R., Dolejš, D., 2010. Incipient eclogite facies metamorphism in the 916 Moldanubian granulites revealed by mineral inclusions in garnet. Lithos 114, 54–69. 917 918 Faryad, S.W., Kachlík, V., Sláma, J., Hoinkes, G., 2015. Implication of corona formation in a 919 metatroctolite to the granulite facies overprint of HP-UHP rocks in the Moldanubian Zone 920 (Bohemian Massif). Journal of Metamorphic Geology 33, 295–310. 921 922 Ferry, J.M., Watson, E.B., 2007. New thermodynamic models and revised calibrations for the Ti-in-923 zircon and Zr-in-rutile thermometers. Contributions to Mineralogy and Petrology 154, 429–437. 924 925 Fiala, J., Matejovska, O., Vankova, A., 1987. Moldanubian granulites: source material and 926 petrogenetic considerations. Neues Jahrbuch für Mineralogie-Abhandlungen 157, 133-65. 927 928 Finger, F., Gerdes, A., Janoušek, V., René, M., Riegler, G., 2007. Resolving the Variscan evolution 929 of the Moldanubian sector of the Bohemian Massif: the significance of the Bavarian and the 930 Moravo-Moldanubian tectonometamorphic phases. Journal of Geosciences 52, 9–28. 931 932 Frank, W., Hammer, S., Popp, F., Scharbert, S., Thöni, M., 1990. Isotopengeologische 933 Neuergebnisse zur Entwicklungsgeschichte der Böhmischen Masse. Österreichische Beiträge zu 934 Meteorologie und Geophysik 3, 185–228. 935 936 Franke, W., 2000. The mid-European segment of the Variscides: tectonostratigraphic 937 units, terrane boundaries and plate evolution. In: Franke, W., Haak, V., Oncken, O., 938 Tanner, D. (Eds.), Orogenic Processes: Quantification and Modelling in the Variscan 939 Belt. Geol. Soc. London, Spec. Publ., London, 179, pp. 35-61.

- 941 Friedl, G., Fritz, F., Paquette, J-L., on Quadt, A., McNaughton, N.J., Fletcher, I.R., 2004. Pre-942 Variscan geological events in the Austrian part of the Bohemian Massif deduced from U-Pb zircon 943 ages. International Jouranl of Earth Sciences 93, 802-823. 944 945 Friedl, G., Cooke, R.A., Finger, F., McNaughton, N.J., Fletcher, I.R., 2011. Timing of Variscan HP-HT metamorphism in the Moldanubian Zone of the Bohemian Massif: U-Pb SHRIMP dating on 946 947 multiply zoned zircons from a granulite from the Dunkelsteiner Wald Massif, Lower Austria. 948 Mineralogy and Petrology 102, 63–75. 949 950 Fuchs, G., Matura, A., 1968. Die Böhmische Masse in Österreich, in: Geologische Bundesanstalt 951 (Eds.), Der Geologische Aufbau Österreichs. Springer, Vienna, pp. 121–143. 952 953 Fuhrman, M.L., Lindsley, D.H., 1988. Ternary-feldspar modeling and thermometry. American 954 Mineralogist 73, 201–215. 955 956 Harley, S.L., 1998. On the occurrence and characterization of ultrahigh-temperature crustal 957 metamorphism. In: Treloar, P.J., O'Brien, P.J. (Eds.), What Drives Metamorphism and Metamorphic 958 Reactions? Special Publications 138, Geological Society, London, 81–107. 959 960 Hauzenberger, C.A., Robl, J., Stüwe, K., 2005. Garnet zoning in high pressure granulite-facies 961 metapelites, Mozambiquebelt, SE-Kenya: constraints on the cooling history. European Journal of Mineralogy 17, 43–55. 962 963
- Henry, D.J., Guidotti, C.V, Thomason, J.A., 2005. The Ti-saturation surface for low-to-medium
   pressure metapelitic biotites: Implications for geothermometry and Ti-substitution mechanisms.
   American Mineraologies 90, 316–328.

- Jochum, K.P., Weis, U., Stoll, B., Kuzmin, D., Yang, Q., Raczek, I., Jacob, D. E., Stracke, A.,
- 993 Birbaum, K., Frick, D. A., Günther, D., Enzweiler, J., 2011. Determination of reference values for
- 994 NIST SRM 610–617 glasses following ISO guidelines. Geostandards and Geoanalytical Research
- 995 35, 397–429.

- 897 Kelly, N.M., Harley, S.L., 2004. Orthopyroxene–corundum in Mg–Al-rich granulites from the
- 998 Oygarden Islands, East Antarctica. Journal of Petrology 45, 1481–1512.

999

- 1000 Kotková, J., 2007. High-pressure granulites of the Bohemian Massif: recent advances and open
- 1001 questions. Journal of Geosciences 52, 45–71.

1002

- Kotková, J., Harley, S.L., 1999. Formation and evolution of high-pressure leucogranulites:
- experimental constraints and unresolved issues. Physics and Chemistry of the Earth, Part A: Solid
- 1005 Earth and Geodesy 24, 299–304.

1006

- 1007 Kotková, J., Harley, S.L., 2010. Anatexis during High-pressure Crustal Metamorphism: Evidence
- 1008 from Garnet–Whole-rock REE Relationships and Zircon–Rutile Ti–Zr Thermometry in
- Leucogranulites from the Bohemian Massif. Journal of Petrology 51, 1967–2001.

1010

- Koziol, A.M., 1989. Recalibration of the garnet-plagioclase Al2SiO5-quartz (GASP) geobarometer
- and applications for natural parageneses. EOS Transactions American Geophysical Union 70, 493.

1013

- Kroll, H., Evangelakakis, C., Voll, G., 1993. Two-feldspar geothermometry: a review and revision
- for slowly cooled rocks. Contributions to Mineralogy and petrology 114, 510–518.

1017 Kröner, A., O'Brien, P.J., Nemchin, A.A., Pidgeon, R.T., 2000. Zircon ages for high pressure 1018 granulites from South Bohemia, Czech Republic, and their connection to Carboniferous high 1019 temperature processes. Contributions to Mineralogy and Petrology 138, 127–42. 1020 1021 Loomis, T.P., Ganguly, J., Elphick, S.C., 1985. Experimental determination of cation diffusivities in 1022 aluminosilicate garnets II. Multicomponent simulation and tracer diffusion coefficients. 1023 Contributions to Mineralogy and Petrology 90, 45–51. 1024 1025 Massone, H.J., 2006. Early metamorphic evolution and exhumation of felsic high-pressure 1026 granulites from the north-western Bohemian Massif. Mineralogy and Petrology 86, 177–202. 1027 1028 Müller, T., Watson, E.B., Harrison, T.M., 2010. Applications of diffusion data to high-temperature 1029 earth systems. Reviews in mineralogy and geochemistry 72, 997–1038. 1030 1031 Müller, T., Massone, H.-J., Willner, A.P., 2015. Timescales of exhumation and cooling inferred by 1032 kinetic modelling: An example using a lamellar garnet pyroxenite from Variscan Granulitgebirge, E 1033 Germany. American Mineralogist 100, 747–759. 1034 1035 Nakamura, N., 1974. Determination of REE, Ba, Fe, Mg, Na and K in carbonaceous and ordinary 1036 chondrites. Geochimica et Cosmochimica Acta 38, 757–775. 1037 1038 O'Brien, P.J., Kröner, A., Jaeckel, P., Hegner, E., Zelazniewicz, A., Kryza, R., 1997. Petrological 1039 and isotopic studies on Palaeozoic high-pressure granulites, Gory Sowie Mts, Polish Sudetes. 1040 Journal of Petrology 38, 433–456.

1042 O'Brien, P.J., Rötzler, J., 2003. High-pressure granulites: formation, recovery of peak conditions 1043 and implications for tectonics. Journal of Metamorphic Geology 2, 3–20. 1044 1045 Osanai, Y., Sajeev, K., Owada, M., Kehelpannala, K.V.W., Prame, W.K.B., Nakano, N., Jayatileke, 1046 S., 2006. Metamorphic evolution of high-pressure and ultrahigh-temperature granulites from the 1047 Highland Complex, Sri Lanka. Journal of Asian Earth Sciences 28, 20–37. 1048 1049 Patiño Douce, A.E., 2005. Vapor-absent melting of tonalite at 15–32 kbar. Journal of Petrology 46, 1050 275–290. 1051 1052 Perraki, M., Faryad, S.W., 2014. First finding of microdiamond, coesite and other UHP phases in 1053 felsic granulites in the Moldanubian Zone: Implications for deep subduction and a revised 1054 geodynamic model for Variscan Orogeny in the Bohemian Massif. Lithos 202, 157–166. 1055 1056 Petrakakis, K., 1997. Evolution of Moldanubian rocks in Austria: review and synthesis. Journal of 1057 Metamorphic Geology 15, 203–222. 1058 1059 Powell, R., Holland, T.J.B., 1999. Relating formulations of the thermodynamics of mineral solid 1060 solutions: activity modeling of pyroxenes, amphiboles, and micas. American Mineralogist 84, 1–14. 1061 1062 Prince, C.I., Košler, J., Vance, D., Günter, D., 2000. Comparison of laser ablation ICP-MS and 1063 isotope dilution REE analyses—implications for Sm-Nd garnet geochronology. Chemical Geology 1064 168, 255–274. 1065

- 1066 Raase, P., 1998. Feldspar thermometry: A valuable tool for deciphering the thermal history of
- granulite-facies rocks, as illustrated with metapelites from Sri Lanka. The Canadian Mineralogist
- 1068 36, 67–86.

- Robert, J.L., 1976. Titanium solubility in synthetic phlogopite solid solutions. Chemical Geology
- 1071 17, 213–227.

1072

- 1073 Rötzler, J., Romer, R.L., 2001. P-T-t evolution of ultrahigh-temperature granulites from the Saxon
- 1074 Granulite Massif, Germany. Part I: petrology. Journal of Petrology 42, 1995–2013.

1075

- Sandiford, M., Neale, F., Powell, R., 1987. Metamorphic evolution of aluminous granulites from
- Labwor Hills, Uganda. Contributions to Mineralogy and Petrology 95, 217–225.

1078

- Scharbert, H.G., Kurat, G., 1974. Distribution of some elements between coexisting ferromagnesian
- minerals in Moldanubian granulite facies rocks, Lower Austria, Austria. Tschermaks
- 1081 Mineralogische und Petrographische Mitteilungen 21, 110–134.

1082

- Schnabel, W., Bryda, G., Egger, H., Fuchs, G., Matura, A., Krenmayr, H.G., Mandl, G.W.,
- Nowotny, A., Roetzel, R., Scharbert, S., Wessely, G., 2002. Geologische Karte von Niederösterreich
- 1:200000. Land Niederösterreich und Geologische Bundesanstalt.

1086

- 1087 Schulmann, K., Konopásek, J., Janoušek, V., Lexa, O., Lardeaux, J.-M., Edel, J.B., Štípská, P.,
- 1088 Ulrich, S., 2009. An Andean type Palaeozoic convergence in the Bohemian Massif. Comptes
- 1089 Rendus Geoscience 341, 266–286.

- 1091 Sizova, E., Gerya, T., Brown, M., Stüwe, K., Hauzenberger, C., Fritz, H., Faryad, S.W., 2018. 1092 Overprinting metamorphic events during continental collision: Insight from geodynamic modelling. 1093 Granulites and Granulites 2018, Ullapool, Scotland. 1094 1095 Spear, F. S., 2017. Garnet growth after overstepping. Chemical Geology 466, 491–499. 1096 1097 Spear, F.S., Kohn, M.J., 1996. Trace element zoning in garnet as a monitor of crustal melting. 1098 Geology 24, 1099–1102. 1099 1100 Štípská, P., Powell, R., 2005. Does ternary feldspar constrain the metamorphic conditions of high-1101 grade meta-igneous rocks? Evidence from orthopyroxene granulites, Bohemian Massif. Journal of 1102 Metamorphic Geology 23, 627–647. 1103 1104 Stüwe, K., 1997. Effective bulk composition changes due to cooling: a model predicting 1105 complexities in retrograde reaction textures. Contributions to Mineralogy and Petrology 129, 43– 1106 52. 1107 1108 Svojtka, M., Košler, J., Venera, Z., 2002. Dating granulite-facies structures and the exhumation of 1109 lower crust in the Moldanubian Zone of the Bohemian Massif. International Journal of Earth 1110 Science 91, 373–385. 1111 1112 Tajčmanová, L., Konopásek, J. Schulmann, K., 2006. Thermal evolution of the orogenic lower crust
- during exhumation within a thickened Moldanubian root of the Variscan belt of Central Europe.

  Journal of Metamorphic Geology 24, 119–134.

1116 Tajčmanová, L., Connolly, J.A.D., Cesare, B., 2009. A thermodynamic model for titanium and ferric 1117 iron solution in biotite. Journal of metamorphic Geology 27, 153–165. 1118 1119 Tomkins, H.S., Powell, R., Ellis, D.J., 2007. The pressure dependence of the zirconium-in-rutile 1120 thermometer. Journal of Metamorphic Geology 25, 703–713. 1121 Tropper, P., Hauzenberger, C., 2015. How well do pseudosection calculations reproduce simple 1122 1123 experiments using natural rocks: an example from high-P high-T granulites of the Bohemian 1124 Massif. Austrian Journal of Earth Sciences 108, 123–138. 1125 1126 Usuki, T., Iizuka, Y., Hirajima, T., Svojtka, M., Lee, H.Y., Jahn, B.M., 2017. Significance of Zr-in-1127 Rutile Thermometry for Deducing the Decompression P–T Path of a Garnet–Clinopyroxene 1128 Granulite in the Moldanubian Zone of the Bohemian Massif. Journal of Petrology 58, 1173–1198. 1129 1130 Vielzeuf, D., Holloway, J.R., 1988. Experimental determination of the fluid-absent melting relations 1131 in the pelitic system: Consequences for crustal differentiation. Contribution to Mineralogy and 1132 Petrology 98, 257–276. 1133 1134 Vrána, S., 1992. The Moldanubian Zone in southern Bohemia: polyphase evolution of imbricated 1135 crustal and upper mantle segments. in: Kukal, Z. (Eds.), International Conference on Bohemian 1136 Massif. Czech Geological Survey, Prague, pp. 331–336. 1137 1138 Vrána, S., Štědrá, V., Fišera, M., 2005. Petrology and geochemistry of the Běstvina granulite body 1139 metamorphosed at eclogite facies conditions, Bohemian Massif. Journal of the Czech Geological 1140 Society 50, 81–94.

1142 White, R.W., Powell, R., Holland, T.J.B., 2001. Calculation of partial melting equilibria in the 1143 system Na2O-CaO-K2O-FeO-MgO-Al2O3-SiO2-H2O (NCKFMASH). Journal of Metamorphic 1144 Geology 19, 139–153. 1145 1146 Whitney, D.L., Evans, B. W., 2010. Abbreviations for names of rock-forming minerals. American 1147 Mineralogist 95, 185–187. 1148 1149 Yokoyama, T., Nakamura, E., 2002. Precise determination of ferrous iron in silicate rocks. 1150 Geochimica et Cosmochimica Acta 66, 1085–1093. 1151 1152 Zack, T., Moraes, R., Kronz, A., 2004. Temperature dependence of Zr in rutile: empirical calibration 1153 of a rutile thermometer. Contributions to Mineralogy and Petrology 148, 471–488. 1154 1155 **Figure Captions** 1156 1157 Fig. 1. (a) Simplified geological framework of the Bohemian Massif (modified after Franke, 2000). 1158 Upper left inset shows the tectonic subdivision of the central European Variscides. Letters indicate 1159 granulite bodies in the Moldanubian Zone: DW – Dunkelsteinerwald granulite, PW – Pöchlarn-1160 Wiselburg granulite, SL – St. Leonhard granulite, B – Blumau granulite, J – Jemnice granulite, Mo – 1161 Mohelno granulite, SU – Strážek Unit granulite, KH – Kutná Hora granulite, L – Lišov granulite, Bl 1162 – Blanský les granulite, P – Prachatice granulite, K – Křištánov granulite. (b) Simplified geological 1163 map of the southeastern Bohemian Massif (modified after Schnabel et al., 2002). 1164 1165 Fig. 2. Hand-specimen photographs and corresponding photomicrographs of (a) a felsic granulite 1166 containing (b) the HP granulite facies peak mineral assemblage of garnet + kyanite + peritectic 1167 alkali-feldspar + rutile + quartz; (c) a felsic granulite with slightly darker bands where (d, e)

retrogressive biotite-flakes interpenetrate sillimanite and ilmenite to form masses oriented parallel to the foliation, mainly defined by quartz ribbons; (f) a fresh mafic granulite with (g) large porphyroblasts of peak garnet and antiperthitic plagioclase and randomly distributed, small secondary orthopyroxene and biotite in a quartzo-feldspathic matrix; (h) a strongly retrograde mafic granulite with (i, j) secondary amphibole, biotite and ilmenite intergrown with small garnet.

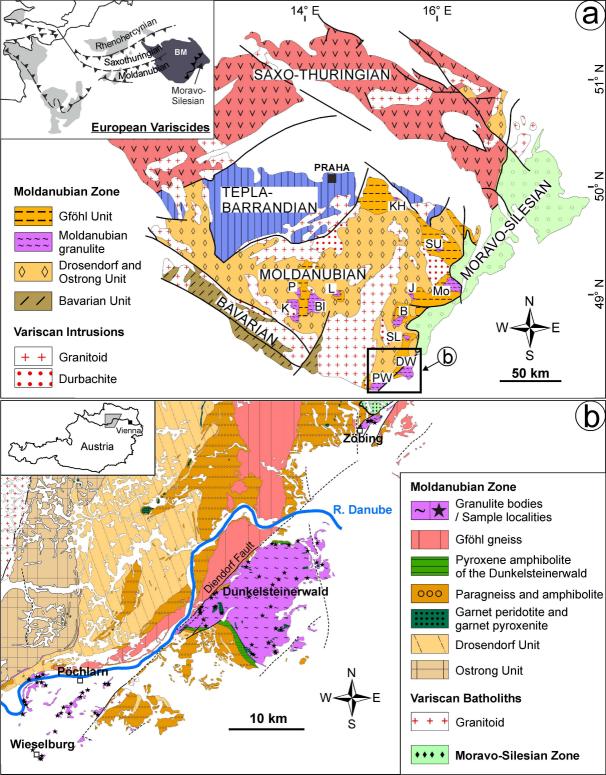
**Fig. 3.** BSE images and major element zoning profiles of representative garnets from felsic (a, b, c, d, e) and mafic (f) granulites. Y-axes indicates mol. % of garnet endmembers; x-axes indicate rimcore-rim distances in millimetres.

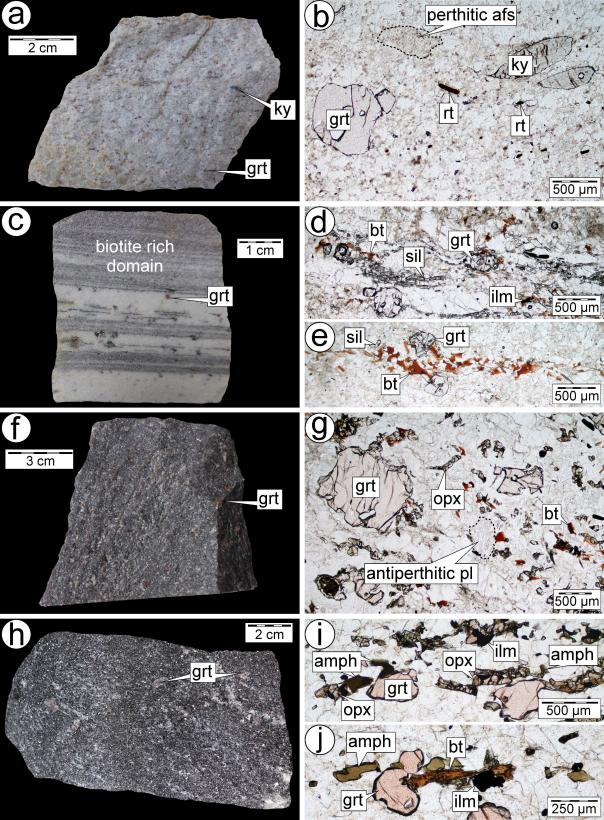
Fig. 4. Photomicrographs of representative inclusions. (a) Rounded, anhedral rutile within garnet. (b) Euhedral inclusion of fresh high-Ti biotite in garnet core. (c) Perthitic alkali-feldspar within kyanite reflecting the equilibrium coexistence between ternary feldspar and kyanite at granulite facies peak conditions. (d) Euhedral-shaped diopside dominated clinopyroxene in the medium to low Ca garnet zone of a mafic granulite, note this is a garnet rim section. (e) Relics of white mica, quartz, biotite and rutile form a polyphase inclusion in the Ca-rich garnet core region; (f) Inclusion of kaolinite, K-feldspar and randomly decomposed quartz in garnet core, most probably formed after the muscovite break-down. (g) Numerous small melt inclusions within garnet core and rim areas. Inset shows a zoom-in where the euhedral-shaped melt inclusions are located in a crack-free garnet domain. (h, i) Euhedral-shaped polycrystalline melt inclusion composed of quartz, K-feldspar and biotite.

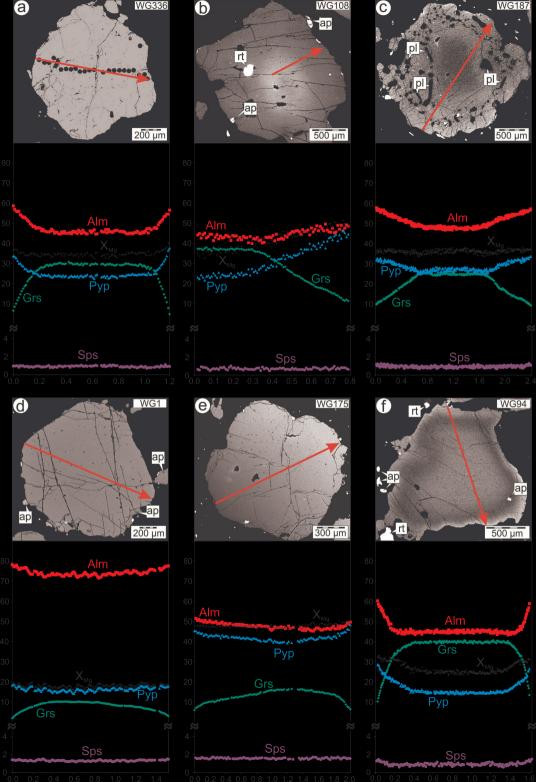
**Fig. 5.** Garnet profile type I from felsic granulite WG336, major element compositional maps of Ca, Fe, Mg, (b–d), major element zoning (e), trace element and REE zoning (f–p) and chondrite normalized Rare Earth Element plot (q) for garnet core and garnet rim. Y-axes indicates ppm of trace elements; x-axes indicate rim-core-rim distances in millimetres. Note zoning of selected trace

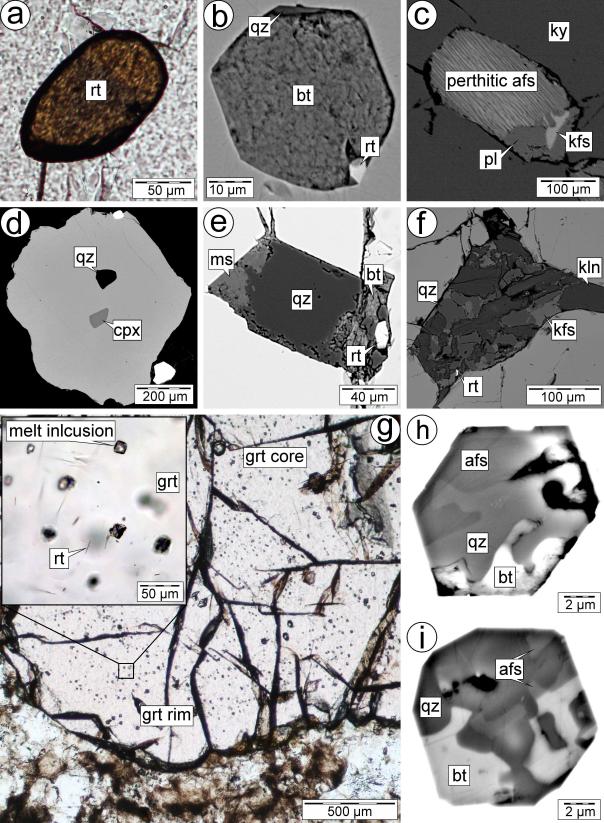
1194 elements were slightly smoothed. Rim-core-rim boundaries are based on the trace element changes 1195 in (e). 1196 1197 Fig. 6. Chondrite normalized Rare Earth Element plot for (a) apatite in garnet core, garnet rim and 1198 rock matrix and (b) perthitic alkali-feldspar. 1199 1200 Fig. 7. Plot of calculated Zr-in-rutile temperatures against (a, b)  $X_{Grs}$  of garnet host enclosing rutile 1201 in felsic granulites and (c, d)  $X_{Grs}$  of garnet host enclosing rutile in mafic granulites. Red squares 1202 and green diamonds indicate measured rutiles in low grossular garnet rim and high grossular garnet 1203 core regions, respectively. (c, d) Zr-contents of matrix rutiles (grey diamonds) in felsic and mafic 1204 granulites vs calculated temperatures. Temperature estimates are after Zack et al. (2004) - Z (04) and 1205 Tomkins et al. (2007) - (T07) for an assumed pressure of 1.6 GPa. 1206 1207 Fig. 8. Exemplary feldspar pairs using the one feldspar (open symbols) and two feldspar (full 1208 symbols) thermometry for a given pressure of 1.60 GPa. Temperature isopleths are obtained using 1209 the recent interaction parameters of Benisek et al. (2010) for 1.60 GPa. 1210 1211 Fig. 9. PT pseudosection for the granulite facies peak mineral assemblage. (a) Presents fields of 1212 stable mineral assemblages and volume isopleths of garnet. Important phase transitions are indicated 1213 as bold coloured lines. Labels for small PT fields are omitted for avoiding confusion. (b) Presents 1214 isopleths of grossular and anorthite in ternary feldspar. 1215 1216 Fig. 10. PT pseudosection for the retrograde mineral assemblage. (a) Presents fields of stable 1217 mineral assemblages and volume isopleths of garnet. Important phase transitions are indicated as 1218 bold coloured lines. Labels for small PT fields are omitted for avoiding confusion. (b) Presents 1219 isopleths of grossular.

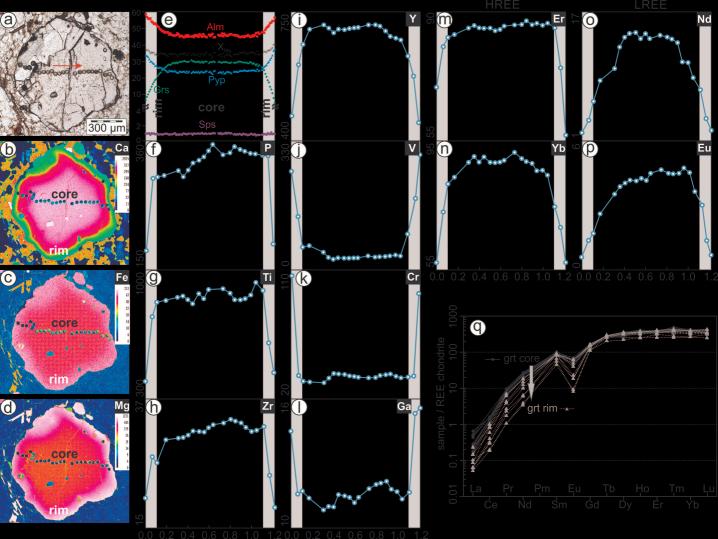
1220 1221 Fig. 11. Representative fits for the measured and calculated (diffusion model) almandine and pyrope 1222 profiles from sample (a) WG1 and (b) WG336. 1223 1224 Fig. 12. PT paths reported for the Moldanubian granulites (modified after Jedlička et al., 2015). 1 -1225 Kutná Hora (Perraki and Faryad, 2014; Jedlička et al., 2015), 2 - Strážek Unit (Tajčmanová et al., 2009), 3 - Blanský les and Lišov (Vrána, 1992; Kotková and Harley, 1999, 2010), 4 -1226 1227 Dunkelsteinerwald and St. Leonhard (Carswell and O'Brien, 1993; O'Brien and Rötzler, 2003), 5 -1228 St. Leonhard (Cooke, 2000; Cooke et al. 2000). 1229 1230 Fig. 13. Reconstructed PT paths and estimated exhumation and cooling rates for the Moldanubian 1231 granulites in the southeastern Bohemian Massif. Field a and b indicates estimated PT conditions for 1232 the formation of the metamorphic peak and the retrograde mineral assemblage, respectively. 1233 Peritectic garnet growth reactions (1) bt + als + qz = ms + grt + melt, (2) bt + ms + qz = grt + kfs + grt + melt1234 melt, (3) ms + qz = grt + kfs + als + melt, (4) bt + als + qz = grt + kfs + melt (5) ms + cpx + qz = grt1235 + kfs + melt are from Vielzeuf and Holloway (1988) and Patiño Douce (2005). Biotite stability is 1236 from Hermann (2002).

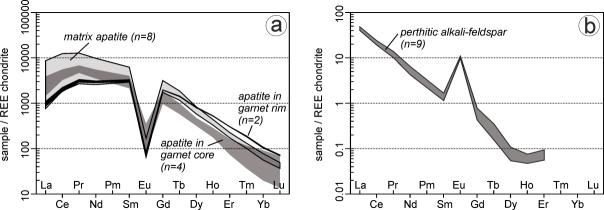


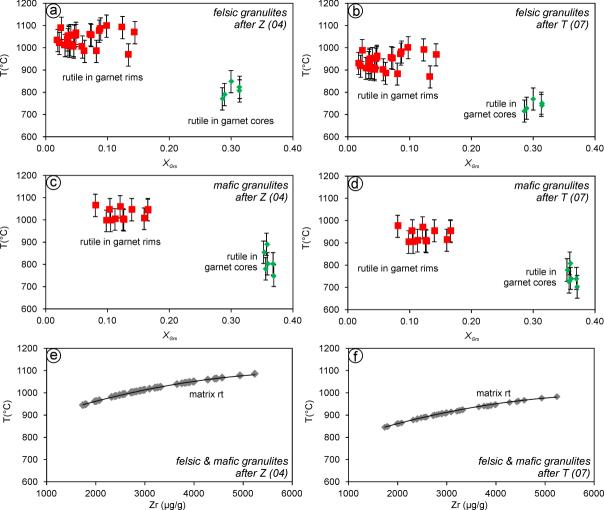


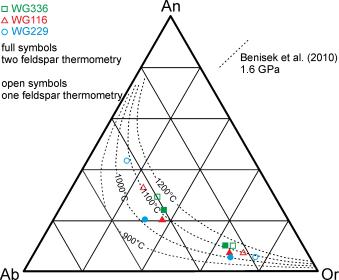


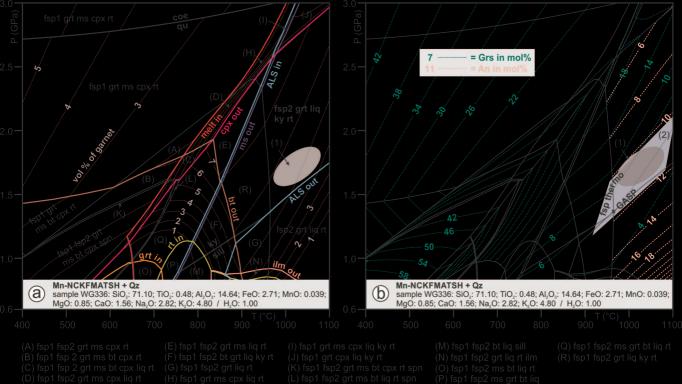


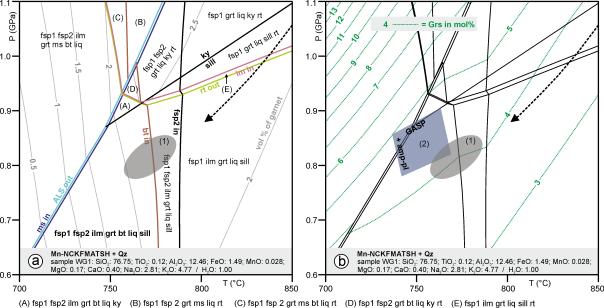


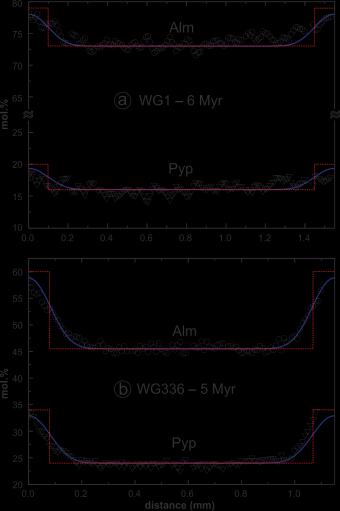


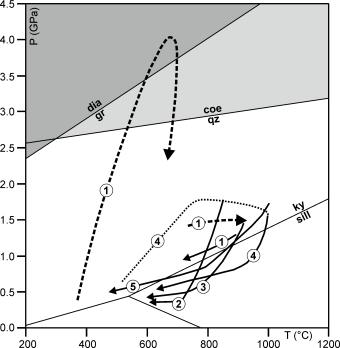












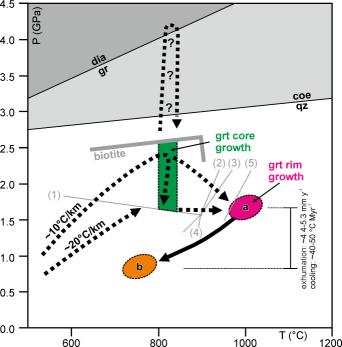


Table 1 Representative composition of garnet and clinopyroxene inclusions in garnet.

| Mineral                        | garnet                           |          |       |        |        |       |       |       |        |       |       |       |       |       |       |       |       |        |       |        | срх   |         |
|--------------------------------|----------------------------------|----------|-------|--------|--------|-------|-------|-------|--------|-------|-------|-------|-------|-------|-------|-------|-------|--------|-------|--------|-------|---------|
| Rock type                      | felsic granulite mafic granulite |          |       |        |        |       |       |       |        |       |       |       |       |       |       |       |       |        |       |        |       |         |
| Sample WG                      |                                  |          | 1     |        | 10     | 8     | 1     | 75    | 18     | 37    | 33    | 36    | 9     | 3     | ç     | 94    | 3     | 42     | 3     | 45     | 3,    | 44      |
| Location*                      | r                                | С        | #     | #      | r      | С     | r     | С     | r      | С     | r     | С     | r     | r     | r     | С     | r     | r      | r     | r      | ir    | nc      |
| SiO <sub>2</sub> wt.%          | 36.90                            | 36.63    | 36.83 | 37.03  | 39.15  | 38.29 | 38.54 | 37.72 | 38.91  | 38.85 | 37.76 | 38.15 | 36.19 | 37.54 | 38.00 | 38.54 | 37.30 | 37.78  | 36.38 | 37.05  | 51.71 | 51.78   |
| TiO <sub>2</sub>               | 0.11                             | 0.13     | b.d.  | 0.13   | 0.03   | 0.21  | b.d.  | 0.12  | 0.16   | 0.16  | b.d.  | 0.19  | b.d.  | b.d.  | b.d.  | b.d.  | b.d.  | 0.22   | b.d.  | b.d.   | 0.21  | 0.34    |
| $Al_2O_3$                      | 21.21                            | 21.66    | 21.04 | 21.66  | 22.04  | 22.26 | 22.45 | 22.50 | 22.48  | 23.18 | 22.11 | 21.87 | 20.64 | 21.02 | 21.60 | 21.46 | 20.56 | 21.24  | 20.96 | 20.96  | 1.84  | 1.71    |
| Cr <sub>2</sub> O <sub>3</sub> | b.d.                             | 0.10     | 0.06  | b.d.   | 0.06   | 0.06  | 0.05  | 0.00  | 0.15   | 0.09  | b.d.  | b.d.  | b.d.  | b.d.  | b.d.  | b.d.  | 0.07  | b.d.   | b.d.  | b.d.   | b.d.  | b.d.    |
| FeO                            | 35.19                            | 33.33    | 34.72 | 34.89  | 23.95  | 20.02 | 24.99 | 23.62 | 25.84  | 21.64 | 28.01 | 22.59 | 34.94 | 28.37 | 27.96 | 21.09 | 30.91 | 25.62  | 30.98 | 30.69  | 14.70 | 12.94   |
| MnO                            | 0.57                             | 0.46     | 0.63  | 0.57   | 0.39   | 0.35  | 0.72  | 0.67  | 0.56   | 0.38  | 0.43  | 0.42  | 1.33  | 0.73  | 0.59  | 0.45  | 0.98  | 0.59   | 1.06  | 1.00   | 0.07  | 0.16    |
| MgO                            | 4.09                             | 4.05     | 4.28  | 4.29   | 10.79  | 5.70  | 11.39 | 9.77  | 8.34   | 6.98  | 8.52  | 6.07  | 3.06  | 2.56  | 7.54  | 4.64  | 4.16  | 4.57   | 4.62  | 4.75   | 10.22 | 11.13   |
| CaO                            | 1.38                             | 3.44     | 1.40  | 1.43   | 3.79   | 12.82 | 1.72  | 4.95  | 3.63   | 8.62  | 2.32  | 10.63 | 2.61  | 9.51  | 3.62  | 13.34 | 5.88  | 10.30  | 5.39  | 5.62   | 19.79 | 20.57   |
| Na₂O                           | b.d.                             | b.d.     | b.d.  | b.d.   | b.d.   | b.d.  | b.d.  | b.d.  | b.d.   | b.d.  | b.d.  | b.d.  | b.d.  | b.d.  | b.d.  | b.d.  | b.d.  | b.d.   | b.d.  | b.d.   | 0.52  | 0.53    |
| Total                          | 99.45                            | 99.80    | 98.96 | 100.00 | 100.20 | 99.71 | 99.86 | 99.35 | 100.07 | 99.90 | 99.15 | 99.92 | 98.77 | 99.73 | 99.31 | 99.61 | 99.86 | 100.32 | 99.39 | 100.07 | 99.06 | 99.16   |
|                                | atoms                            | per 12 C | )     |        |        |       |       |       |        |       |       |       |       |       |       |       |       |        |       |        | atoms | per 6 O |
| Si                             | 2.968                            | 2.921    | 2.972 | 2.954  | 2.963  | 2.945 | 2.926 | 2.887 | 2.986  | 2.968 | 2.939 | 2.942 | 2.948 | 2.983 | 2.967 | 2.990 | 2.961 | 2.941  | 2.894 | 2.924  | 1.985 | 1.976   |
| Ti                             | 0.007                            | 0.008    | 0.002 | 0.008  | 0.002  | 0.012 | 0.000 | 0.007 | 0.009  | 0.009 | 0.000 | 0.011 | 0.000 | 0.000 | 0.000 | 0.005 | 0.000 | 0.013  | 0.000 | 0.000  | 0.006 | 0.010   |
| Al                             | 2.010                            | 2.036    | 2.001 | 2.037  | 1.966  | 2.018 | 2.009 | 2.030 | 2.033  | 2.087 | 2.028 | 1.987 | 1.981 | 1.969 | 1.988 | 1.962 | 1.924 | 1.949  | 1.965 | 1.950  | 0.083 | 0.077   |
| Cr                             | 0.000                            | 0.006    | 0.004 | 0.002  | 0.004  | 0.004 | 0.003 | 0.000 | 0.009  | 0.005 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |       |       | 0.000  | 0.000 | 0.000  | 0.000 | 0.000   |
| Fe <sup>3+</sup>               | 0.041                            | 0.100    | 0.048 | 0.037  | 0.101  | 0.063 | 0.136 | 0.182 | 0.000  | 0.000 | 0.095 | 0.107 | 0.123 | 0.064 | 0.078 | 0.048 | 0.149 | 0.142  | 0.246 | 1.823  | 0.000 | 0.000   |
| Fe <sup>2+</sup>               | 2.326                            | 2.122    | 2.295 | 2.291  | 1.415  | 1.224 | 1.451 | 1.330 | 1.658  | 1.382 | 1.728 | 1.349 | 2.257 | 1.821 | 1.748 | 1.320 | 1.903 | 1.526  | 1.816 | 0.203  | 0.472 | 0.413   |
| Mn                             | 0.039                            | 0.031    | 0.043 | 0.039  | 0.025  | 0.023 | 0.046 | 0.043 | 0.036  | 0.025 | 0.028 | 0.027 | 0.092 | 0.049 | 0.039 |       | 0.066 | 0.039  | 0.071 | 0.067  |       | 0.005   |
| Mg                             | 0.490                            | 0.481    | 0.515 | 0.510  | 1.217  | 0.654 | 1.289 | 1.115 | 0.954  | 0.795 | 0.989 | 0.698 | 0.372 | 0.303 |       | 0.537 |       | 0.530  | 0.548 | 0.559  |       | 0.633   |
| Ca                             | 0.119                            | 0.294    | 0.121 | 0.122  | 0.307  | 1.057 | 0.140 | 0.406 | 0.298  | 0.706 | 0.193 | 0.878 | 0.228 | 0.810 | 0.303 | 1.109 | 0.500 | 0.859  | 0.459 | 0.475  |       | 0.841   |
| Na                             |                                  |          |       |        |        |       |       |       |        |       |       |       |       |       |       |       |       |        |       |        |       |         |
| Σ Cat.                         | 8.000                            | 7.999    | 8.001 | 8.000  | 8.000  | 8.000 | 8.000 | 8.000 | 7.984  | 7.977 | 8.000 | 7.999 | 8.000 | 8.000 |       |       | 8.000 | 8.000  | 8.000 | 8.000  | 3.986 | 3.995   |
| Alm <i>mol%</i>                | 78.2                             | 72.5     | 77.2  | 77.3   | 47.7   | 41.4  | 49.6  | 46.0  | 56.3   | 47.5  | 58.8  | 45.7  | 76.6  | 61.0  | 58.9  | 44.1  | 64.3  | 51.6   | 62.7  | 62.3   |       |         |
| Рур                            | 16.5                             | 16.4     | 17.3  | 17.2   | 41.1   | 22.1  | 44.1  | 38.5  | 32.4   | 27.3  | 33.6  | 23.6  | 12.6  | 10.2  | 29.6  | 17.9  | 16.6  | 18.0   | 18.9  | 19.1   |       |         |
| Grs                            | 4.0                              | 10.0     | 4.1   | 4.1    | 10.4   | 35.7  | 4.8   | 14.0  | 10.1   | 24.3  | 6.6   | 29.7  | 7.7   | 27.1  | 10.2  | 37.0  | 16.9  | 29.1   | 15.9  | 16.3   |       |         |
| Sps                            | 1.3                              | 1.1      | 1.4   | 1.3    | 0.8    | 8.0   | 1.6   | 1.5   | 1.2    | 0.8   | 1.0   | 0.9   | 3.1   | 1.6   | 1.3   | 1.0   | 2.2   | 1.3    | 2.5   | 2.3    |       |         |
| $X_{Mg}$                       | 0.174                            | 0.185    | 0.183 | 0.182  | 0.462  | 0.348 | 0.470 | 0.456 | 0.365  | 0.365 | 0.364 | 0.341 | 0.141 | 0.143 | 0.334 | 0.289 | 0.205 | 0.258  | 0.232 | 0.734  |       | 0.605   |
| X <sub>Na</sub>                |                                  |          |       |        |        |       |       |       |        |       |       |       |       |       |       |       |       |        |       |        | 0.046 | 0.044   |
| Al <sup>IV</sup>               |                                  |          |       |        |        |       |       |       |        |       |       |       |       |       |       |       |       |        |       |        | 0.015 | 0.024   |

<sup>\*</sup>specifies textural position of analyzed mineral: r-rim; c-core; #-garnet in biotite and sillimanite rich domains; inc-inclusion in garnet

Table 2 Representative composition of muscovite, biotite, orthopyroxene and amphibole.

| Mineral               | neral muscovite |       |                  |       |           | orthop          | yroxene | amphibole |        |
|-----------------------|-----------------|-------|------------------|-------|-----------|-----------------|---------|-----------|--------|
| Rock type             | felsic          | mafic | felsic granulite |       | mafic gra | mafic granulite |         |           |        |
| Sample WG             | 336             | 344   | 4 178            |       | 345       | 87              | 342     | 345       |        |
| Location*             | inc             | inc   | mx               | inc   | mx        | core            | rim     | rim       | core   |
| SiO <sub>2</sub> wt.% | 46.90           | 47.57 | 38.60            | 38.18 | 35.87     | 48.00           | 49.88   | 39.89     | 40.24  |
| TiO <sub>2</sub>      | b.d.            | b.d.  | 1.62             | 6.13  | 4.34      | 0.10            | 0.11    | 2.26      | 2.02   |
| $Al_2O_3$             | 32.75           | 37.43 | 15.37            | 15.39 | 15.38     | 0.44            | 1.19    | 11.65     | 10.80  |
| $Cr_2O_3$             | b.d.            | b.d.  | 0.06             | b.d.  | b.d.      | b.d.            | b.d.    | b.d.      | b.d.   |
| FeO                   | 2.47            | 1.68  | 13.57            | 8.46  | 21.26     | 43.06           | 33.78   | 20.44     | 20.20  |
| MnO                   | 0.00            | b.d.  | b.d.             | b.d.  | b.d.      | 0.42            | 0.43    | 0.12      | 0.14   |
| MgO                   | 1.44            | 0.90  | 16.02            | 17.21 | 9.50      | 6.80            | 14.21   | 7.45      | 8.06   |
| CaO                   | 0.05            | b.d.  | b.d.             | b.d.  | 0.05      | 1.06            | 0.57    | 10.95     | 10.91  |
| Na₂O                  | 0.26            | 0.94  | 0.07             | 0.25  | b.d.      | b.d.            | b.d.    | 1.70      | 1.56   |
| K <sub>2</sub> O      | 10.73           | 9.97  | 9.94             | 9.91  | 9.38      |                 |         | 1.86      | 1.75   |
| F                     | 0.43            | b.d.  | 5.40             | 2.32  | 0.48      |                 |         | 0.06      | 0.05   |
| Cl                    | b.d.            | b.d.  | b.d.             | 0.09  | 0.05      |                 |         | 0.35      | 0.35   |
| Total                 | 95.03           | 98.49 | 100.65           | 97.94 | 96.31     | 99.88           | 100.17  | 96.73     | 96.08  |
|                       | atoms per 11 C  | )     |                  |       |           | atoms           | per 6 O | atoms per | 23 O   |
| Si                    | 3.164           | 3.054 | 2.859            | 2.762 | 2.751     | 1.992           | 1.960   | 6.229     | 6.302  |
| Ti                    | 0.000           | 0.000 | 0.090            | 0.333 | 0.250     | 0.003           | 0.003   | 0.265     | 0.238  |
| Al <sup>IV</sup>      | 0.836           | 0.946 | 1.141            | 1.238 | 1.249     | 0.008           | 0.040   | 1.771     | 1.698  |
| $AI^{VI}$             | 1.768           | 1.886 | 0.201            | 0.073 | 0.141     | 0.014           | 0.016   | 0.373     | 0.295  |
| Cr                    | 0.000           | 0.000 | 0.004            | 0.000 | 0.000     | 0.000           | 0.000   | 0.000     | 0.000  |
| Fe <sup>3+</sup>      | 0.000           | 0.000 | 0.000            | 0.000 | 0.000     | 0.000           | 0.018   | 0.203     | 0.284  |
| Fe <sup>2+</sup>      | 0.139           | 0.090 | 0.841            | 0.512 | 1.364     | 1.494           | 1.093   | 2.467     | 2.361  |
| Mn                    | 0.000           | 0.000 | 0.000            | 0.000 | 0.000     | 0.015           | 0.014   | 0.016     | 0.019  |
| Mg                    | 0.145           | 0.086 | 1.769            | 1.856 | 1.086     | 0.421           | 0.833   | 1.734     | 1.882  |
| Ca                    | 0.004           | 0.000 | 0.000            | 0.000 | 0.004     | 0.047           | 0.024   | 1.832     | 1.831  |
| Na                    | 0.034           | 0.117 | 0.010            | 0.035 | 0.000     | 0.000           | 0.000   | 0.515     | 0.474  |
| K                     | 0.923           | 0.817 | 0.939            | 0.914 | 0.918     |                 |         | 0.371     | 0.350  |
| F                     | 0.092           | 0.000 | 1.265            | 0.531 | 0.116     |                 |         | 0.030     | 0.025  |
| Cl                    | 0.000           | 0.000 | 0.000            | 0.011 | 0.006     |                 |         | 0.093     | 0.093  |
| Σ Cat.                | 7.013           | 6.996 | 7.853            | 7.724 | 7.763     | 3.994           | 4.001   | 15.775    | 15.734 |
| $X_{Mg}$              | 0.511           | 0.489 | 0.678            | 0.784 | 0.443     | 0.220           | 0.433   | 0.413     | 0.444  |

<sup>\*</sup>specifies textural position of analyzed mineral: inc-inclusion in garnet; mx-matrix;

Table 3 Representative composition of former ternary feldspar and K-feldspar.

| Mineral               | former ternary feldspar |       |              |       |              |       |              |        |              |           |        |  |  |
|-----------------------|-------------------------|-------|--------------|-------|--------------|-------|--------------|--------|--------------|-----------|--------|--|--|
| Rock type             | felsic gran             | ulite |              |       |              |       |              |        | mafic g      | granulite |        |  |  |
| Sample WG             | 11                      | 6     | 32           | 329   |              | 336   |              | 192    |              | 94        |        |  |  |
| Location*             | ho                      | ex    | ho           | ex    | ho           | ex    | ho#          | ex#    | ex           | ho        | mx     |  |  |
| SiO <sub>2</sub> wt.% | 64.57                   | 62.95 | 65.21        | 63.07 | 64.96        | 62.49 | 65.29        | 65.27  | 66.11        | 58.98     | 64.40  |  |  |
| $Al_2O_3$             | 19.01                   | 22.57 | 18.77        | 22.75 | 18.78        | 23.30 | 18.01        | 22.23  | 18.01        | 26.17     | 18.91  |  |  |
| CaO                   | 0.12                    | 4.29  | 0.05         | 3.93  | 0.12         | 4.76  | b.d.         | 2.76   | b.d.         | 7.94      | 0.09   |  |  |
| BaO                   | 0.17                    | b.d.  | b.d.         | b.d.  | 0.14         | b.d.  | b.d.         | b.d.   | b.d.         | b.d.      | 0.58   |  |  |
| Na₂O                  | 1.05                    | 9.01  | 1.10         | 9.08  | 1.29         | 8.91  | 1.15         | 9.93   | 0.73         | 6.94      | 0.95   |  |  |
| K <sub>2</sub> O      | 15.44                   | 0.26  | 15.27        | 0.67  | 14.86        | 0.18  | 15.31        | 0.13   | 15.14        | 0.27      | 15.23  |  |  |
| Total                 | 100.36                  | 99.08 | 100.40       | 99.50 | 100.15       | 99.64 | 99.76        | 100.32 | 99.99        | 100.30    | 100.16 |  |  |
| Si per 8 O            | 2.971                   | 2.806 | 2.987        | 2.805 | 2.985        | 2.777 | 3.014        | 2.858  | 3.025        | 2.615     | 2.974  |  |  |
| Al                    | 1.031                   | 1.186 | 1.013        | 1.192 | 1.017        | 1.220 | 0.980        | 1.152  | 0.971        | 1.368     | 1.029  |  |  |
| Ca                    | 0.006                   | 0.205 | 0.002        | 0.187 | 0.006        | 0.227 | 0.000        | 0.129  | 0.000        | 0.377     | 0.004  |  |  |
| Ва                    | 0.003                   | 0.000 | 0.000        | 0.000 | 0.003        | 0.000 | 0.000        | 0.000  | 0.000        | 0.000     | 0.010  |  |  |
| Na                    | 0.094                   | 0.779 | 0.098        | 0.783 | 0.115        | 0.768 | 0.103        | 0.843  | 0.065        | 0.597     | 0.085  |  |  |
| K                     | 0.906                   | 0.015 | 0.892        | 0.038 | 0.871        | 0.010 | 0.902        | 0.007  | 0.884        | 0.015     | 0.897  |  |  |
| Σ Cat.                | 5.011                   | 4.991 | 4.992        | 5.005 | 4.997        | 5.001 | 4.999        | 4.989  | 4.945        | 4.972     | 4.999  |  |  |
| An <i>mol%</i>        | 0.6                     | 20.5  | 0.2          | 18.6  | 0.6          | 22.6  | 0.0          | 13.2   | 0.0          | 38.1      | 0.4    |  |  |
| Ab                    | 9.3                     | 78.0  | 9.9          | 77.7  | 11.6         | 76.4  | 10.2         | 86.1   | 6.8          | 60.4      | 8.6    |  |  |
| Or                    | 90.1                    | 1.5   | 89.9         | 3.8   | 87.8         | 1.0   | 89.8         | 0.7    | 93.2         | 1.5       | 91.0   |  |  |
|                       | reintegrated            |       | reintegrated |       | reintegrated |       | reintegrated |        | reintegrated |           |        |  |  |
| An <i>mol%</i>        | 8.5                     |       | 4.9          |       | 11.0         |       | 5.9          |        | 38.9         |           |        |  |  |
| Ab                    | 21                      | .4    | 16.9         |       | 25.2         |       | 25.8         |        | 34.6         |           |        |  |  |
| Or                    | 70.2                    |       | 78.2         |       | 63.8         |       | 68.4         |        | 26.4         |           |        |  |  |

<sup>\*</sup>specifies textural position of analyzed mineral: ho-host; ex-exsolution; #-feldspar enclosed in kyanite

 Table 4 Representative composition of plagioclase.

| Mineral               | plagiocla  | ise    |                 |       |       |  |
|-----------------------|------------|--------|-----------------|-------|-------|--|
| Rock type             | felsic gra | nulite | mafic granulite |       |       |  |
| Sample WG             | 116        | 322    | 336             | 87    | 345   |  |
| Location*             | mx         | mx     | mx              | mx    | mx    |  |
| SiO <sub>2</sub> wt.% | 63.40      | 64.14  | 62.46           | 61.04 | 61.53 |  |
| $Al_2O_3$             | 22.88      | 22.66  | 23.34           | 23.98 | 23.65 |  |
| CaO                   | 4.32       | 3.51   | 5.01            | 5.73  | 5.58  |  |
| BaO                   | b.d.       | b.d.   | b.d.            | b.d.  | b.d.  |  |
| Na₂O                  | 8.89       | 9.15   | 8.54            | 8.15  | 8.22  |  |
| K <sub>2</sub> O      | 0.26       | 0.50   | 0.24            | 0.48  | 0.35  |  |
| Total                 | 99.75      | 99.96  | 99.59           | 99.38 | 99.33 |  |
| Si per 8 O            | 2.803      | 2.828  | 2.775           | 2.725 | 2.747 |  |
| Al                    | 1.192      | 1.178  | 1.222           | 1.262 | 1.245 |  |
| Ca                    | 0.205      | 0.166  | 0.238           | 0.274 | 0.267 |  |
| Ва                    | 0.000      | 0.000  | 0.000           | 0.000 | 0.000 |  |
| Na                    | 0.762      | 0.782  | 0.736           | 0.705 | 0.712 |  |
| K                     | 0.015      | 0.028  | 0.014           | 0.027 | 0.020 |  |
| Σ Cat.                | 4.977      | 4.982  | 4.985           | 4.993 | 4.991 |  |
| An <i>mol%</i>        | 20.9       | 17.0   | 24.1            | 27.2  | 26.7  |  |
| Ab                    | 77.6       | 80.1   | 74.5            | 70.1  | 71.3  |  |
| Or                    | 1.5        | 2.9    | 1.4             | 2.7   | 2.0   |  |

<sup>\*</sup>specifies textural pos. of analyzed mineral: mx-matrix