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4	Establishing the <i>P–T</i> path of UHT granulites by geochemically distinguishing	
5	peritectic from retrograde garnet	
6	Shujuan Jiao <sup>1, 2, 3*</sup> , Noreen J. Evans <sup>3, 4</sup> , Jinghui Guo <sup>1, 2, 6</sup> , Ian C. W. Fitzsimons <sup>3</sup> ,	
7	Jian-Wei Zi <sup>4, 5</sup> , Bradley J. McDonald <sup>3, 4</sup>	
8	<sup>1</sup> State Key Laboratory of Lithospheric Evolution, Institute of Geology and Geophysics,	
9	Chinese Academy of Sciences, Beijing 100029, China	
10	<sup>2</sup> Innovation Academy for Earth Science, CAS, Beijing 100029, China	
11	<sup>3</sup> School of Earth and Planetary Sciences, Curtin University, Perth 6845, Australia	
12	<sup>4</sup> John de Laeter Center, Curtin University, Perth 6845, Australia	
13	<sup>5</sup> State Key Laboratory of Geological Processes and Mineral Resources, China University	
14	of Geosciences, Wuhan 430074, China	
15	<sup>6</sup> College of Earth and Planetary Sciences, University of Chinese Academy of Sciences,	
16	Beijing 100049, China	
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21	*Corresponding author.	
22	Dr. Shujuan Jiao, jiaoshujuan0215@126.com	
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### Abstract

The P-T evolution (and particularly the prograde path segment) of ultrahigh-temperature 25 (UHT) granulites is commonly ambiguous, hampering our understanding of deep crustal 26 processes. Here, we establish the P-T path by distinguishing garnet origin (peritectic or 27 retrograde) based on the combined Ca, Ti, Zr and Y + REE chemical signatures, using the 28 29 residual UHT granulites of the Khondalite Belt, North China Craton as a test case. In these rocks, peritectic garnet is characterized by rare inclusions, whereas retrograde 30 garnet has overprinted the main foliation, and is characterized by abundant biotite and 31 32 sillimanite inclusions, which are interpreted to have grown together with retrograde garnet during cooling. Zirconium in peritectic garnet increases from 10 to 50 ppm with 33 garnet growth. In contrast, Zr in retrograde garnet generally decreases from 60 to 10 ppm 34 with garnet growth. A similar trend is observed for Ti. Temperatures calculated from the 35 Ti-in-garnet geothermometer increase from 830 °C to 980 °C based on Ti in peritectic 36 garnet, indicating prograde partial melting, whereas decrease from 900 °C to 700 °C 37 based on Ti in retrograde garnet, indicating post-peak cooling. Peritectic and retrograde 38 garnets show distinct Eu/Eu\* (0.2–0.5 vs. 0.05–0.2, respectively) and Ca contents (6000– 39 40 12000 ppm vs. 4000–6000 ppm, respectively), which generally decrease with progressive garnet crystallization. The pressures calculated from the Ca-in-garnet geobarometer in 41 42 peritectic and retrograde garnet are 9–11 kbar and 7–9 kbar, respectively. Peritectic garnet 43 shows a bell-shaped Y (80–340 ppm) pattern, whereas retrograde garnet shows an increase in Y content (20–100 ppm) toward rims. Taken together, these results establish a 44 P-T path comprised of an earlier high-pressure peritectic garnet formation during 45 46 prograde partial melting before the UHT peak and a late abundant retrograde formation

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47	during post-peak cooling stage. We conclude that change of Zr and other elements (e.g. Ti,
48	Ca, Y, and Eu/Eu*) can well distinguish different garnet formation events in UHT
49	granulites, which is critical for the $P-T$ path establishment, and further sheds light on the
50	cause of UHT metamorphism and the geodynamic evolution.
51	<b>Keywords</b> : Garnet, $P-T$ path, Trace element, UHT, Khondalite Belt, North China Craton
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53	Introduction
54	The metamorphic $P$ T path is one of the fundamental features used to elucidate doop
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55	crustal geologic processes and major and trace element zonation in garnet can reveal
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55 56 57	rustal geologic processes and major and trace element zonation in garnet can reveal metamorphic $P-T$ -fluid evolution (e.g. Tuccillo et al. 1990; Spear and Kohn 1996; Kohn et al. 2001). Garnet in metapelites can be formed by sub-solidus reaction (e.g. Rivers
55 56 57 58	The metanlorphic $T-T$ path is one of the fundamental features used to enclude deep crustal geologic processes and major and trace element zonation in garnet can reveal metamorphic $P-T$ -fluid evolution (e.g. Tuccillo et al. 1990; Spear and Kohn 1996; Kohn et al. 2001). Garnet in metapelites can be formed by sub-solidus reaction (e.g. Rivers 1983; Pyle and Spear 1999; Yang and Rivers 2001), defined as prograde garnet, and

between sapphirine/spinel and quartz/liquid (White et al. 2002; Holder et al. 2018), and be defined as retrograde garnet. More than one garnet generation could be preserved in metapelitic granulite, and therefore determining garnet formation events and P-Tconditions will shed light on overall P-T evolution. Sufficient diffusion of major divalent cations at elevated temperatures (e.g. Florence and

peritectic garnet. Alternately, garnet can occur as a retrograde product of the reaction

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Sumerent diffusion of major divarent cations at elevated temperatures (e.g. Fiorence and Spear 1991), retrograde exchange and net transfer reactions (Selverstone and Chamberlain 1990; Kohn and Spear 2000) can flatten garnet growth zoning in the case of granulites (Pattison et al. 2003). This can lead to potential misinterpretation of P-T paths and inaccurate tectonic interpretations (Selverstone and Chamberlain 1990), and the

situation can be exacerbated in UHT granulites, where peak temperatures exceeded 900  $^{\circ}$ C (Harley 1998). Therefore, the *P*–*T* path experienced by UHT granulites (particularly the prograde segment) is commonly ambiguous.

The larger ionic radius of Ca means it has an order of magnitude lower rate of diffusion in garnet compared to Fe and Mg (Vielzeuf et al. 2007), and therefore Ca content and zonation may reflect original garnet growth zoning. Rare-earth elements (REEs) have a slower diffusion rate than major divalent cations in garnet (i.e. Tirone et al. 2005; Carlson 2012). Moreover, garnet strongly fractionates HREE and Y, which can provide a record of formation history when coupled with Ca (Chernoff and Carlson 1997, 1999), and other trace elements (e.g. Axler and Ague 2015; Raimondo et al. 2017; George et al. 2018).

The Khondalite Belt is one of the Paleoproterozoic orogens in the North China Craton 80 81 (NCC) with predominant upper amphibolite- to granulite-facies metasedimentary rocks (Fig. 1a; e.g. Zhao et al. 2005; Peng et al. 2014). Evidence for UHT metamorphism has 82 been recognized from several localities (Fig. 1b). These UHT granulites were interpreted 83 to record an initial post-peak near isobaric cooling (IBC) P-T path, and followed by a 84 stage of near isothermal decompression (ITD) or decompression-heating (as review in 85 Jiao and Guo 2020). However, the prograde P-T path before the UHT-peak is poorly 86 constrained. The UHT granulites have long been considered to have experienced an 87 anticlockwise P-T path with near isothermal pressure increase before IBC stage (Santosh 88 et al. 2007a, 2009a, 2012; Tsunogae et al. 2011), whereas a complex clockwise P-T path 89 was proposed by more recent studies with a decompression-heating stage before the 90 UHT-peak (Jiao et al. 2017; Li and Wei 2018). 91

92 In this study, trace elements and Ca contents of garnet in the aluminous granulites from a

93 well-studied UHT locality (i.e. Dongpo; Fig. 1b) in the Khondalite Belt, NCC, were 94 measured by laser ablation inductively coupled plasma mass spectrometry (LA–ICP–MS). 95 These data in combination with phase equilibria modeling and the application of 96 Ti-in-garnet geothermometer and Ca-in-garnet geobarometer are used to document garnet 97 formation events during the UHT metamorphic evolution, and better constrain the P-T98 path and shed light on the tectono-thermal evolution of the Khondalite Belt.

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### Geological setting

101 The NCC is composed of multiple micro-blocks of Archean to Paleoproterozoic basement, separated by several Paleoproterozoic orogenic/mobile belts (Fig. 1a; e.g. Zhao et al. 102 2005; Zhai et al. 2014). The EW-trending Khondalite Belt is thought to have formed by 103 continental-continental collision between the Yinshan Block in the north and the Ordos 104 Block in the south at ca. 1.95 Ga (Fig. 1a; Zhao et al. 2005). The final amalgamation of 105 the NCC was accomplished during continental-continental collision along the 106 Trans-North China Orogen between the Western Block and the Eastern Block at ca. 1.85 107 Ga (Fig. 1a; e.g. Zhao et al. 2005). 108

109 The Khondalite belt is located adjacent to the western segment of the Trans-North China Orogen (Fig. 1b) and is commonly divided into three terranes from west to east: 110 111 Helanshan–Qianlishan, Ulashan–Daqingshan and Jining-Liangcheng-Fengzhen 112 (simplified here to Jining) terranes. The belt is mainly composed of ENE-trending upper amphibolite- to granulite-facies metasedimentary rocks including garnet-sillimanite 113 gneiss, quartzo-feldspathic granofels, feldspathic quartzite, mafic granulite, marble, 114 115 calc-magnesium silicate rocks and minor graphite gneiss (Fig. 1b; Lu and Jin 1993).

These rocks are usually associated with extensive garnet-bearing potassic granite and charnockite, and metamorphosed gabbroic and noritic to dioritic intrusions (Fig. 1b; Lu and Jin 1993). The protolith of the metasedimentary rocks in the Khondalite Belt was thought to have been deposited on an active continental margin at ca. 2.04–1.95 Ga (e.g. Dan et al. 2012).

The majority of metapelites consist of garnet + sillimanite-bearing assemblages in the 121 Khondalite Belt, whereas minor high-pressure (HP) metapelites with garnet + kyanite + 122 perthite assemblage were also recognized (Yin et al. 2015). The metapelites were 123 suggested to have experienced clockwise P-T paths with peak P-T conditions of ca. 8–12 124 125 kbar and 750–880  $^{\circ}$ C, including near-isothermal decompression (ITD) stages (Yin et al. 2015). As stated above, the UHT granulites experienced post-peak cooling before the 126 decompression-heating or ITD stages (e.g. Santosh et al. 2012; Li and Wei 2018; Jiao 127 and Guo 2020), but the overall shape of the P-T path is controversial due to the 128 ambiguity of the pre-peak prograde *P*–*T* path segment. 129

There are a wide range of metamorphic ages (ca. 1.96–1.80 Ga) reported from the Khondalite Belt (Peng et al. 2014; Jiao et al. 2020b). The timing of HP metamorphism was constrained to be 1.96–1.94 Ga (Yin et al. 2011), while the HT–UHT metamorphism was long-lived from 1.94–1.80 Ga (Santosh et al., 2007b, 2009b; Jiao et al. 2020a, b; Jiao and Guo, 2020).

At the Dongpo locality (GPS: 40°57′ 8.2″ N and 111°09′ 16.5″ E; Fig. 1b), garnetiferous leucogneiss, garnet-sillimanite gneiss, aluminous garnet-sapphirine or garnet-spinel granulite, mafic granulite and quartz-K-feldspar vein occur as layers in the host orthopyroxene-bearing orthogneiss (Fig. 1b; Jiao et al. 2020b). These rocks

commonly show a strong or weak NEE-trending, steeply dipping foliation. Three
aluminous granulite samples that were interpreted to have experienced UHT
metamorphism are studied here.

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### Sample description

The three samples (sample 10DP01 with three thin sections 10DP01a, 10DP01b, and 144 10DP01c, and samples 08JDP08 and 08JDP11, each with one thin section) are residual 145 granulites, depleted in SiO<sub>2</sub> (39–40 wt.%) and K<sub>2</sub>O (1–2 wt.%), but enriched in Al<sub>2</sub>O<sub>3</sub> 146 (28–30 wt.%), FeO (11–14 wt.%) and MgO (7–8 wt.%) (Details in Jiao et al. 2017). They 147 contain garnet (10-50 mass%; calculated by TIMA (TESCAN Integrated Mineral 148 Analyser), sillimanite (1–7 mass%), plagioclase (15–47 mass%), biotite (10–27 mass%), 149 spinel (1.4–4.7 mass%), sapphirine (3–17 mass%), and accessory minerals including 150 rutile, ilmenite, cordierite, corundum, monazite and zircon. The samples contain very rare 151 quartz as inclusions in garnet, and no K-feldspar. The only potassium-bearing mineral is 152 biotite and the only leucocratic mineral is plagioclase. 153

Garnet, spinel, sapphirine and plagioclase occur as two different types. Garnet is variable 154 155 in grain size (from less than 0.5 mm to 12 mm) and irregular in shape. The first type of garnet occurs as inclusion-rare single grains (Fig. 2a) or as cores that are mantled by the 156 second type of garnet (Fig. 2b-c), rich in fibrous sillimanite and biotite inclusions and 157 158 locally containing minor plagioclase, sapphirine and spinel inclusions. The major foliation, defined by oriented biotite, prismatic sillimanite and sometimes sapphirine and 159 160 spinel, passes along the boundaries of the inclusion-rare garnet and sometimes forms 161 pressure shadows (Fig. 2a), but the foliation is overprinted by the inclusion-rich garnet

162	(Fig. 2b–c). Spinel occurs as irregular grains in the matrix, or occurs as intergrowths with
163	plagioclase taking the shape of sillimanite. Sapphirine occurs as coronae on spinel, or as
164	intergrowths with plagioclase replacing sillimanite. Plagioclase occurs as coarse-grained
165	crystals in the matrix, or as fine-grained intergrowths with spinel and/or sapphirine.
166	Zircon and monazite commonly occur as inclusions in inclusion-rich garnet, and in the
167	matrix, but rarely as inclusions in inclusion-rare garnet.
168	Photomicrograph scans of two representative thin section samples (i.e. 08JDP11 and
169	10DP01a) are shown in the Appendix materials (Figs. A1–A2).

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### Results

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### 173 Garnet trace elements

A total of 234 analytical spots were measured by LA–ICP–MS along continuous traverses through 9 garnet grains in five thin sections, and the other grains were analyzed with a random spot distribution. Detailed methods, standards and analytical uncertainties are in the Appendix materials.

The results show that inclusion-rare garnet and inclusion-rich garnet have different chemical features that are generally not grain-size related. The inclusion-rare garnet is characterized by a high-Ca content (mostly 6000–12000 ppm), and the inclusion-rich garnet is low-Ca (mostly 4000–6000 ppm; Fig. 7b). The Ca content in the inclusion-rare garnet shows a range of Ca concentration patterns across grains. Ca can increase and then decrease rimwards (Fig. 3f), or remain constant and then decrease rimwards (Figs. 4c, 5c).

In contrast, the inclusion-rich garnet preserves consistent (Fig. 3f), and slightly decreasing Ca zoning rimwards (Figs. 4c, 5c, and 6c), and sometimes has Ca-enriched outermost rims (Figs. 4c, 6c).

The inclusion-rare garnet has high Eu/Eu\* (Eu/ $\sqrt{(Sm \times Nd)}$ ); mostly in the range of 0.2– 0.5, whereas inclusion-rich garnet has low Eu/Eu\* (0.05–0.2). In general, zonation in Eu/Eu\* varies consistently with Ca content (Figs. 3f, 4c, 5c, and 6c), with Eu/Eu\* positively correlated with Ca (Fig. 7b).

The inclusion-rare garnet shows a large variation in Y content between samples, and the 191 192 inclusion-rare garnet from sample 08JDP11 has a higher Y content (100–340 ppm) than that from samples 10DP01b and 08JDP08 (80-110 ppm) (Figs. 3g, 4d, 5d, and 7a). In 193 194 contrast, the inclusion-rich garnet has a relatively uniform Y content (20 to 100 ppm) among samples, but can contain up to 180 ppm Y in some outermost rims (Figs. 3g, 4d, 195 5d, and 7a). The inclusion-rare garnet preserves bell-shaped (Figs. 3g, 4d) or flat Y 196 zoning (Fig. 5d), and the inclusion-rich garnet preserves flat and increased Y zoning 197 rimwards (Figs. 3g, 4d, 5d and 6d). The Y-enriched outermost rims (less than 0.8 mm) are 198 preserved in both the inclusion-rich garnet and the inclusion-rare garnet (Fig. 5d). 199

The inclusion-rare garnet shows positive to flat HREE slopes (Figs. 3d–e, 4b, 5b), with Lu<sub>N</sub>/Gd<sub>N</sub> in the range of 0.5–12, whereas the inclusion-rich garnet normally shows negative HREE slopes (Figs. 3d–e, 4b, 5b, and 6b) with Lu<sub>N</sub>/Gd<sub>N</sub> mostly less than 0.6. In general, Lu<sub>N</sub>/Gd<sub>N</sub> shows a consistent variation with Y (Figs. 3g, 4d, 5d, and 6d).

The inclusion-rare garnet contains less Gd (8–14 ppm) than inclusion-rich garnet (10–27 ppm). The inclusion-rare garnet shows a bowl-shaped Gd abundance pattern across a grain, whereas the inclusion-rich garnet shows variable and asymmetric Gd patterns, from

flat, to decreased or increased Gd contents toward the rims (Figs. 3h, 4e, 5e, and 6e). The inclusion-rare and inclusion-rich garnets contain comparable Sc (40–100 ppm), but the inclusion-rare garnet has a bowl-shaped Sc pattern (like Gd), whereas the inclusion-rich garnet shows variable and asymmetric patterns of Sc enrichment across grains, from flat, to decreased or increased contents toward the rims (Figs. 3h, 4e, 5e, and 6e).

212 The inclusion-rare garnet contains more Ti (140–280 ppm) than the inclusion-rich garnet (60–250 ppm) (Fig. 7c). The inclusion-rare garnet shows increased Ti toward garnet inner 213 rims and decreasing Ti toward the outermost rims, whereas the inclusion-rich garnet 214 215 shows complex Ti zoning which is generally characterized by less Ti toward the rims, but sometimes shows inflections (Figs. 3i, 4f, 5f, and 6f). The inclusion-rare garnet has 216 slightly less Zr (10–40 ppm) than the inclusion-rich garnet (10–60 ppm) (Fig. 7f). The 217 inclusion-rare garnet commonly shows a bowl-shaped Zr enrichment pattern across a 218 grain, whereas the inclusion-rich garnet shows variable Zr, mostly decreasing trends 219 toward the rims, but sometimes increasing rimwards, or with inflections (Figs. 3i, 4f, 5f, 220 and 6f). 221

In summary, the inclusion-rare garnet and inclusion-rich garnet are characterized by different Ca (6000-12000 vs. 4000-6000 ppm), Eu/Eu\* (0.2-0.5 vs. 0.05-0.2), Y (80-340 vs. 20–100 ppm), Lu<sub>N</sub>/Gd<sub>N</sub> (0.5-12 vs. 0.01-0.6), and Gd (8-14 vs. 10-27 ppm), respectively. The variation of these chemical components and Eu/Eu\* ratios is generally consistent across all inclusion-rare garnets, but variable among inclusion-rich garnets as summarized in Table 1.

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### 229 *P*–*T* pseudosections

Two thin sections were selected for pseudosection calculations. Sample 10DP01b mainly 230 consists of coarse-grained garnet and has the highest garnet abundance ( $\sim 50$  mass%), 231 while sample 10DP01c mainly consists of fine-grained garnet and has the lowest garnet 232 abundance ( $\sim 10 \text{ mass}\%$ ). The bulk compositions of these two thin sections were used for 233 234 the calculations (Fig. 8). Detailed methods and procedures can be found in the Appendix materials. The P-T pseudosection was calculated in a P-T range of 6–14 kbar and 750– 235 1100 °C, and we show the result from sample 10DP01c here, while results for sample 236 10DP01b can be found in the Appendix materials. The full topological characteristics can 237 also be found in the Appendix materials. 238

The predominant mineral assemblage is in the Grt + Sil + Bt + Spr + Lig field, defined as 239 240 M2 (the second metamorphic stage), while spinel belongs to an early stage, defined as M1 (the first metamorphic stage). Mineral growth and consumption are inferred based on 241 242 the change of mineral modes in the pseudosection. Garnet mode does not change much in 243 the Grt + Bt + Spr + Liq and Grt + Sil + Bt + Spr + Liq fields, but it is clear that garnet mode increases during cooling and decreases during decompression (Fig. 8b). Change of 244 biotite mode is mainly T-related in Crd-absent fields (Fig. 8c). Biotite mode increases 245 during cooling, and distinctly changes across the Sil-in line (Fig. 8c). Change of 246 plagioclase mode is also T-related in Crd-absent, Crn-absent fields (Fig. 8d). Plagioclase 247 mode increases during cooling, and is stable across the Sil-in line (Fig. 8d). In summary, 248 it is inferred that garnet, biotite, plagioclase and sillimanite grew during a cooling stage. 249 During this cooling stage, Ca-in-Grt (= Ca/(Ca + Mg +Fe)  $\approx$  Grs mol.%) decreased at 250 251 first, then stabilizes and finally increases a little based on the change of modeled

252 Ca-in-Grt isopleths (Fig. 8a).

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### Discussion

### 255 A metamorphic framework of the Dongpo UHT granulite

Previous works found that the Dongpo granulites experienced Paleoproterozoic UHT 256 metamorphism with peak P-T conditions of 8–12 kbar and 910–980 °C, constrained by 257 pseudosection calculations (Tsunogae et al. 2011; Guo et al. 2012; Jiao et al. 2017; Jiao 258 and Guo 2020) and using the Zr-in-rutile geothermometer (Jiao et al. 2011). It is quite 259 260 clear that there were two retrograde stages of post-peak IBC (M2) from ca. 980 °C to ca. 830 °C at ca. 9 kbar, and subsequent decompression-heating (i.e. M3) to ca. 7 kbar and ca. 261 900 °C, based on phase equilibria modeling using effective bulk compositions of three 262 sapphirine-bearing microdomains (Jiao and Guo 2020). The P-T pseudosections modeled 263 here show that garnet, together with biotite, plagioclase, and sillimanite, grew during a 264 cooling stage (Fig. 8), which further supports the conclusion of post-peak IBC stage (M2) 265 by Jiao and Guo (2020). 266

Two types of garnet are recognized here based on textural and geochemical features, with 267 268 the inclusion-rare garnet forming prior to the major foliation defined by aligned biotite and sillimanite, and the inclusion-rich garnet forming after, or concurrently with, the 269 foliation (Fig. 9). The inclusion-rich garnet occurs in higher abundance than the 270 271 inclusion-rare garnet, and is commonly associated with biotite and sillimanite, and therefore we suggest that the modeled pseudosections show the inclusion-rich garnet 272 273 formation process. However, the formation of inclusion-rare garnet (only a small 274 percentage of the whole thin section) is unclear in the pseudosections, because these

granulites are strongly evolved residual melt phases, and domainal in compositions (Jiao
and Guo 2020). For this reason, prograde metamorphism cannot be well constrained.
Tsunogae et al. (2011) have inferred a nearly isothermal compression before the thermal
peak, whereas Jiao et al. (2017) proposed two alternative scenarios; decompression–
heating or an early decompression followed by heating before the UHT peak.

280 The pseudosections generally represent the metamorphic evolution of these granulites, considering the consistency between observed and modeled mineral assemblages and 281 282 their modes. However, two major inconsistencies still exist. First, spinel, a common 283 mineral in these rocks, was only calculated to be stable at lower pressure and/or higher temperature, and no spinel + garnet stable fields were calculated. Second, retrograde 284 garnet that makes up a significant proportion of the total garnet in the rocks only shows a 285 few percent growth with cooling in the pseudosections. The limitation and uncertainty 286 associated with the phase equilibria modeling mean that the exact mineral assemblage 287 288 cannot be always reproduced. Importantly, however, retrograde garnet growth is predicted, even if the amount of garnet growth is not modeled accurately, because the precise 289 predicted amount of retrograde garnet growth depends significantly on the details of the 290 291 interpreted P-T path (Fig. 8). Some of the modeling limitations might be related to the highly residual composition of these rocks (low-Si, low-K, high-Al, high-Fe and 292 high-Mg), which differs substantially from the average pelite for which current a-x 293 294 models are typically applied.

295 Comparison between pseudosections based on datasets of ds55 and ds62 is shown in the 296 Appendix materials. An in-depth discussion of the uncertainties associated with phase 297 equilibria modeling using different datasets were discussed by Korhonen et al. (2014) and

298 Guevara and Caddick (2016). Korhonen et al. (2014) concluded that ds62 provided better agreement to their interpreted metamorphic reaction history than ds55s, although several 299 observations were not successfully accounted for in their ds62 models. Guevara and 300 Caddick (2016) showed that generally similar interpretations were obtained with ds55 301 and ds62, but the absolute values of P and T for interpreted parageneses differed and 302 303 some interpreted parageneses were not successfully modeled in ds62. Using ds62 in this study, garnet + spinel, but not sapphirine, were calculated to be stable within the 304 investigated P-T range; retrograde garnet growth within the biotite stability field was not 305 306 predicted either. In contrast, ds55 calculations predict garnet-sapphirine stability and retrograde garnet growth within the biotite stability field, but not garnet-spinel stability. 307 Thus, neither dataset predicts all of the interpreted parageneses, requiring independent 308 verification of the estimated *P*–*T* conditions (i.e. the Ca and Ti in garnet in the following 309 sections), which support the overall interpretation of a UHT clockwise P-T path and two 310 generations of garnet growth. 311

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### 313 Mechanisms controlling trace element distribution in garnet

Trace element distribution in garnet is complex and commonly shows decoupling between elements. Related to the variable length scale of chemical equilibrium, garnet trace element distribution is controlled by a number of factors including elemental partition coefficients between garnet and the matrix, limited intergranular diffusion of cations, changes of intensive parameters (i.e. P, T), changes of major and accessory mineral assemblages, and (potentially) fluid infiltration (Lanzirotti 1995; Pyle and Spear 1999; Otamendi et al. 2002; Konrad-Schmolke et al. 2008; Moore et al. 2013; Rubatto et

321 al. 2020).

The chemical composition of garnet in the Dongpo granulites is Alm (50–60 mol.%)–Prp 322 (37–47 mol.%) solid solution with  $X_{Mg}$  of 0.38–0.51, Grs content of 2–4 mol.% and Sps 323 content of 0.6-1.0 mol.% (Jiao and Guo 2020). Zonation of Mg, Fe and Mn has been 324 flattened by strong diffusion and, while the outermost rims were affected by retrograde 325 326 Fe-Mg exchange, Ca zonation is preserved (Jiao et al. 2017; Jiao and Guo 2020). A change in garnet major element composition is therefore not considered to be the major 327 mechanism controlling trace element distribution. A recent study has certified that 328 329 diffusion-limited uptake is not a dominant mechanism at high T (Rubatto et al. 2020). There is no evidence of a sharp peak or spike in trace element zonation, also arguing 330 against the mechanisms of limited intergranular diffusion and fluid alteration. In summary, 331 the observed trace element (i.e. HREE + Y, Ti, Zr, and Sc) zonation in garnet from the 332 Dongpo granulites mainly reflects growth zoning since garnet formation, and the 333 equilibrium partitioning of these elements between garnet and the matrix, preserves 334 indicators of P-T condition change, and was influenced by the formation and breakdown 335 of other major and accessory minerals. However, diffusion relaxation under UHT 336 337 conditions may have smoothed the patterns somewhat, and the characteristic diffusion length scales are less than 2.2 mm, calculated using a duration of 100 Myr by both zircon 338 and monazite U-Pb dating (Jiao et al., 2020a, b) and T of 900 °C, with Y diffusion 339 coefficient (i.e.  $Log(D_Y) = -21.45$ ) from Carlson (2012) and Ca diffusion coefficient (i.e. 340  $Log(D_{Ca}) = -21.43$ ) from Vielzeuf et al. (2007). 341

Manganese and Y are strongly compatible in garnet, and therefore garnet growth causes progressively depleted Mn and Y, and generates bell-shaped zonation across the grain

(Pyle and Spear 1999; Otamendi et al. 2002; Moore et al. 2013). Manganese is commonly used as a chemical proxy to represent progressive garnet growth in low-grade metamorphism, while Y is used for high-grade metamorphism. In this study, Eu/Eu\* is used as a proxy to represent progressive garnet growth, which commonly decreases from core to rim (like Y) in the two types of garnet (Fig. 7a), with Y being enriched in garnet outermost rims. The other trace elements and Ca are plotted against Eu/Eu\* to show changes with garnet growth (Fig. 7), as discussed in more detail below.

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### 352 Peritectic garnet formation during prograde partial melting

The bell-shaped HREE + Y zoning has been attributed to Rayleigh fractionation during garnet formation (where mineral assemblages remain unchanged), commonly under sub-solidus conditions (Pyle and Spear 1999; Otamendi et al. 2002; Moore et al. 2013; Rubatto et al. 2020). The inclusion-rare garnet shows bell-shaped or sometimes flat Y zoning, irrespective of grain size, indicating that Rayleigh fractionation is not the sole explanation. Some other considerations are discussed below.

Scandium is strongly compatible in garnet, like Y and Mn, but the variation in Sc content 359 360 from core to rim is in contrast to the variation in Y + HREE (Figs. 3g, 4d, 5d and 6d), and similar to the variation in Gd content (representative of MREE)(cf. Figs. 3h, 4e, 5e and 361 6e). The transition from bell-shaped to bowl-shaped zonation with decreased REE atomic 362 363 number is consistent with observations of garnet zoning in other studies (Lapen et al. 2003; Skora et al. 2006; Konrad-Schmolke et al. 2008; Moore et al. 2013; Raimondo et al. 364 365 2017; George et al. 2018), with general core–rim decreases in Y + HREE and increases in 366 M-LREE due to REE fractionation during garnet growth (e.g. Lapen et al. 2003) with

possible variability due to superimposed effects of matrix-mineral reactions (e.g.Konrad-Schmolke et al. 2008).

The zonation of Ca and Ti in garnet (Figs. 7b–e) reflects a change of metamorphic P and 369 T. The P results are calculated to be 9.2–11.4 kbar (at 900 °C) using a newly calibrated 370 Ca-in-Grt geobarometer (Wu 2019), which are consistent with the pressure results of 9.6– 371 10.9 kbar (at 900 °C) calculated using the GASP geobarometer (Holdaway 2001). These 372 P results are taken as maximum estimates considering the silica-undersaturated 373 conditions, but phase equilibria modeling using the whole-rock composition constrains 374 375 similar P conditions at 9–10 kbar with T estimates of 850–920 °C (Jiao et al. 2017). An experimental study has shown that Ti in garnet is positively correlated with 376 metamorphic T (Kawasaki and Motoyoshi 2016). The Ti content slightly increases in the 377 inner part of inclusion-rare garnet, followed by sharp Ti content decrease at the rim (Figs. 378 3i, 7c), confirming that metamorphic T increased during prograde metamorphism. The T 379 380 calculated by the Ti-in-Grt geothermometer (calibrated by Kawasaki and Motoyoshi (2016)) increases from 830 to 980 °C across the inclusion-rare garnet (Fig.7d). These are 381 minimum estimates due to the absence of quartz and may show bias because of the 382 absence of orthopyroxene, but these temperature results are consistent with T calculated 383 from rutile without adjacent ilmenite or zircon using the Zr-in-rutile geothermometer 384 (850–980 °C), and with the results from pseudosection modeling (Jiao et al. 2017; Jiao 385 and Guo 2020). The Ti-depleted outermost rims may reflect decreased T during the 386 subsequent retrogression, or may indicate Ti interface coupled dissolution-reprecipitation 387 (Ague and Axler 2016). The latter is more likely given the fact that the outermost rims of 388 389 most analyzed garnets have decreased Ti contents (e.g., Figs. 3i, 4f, 5f, and 6f).

390 Zirconium zonation in garnet is similar to that of Ti, and also regarded as temperature-dependent (Kohn et al. 2015), if zircon exists during the whole metamorphic 391 evolution, that means the  $ZrO_2$  activity is unity. The increase of Zr content with garnet 392 growth in inclusion-rare garnet (Fig. 7f), supports the conclusion of peritectic garnet 393 formation during prograde partial melting. The increase of V, Cr, Zr, Y and M-HREE in 394 395 peritectic garnet was also recognized by Rubatto et al. (2020), but they suggest that it is related to the dehydration melting of biotite and the solubility of accessory minerals in 396 the melt, such as zircon and monazite. 397

398 The inclusion-rare garnet coexists with spinel and plagioclase in the matrix of the Dongpo granulites, and all are assigned as M1 phases (Fig. 9). These mineral 399 assemblages can be produced by biotite dehydration melting at high-pressure (ca. 10 kbar) 400 and high-temperature (> 1000 °C; Patiño Douce and Johnston 1991), probably under 401 silica-undersaturated conditions. A decrease in Eu/Eu\* with garnet formation (Figs. 3f 402 and 4c) suggests K-feldspar grew together with inclusion-rare garnet during biotite 403 dehydration melting (Patiño Douce and Johnston 1991). K-feldspar is absent from the 404 Dongpo granulites, but K-feldspar could have been produced by biotite dehydration 405 melting, but have been extruded during melt loss. Alternatively, the Eu content could 406 simply be a function of the grossular content, because trace-element incorporation into 407 pure grossular is different from that in pure almandine or pyrope. 408

In summary, we interpret the inclusion-rare garnet to have formed as a peritectic phase,by biotite dehydration melting reaction during the high-pressure, high-temperature

411 prograde metamorphism before the UHT peak.

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## 413 Retrograde garnet formation and garnet resorption during post-peak retrograde 414 stages

Abundant aligned biotite and sillimanite inclusions occur in inclusion-rich garnet but are 415 rarely found in the inclusion-rare garnet, indicating that there could have been a cooling 416 stage between the two garnet generations, or that the inclusion-rich garnet formed 417 418 together with sillimanite and biotite during the cooling stage (Fig. 9). Boger et al (2012) has reported similar garnet with aligned sillimanite and biotite inclusions and some garnet 419 surrounding magnetite, ilmenite and spinel, and suggested that these garnets have formed 420 421 by biotite dehydration melting. However, we think the former is more likely given the following considerations. 422

The zonation of Gd, Sc, Ti and Zr in the inclusion-rich garnet is variable and complex compared to that in the inclusion-rare garnet. The Zr content in inclusion-rich garnet generally decreases toward the rim, indicating that temperature decreases with garnet formation (Fig. 7f).

Temperatures calculated from Ti-in-Grt geothermometer (Kawasaki and Motoyoshi 2016) 427 are 700–900 °C, lower than those calculated from inclusion-rare garnet (Fig. 7d). Pressure 428 results calculated by the Ca-in-Grt geobarometer (Wu 2019) are 7–9 kbar (at 900  $^{\circ}$ C), 429 and 7-8 kbar by GASP geobarometer (Holdaway 2001), both also lower than estimates 430 from inclusion-rare garnet. The inflection of Ca/Ti ratios between inclusion-rare garnet 431 432 and inclusion-rich garnet represents the transition from prograde partial melting with decreased P/T, to post-peak cooling with increased P/T (Fig. 7e). The Y content of 433 inclusion-rich garnet is relatively homogeneous compared to that of inclusion-rare garnet, 434 435 with the exception of occasional Y-enriched outermost rims (Fig. 7a), implying bulk

equilibrium as garnet formed during slow cooling from UHT conditions. The Eu/Eu\* in
inclusion-rich garnet mostly decreases toward the rim (Fig. 7a–f), which can be explained
by plagioclase formation together with garnet during the cooling stage (Fig. 8).

Biotite occurs as inclusions in inclusion-rich garnet and extensively in the matrix in the 439 Dongpo granulites, and contains consistent and enriched  $TiO_2$  (3–7 wt%), indicating that 440 441 the two occurrences of biotite were likely formed simultaneously (Jiao and Guo 2020). Petrographic study indicates that the inclusion-rich garnet is in straight contact with 442 biotite in the matrix, suggesting they were in equilibrium. Taken together, the results 443 support the coeval formation of inclusion-rich garnet with biotite, both as inclusions and 444 in the matrix. A similar case should be true for sillimanite. These petrographical 445 observations are consistent with the change of mineral mode in the pseudosection (Fig. 446 8). 447

Therefore, the inclusion-rich garnet and extensive biotite and sillimanite, together with sapphirine coronae after spinel in the matrix, was more likely to have formed during the post-peak IBC stage (Jiao and Guo 2020). Minor spinel and sapphirine inclusions in garnet support this conclusion (Holder et al. 2018). Change of Ca in retrograde garnet (Table 1), is also consistent with the modeled isopleths along the post-peak IBC stage (Fig. 8a).

The Y-enriched outermost rim in garnet from the Dongpo granulites can be explained by garnet resorption and back diffusion (Fig. 7a), following similar explanations elsewhere (e.g. Hickmott and Spear 1992; Rubatto et al. 2006). The formation of sapphirine ± spinel + plagioclase intergrowths, plagioclase coronae and minor cordierite supports garnet breakdown during the M3 stage (Fig. 9) and indicates a decompression–heating stage to

459 ca. 7 kbar at ca. 900 °C in the P-T pseudosection calculated using effective bulk 460 composition of the sapphirine + plagioclase symplectite-dominated microdomain (Jiao 461 and Guo 2020).

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### 463 Interpretation of HP partial melting before UHT metamorphism

Given the evidence discussed above, we have documented early high-pressure, 464 high-temperature peritectic garnet formation during prograde partial melting before the 465 UHT peak (M1 stage), and late retrograde garnet formation during the post-peak 466 low-pressure IBC processes (M2 stage), and garnet resorption during decompression-467 heating (M3 stage) (Figs. 8, 10). This high-pressure prograde partial melting before UHT 468 metamorphism is the first documented example in the Khondalite Belt, NCC. A pre-UHT 469 high-pressure partial melting stage to UHT thermal peak along decompression clarifies 470 the previous debate over the overall shape of the P-T path, and therefore the clockwise 471 *P*–*T* path is certified (Fig. 10). 472

The clockwise P-T path documented here is distinct from that in high-pressure 473 metapelites in Helanshan and Qianlishan Terranes, for which post-peak ITD has been 474 shown (Yin et al. 2015). High-pressure granulite-facies metamorphism was dated at 1.96-475 1.95 Ga by zircon and monazite U-Pb geochronology (Fig. 10; Yin et al. 2011; Gou et al. 476 2019), representing the timing of collision between the Yinshan Block and the Ordos 477 478 Block within the Nuna supercontinent. The timing of prograde partial melting before UHT peak was constrained at 1.94–1.90 Ga, whereas the timing of post-peak long-lived 479 cooling at 1.90-1.80 and thermal peak very close to ca. 1.90 Ga (Jiao et al. 2020b). The 480 481 high-pressure prograde partial melting metamorphism before UHT peak confined here

implies the regional HP granulite-facies metamorphism and UHT metamorphism 482 occurred in sequence in the same tectono-thermal scenario in the Khondalite Belt, and 483 argue against an inferred paired metamorphic belt during Late Paleoproterozoic 484 orogenesis. The temporal change from HP partial melting to achieving UHT conditions 485 along decompression, indicates that the transition of compressed to extensional tectonic 486 487 regime occurred as early as ca. 1.94 Ga, whereas these granulites have retained in lower crust level at high-temperature conditions for protracted timescale, until another 488 decompression-heating metamorphic episode. This case study sheds light on the cause of 489 490 UHT metamorphism and favors the post-collisional extension environment and possible asthenospheric upwelling for the cause of UHT metamorphism, following initial heating 491 and higher-pressure granulite metamorphism during collision. 492

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### Implications

We investigated garnet behavior using samples of Dongpo residual UHT granulites in the 495 Khondalite Belt, NCC. The Ca, Ti, Zr and Y + REE chemical signatures, coupled with the 496 application of the Ti-in-Grt geothermometer and the Ca-in-Grt geobarometer, can 497 498 distinguish garnet origin and determine P-T conditions. The integrated results allow us to formulate an earlier, high-pressure, high-temperature garnet formation and a later 499 abundant retrograde garnet formation during post-peak cooling. This is the first time 500 501 high-pressure peritectic garnet formation before UHT metamorphism has been documented in the Khondalite Belt. It attests to the genetic correlation between HP 502 503 granulite-facies and UHT metamorphism, which, otherwise, do not constitute an ancient 504 paired metamorphic belt.

505 Our study also argues that garnet with abundant sillimanite and biotite inclusions can be 506 retrograde rather than peritectic. The inclusions and partial inclusions in garnet are not 507 always formed as prograde mineral assemblages.

Garnet commonly occurs in UHT granulites in other Khondalite Belt localities and the new approach introduced here can be used to constrain the P-T paths in other high-grade terranes. Moreover, the identification of garnet origin is significant for future studies involving Lu–Hf, Sm–Nd, O and Fe isotopic investigations of garnet, and understanding the petrogenetic link between zircon/monazite and garnet.

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### 527 Appendix A. Supplementary material

528 Supplementary material related to this article can be found online.

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### **Figure captions**

Figure 1. (a) Location of the North China Craton (NCC), and its simplified tectonic
subdivisions (modified after Zhao et al. 2005). Abbreviations: EB = the Eastern Block.
TNCO = the Trans-North China Orogen. WB = the Western Block which is composed of
YB, OB and the Khondalite Belt. YB = the Yinshan Block. OB = the Ordos Block. H–Q

the Helanshan–Qianlishan Terrane, U–D = the Ulashan–Daqingshan Terrane, J = the
Jining Terrane. (b) Sample locations and distribution of high-grade metamorphic rocks in
the eastern segment of the Khondalite Belt, NCC (modified after Jiao and Guo 2020). All
samples studied here were collected from the Dongpo locality.

**Figure 2.** Representative photomicrographs showing microtextures of the two types of garnet. (a) Inclusion-rare garnet surrounded by biotite in sample 08JDP11. Analytical traverse results shown in Fig. 3c–i. (b) Inclusion-rare garnet core mantled by inclusion-rich garnet rim in sample 08JDP11. Analytical traverse results shown in Figs. 3b, 3d–i. (c) Inclusion-rare garnet core mantled by inclusion-rich garnet rim in sample 10DP01b. Analytical traverse results shown in Fig. 4. Mineral abbreviations follow Whitney and Evans (2010).

Figure 3. (a–c) X-ray mapping of Ca showing three analyzed garnets in sample 08JDP11, with stars marking zircon localities. The yellow arrows indicate the path of the analytical traverse. A thin section image is shown in Fig. A2. (d) Chondrite-normalized REE patterns for Grt1 and Grt3. (e) Chondrite-normalized REE pattern for Grt2. (f) Eu/Eu\* and Ca zoning along analytical traverses. (g) Y and Lu<sub>N</sub>/Gd<sub>N</sub> zoning. (h) Gd and Sc zoning. (i) Ti and Zr zoning. Chondrite values taken from Sun and McDonough (1989).

Figure 4. (a) TIMA image showing the analyzed garnet in sample 10DP01b, with stars
marking zircon localities. The yellow arrow shows the path of the analytical traverse. (b)
Chondrite-normalized REE pattern for the analyzed garnet. (c) Eu/Eu\* and Ca zoning
along the analyzed traverse. (d) Y and Lu<sub>N</sub>/Gd<sub>N</sub> zoning. (e) Gd and Sc zoning. (f) Ti and
Zr zoning. Chondrite values taken from Sun and McDonough (1989).

Figure 5. (a) TIMA image showing analyzed garnet from sample 08JDP08, with stars

756	marking zircon localities. The yellow arrows mark analytical traverses. Mineral legend
757	the same as Fig. 4. (b) Chondrite-normalized REE pattern. (c) Eu/Eu* and Ca zoning
758	along analyzed traverses. (d) Y and $Lu_N/Gd_N$ zoning. (e) Gd and Sc zoning. (f) Ti and Zr
759	zoning. Chondrite values taken from Sun and McDonough (1989).
760	Figure 6. (a) TIMA image showing analyzed garnet in sample 10DP01c, with stars
761	marking zircon localities. The yellow arrows show analytical traverses. Mineral legend
762	the same as Fig. 4. (b) Chondrite-normalized REE pattern. (c) Eu/Eu* and Ca zoning
763	along analyzed traverses. (d) Y and Lu_N/Gd_N zoning. (e) Gd and Sc zoning. (f) Ti and Zr
764	zoning. Chondrite values taken from Sun and McDonough (1989).
765	Figure 7. The Ca and trace element chemical features in terms of Eu/Eu* in the two types
766	of garnet. Light shaded region denotes peritectic garnet while darker shaded region
767	encompasses retrograde garnet. The arrows represent changes of Ca and trace elements
768	during progressive garnet growth from core to rim in each garnet type. (a) Y (ppm) versus
769	Eu/Eu*. (b) Ca (ppm) versus Eu/Eu*. (c) Ti (ppm) versus Eu/Eu*. (d) The Ti-in-Grt
770	temperatures (°C) (calculated using the Kawasaki and Motoyoshi (2016) model) versus
771	Eu/Eu*. (e) Ca/Ti ratios versus Eu/Eu*. (f) Zr (ppm) versus Eu/Eu*.
772	Figure 8. (a) $P-T$ pseudosection calculated based on the bulk composition of sample
773	10DP01c. Isopleths of Ca-in-Grt (= Ca/(Ca + Mg +Fe) $\approx$ Grs mol.%) in the range of
774	0.014-0.086 are shown. The interval is 0.002. (b) Change of Grt mode in the range of
775	0.02-0.25. The interval is 0.01. (c) Change of Bt mode in the range of 0.02-0.24. The
776	interval is 0.02. (d) Change of Pl mode in the range of 0.21–0.47. The interval is 0.01.

The interpreted retrograde P-T path from Jiao and Guo (2020) is shown.

**Figure 9.** The summarized sketch map showing garnet behavior during the metamorphic

evolution of the Dongpo UHT granulite. At M1 stage (decompression-heating), peritectic
garnet formed together with spinel; At M2 stage (Post-peak IBC), retrograde garnet
formed together with abundant sillimanite, biotite and plagioclase and sapphirine coronae
on spinel; At M3 stage (decompression-heating), garnet broke down and
sapphirine/spinel + plagioclase symplectites formed.

- **Figure 10.** The overall P-T path of Dongpo UHT granulites involving peritectic garnet
- formation at M1 stage and retrograde garnet formation at M2 stage documented here and
- garnet resorption at M3 stage from Jiao and Guo (2020). Previous P-T paths (grey
- 787 colored) of HP granulite-facies metamorphism (Yin et al. 2015) and of UHT
- metamorphism at this locality (Tsugogae et al. 2011; Jiao et al. 2017) and from the
- 789 Tuguiwula locality (Li and Wei, 2018) are compared.

Classification	Inclusion-rare garnet	Inclusion-rich garnet
Ca	> 6000 ppm; consistent/increased and then decreased zoning rimwards	4000-6000; flat, consistent or slightly decreased zoning rimwards and sometimes Ca-enriched outermost rims
Eu/Eu*	0.2-0.5; decreased zoning rimwards	0.05-0.2; consistent or slightly decreased zoning rimwards and sometimes higher Eu/Eu* outermost rims
Y	80-340; bell-shaped or flat zoning, and sometimes sharply enriched outermost rims	20-100; flat or increased zoning rimwards
Lu <sub>N</sub> /Gd <sub>N</sub>	0.5-12; bell-shaped or flat zoning, and sometimes sharply enriched outermost rims	<0.6; flat or increased zoning rimwards
Gd	8-14; bowl-shaped zoning	10-27; variable zoning
Sc	40-100; bowl-shaped zoning	40-100; variable zoning
Ti	140-280; increased and then decreased trends rimwards	60-250 ppm; complex but generally decreased zoning rimwards
Zr	10-40; bowl-shaped zoning	10-60 ppm; variable but generally decreased zoning rimwards

Table 1 Chemical features of two types of garnet in Dongpo granulites



















Fig. 5

![](_page_41_Picture_0.jpeg)

![](_page_41_Figure_1.jpeg)

Fig. 6

![](_page_42_Figure_0.jpeg)

Fig. 7

![](_page_43_Figure_0.jpeg)

![](_page_43_Picture_1.jpeg)

# M1

# Peritectic Grt formation

![](_page_44_Picture_2.jpeg)

# M2

![](_page_44_Picture_4.jpeg)

# Retrograde Grt formation

![](_page_44_Picture_6.jpeg)

# M3

# Grt resorption and HREE + Y back-diffusion

![](_page_44_Picture_9.jpeg)

![](_page_44_Picture_10.jpeg)

![](_page_45_Picture_0.jpeg)

![](_page_45_Figure_1.jpeg)

![](_page_45_Picture_2.jpeg)