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1	Timescales of exhumation and cooling informed by kinetic modelling. An
4	Timescales of exhumation and cooling interfed by kinetic modeling. An
5	example using a lamellar garnet pyroxenite from the Variscan
6	Granulitgebirge, E Germany
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23	Abstract

24 We present a numerical modeling approach to infer timescales of the exhumation and cooling history recorded in the chemical composition of minerals in a garnet pyroxenite from the 25 26 Granulitgebirge, Saxony/Germany. The studied sample contains remarkable exsolution 27 textures from former megacrysts that produced up to mm-wide, alternating lamellae of garnet (grt) and clinopyroxene (cpx). Compositional profiles of major and minor elements measured 28 29 with the electron microprobe perpendicular to the grt-cpx interfaces reveal systematic zoning patterns for Fe, Mg, Al, Si, Cr, Ti in clinopyroxene and Ca, Fe, Mg, Mn in garnet, 30 respectively. In addition to simple thermal modelling that is used to constrain the conditions 31 32 of emplacement of the Granulitgebirge Massif at shallow crustal levels, we combine 33 thermodynamic data with a numerical finite difference scheme that simulates growth and 34 simultaneous diffusive exchange between garnet and clinopyroxene along a virtual cooling 35 path. The latter model assumes local equilibrium at the interface. Diffusive fluxes are constrained by mass balance. It is shown that zoning patterns such as Fe-Mg exchange 36 between garnet and clinopyroxene can be used to extract cooling rates and thus timescales of 37 exhumation, while the profiles for the minor elements are provisionally related to the growth 38 history of the lamellae. Furthermore, zoning profiles in the lamellae can only be reproduced 39 40 with ultrahigh cooling rates similar to contact metamorphic conditions. This in turn, suggests that the massif was emplaced at temperatures above 900°C in agreement with the observed 41 spatial extent of a contact aureole within low-grade metasedimentary rocks surrounding the 42 43 granulite massif as predicted by thermal modeling. Exhumation of the massif without cooling below 900°C requires an exhumation rate of several cm/yr. Thus, we propose an almost 44

isothermal exhumation period of ~1Ma followed by isobaric cooling from 900 to 600°C
within less than 10 ka.

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48 Introduction

49 Metamorphic textures and mineral compositions are records of complex geodynamic 50 processes such as subduction, orogenesis or exhumation. Determination of pressure and 51 temperature conditions at various stages is one of the key tools to constrain the evolution of 52 rock units on a larger scale. Commonly, thermodynamic calculations are used to infer P-T 53 conditions based on observed phase assemblages and mineral compositions. The use of 54 thermodynamic data is founded on the assumption that phases in a given sample are effectively able to adjust their composition up to a certain point in time and remain perfectly 55 56 closed afterwards, i.e. without any further exchange reaction on the retrograde path. 57 Especially in medium to high grade metamorphic rocks this assumption is questionable as 58 virtually every system, evolving along a T-t path, is subject to diffusive re-equilibration to 59 different extents. In the last decade, an increasing number of studies investigated nonequilibrium aspects with regard to textural and compositional records in rocks on various 60 scales (e.g., Roselle et al., 1997; Mueller et al., 2004; Gaidies et al., 2008a; Gaidies et al., 61 2008b; Mueller et al., 2008; Caddick et al., 2010; Mueller et al., 2010; Gaidies et al., 2011). 62 Rather than a limitation, the incomplete readjustment of mineral compositions during 63 64 metamorphism should be regarded as an additional source of information on the mechanism 65 and rates of processes, such as element / isotope exchange during large scale geodynamic 66 processes with significantly changing P-T conditions (see also review by Mueller et al., 2010). 67 Lasaga (1983) published a landmark paper in which he used the temperature dependent ability of diffusive compositional adjustment to infer exhumation rates based on the cooling history 68 69 recorded in diffusion profiles of elements in minerals which led to the concept of 70 "geospeedometry". While the original focus of this approach was on exhumation rates, i.e. the

71 determination of speed in mm/year, it has also often been misleadingly used to estimate 72 timescales of igneous and metamorphic processes (for a detailed description see review by 73 Costa et al., 2008). However, the concept of the determination of rates and durations of processes for isothermal and non-isothermal histories can successfully be applied if the 74 75 relevant transport parameters, e.g. diffusion coefficients and information on other factors 76 controlling the diffusive flux (e.g. grain size, modal abundance) are available. As a 77 consequence, cooling histories of metamorphic terrains have been determined using this kinetic modeling approach (Lasaga et al., 1977; Spear and Florence, 1992; Ducea et al., 2003; 78 79 Trepmann et al., 2004; Hauzenberger et al., 2005). Element exchange driven by diffusion is 80 largely dependent on temperature, which directly relates the applicability of geospeedometry 81 and geothermobarometry to the concept of diffusive closure of a mineral (Dodson, 1973; 82 Dodson, 1986; Ganguly and Tirone, 1999). However, a complete description of the dynamic 83 system governing the geochemical fluxes, in turn, allows evaluating whether mineral 84 compositions are reset during heating, cooling and/or decompression and if so, to which extent. For example, the effect of mixed-volatile reaction, volume diffusion, and exsolution 85 has been studied to successfully reproduce variations in measured calcite-dolomite 86 87 thermometric data in contact metamorphic settings (Mueller et al., 2008). Recently, the Fe-Mg interdiffusion data for various ferromagnesian minerals such as garnet (Borinski et al., 2012), 88 89 spinel (Liermann and Ganguly, 2002), clinopyroxene (Mueller et al., 2013), and 90 orthopyroxene (Ganguly and Tazzoli, 1994) have been determined. Knowledge of these 91 kinetic parameters in turn was used to evaluate the effect on the element distribution and thus on apparent thermometric data for typical cosmochemical and geological settings (Ganguly et 92 93 al., 2013; Mueller et al., 2013).

In this paper, we use numerical models of kinetically controlled element exchange between co-existing garnet (grt) and clinopyroxene (cpx) exsolution lamellae to study the effect and timescales of diffusive compositional adjustment during a cooling and exhumation

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97 event. Such lamellae occur in an ultrabasic rock intercalated within a complex of high 98 pressure granulite in the Variscan Granulitgebirge (Saxony/Germany). This metamorphic 99 complex is a suitable example for two reasons: (1) the geological setting is simple enough to 100 place solid constraints on the geometry, different lithologies, and tectonic setting (Fig. 1 and 101 Reinhardt and Kleemann, 1994) and (2) there are a large number of studies which focused on 102 the P-T evolution using exchange reactions and thermodynamic calculations (Roetzler and 103 Romer, 2001; Massonne and Bautsch, 2002; Roetzler et al., 2004; Hagen et al., 2008; Roetzler 104 et al., 2008; Schmaedicke et al., 2010) in addition to geochronological data that provide 105 independent estimates for the timescale of the exhumation process (von Quadt, 1993; Kroener 106 et al., 1998; Romer and Roetzler, 2001; Roetzler and Romer, 2010). It is shown here that a 107 combination of equilibrium phase petrology and modeling of mass and heat transport can 108 improve the reconstructed P-T-t exhumation path. Finally, the new results are discussed in the context of a large scale geodynamic exhumation model comparing previous petrological 109 110 findings.

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112 Geological settings and previously derived P-T-t evolution of the Granulitgebirge

113 The Variscan orogen of Europe formed by collision of the palaeocontinents Laurussia 114 and Gondwana in the Late Palaeozoic. Many researchers assume that Gondwana-derived 115 terrains collided with Laurussia first before Gondwana came in contact with Laurussia (e.g., Kroner and Romer, 2013). The eastern part of this orogen is represented by the Bohemian 116 117 Massif, a collage of diverse basement blocks, which include units of high temperature, high to ultrahigh pressure metamorphic rocks from the root of the collisional orogen. These rock 118 119 assemblages include garnet peridotite, eclogite, high pressure mafic and felsic granulite as well as related quartzofeldspathic rocks with a wide range of maximum P-T estimates [700° to 120 121 1100°C, 0.4 to 4.5 GPa (for summary see Massonne, 2011)]. The ages of high-pressure 122 metamorphism in the Bohemian Massif are bimodal (Kroener and Willner, 1998): 400-380 4

Ma in the Gory Sowie, Tepla Barrandian Unit, and Münchberg Complex and 350-335 Ma in the Erzgebirge, Granulitgebirge, Snieznik, and Gföhl Unit (Fig. 1a). Evolution and mechanism of exhumation of these high pressure rocks are still a matter of debate (e.g., Willner et al., 2002; Kroner and Goerz, 2010).

The Granulitgebirge in Saxony (Germany) in the northern part of the Bohemian Massif 127 128 represents a key unit for the younger high-pressure event, where geodynamic processes were 129 studied in detail within a rather small area. The Granulitgebirge forms an oval-shaped dome structure composed of high-pressure felsic granulite including lenses of mafic granulite and 130 garnet peridotite (Werner, 1987; Roetzler et al., 1992; Reinhardt and Kleemann, 1994; 131 132 Roetzler and Romer, 2010). Protoliths of the granulites are Cambro-Ordovician igneous rocks with calcalkaline and tholeiitic affinities (Werner, 1987; Kroener et al., 1998). The contact of 133 the Granulitgebirge to the surrounding rocks, which are low-pressure siliciclastic 134 metasediments of early Palaeozoic to late Devonian age, is represented by a major extensional 135 136 detachment zone. This shear zone comprises (1) the rim of the granulite complex, (2) 137 dismembered slivers of medium-pressure garnet-cordierite gneiss and ophiolitic rocks, and (3) 138 the lower part of the metasedimentary cover, and it shows a top-to-SE tectonic transport 139 (Roetzler et al., 1992; Reinhardt and Kleemann, 1994). Various peak P-T conditions were estimated for the felsic and mafic granulites: >1 GPa, >800 °C (Grew, 1986; Roetzler et al., 140 141 1992), 2.2-2.3 GPa, >1000 °C (Roetzler and Romer, 2001; Roetzler et al., 2004; Hagen et al., 2008; Roetzler et al., 2008; Roetzler and Romer, 2010) and 1.4 GPa, > 800 °C (Massonne, 142 143 2006). The P-T estimates for the garnet peridotite and associated garnet pyroxenite and eclogite are in the range 1.9-3.3 GPa, 1000-1070 °C (Roetzler and Romer, 2001; Massonne 144 145 and Bautsch, 2002; Schmaedicke et al., 2010). Later equilibration stages in the granulite during the exhumation were estimated to 0.9-0.95 GPa, 890-940 °C (Roetzler and Romer, 146 2001), 1.0-1.05 GPa, 940-980 °C [symplectite stage (Roetzler et al., 2008)] and 0.25 GPa, 740 147 °C [final emplacement stage (Roetzler et al., 2004)]. The age of the peak pressure conditions 148

was constrained by dating of zircon (341.5±0.8 Ma) and titanite (342±0.8 Ma) with the U/Pb
system (Romer and Roetzler, 2001). The obtained data agree with earlier zircon ages derived
by von Quadt (1993) and Kroener et al. (1998). From the study of the garnet-cordierite gneiss,
a decompression-heating path of 0.65 GPa, 730 °C to 0.5 GPa, 790°C was invoked by
Roetzler & Romer (2010). These authors interpreted this partial P-T path as being due to heat
transfer from the rising granulite.

155 The low-pressure metasediments (phyllite) surrounding the granulites show a progressive metamorphic zonation from very low grade metamorphic conditions towards 156 157 incipient migmatization near the contact to the granulites at a depth corresponding to 0.2-0.3 158 GPa (Roetzler et al., 1992; Reinhardt and Kleemann, 1994). Subsequent growth of chlorite, andalusite, staurolite, cordierite, garnet, and sillimanite is observed in these metasediments 159 160 (schist mantle). This $\sim 1-3$ km wide halo around the granulite complex is interpreted as the result of heating after emplacement of this complex during exhumation (Roetzler et al., 1992; 161 162 Reinhardt and Kleemann, 1994; Roetzler and Romer, 2010). Rb/Sr ages of white mica in the low-pressure metasediments can be grouped into three categories according to Roetzler & 163 164 Romer (2010): (1) ages of 348.6 ± 3.5 Ma and 349.4 ± 3.5 Ma at more than 600 m from the 165 contact reflect the age of regional metamorphism of the sediments prior to emplacement of the 166 granulites; (2) an age of 337.6±3.6 in the garnet-cordierite gneiss at the contact overlaps with 167 the age of the peak of metamorphism in the granulite complex and is interpreted as the age of its juxtaposition with the granulite complex; (3) an age of 333.6 ± 4.2 Ma in the schists at the 168 169 contact is consistent with Ar-Ar ages of white mica of 334.2±1.9 Ma and 332.6±4 Ma (Werner and Reich, 1997) in these schists and a Pb-Pb single-zircon evaporation age of 170 171 333.1±1.0 Ma for a concordant granite intrusion into the schists (Kroener et al., 1998). The latter ages are interpreted as the time of the arrival of the granulite complex at shallow crustal 172 depth and the formation of the contact metamorphic halo (Roetzler and Romer, 2010). The 173 determined time interval for the exhumation of ~7 Myrs results in an exhumation rate of 7-13 174 6

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mm/yr and a cooling rate of 40-70 °C/Myr (Roetzler and Romer, 2010). This very rapid 175 176 extensional unroofing of the granulite complex from the root of a thickened crust (Reinhardt 177 and Kleemann, 1994) is matched by comparable exhumation rates and mechanisms of high-178 pressure rocks in the Erzgebirge in the south (Willner et al., 2000; Willner et al., 2002; 179 Massonne et al., 2007). Extensional unroofing in an "exhumation channel" is thought to be 180 balanced by concomitant stacking at depth during ongoing convergence. Delamination of the 181 lithospheric mantle was envisaged as primary cause for the rapid exhumation of the 350-335 Ma high-pressure rocks from the crustal root throughout the Bohemian Massif, where a 182 thickened crust was likely maintained since the time of collision at 400-380 Ma (Massonne 183 184 and O'Brien, 2003; Massonne, 2006), when the older high-pressure units of the Bohemian Massif originated. Other geodynamic models invoke intracontinental subduction (Kroner and 185 186 Goerz, 2010; Kroner and Romer, 2013) or considerable crustal stacking after deep crustal subduction (O'Brien, 2008). 187

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189 Sample description, mineral composition and origin of lamellar megacrysts

190 We studied a garnet pyroxenite from the abandoned serpentinite quarry at the village 191 of Reinsdorf, Saxony (Germany). The garnet pyroxenite, which was first described by 192 Hentschel (1937) and originally named as "Eklogit von Gilsberg", forms several centimeter to 193 decimeter thick, boudinaged layers in the serpentinite body. These layers are parallel to each 194 other. In some instances, alternating lamellae of garnet and clinopyroxene are discernable in 195 the garnet pyroxenite (Fig. 2). Such domains of lamellar fabric are surrounded by more or less 196 equigranular domains, which consist of mm-sized grains of garnet and clinopyroxene 197 representing an equilibrium texture (Fig. 2). Both types of fabric can occur in homogeneous domains of several cm³ in our sample. The equilibrium texture was the result of 198 199 recrystallization of the lamellae proven by intermediate stages (e.g. curved and partially 200 recrystallized lamellae as the result of deformation) between both types of fabric (Massonne

201 and Bautsch, 2002). The garnet lamellae are topotaxially intergrown with clinopyroxene [cpx: 202 [001]cpx//[100]grt well (100)cpx//(100)grt(100)cpx//(110)grtand as as and 203 [001]cpx//[110]grt (Reiche and Bautsch, 1984; Jekosch and Bautsch, 1991)]. Therefore, the 204 lamellar texture was interpreted to be the result of exsolution of garnet from clinopyroxene 205 (Reiche and Bautsch, 1985) because of the dominance of clinopyroxene lamellae [vol.% 206 cpx/grt = 7:3, (Massonne and Bautsch, 2002)]. As the lamellae can extend parallel over 207 several cm, the invoked clinopyroxene originally occurred as megacrysts up to 10 cm in size forming once monomineralic layers in the exposed, now serpentinized mantle fragment. 208

209 Especially thick garnet lamellae without visible symplectites [composed of 210 orthopyroxene, spinel, clinopyroxene and anorthite-rich plagioclase (Massonne and Bautsch, 2002)] were selected for detailed compositional profiles perpendicular to the interface 211 212 between lamellae. Electron microprobe measurements have been performed using a Cameca 213 SX 100 at Universität Stuttgart. Garnet and clinopyroxene composition have been analyzed at 214 15 kV and a beam current of 30 or 40 nA. A total of ten profiles for adjacent grt-cpx lamellae 215 have been measured at different positions within the limits of a former megacryst. No 216 significant difference can be observed and representative compositional profiles are shown in 217 figure 3. Measured profiles reveal almost flat, but often slightly zoned patterns with 218 increasing pyrope and almandine and decreasing grossular component from the garnet center 219 towards the interface (Fig. 3), and almost no zoning of any major element from core to rim can be observed in the adjacent clinopyroxene (Fig. 3; see also Massonne and Bautsch, 2002). 220 221 Spatially resolved minor element compositions show an increase in concentration of Cr, V 222 and Ti towards the clinopyroxene rim. In contrast, no zoning for Cr and V can be observed in 223 the garnet, which is also nearly free of titanium (Fig. 3).

In a previous study, Massonne and Bautsch (2002) determined the original megacryst composition on the basis of the compositions of the slightly chemically zoned clinopyroxene and garnet and their abundance. They concluded that the megacrysts were either Al-rich

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227 clinopyroxenes formed at about 1.7 GPa and 1400°C or Ca-majoritic garnets from an upper 228 portion of the mantle transition zone. The question of the original host phase, i.e. whether 229 garnet exsolved from clinopyroxene or vice versa, has important consequences for the 230 reconstruction of the P-T evolution as argued by Massonne and Bautsch (2002). These authors 231 used bulk rock trace element compositions to argue for a majoritic garnet to be the former 232 host phase. In contrast, Reiche and Bautsch (1985) proposed cpx as the original phase based 233 on the higher abundance of cpx compared to garnet. Roetzler and Romer (2010) argued that 234 Al-rich spinel inclusions measured in garnet crystals of the matrix support the case of a cpx host. In fact, it is not essential to the purposes of this paper to determine the original host 235 236 phase, but the spatially resolved compositional trace element profiles potentially contain the information needed to answer this question. For example, the virtually Ti-free garnet and the 237 238 visible Ti-zoning in clinopyroxene (Fig. 3) could be interpreted as the consequence of 239 titanium accumulation in clinopyroxene during the growth of the garnet lamella in which Ti is 240 rather incompatible. Consequently, back diffusion of Ti into the residual clinopyroxene 241 lamellae would then lead to the observed compositional profile as observed in other studies

for Nb in rutile after reaction to titanite (Lucassen et al., 2011; Cruz-Uribe et al., 2014).

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244 Numerical modeling

245 Peak metamorphic conditions are typically determined with geothermobarometers, for example the temperature dependent exchange of elements between two minerals (e.g. Fe-Mg 246 247 between garnet and biotite). Based on thermodynamics, corresponding calculations constrain 248 equilibrium between minerals that is the direct record of intrinsic, external variables such as temperature, pressure or a partition coefficient. A very important assumption for the 249 250 interpretation of this concept to metamorphic rocks is that minerals are thought to adjust their composition infinitely fast according to the external conditions at least during prograde 251 metamorphism, which includes formation of new minerals by net transfer reaction, 252

253 recrystallization and/or fast diffusive homogenization at elevated temperatures. In contrast, 254 retrograde adjustment of mineral compositions during cooling is often interpreted to be 255 sluggish which has led many researchers to the erroneous interpretation that only mineral rim 256 compositions are affected by retrograde element exchange whereas core compositions are 257 likely to reflect peak metamorphic conditions. The later assumption has been shown to depend 258 on a number of parameters such as cooling rate, grain size, modal abundances, which all 259 determine the transport properties of elements along grain boundaries and within crystals and thus the effective flux of elements (Fisher, 1978; Ganguly and Tirone, 1999; Dohmen and 260 261 Chakraborty, 2003; Mueller et al., 2010). Thus, it is necessary to evaluate which part of the 262 thermal history is recorded in the chemical zoning pattern for a given mineral pair and set of parameters given above. Dodson (1973) developed a formulation to compute the so-called 263 264 "closure temperature" being the mean temperature at which declining diffusion rates preclude 265 significant exchange of elements by diffusion at a given cooling rate and grain size under the 266 assumption of a simple mineral geometry and effectively infinite reservoir to exchange with. 267 Later, some modifications allowed the spatial resolution of the closure temperature for 268 different parts of a crystal (e.g., Dodson, 1986; Ganguly and Tirone, 1999). However, in the 269 present case, interdiffusion rates of Fe-Mg in clinopyroxene (Mueller et al., 2013) and garnet 270 (Borinski et al., 2012) are very similar, i.e. the assumption of an effectively infinite reservoir 271 and thus the above formulation cannot be used to evaluate the compositional resetting of a cpx-grt pair during cooling. In recent studies, Ganguly et al. (2013) and Mueller et al. (2013) 272

stated that there is no analytical solution for this problem and they developed a 1-D numerical model for a polythermal diffusive element exchange between two phases without net mass transfer under isobaric conditions using a temperature dependent partition coefficient. The model of Mueller et al. (2013), specifically focused on the Fe-Mg exchange between ferromagnesian mineral pairs (spinel, garnet, olivine, ortho- and clinopyroxene). Modeling results revealed that for most geologically relevant conditions the mineral pairs efficiently

adjust their chemical composition above 1000-1100 °C independent of the cooling rate.

In this study, we extended the simple polythermal diffusive element exchange model to incorporate the effect of exhumation (i.e., decompression) and mineral growth (i.e., net mass transfer) and applied this to the grt-cpx lamellae in our sample. The length of the modeled compositional profiles perpendicular to the interface between the lamellae are negligible compared to the extent of the lamellae parallel to the interface which justifies the application of the 1-D model geometry excluding additional element fluxes in a second or even third dimension. For both adjacent lamellae we solved the diffusion equation:

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$$\left(\frac{\partial C_{F_{e}/M_g}}{\partial t}\right)^{\alpha} = \frac{\partial}{\partial X} \left(D_{F_{e}-M_g}^{\alpha} \left(\frac{\partial C_{F_{e}/M_g}}{\partial X}\right)^{\alpha}\right)$$
(1)

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290 using a finite difference scheme where α denotes the mineral phase. In this equation, the 291 actual change in concentrations of Fe and Mg ($C_{\text{Fe/Mg}}$) are calculated for each node (with node 292 spacing X) within the crystal for a given time interval t and the effective diffusion coefficient 293 $D_{\rm Fe-Mg}$ that is re-calculated after every time step according to the current temperature. Based 294 on the results by Mueller et al. (2013), an efficient adjustment of mineral compositions in both phases above 1000 °C was assumed leading to initially flat concentration profiles. 295 296 Temperature dependent diffusion coefficients are calculated using the experimental data for 297 Fe-Mg interdiffusion in garnet (Borinski et al., 2012) and clinopyroxene (Mueller et al., 2013). Fe and Mg concentrations for both phases at the interface are set to be in local 298 299 equilibrium, i.e. these concentrations followed a pressure and temperature dependent partitioning: 300

$$K_D^{grt-cpx} = \frac{\left(\frac{Fe}{Mg}\right)^{grt}}{\left(\frac{Fe}{Mg}\right)^{cpx}} = f(P,T)$$
(2)

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For this study, we used the partition coefficient derived by Ganguly et al. (1996). It is important to bear in mind that the subtle differences in the transport properties of Fe and Mg in clinopyroxene and garnet require an additional constraint to calculate the element fluxes correctly. This becomes especially important in the case of simulated lamellae growth. Consequently, mass balance is maintained for fluxes across the interface by:

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$$D_{Fe-Mg}^{grt} \left(\frac{\partial C_{Fe/Mg}}{\partial X}\right)^{grt} = D_{Fe-Mg}^{cpx} \left(\frac{\partial C_{Fe/Mg}}{\partial X}\right)^{cpx}$$
(3)

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Diffusion and partition coefficients are updated to the pressure and temperature corresponding to the conditions attained at the time along a predefined exhumation and cooling path. Resulting concentration profiles are calculated iteratively and final, frozen compositional profiles are presented ranging from the center of the garnet lamella over the interface to the center of the clinopyroxene lamella.

317 In the following, we explore three different model scenarios in order to separate and 318 evaluate the effects of cooling, exhumation and lamellae growth on the resulting recorded chemical profile and compare the model results with the measured $X_{\rm Fe}$ distribution in the 319 320 natural sample. Final half-lamella dimensions of 80 μ m for the garnet and 150 μ m for the 321 clinopyroxene have been chosen to allow direct comparison of model results and natural 322 samples. The initial concentration in the garnet lamella has arbitrarily been set to $X_{\rm Fe}=0.21$ and the corresponding clinopyroxene composition has been calculated to be in equilibrium 323 324 with the garnet at the P-T-conditions at the start of the model run using equation 2. For

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simplicity, we selected a simple linear cooling and exhumation path for model runs with a total duration of $2x10^3$, $2x10^4$, and $2x10^5$ years, which corresponds to cooling rates of $2x10^5$, $2x10^4$, and $2000 \,^{\circ}$ C/Ma, respectively.

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329 *Case 1 – isobaric cooling / no lamellae growth*

A first set of models evaluate the effect of cooling on the compositional profiles 330 331 recorded in both the garnet and the clinopyroxene lamellae. Based on the results of Mueller et 332 al. (2013) which suggested complete (instantaneous) adjustment of compositions above 1000-333 1100 °C and an apparent closure between 600 and 700 °C, we modeled a linear cooling from 334 1000 to 600 °C with different cooling rates. The pressure was chosen to 0.2 GPa which 335 corresponds to the final depth of emplacement of the massif. Our initial garnet composition of 336 $X_{\rm Fe}=0.21$ results in an initial $X_{\rm Fe}$ of 0.1 in the clinopyroxene. We note that these values closely 337 correspond to the measured core compositions of both lamellae.

338 Modeling results for the case 1 scenario are shown in figure 4 (case 1). The recorded profiles reveal a general increase in Fe in the garnet coupled to decrease of $X_{\rm Fe}$ in the 339 340 clinopyroxene, which is in agreement with the partition coefficient reflecting that Fe is more 341 compatible in garnet than in clinopyroxene with decreasing temperatures. Remarkably, both 342 lamellae exhibit a different Fe-zoning pattern with a slight increase from the center of the 343 garnet lamella towards the interface and a steep decrease of Fe concentration in clinopyroxene 344 towards the interface. The observed difference for the zoning pattern is the consequence of 345 two factors: (1) the smaller size of the garnet lamella results in a more efficient 346 homogenization. In addition, there is a Fe influx from the opposite grt-cpx interface which is 347 further promoted by (2) the higher diffusivity of Fe-Mg in garnet compared to clinopyroxene. The slower transport of Fe and Mg through the clinopyroxene lattice causes an apparent 348 "depletion" of Fe near the interface. In other words, the limited supply of Fe from the lamella 349 interior produces a Fe-concentration gradient towards the interface. Sluggish diffusion within 350 13

the clinopyroxene also results in the preservation of the initial concentration for cooling histories below $2x10^4$ years, i.e. cooling rates above $2x10^4$ °C/Ma. In addition, we noted that the original clinopyroxene composition is completely reset at slower cooling rates. In contrast, the smaller lamella size combined with faster diffusion erases the original garnet composition for all cooling histories lasting longer than ~10,000 years, i.e. only extremely high cooling rates of > $4x10^4$ °C/Ma, typical of contact metamorphism, will preserve the initial element distribution in the center of the garnet lamella.

Comparison of the measured concentrations reveal that very short cooling histories with very high cooling rates are necessary to produce modeled element distributions that are in agreement with the observed ones. Slower cooling rates allowing more diffusive exchange inevitably result in a stronger Fe-zoning in the clinopyroxene lamella which is not observed in the natural sample. In the case of garnet, the model predicts the zoning profile, but much higher Fe-concentrations would be expected.

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365 *Case 2 – polybaric cooling / no lamellae growth*

366 In the second set of models we have explored the modification of the preserved 367 cooling profile due to the different temporal evolution of the partition coefficient if 368 exhumation, i.e. changes in the confining pressure, is taken into account. In theory, diffusive 369 migration of elements through the crystal lattice is also affected by changes in pressure, but to our knowledge, no pressure dependent Fe-Mg interdiffusion data exist for clinopyroxene and 370 371 garnet. However, in most cases this pressure effect on diffusion becomes only significant at 372 very high pressures (Watson and Baxter, 2007; Mueller et al., 2010). Thus, we neglect a 373 possible minor pressure dependence of Fe-Mg interdiffusion for the purpose of this study. 374 Modeling results of this scenario are shown in figure 4 (case 2).

For the same initial garnet composition ($X_{Fe} = 0.21$) a starting composition for the clinopyroxene of $X_{Fe} = 0.09$ results, which is slightly below the measured natural 14 377 concentration. We applied the same thermal histories as in case 1. The modeling results 378 exhibit similar features, i.e. formation of zoning patterns in both lamellae and a comparable 379 extent of increasing X_{Fe} in garnet countered by a decrease of X_{Fe} in clinopyroxene. 380 Nevertheless, subtle differences can be observed in both lamellae that are a direct 381 consequence of the partition coefficient being a function of pressure and temperature. Here, 382 decreasing pressure favors Fe incorporation into pyroxene, whereas decreasing temperatures 383 act in the opposite direction. As a consequence, the effective influx of iron into the garnet is 384 somewhat smaller which reduces the total increase in Fe-content. Nevertheless, cooling timescales greater than 10⁴ years for the cooling from 1000 °C to 600 °C modify the entire 385 386 initial lamellae compositions and produce a slight zoning pattern with increasing $X_{\rm Fe}$ towards 387 the interface. For the clinopyroxene, the model predicts an extended depletion of Fe near the 388 interface even for a short period of time of 2,000 years, but the initial composition is still preserved in the center for cooling histories shorter than 10⁵ years. Longer cooling times yield 389 390 flatter Fe-zoning compared to the case 1 scenario. In addition, the zoning significantly extends into the lamella interior, which is in clear disagreement with the measured data. 391

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393 *Case 3 – isobaric cooling / lamellae growth*

The effect of lamella growth on the developing concentration profile is the focus of the 394 395 third set of models. Given the minor impact of pressure changes on the recorded profiles in 396 case 2 scenarios and to separate each parameter, we decided to run this set of models at a 397 constant pressure of 0.2 GPa. Thus, all model parameters are the same as in case 1 models. 398 The garnet lamella with an initial thickness of 40 μ m (cpx = 190 μ m) grows linearly with time 399 by 40 µm to a final thickness of 80 µm over the duration of the calculation. The same amount 400 of clinopyroxene was consumed, ignoring any volume change induced by this reaction. Figure 4 (case 3) shows the modeling results for the case of isobaric cooling from 1000 °C to 600 °C 401 402 accompanied by the final growth stage of the garnet lamella at the expense of clinopyroxene.

403 The calculated final concentration profiles are generally similar to all previous model 404 scenarios. Again, spatial variations in the zoning pattern and differences in total Fe-content of 405 garnet can be observed. In the present case, the original garnet lamella composition is 406 completely modified even for short run durations of only 2,000 years. This is a direct 407 consequence of the small initial lamella size, which allows diffusion to efficiently transport Fe 408 to the center of the lamella. Interestingly, the model predicts only a very narrow Fe-zoning in 409 clinopyroxene near the interface. The reason for this is that the growing garnet basically "consumes" the developing depletion in the clinopyroxene lamella progressively. Retention of 410 411 the original clinopyroxene composition in the center of the lamella corresponds exactly to the case 1 models, i.e. preservation for thermal histories with cooling rates above $2x10^4$ °C/Ma. 412

413

414 **Discussion**

The crystallization history of co-existing mineral phases is typically recorded in their 415 416 chemical compositions, the basic concept of geothermobarometry. Many metamorphic studies 417 have applied this concept to decipher the P-T evolution of a metamorphic rock and placed the 418 results into a larger geodynamic context. For example, a number of studies reconstructed P-T-419 paths for rocks from the Bohemian Massif, particularly for those of higher metamorphic 420 grade. Such rocks occur in the Granulitgebirge (e.g., Roetzler and Romer, 2001; Massonne 421 and Bautsch, 2002; Roetzler et al., 2004; Roetzler et al., 2008; Schmaedicke et al., 2010). 422 While there is a general agreement over a clockwise P-T-path, it is often based on exchange 423 reactions applied to mineral pairs which are subject to retrograde, diffusive modification. In 424 addition, information on the timescales of geodynamic processes is mostly restricted to 425 geochronological data obtained on different minerals. To both ends, kinetic modeling allows the placing of time constraints and evaluates if a mineral composition is reset and if so, to 426 what extent. In the following sections, we consider both equilibrium phase petrology and 427

kinetic modeling to determine timescales of different stages in the P-T evolution of rocksfrom the Granulitgebirge in Saxony and compare our findings with previous studies.

430

431 *Reconstruction of the P-T-t path*

432 Decompression during exhumation, cooling and net mass transfer reactions are 433 recorded in the concentration profiles of the studied garnet and clinopyroxene lamellae 434 exsolved from a former megacryst. Mueller et al. (2013) presented convincing evidence that mineral compositions rapidly adjust at temperatures above 1000 °C for most geological 435 436 settings. Therefore, modeling of the element distribution in the studied lamellae will only give 437 information on the thermal history below this temperature. The predicted profiles of all model scenarios clearly suggest that cooling from 900-1000 °C was very fast (<< 10,000 years) 438 439 indicated by the absence of pronounced zoning patterns, which are predicted for slower cooling rates (Fig. 4). This short period of time, which is typical for contact metamorphic 440 441 aureoles such as that around the Adamello Batholith (Berger and Herwegh, 2004), and 442 Ubehebe Peak (Roselle et al., 1999; Mueller et al., 2008), is the first key observation that 443 result from the diffusion modeling presented here.

444 The first model of isobaric cooling at shallow crustal levels (mimicking simple contact metamorphism) produced concentration profiles that do not exactly match the observed, 445 measured profiles (Fig. 4 - case 1). On the one hand, the concentration in the center of the 446 447 clinopyroxene lamella is in agreement with the measured data and represents the original 448 composition. On the other hand, the central garnet composition increased slightly, but not 449 sufficiently to exactly match the observed data for the 2,000 year cooling episode. 450 Surprisingly, the addition of continuously changing pressure conditions during cooling to account for the exhumation of the massif does not improve the fittings (Fig. 4 - case 2). In 451 452 this case, the short time scales necessary to limit the spatial extent of the zoning patterns will 453 also preserve the initial clinopyroxene lamella composition in the center. Using the pressure 17

and temperature dependent partition coefficient we calculated an initial Fe-content which is 454 455 slightly below the observed data. As this calculation is a direct consequence of the arbitrarily 456 defined starting composition in garnet, this difference could be minimized by an increase of 457 the Fe-content in initial garnet. However, the pressure effect on the partition coefficient leads 458 to a flatter and broader zoning pattern in the clinopyroxene lamella in apparent contrast to the measured profile (Fig. 4 – case 2). Hence, we interpret the apparent deviation of the predicted 459 460 profiles as an indication that the vast majority of the cooling history below 1000 °C took place at or near the final depth of emplacement, i.e. at a pressure of about 0.2 GPa. 461

462 The effect of lamella growth on the final profiles is not substantial, but is discernable 463 in the final shape of the zoning pattern (Fig. 4 – case 3). Based on thermodynamic constraints we assume that the garnet lamella grew about 50 % of its final size during cooling. The garnet 464 465 growth, in turn, results in a more efficient homogenization of the garnet leading to an increase in the Fe-content up to the center of the lamella, which is in perfect agreement with the 466 467 measured data. At the same time, the progressive growth of garnet will consume the depletion of Fe in clinopyroxene, resulting in a very narrow and steep zoning profile (Fig. 4 – case 3). 468 469 In conclusion of the diffusion modeling we interpret the observed Fe-Mg profiles in adjacent 470 grt-cpx lamellae to be the result of isobaric cooling from at least 900 - 600 °C within ~10,000 471 years at shallow crustal levels (~6 km depth).

The high cooling rates (> $2x10^5$ °C/Ma) predicted by the diffusion modeling are 472 common for contact aureoles as mentioned above. The presence of the schist mantle 473 474 surrounding the tectonically separated granulite complex of the Granulitgebirge (Fig. 1c) is the consequence of contact metamorphism during the emplacement (Roetzler and Romer, 475 476 2010), which is in agreement with increasing metamorphic grade towards the tectonic contact 477 and has already been suggested by Frech (1917). The spatial extent of the contact metamorphic halo in the schist mantle provides an excellent opportunity to independently 478 479 constrain the temperature of the Massif during emplacement of the granulite complex with a

480 simple thermal model. To that end, we modeled the T-t evolution of the granulite complex 481 and surrounding country rocks. The model assumes a tabular shape of the granulite complex 482 with a radius of 10 km. Figure 5 presents the temporal evolution of the thermal history in 483 rocks surrounding the Massif. Metamorphic temperatures necessary to form the exposed 484 phyllite from pelitic sediments are around 350 °C. Reported migmatites near the tectonic 485 contact require temperatures near 700 °C. Inspection of figure 5 reveals a maximum 486 dimension of about 1-3 km for the contact aureole in the western part. The spatial extension in the eastern area is less, but this may be a cut effect of the current topography or the exact 3-D 487 488 position of the granulite complex. In addition, we monitor the cooling history of a rock 489 located about 1 km away from the contact within the granulite complex. This position is 490 approximately the location of the investigated lamellar garnet pyroxenite. Calculated thermal 491 histories are shown in figure 5. It can be seen that both, the spatial extent of the predicted 492 contact-metamorphic halo (Fig. 5) and cooling rates corresponding to those determined by the 493 diffusion modeling (Fig. 5 - inset), can well be estimated with this simplified thermal model 494 for a contact aureole assuming an initial temperature of \geq 950 °C for the granulite complex. A 495 more detailed and sophisticated thermal model would be necessary to really constrain exact 496 initial temperatures, which is beyond the scope of this study. We note, however, that a 497 simplified thermal model is an independent second line of arguments supporting the results of 498 our diffusion modeling, i.e. the major cooling history that took place at almost isobaric 499 conditions after emplacement.

500 One major goal of this study is to place time constraints on different stages of the P-T-t 501 path. The heat and diffusion modeling provided two solid constraints. First, the major portion 502 of the cooling history from ~1000-600 °C took place at almost isobaric conditions and 503 secondly this cooling episode occurred at a short timescale of several thousand years only. 504 Thus, the exhumation of the granulite complex is likely to follow an almost isothermal 505 decompression path (Fig. 6). Several studies have estimated the peak P-T conditions for most 19

506 rocks from the granulite complex to be around 2.2-2.3 GPa and >1000°C (Roetzler and 507 Romer, 2001; Massonne and Bautsch, 2002; Roetzler et al., 2004; Roetzler et al., 2008; 508 Schmaedicke et al., 2010) ignoring the higher temperatures for the magmatic formation of the 509 megacrysts preceding the garnet pyroxenite from Reinsdorf. It is important to keep in mind 510 that determination of the above P-T conditions are based on geothermobarometry using the 511 core compositions of co-existing mineral pairs (e.g. grt-cpx). The modeling results of the 512 diffusive element exchange during cooling indicate that in the present case only the central 513 clinopyroxene composition remained unchanged. The garnet composition, in contrast, was 514 completely reset during cooling as a consequence of the smaller lamella size and faster 515 diffusion. Under these circumstances, conventional thermometry using core-core 516 compositions of co-existing mineral phases will either overestimate the pressure or 517 underestimate the temperature if the P-T dependent partition coefficient of Ganguly et al. 518 (1996) is applied. However, the results generally suggest a very limited cooling during the 519 exhumation process. While the exact reaction history remains unclear as discussed above, the 520 presence of a nearly isothermal decompression path sets some thermal constraints on the 521 timescale of exhumation. To that end, one can again use a very simplified thermal model to 522 evaluate the minimum exhumation rate for a block that cooled progressively inwards during 523 exhumation due to the decreasing temperature of the surrounding rocks within an 524 "exhumation channel". Figure 7 shows the predicted temperature distribution after 1, 3 and 7 525 Ma for the block with the same geometry and heat transport properties as in the previous 526 calculation. In this model the contact temperature decreases linearly from 1200 °C 527 representing the original root zone to 350 °C mimicking the temperature of the sediments at

527 representing the original root zone to 550°C minineking the temperature of the sedments at 528 the final depth of emplacement at 0.2 GPa. It is important to keep in mind that the results of 529 the diffusive element exchange as well as the modeling of the thermal history of the aureole 530 revealed a minimum temperature of 900 °C for the garnet-pyroxenite sample located about 1 531 km away from the contact. The simplified thermal model for the exhumation event of the 20 532 granulite complex suggests a maximum integrated time of exhumation to be less than 1 Ma. 533 which translates into an average exhumation rate of 4-5 cm/year. Slower exhumation rates are 534 likely to cool the outermost kilometer of the granulite complex to temperatures significantly 535 below 900 °C which is incompatible with the finding of the diffusion model. We note, that our 536 model has many simplifying assumptions, e.g. that there is no friction, latent heat of 537 crystallization, etc., and thus the extracted exhumation rates could be somewhat 538 overestimated. Again, we emphasize that a much more detailed thermal model is required to 539 constrain exact information of the thermal evolution of the granulite complex during exhumation and cooling in order to verify our conclusions. However, our simple thermal 540 541 model calculations provide at least rough, but independent estimates which all point to the same P-T-t evolution of the studied sample. 542

543

544 *Comparison with previous P-T-t estimates*

545 We combined our modeling results to construct a P-T-t path presented as path A in 546 figure 6. For comparison we added the reported P-T evolution of Roetzler and Romer (2001), 547 Roetzler et al. (2004, 2008) Schmaedicke et al. (2010), Massonne and Bautsch (2002), 548 Massonne (2006), and O'Brien (2008). The latter author studied the P-T path of co-existing 549 garnet and clinopyroxene in rocks from the southern Bohemian Massif which belongs to the 550 same overall geological setting, but has a different final depth of emplacement (0.8 GPa). The P-T-path of Roetzler and Romer (2001), and Roetzler et al. (2004, 2008) derived by a series of 551 552 studies summarized in Roetzler and Romer (2010) and the geological settings of the current study, is based on conventional thermobarometry and multivariant reactions (path C in figure 553 554 6). For example, peak P-T conditions are estimated on felsic and mafic granulite using the Fe-Mg exchange thermometry between co-existing garnet and clinopyroxene, re-integrated 555 feldspar composition and equilibrium oxygen isotope fractionations. All approaches, 556 including the geothermobarometry data of Massonne and Bautsch (2002) and Schmaedicke 557 21

558 (2010), yield a very narrow range of apparent peak temperatures around 1000 °C. However, in 559 the light of this study it could be that this coincidence is an artefact of efficient element and 560 isotope exchange leading to an effective preservation of the compositional record at 561 temperatures below 1000 °C. This is certainly true for element and isotope exchange 562 processes which are kinetically controlled, i.e. Fe-Mg exchange and oxygen isotope 563 thermometry. Re-integration of feldspar composition might give more robust information. 564 Roetzler & Romer (2001) and Roetzler et al. (2004, 2008) applied the commonly used GASP barometer to estimate the peak pressure conditions. Again, caution is necessary when 565 566 applying this barometer using the possibly modified garnet composition. To account for this 567 we expanded the P-T pressure range extracted by Roetzler and Romer (2001), Roetzler et al. (2004, 2008), Massonne and Bautsch (2002) and Schmaedicke (2010) to include lower and 568 569 higher temperatures.

570 P-T estimates for the garnet-cordierite-gneiss were used as a second constraint for the 571 P-T-path by Romer and Rötzler (2010) who proposed a decompression-heating path for the 572 rocks that have been incorporated into the ascending granulite complex. Several models exist 573 for the exhumation mechanism of the Varisican HP-HT rocks (Franke and Stein, 2000; 574 Willner et al., 2002; Massonne, 2006; Kroner et al., 2007). For the purpose of this study it is 575 not necessary to discriminate between the many existing models as only the time response of 576 mineral compositions on the exhumation process is considered here. A schematic model for 577 the ascent of the granulite core in an "exhumation channel" (Fig. 8) illustrates the 578 consequences of the P-T conditions determined for the garnet-cordierite gneiss (Fig. 8) on the 579 P-T-t path of the studied garnet-pyroxenite sample. There is general agreement that the 580 garnet-cordierite gneiss became attached on the granulite complex during exhumation. During 581 this uptake, this rock was heated by the rising granulite complex which is documented by the decompression-heating path proposed by Romer and Roetzler (2001). These authors 582 concluded that the granulite complex had the same temperature as the surrounding gneiss 583

584 which is represented by the cooling path in figure 6 (path C3 and C). Again, transport of heat 585 is not instantaneous and thus the heating of the uptaken rock portion can be imagined as a 586 contact metamorphic event along the short-lived exhumation process. In other words, while 587 there is no doubt that the metamorphic garnet-cordierite gneiss experienced the proposed 588 decompression-heating path, there is no direct evidence of similar low temperatures for the 589 central part of the granulite complex. In contrast, sluggish heat transfer is likely to decouple 590 the thermal history for the different lithologies leaving the thermal evolution of the original 591 block near its isothermal behavior due to adiabatic cooling only in agreement with our 592 modeling results (Fig. 8).

593 In a recent study, Schmaedicke et al. (2010) presented a series of thermometric data of 594 the garnet peridotites and garnet pyroxenites exhibiting kelyphitic reaction textures 595 surrounding garnet crystals of the same locality. Thermometry data based on Fe-Mg exchange 596 revealed the same P-T estimates for grt-cpx and grt-olivine pairs (~ 2.4 GPa, ~ 1000 °C). 597 However, co-existing opx-cpx pairs in the kelyphitic reaction rims yield systematically lower 598 temperatures ranging from 890-940 °C for the garnet peridotite (at 2.0 GPa) and 840 °C at 1.5 599 GPa for the garnet pyroxenite, respectively. We note that the symplectites observed in our 600 sample replacing garnet have to be formed after the formation of the grt-cpx lamellae, i.e. 601 after exhumation to approximately 0.2 GPa. However, the lower temperature estimates have 602 led Schmaedicke (2010) to shift the reconstructed P-T-path to be located around 100 °C 603 lower, but parallel to previous estimates (path E in Fig. 6). This interpretation favors the opx-604 cpx data and neglects the results of the grt-cpx and feldspar thermometry. In the light of our 605 modeling results, however, it is likely that the opx-cpx pairs have experienced a more efficient 606 element exchange, which results in a larger reset of the preserved, i.e. measured temperatures. 607 While the diffusion coefficients of Fe-Mg interdiffusion in grt and opx are similar at the relevant temperature range (Mueller et al., 2013), this interpretation is supported by the 608 609 mostly pressure sensitive, continuous reaction forming the opx-cpx-spinel kelyphite texture at 23

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610 pressures below 2.0 GPa. Modeling results of our case 3 scenarios revealed that mineral 611 growth leads to more efficient homogenization and thus the progressive cooling would be 612 preferentially recorded in cpx-opx pairs while already existing grt-cpx pairs experience more 613 sluggish adjustment of central compositions. Hence, we attribute the lower temperatures 614 extracted by opx-cpx thermometry in kelyphitic reaction rims to diffusive closure of element 615 exchange at lower temperatures and thus at a later stage during cooling on the retrograde path. 616 Excluding the opx-cpx thermometric data in the study of Schmaedicke et al. (2010) would 617 shift the resulting P-T path towards higher temperatures and thus perfectly fit the data of 618 Roetzler and Romer (2008).

619 In a very thorough study of rocks from the southwestern part of the Bohemian Massif, O'Brien (2008) presented convincing evidence for a very similar isothermal decompression 620 621 path around 1000 °C using thermodynamic phase equilibria calculations on whole rock 622 chemistry and element zoning in grt-cpx pairs (path G in figure 6). In this case, the isothermal 623 exhumation is followed by an almost isobaric cooling episode at approximately 0.8 GPa. 624 Here, the metamorphic block is supposed to have not been exhumed to the same extent as in 625 the granulite complex. Given the greater depth of emplacement, the reconstructed P-T 626 evolution of O'Brien (2008) is in good agreement with our findings. We thus interpret all of 627 these rocks to have been exhumed by the same, although unknown mechanism and most 628 likely the same rates, but to different final depths. This interpretation highlights the potential 629 of combining equilibrium phase petrology with kinetic modeling to decipher rates and 630 mechanisms of large-scale geodynamic processes.

631

632 Implications

We applied kinetic modeling to decipher the effect of changing external parameters,
i.e. pressure and temperature, on the evolution of concentration profiles in minerals which are
direct recorders of geochemical fluxes in metamorphic rocks. The fact, that minerals adjust

636 their compositions according to external parameters, is typically used to reconstruct the P-T-637 evolution of a rock using a combination of available geothermobarmeters. In this study, we 638 demonstrate that care has to be taken by using geothermobarometric data to reconstruct P-T-639 paths without constraining the kinetically controlled efficiency of geochemical fluxes. While 640 there is no doubt that geochemical exchange records the change of external temperatures and 641 pressures, it often remains the question by how much. In other words, the temperatures 642 determined by rim-rim and core-core compositions may not necessarily reflect peak 643 metamorphic or any other assigned conditions as previously suggested by Dohmen and 644 Chakraborty (2003) and Faryad and Chakraborty (2005). Additional information is necessary 645 to place these data into a larger context within a petrogenetic grid. Modeling of the diffusive element exchange during cooling provides a solid estimate for the extent of reset allowing the 646 647 temperature data to be interpreted as dynamically evolving parameter. Moreover, this study highlights the potential of assigning timescales not only to geological settings with large P-T 648 649 changes over short time-intervals such as contact aureoles, but also on large scale geodynamical processes in regional metamorphic settings. 650

651 The diffusive exchange model was used to extract the major cooling episode at 652 shallow crustal levels which is in agreement with the thermal modeling that requires the 653 emplacement of the granulite block at temperatures above 900 °C in order to produce the 654 observed contact metamorphism in the schist mantle and the phyllite zone. This in turn requires an almost isothermal exhumation from great depth at rates comparable to active plate 655 656 movements of several cm per year. While modeling of the mineral zoning in grt-cpx pairs places narrow limits on the timescales of the final cooling episode, the evaluation of 657 658 timescales for the exhumation is much more complex. Our very simplified thermal model for the exhumation process only suggests a very rapid exhumation and consequently has to be 659 660 regarded as an end-member model. The other extreme would be a slow adiabatic exhumation 661 in which case no time-related information is recorded. Hence, much more detailed thermal 25

662	modeling within the context of geodynamical transport processes is necessary to extract more
663	detailed information on the exhumation rate of the Granulitgebirge. We close this section by
664	emphasizing that every conceptual model explaining a large scale exhumation process needs
665	to fit the geochemical record preserved in the spatial element distribution within minerals.
666 667 668 669 670 671 672 673 674 675	Acknowledgments This study was financially supported by grants from the Ruhr-University Bochum to T. Mueller partly covering the travel expenses for this collaboration. The ideas and models presented here benefited greatly from discussion with Sumit Chakraborty in the course of developing the numerical model. We thank Thomas Theye for the help with the electron microprobe analysis. We greatly acknowledge the constructive reviews of C. Tom Foster and Ryszard Kryza as well as comments and the editorial handling by John Ferry. References
676	Berger, A., and Herwegh, M. (2004) Grain coarsening in contact metamorphic carbonates:
677	effects of second-phase particles, fluid flow and thermal perturbations. Journal of
678	Metamorphic Geology, 22(5), 459-474.
679	Borinski, S.A., Hoppe, U., Chakraborty, S., Ganguly, J., and Bhowmik, S.K. (2012)
680	Multicomponent diffusion in garnets I: general theoretical considerations and
681	experimental data for Fe-Mg systems. Contributions to Mineralogy and Petrology,
682	164(4), 571-586.
683	Caddick, M.J., Konopásek, J., and Thompson, A.B. (2010) Preservation of garnet growth
684	zoning and the duration of prograde metamorphism. Journal of Petrology, 51(11),
685	2327-2347.
686	Costa, F., Dohmen, R., and Chakraborty, S. (2008) Time Scales of Magmatic Processes from
687	Modeling the Zoning Patterns of Crystals. Minerals, Inclusions and Volcanic
688	Processes, 69, 545-594.
689	Cruz-Uribe, A.M., Feineman, M.D., Zack, T., and Barth, M. (2014) Metamorphic reaction
690	rates at ~650–800° C from diffusion of niobium in rutile. Geochimica Et

691 Cosmochimica Acta, 130, 63-77.

- Dodson, M.H. (1973) Closure temperature in cooling geochronological and petrological
- 693 systems. Contributions to Mineralogy and Petrology, 40(3), 259-274.
- -. (1986) Closure profiles in cooling systems. Materials Science Forum, 7, p. 145-153. Trans
 Tech Publications, Aedermannsdorf, Switzerland.
- Dohmen, R., and Chakraborty, S. (2003) Mechanism and kinetics of element and isotopic
- 697 exchange mediated by a fluid phase. American Mineralogist, 88(8-9), 1251-1270.
- Ducea, M.N., Ganguly, J., Rosenberg, E.J., Patchett, P.J., Cheng, W.J., and Isachsen, C.
- 699 (2003) Sm-Nd dating of spatially controlled domains of garnet single crystals: a new
- 700 method of high-temperature thermochronology. Earth and Planetary Science Letters,
- 701 213(1-2), 31-42.
- Fisher, G.W. (1978) Rate laws in metamorphism. Geochimica et Cosmochimica Acta, 42,
 1035-1050.
- Franke, W., and Stein, E. (2000) Exhumation of high-grade rocks in the Saxo-Thuringian
- Belt: geological constraints and geodynamic concepts. Geological Society, London,
 Special Publications, 179(1), 337-354.
- Frech, F. (1917) Allgemeine Geologie I: Vulkane einst und jetzt. Teubner Verlag, Leipzig.
- Gaidies, F., De Capitani, C., Abart, R., and Schuster, R. (2008a) Prograde garnet growth
- along complex P–T–t paths: results from numerical experiments on polyphase garnet
- from the Wölz Complex (Austroalpine basement). Contributions to Mineralogy and
 Petrology, 155(6), 673-688.
- Gaidies, F., Krenn, E., De Capitani, C., and Abart, R. (2008b) Coupling forward modelling of
 garnet growth with monazite geochronology: an application to the Rappold Complex
 (Austroalpine crystalline basement). Journal of Metamorphic Geology, 26(7), 775793.

716	Gaidies, F., Pattison, D., and de Capitani, C. (2011) Toward a quantitative model of
717	metamorphic nucleation and growth. Contributions to Mineralogy and Petrology,
718	162(5), 975-993.
719	Ganguly, J., Cheng, W., and Tirone, M. (1996) Thermodynamics of aluminosilicate garnet
720	solid solution: new experimental data, an optimized model, and thermometric
721	applications. Contributions to Mineralogy and Petrology, 126(1-2), 137-151.
722	Ganguly, J., and Tazzoli, V. (1994) Fe2+-Mg interdiffusion in ortho-pyroxene - retrieval from
723	the data on intercrystalline exchange reaction. American Mineralogist, 79(9-10), 930-
724	937.
725	Ganguly, J., and Tirone, M. (1999) Diffusion closure temperature and age of a mineral with
726	arbitrary extent of diffusion: theoretical formulation and applications. Earth and
727	Planetary Science Letters, 170(1-2), 131-140.
728	Ganguly, J., Tirone, M., Chakraborty, S., and Domanik, K. (2013) H-chondrite parent
729	asteroid: A multistage cooling, fragmentation and re-accretion history constrained by
730	thermometric studies, diffusion kinetic modeling and geochronological data.
731	Geochimica Et Cosmochimica Acta, 105(0), 206-220.
732	Grew, E.S. (1986) Petrogenesis of kornerupine at Waldheim (Sachsen), German-Democratic-
733	Republic. Zeitschrift fuer geologische Wissenschaften, 14(5), 525-558.
734	Hagen, B., Hoernes, S., and Roetzler, J. (2008) Geothermometry of the ultrahigh-temperature
735	Saxon granulites revisited. Part II: Thermal peak conditions and cooling rates inferred
736	from oxygen-isotope fractionations. European Journal of Mineralogy, 20(6), 1117-
737	1133.
738	Hauzenberger, C.A., Robl, J., and Stuwe, K. (2005) Garnet zoning in high pressure granulite-
739	facies metapelites, Mozambique belt, SE-Kenya: constraints on the cooling history.
740	European Journal of Mineralogy, 17(1), 43-55.

- 741 Hentschel, H. (1937) Der Eklogit von Gilsberg im sächs. Granulitgebirge und seine
- 742 metamorphen Umwandlungsstufen. Zeitschrift für Kristallographie, Mineralogie und
 743 Petrographie, 49(1), 42-88.
- Jekosch, U., and Bautsch, H. (1991) Orientierte Entmischungen in Pyroxenen. Zeitschrift für
 Kristallographie: Supplement (XIII European Crystallographic Meeting), 4, p. 134.
- 746 Kroener, A., Jaeckel, P., Reischmann, T., and Kroner, U. (1998) Further evidence for an early
- 747 Carboniferous (similar to 340 Ma) age of high-grade metamorphism in the Saxonian
 748 granulite complex. Geologische Rundschau, 86(4), 751-766.
- 749 Kroener, A., and Willner, A.P. (1998) Time of formation and peak of Variscan HP-HT
- 750 metamorphism of quartz-feldspar rocks in the central Erzgebirge, Saxony, Germany.
- 751 Contributions to Mineralogy and Petrology, 132(1), 1-20.
- 752 Kroner, U., and Goerz, I. (2010) Variscan assembling of the Allochthonous Domain of the
- 753 Saxo-Thuringian Zone–a tectonic model. In U. Linnemann, and R.L. Romer, Eds. Pre-
- 754 Mesozoic Geology of Saxo-Thuringia–from the Cadomian Active Margin to the
- 755 Variscan Orogen. Schweizerbart, Stuttgart, p. 271-286. Schweizerbart, Stuttgart.
- 756 Kroner, U., Hahn, T., Romer, R.L., and Linnemann, U. (2007) The Variscan orogeny in the
- 757 Saxo-Thuringian zone-heterogenous overprint of Cadomian/Paleozoic Peri-Gondwana
- rust. 153 p. Geological Society of Amernica.
- Kroner, U., and Romer, R.L. (2013) Two plates Many subduction zones: The Variscan
 orogeny reconsidered. Gondwana Research, 24(1), 298-329.
- Lasaga, A.C. (1983) Geospeedometry: an extension of geothermometry. Kinetics and
 equilibrium in mineral reactions, p. 81-114. Springer.
- Lasaga, A.C., Richardson, S.M., and Holland, H.D. (1977) The mathematics of cation
- diffusion and exchange between silicate minerals during retrograde metamorphism,. In
- 765 S.K. Saxena, and S. Bhattachanji, Eds. Energetics of Geological Processes, p. 353-
- 766 388. Springer-Verlag, New York.

767	Liermann, HP., and Ganguly, J. (2002) Diffusion kinetics of Fe ²⁺ and Mg in aluminous
768	spinel: experimental determination and applications. Geochimica Et Cosmochimica
769	Acta, 66(16), 2903-2913.
770	Lucassen, F., Franz, G., Dulski, P., Romer, R., and Rhede, D. (2011) Element and Sr isotope
771	signatures of titanite as indicator of variable fluid composition in hydrated eclogite.
772	Lithos, 121(1), 12-24.
773	Massonne, HJ. (2006) Early metamorphic evolution and exhumation of felsic high-pressure
774	granulites from the north-western Bohemian Massif. Mineralogy and Petrology, 86(3-
775	4), 177-202.
776	(2011) Occurrences and PT conditions of high and ultrahigh pressure rocks in the Bohemian
777	Massif. Geolines, 23, 18-26.
778	Massonne, HJ., and Bautsch, H.J. (2002) An unusual garnet pyroxenite from the
779	Granulitgebirge, Germany: Origin in the transition zone (> 400 km depths) or in a
780	shallower upper mantle region? International Geology Review, 44(9), 779-796.
781	Massonne, HJ., Kennedy, A., Nasdala, L., and Theye, T. (2007) Dating of zircon and
782	monazite from diamondiferous quartzofeldspathic rocks of the Saxonian Erzgebirge-
783	hints at burial and exhumation velocities. Mineralogical Magazine, 71(4), 407-425.
784	Massonne, HJ., and O'Brien, P.J. (2003) The Bohemian massif and the NW Himalaya.
785	Mueller, T., Baumgartner, L.P., Foster, C.T., Jr., and Roselle, G.T. (2008) Forward modeling
786	of the effects of mixed volatile reaction, volume diffusion, and formation of
787	submicroscopic exsolution lamellae on calcite-dolomite thermometry. American
788	Mineralogist, 93(8-9), 1245-1259.
789	Mueller, T., Baumgartner, L.P., Foster, C.T., and Vennemann, T.W. (2004) Metastable
790	prograde mineral reactions in contact aureoles. Geology, 32(9), 821-824.
791	Mueller, T., Dohmen, R., Becker, H., ter Heege, J.H., and Chakraborty, S. (2013) Fe-Mg
792	interdiffusion rates in clinopyroxene: experimental data and implications for Fe–Mg 30

793	exchange geothermometers. Contributions to Mineralogy and Petrology, 166(6), 1563-
794	1576.
795	Mueller, T., Watson, E.B., and Harrison, T.M. (2010) Applications of Diffusion Data to High-
796	Temperature Earth Systems. Reviews in Mineralogy and Geochemistry, 72(1), 997-
797	1038.
798	O'Brien, P.J. (2008) Challenges in high-pressure granulite metamorphism in the era of
799	pseudosections: reaction textures, compositional zoning and tectonic interpretation
800	with examples from the Bohemian Massif. Journal of Metamorphic Geology, 26(2),
801	235-251.
802	Reiche, M., and Bautsch, HJ. (1985) Electron microscopical study of garnet exsolution in
803	orthopyroxene. Physics and Chemistry of Minerals, 12(1), 29-33.
804	Reiche, M., and Bautsch, H. (1984) Entmischungsstrukturen in Pyroxenen aus eklogitischen
805	Gesteinen. Freiberger Forschungshefte, 393, 19-33.
806	Reinhardt, J., and Kleemann, U. (1994) Exensional unroofing of granulitic lower crust and
807	related low-pressure, high-temperature metamorphism in the Saxonian Granulite
808	Massif, Germany. Tectonophysics, 238(1-4), 71-94.
809	Roetzler, J., Hagen, B., and Hoernes, S. (2008) Geothermometry of the ultrahigh-temperature
810	Saxon granulites revisited. Part I: New evidence from key mineral assemblages and
811	reaction textures. European Journal of Mineralogy, 20(6), 1097-1115.
812	Roetzler, J., Kurze, M., Linnemann, U., and Troeger, KA. (1992) Zur Petrogenese im
813	sächsischen Granulitgebirge die pyroxenfreien Granulite und die Metapelite ; mit 12
814	Tab. = On the petrogenesis in the Saxon Granulite Massif. Schweizbart, Stuttgart.
815	Roetzler, J., and Romer, R. (2010) The Saxon Granulite Massif: a key area for the
816	geodynamic evolution of Variscan central Europe. Pre-Mesozoic Geology of Saxo-
817	Thuringia-from the Cadomian Active Margin to the Variscan Orogen. Schweizerbart,
818	Stuttgart, 233-252.
	31

819	Roetzler, J., and Romer, R.L. (2001) P-T-t evolution of ultrahigh-temperature granulites from
820	the Saxon Granulite Massif, Germany. Part I: Petrology. Journal of Petrology, 42(11),
821	1995-2013.
822	Roetzler, J., Romer, R.L., Budzinski, H., and Oberhansli, R. (2004) Ultrahigh-temperature
823	high-pressure granulites from Tirschheim, Saxon Granulite Massif, Germany: P-T-t
824	path and geotectonic implications. European Journal of Mineralogy, 16(6), 917-937.
825	Romer, R.L., and Roetzler, J. (2001) P-T-t evolution of ultrahigh-temperature granulites from
826	the Saxon Granulite Massif, Germany. Part II: Geochronology. Journal of Petrology,
827	42(11), 2015-2032.
828	Roselle, G.T., Baumgartner, L.P., and Chapman, J.A. (1997) Nucleation-dominated
829	crystallization of forsterite in the Ubehebe Peak contact aureole, California. Geology,
830	25(9), 823-826.
831	Roselle, G.T., Baumgartner, L.P., and Valley, J.W. (1999) Stable isotope evidence of
832	heterogeneous fluid infiltration at the Ubehebe Peak contact aureole, Death Valley
833	National Park, California. American Journal of Science, 299(2), 93-138.
834	Schmaedicke, E., Gose, J., and Will, T.M. (2010) The P-T evolution of ultra high temperature
835	garnet-bearing ultramafic rocks from the Saxonian Granulitgebirge Core Complex,
836	Bohemian Massif. Journal of Metamorphic Geology, 28(5), 489-508.
837	Spear, F.S., and Florence, F.P. (1992) Thermobarometry in granulites - pitfalls and new
838	approaches. Journal of Precambrian Research, 55, 209-241.
839	Trepmann, C.A., Stockhert, B., and Chakraborty, S. (2004) Oligocene trondhjemitic dikes in
840	the Austroalpine basement of the Pfunderer Berge, Sudtirol - level of emplacement
841	and metamorphic overprint. European Journal of Mineralogy, 16(4), 641-659.
842	von Quadt, A. (1993) The Saxonian Granulite Massif - New aspects from geochronoligal
843	studies. Geologische Rundschau, 82(3), 516-530.

- 844 Watson, E.B., and Baxter, E.F. (2007) Diffusion in solid-Earth systems. Earth and Planetary
- Science Letters, 253(3), 307-327.
- 846 Werner, C.D. (1987) Saxonian granulites: a contribution to the geochemical diagnosis of
- 847 original rocks in high-metamorphic complexes. Gerlands Beiträge der Geophysik, 96,
 848 271-290.
- 849 Werner, O., and Reich, S. (1997) 40Ar/39 Ar Abkühlalter von Gesteinen mit
- 850 unterschiedlicher PT-Entwicklung aus dem Schiefermantel des Sächsischen
- Granulitgebirges. Terra Nostra, 97(5), 196-198.
- 852 Willner, A.P., Krohe, A., and Maresch, W.V. (2000) Interrelated P-T-t-d paths in the Variscan
- 853 Erzgebirge dome (Saxony, Germany): Constraints on the rapid exhumation of high-
- 854 pressure rocks from the root zone of a collisional orogen. International Geology
- 855 Review, 42(1), 64-85.
- 856 Willner, A.P., Sebazungu, E., Gerya, T.V., Maresch, W.V., and Krohe, A. (2002) Numerical
- 857 modelling of PT-paths related to rapid exhumation of high-pressure rocks from the
- 858 crustal root in the Variscan Erzgebirge Dome (Saxony/Germany). Journal of
- 859 Geodynamics, 33(3), 281-314.

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861

862 **Figure captions**

Figure 1: (a) Location of the Granulitgebirge within the Variscan Bohemian Massif of Central Europe with the distribution of high-pressure rocks (redrawn after Willner et al., 2000). (b) Geological Map of the Granulitgebirge modified after Reinhardt and Kleemann (1994) with the location of the garnet pyroxenite sample. (c) Simplified cross section of the Granulitgebirge after Reinhardt and Kleemann (1994). Note that the black units shown in panels (b) and (c) contain both, garnet peridotite and garnet pyroxenite.

Figure 2: Thin section image of garnet-pyroxenite sample under crossed polarized light. (A)
Image showing the dimensions of the former cm-sized megacryst within a matrix of
recrystallized garnet and clinopyroxene. (B) Alternating lamellae of garnet and clinopyroxene
with a final volume ratio of 3:7 are formed within the megacryst during exhumation and
cooling.

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Figure 3: Representative compositional profiles of major and minor elements within adjacent garnet and clinopyroxene lamellae measured with an electron microprobe. Line profiles reveal almost flat, but weakly zoned patterns with increasing X_{Fe} from the garnet center towards the interface. Almost no zoning for X_{Fe} can be observed in the cpx lamella. Minor elements show an increase in concentration for Cr and Ti within the clinopyroxene towards the interface. In contrast, no zoning is visible in the garnet. Note, that the garnet lamella is nearly free of Ti.

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883 Figure 4: Modeling results using a finite difference scheme that simulates diffusive exchange 884 of Fe-Mg between garnet and clinopyroxene along a virtual cooling and exhumation path. The 885 model assumes local equilibrium at the interface and diffusive fluxes are constrained by mass 886 balance. Three different scenarios are modeled to investigate the effect of cooling (case 1), exhumation (case 2) and growth (case 3) on the developing concentration profiles. 887 888 Progressively evolving concentration profiles are shown ranging from the initial step profile 889 up to 0.2 Ma. Note that only a combination of cooling on very short timescales of several 890 thousands of years in combination with growth of the garnet lamella is in agreement with the measured data. 891

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Figure 5: Thermal modeling of the contact metamorphic aureole producing the schist mantle and the phyllite surrounding the granulite block. The numerical 1-D model assumes a tabular shaped geometry of the granulite block and a general thermal diffusivity of 1×10^{-6} m²/s. 896 Temperature profiles are shown for different times ranging from 2k to 200k years. Note, that 897 temperatures necessary to match the spatial extent of the schist mantle and the surrounding 898 phyllite require an emplacement temperature of more than 900 °C for the granulite complex. 899 The black box represents the temperature estimates of the mantle schist as summarized in 900 Roetzler and Romer (2010). Inset: Modeled temperature-time path for the approximate 901 position of the garnet peridotite sample of this study as well as selected locations for rocks of 902 the mantle schist and the phyllite zone. Note that the major cooling episode (950-780 $^{\circ}$ C) of the garnet peridotite takes place in less than 2,000 years, which is in agreement with the short 903 904 modeled time scales for the Fe-Mg concentration profiles presented in figure 4.

905

906 Figure 6: Synopsis of modelled and determined P-T paths in the Granulitgebirge. A -907 modelled P-T path of the granulite complex of this work; B - observed progressive contact 908 metamorphism in the schist mantle after Roetzler et al. (1992), Reinhardt and Kleemann 909 (1994) and Roetzler and Romer (2010); C - observed P-T-path of the granulite complex after 910 Roetzler & Romer (2001; 2010); C1 - observed peak conditions (Roetzler and Romer, 2001; 911 Roetzler et al. 2004, 2008; Hagen et al. 2008); C2 - symplectite stage (Roetzler et al. 2008); 912 C3- observed decompression-heating path of the garnet-cordierite gneiss (Rötzler & Romer 913 2010; D – observed late exhumation path of garnet pyroxenite after Massonne and Bautsch 914 (2002); E - observed late exhumation path of garnet peridotite after Schmaedicke et al. (2010); E1, 2- observed conditions of two symplectite stages (Schmaedicke et al., 2010); F - observed 915 916 local early stage metamorphic conditions (Massonne, 2006); G - observed P-T path of a high-917 pressure granulite from the southwestern Bohemian Massif emplaced at mid-crustal 918 conditions (O'Brien, 2008).

919

920 Figure 7: Simplified numerical model simulating the cooling of the granulite block upon
921 exhumation in contact with an infinite reservoir of country rock with a linear geotherm. The
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922 original temperature of the block and the surrounding was set to 1200 °C according to the 923 assumption of clinopyroxene as original host phase. The country rock is assumed to 924 geothermally equilibrate with depth forming a linear gradient that is opposed to the interface 925 of the exhumed tabular shaped block. Modeled thermal profiles are shown for exhumation 926 times ranging from 1-7 Ma. No external heat source (e.g. friction, latent heat of 927 crystallization, etc.) within an "exhumation channel" was taken into account by this simplified 928 model, which means that the determined timescales have to be regarded as minimum 929 timescales, i.e. maximum rates of exhumation. Nevertheless, the results emphasize the fast 930 exhumation rates in the order of several cm per year are necessary to preserve temperatures 931 higher than 900 °C. Such temperatures are required to match the spatial dimensions of the 932 formed contact aureole.

933

Figure 8: Mechanistic model explaining the observed temperature-time evolution of three rock units between A - the position before the ascent of the granulite complex in extensional detachment zones within an "exhumation channel" (a), i.e. during concomitant convergence and B - after emplacement of the granulite complex within the schist mantle at shallow crustal conditions. Temperature-time evolution of (b) the schist mantle near the contact to the granulite complex, (c) the mid-crustal garnet-cordierite gneiss emplaced during coupled motion at the contact, (d) the granulite complex.



Mueller et al. Figure 1



Figure 2 Müller et al.



Figure 3 Müller et al.







Figure 5 Müller et al.



Mueller et al. Figure 6







Figure 8 Mueller et al. 10/7