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**Application of Ti-in-zircon and Zr-in-rutile thermometers to constrain high-temperature metamorphism in eclogites from the Dabie orogen, central China**

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(Article begins on next page)



## UNIVERSITÀ DEGLI STUDI DI TORINO

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1        1    **Application of Ti-in-zircon and Zr-in-rutile thermometers to**  
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4        2    **constrain long-lived high-temperature metamorphism in**  
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6        3    **granulitized eclogites from the Dabie orogen, central China**

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## Abstract

Granulitized eclogites from the Dabie orogen, central China represent deeply subducted mafic lower continental crust of the South China Block and record a complex polymetamorphic evolution during Triassic continental deep subduction and subsequent exhumation. These eclogites were strongly affected by multiple decompression and re-crystallization processes during multistage exhumation, thus making the determination of peak metamorphic conditions particularly challenging. However, the recently calibrated Ti-in-zircon and Zr-in-rutile thermometers provide new tools to estimate the peak and post-peak temperatures. The obtained results suggest that the eclogites experienced a protracted high- $T$  ( $> 900$  °C) metamorphic evolution from high- $T$ /ultrahigh-pressure (UHP) eclogite-facies to UHT/HP granulite-facies conditions, characterized by near-isothermal decompression during the initial stages of exhumation.

Most of the analyzed zircons contain less than 20 ppm Ti and only 5–10% of them contain up to 60–100 ppm Ti, the latter corresponding to metamorphic temperatures of  $> 900$  °C. The occurrence of decompression textures preserved in robust minerals (e.g., low-Na omphacite inclusions coexisting with quartz, rutile and ilmenite in zircon; clinopyroxene + plagioclase + quartz intergrowths after omphacite in garnet) suggests that, even in robust minerals such as zircon, mineral inclusions may have experienced some degrees of decompression breakdown or retrogression. Therefore, Ti concentrations in zircons and Zr concentrations in rutile grains within garnet and zircon, respectively, may have been strongly modified by re-crystallization or re-equilibration. As a result, only few (5–10 %) zircons record their actual crystallization temperatures. In comparison, the rutile inclusions in zircon generally define higher temperatures, likely corresponding to their formation and preservation in a Zr-saturated environment. We therefore suggest that rutile inclusions in zircon are the most suitable candidates for high-grade  $T$  estimates, especially in strongly retrogressed eclogites.

This study also provides thermometric evidence that supports the previously

1 51 proposed Neoproterozoic mantle plume that led to the breakup of the supercontinent  
2 52 Rodinia, especially along the northern periphery of the South China Block.  
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4 53  
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6 54 *Keywords:* Eclogite; high-temperature metamorphism; Ti-in-zircon and Zr-in-rutile  
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8 55 thermometers; continental deep subduction; multistage exhumation.  
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## 1. Introduction

Peak and post-peak temperature estimates are crucial for better understanding the genesis and evolution of high-pressure (HP) and ultrahigh-pressure (UHP) eclogites and related metamorphic rocks in subduction zones. However, this task is challenging when investigating high-grade rocks, particularly those formed under extreme metamorphic conditions such as ultrahigh-temperature (UHT) metamorphism (Harley, 1998, 2008; Brown, 2007; Kelsey, 2008; Santosh and Kusky, 2010). Temperatures of  $> 900$  °C are, in fact, higher than the closure temperature of most conventional thermometers (Baldwin et al., 2007). An accurate estimate of peak temperature for high-grade rocks is often hampered by the significant re-equilibration or re-crystallization during retrogression and cooling. This has led to the recent development of trace-element thermometers such as those based on titanium concentration in zircon and zirconium concentration in rutile, which may provide a more precise link between the  $P$ - $T$  path and geochronological data (e.g., Watson and Harrison, 2005; Watson et al., 2006; Timms et al., 2011). Since their earlier development, the new Ti-in-zircon and Zr-in-rutile thermometers (Zack et al., 2004; Watson et al., 2006; Ferry and Watson, 2007; Baldwin et al., 2007; Tomkins et al., 2007) have been more and more successfully used to estimate the peak and post-peak temperatures of polymetamorphic rocks (e.g., Zack and Luvizotto, 2006; Spear et al., 2006; Baldwin et al., 2007; Miller et al., 2007; Tomkins et al., 2007; Chen and Li, 2008; Liu et al., 2010a; Zhang et al., 2010; Jiao et al., 2011; Meyer et al., 2011; Zheng et al., 2011; Kooijman et al., 2012; Ewing et al., 2013).

Zircon and rutile are common accessory minerals in metamorphic rocks. Therefore, although the possibility of diffusive resetting at high temperature may complicate the interpretation of apparent temperatures and zoning profiles (Watson et al., 2006), Ti-in-zircon and Zr-in-rutile thermometers may allow precise temperature estimates of metamorphism (Zack et al., 2004; Spear et al., 2006; Watson et al., 2006; Baldwin et al., 2007; Ferry and Watson, 2007; Page et al., 2007; Tomkins et al., 2007). Zircon is a robust mineral (Dobrzhinetskaya et al., 2003; Watson et al., 2006) and is

1 86 extensively used for U–Pb geochronology, giving useful information about a wide  
2 87 range of tectonic events and related processes (e.g., Rubatto et al., 1999; Hermann et  
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4 88 al., 2001; Möller et al., 2002; Liu et al., 2011a). Furthermore, the Ti-in-zircon  
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6 89 thermometer has the potential to create an invaluable link between U-Pb ages and  
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8 90 temperatures measured *in-situ* in zircon (e.g., Baldwin and Brown, 2008): this is  
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10 91 particularly true for multiple metamorphic rocks, because internal fine-scaled growth  
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12 92 structures in zircon may be directly correlated with variations in the physicochemical  
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14 93 conditions and the duration of each metamorphic event (e.g., Rubatto et al., 1999;  
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16 94 Corfu et al., 2003; Whitehouse and Platt, 2003). Application of this thermometer to  
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18 95 two typical UHT granulite localities demonstrated that it is a powerful method to  
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20 96 determine the peak temperatures of zircons (Baldwin et al., 2007). However, there are  
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22 97 also studies that show zircon re-crystallized post-peak and did not preserve UHT  
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24 98 temperatures, whereas rutile in the same samples did (Ewing et al., 2013).

27 99 Zr-in-rutile thermometry, based on the Zr content in rutile coexisting with quartz  
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29 100 and zircon, is an alternative and complementary method for estimating temperature of  
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31 101 metamorphism, especially useful for eclogites. Earlier calibrations of the Zr-in-rutile  
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33 102 thermometer focused on the strong effect of temperature (Zack et al., 2004; Watson et  
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35 103 al., 2006; Ferry and Watson, 2007), without including a correction for pressure. The  
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37 104 pressure dependence was incorporated into this thermometer with the calibration of  
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39 105 Tomkins et al. (2007). This revised thermometer has been demonstrated to be a  
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41 106 reliable method for the estimate of the peak temperatures in UHT rocks (e.g., Jiao et  
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43 107 al., 2011; Meyer et al., 2011; Kooijman et al., 2012). Also, Luvizotto and Zack (2009)  
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45 108 obtained Zr-in-rutile temperatures of up to 850–930 °C for rutile from granulite facies  
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47 109 metapelites from Val Strona and Val d’Ossola, but with significant resetting of  
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49 110 Zr-in-rutile temperatures to a spread of lower values.

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52 111 As a result, a combined Ti-in-zircon and Zr-in-rutile thermometry is required to  
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54 112 constrain peak and post-peak metamorphic temperatures for eclogites and related  
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56 113 high-grade rocks involved in complex processes. A suitable lithology to usefully apply  
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58 114 these two novel techniques is the granulitized eclogites of the Luotian dome in the  
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60 115 southwestern part of the North Dabie complex zone (NDZ), central China, which is a

1 116 portion of deeply subducted mafic lower continental crust of the South China Block  
2 117 (Liu et al., 2007a). The eclogites underwent UHP and HP eclogite-facies  
3 118 metamorphism, followed by HP granulite-facies overprint and later amphibolite-facies  
4 119 retrogression, during continental subduction and exhumation (Liu et al., 2011b). The  
5 120 peak metamorphic assemblages and compositions of such UHP rocks are commonly  
6 121 obliterated or overprinted by subsequent retrograde metamorphism at UHT  
7 122 (905–917 °C) conditions (Liu et al., 2011b). These metamorphic temperatures  
8 123 approximated or exceeded the closure temperatures of the Fe–Mg exchange  
9 124 thermometer between garnet and clinopyroxene (e.g., Raheim and Green, 1974;  
10 125 Baldwin et al., 2007). In this context, it is generally difficult, using conventional  
11 126 geothermometers, to precisely constrain the actual metamorphic temperatures  
12 127 experienced by the eclogites during the various stages of their evolution; nevertheless  
13 128 this information is essential for a robust understanding of the genetic and evolutionary  
14 129 processes of the UHP rocks in the NDZ.

15 130 Zircon is extremely robust to thermal disturbance and its U–Pb and REE  
16 131 systematics can remain preserved despite multiple (U)HT metamorphic episodes and  
17 132 re-equilibration, thus providing reliable ages and genetic information (Kooijman et al.,  
18 133 2011; and references therein). Although the NDZ eclogites experienced a complex  
19 134 metamorphic evolution and multistage retrograde overprinting, zircons from the  
20 135 eclogites still preserve multiple metamorphic age-records with REE and mineral  
21 136 inclusion constraints (Liu et al., 2011a). Combining the zircon U–Pb ages and the  
22 137 estimated temperatures and pressures, the whole  $P$ – $T$ – $t$  path of the eclogites during  
23 138 subduction and exhumation may be therefore constrained in detail. In this study, we  
24 139 applied Ti-in-zircon and Zr-in-rutile thermometers to the NDZ granulitized eclogites.  
25 140 The results provide unambiguous evidence of a multistage high- $T$  evolution in the  
26 141 NDZ. In addition, the applicability of the zircon and rutile thermometers to  
27 142 granulitized eclogites is tested. The implications of our results on the  $P$ – $T$ – $t$  evolution  
28 143 of the NDZ are discussed, shedding new light on the formation and exhumation of the  
29 144 UHP metamorphic belt in the Dabie orogen.

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## 2. Geological setting

The Dabie orogen is a well known UHP terrain, located in the intermediate segment of the Qinling-Dabie-Sulu orogenic belt formed by the Triassic continental collision between the North China Block and South China Block. It comprises several fault-bounded terranes with varying metamorphic grades and evolutionary histories, and is subdivided into five major lithotectonic units from north to south (Xu et al., 2003; Liu et al. 2007a): (1) the Beihuaiyang zone (BZ); (2) the North Dabie complex zone (NDZ); (3) the Central Dabie UHP metamorphic zone (CDZ); (4) the South Dabie low-*T* eclogite zone (SDZ); and (5) the Susong complex zone (SZ) (Fig. 1). These zones are separated by the Xiaotian-Mozitan fault, Wuhe-Shuihou fault, Hualiangting-Mituo fault and Taihu-Shanlong fault, respectively. Zone (1) is a low-grade composite unit comprising the Foziling (or Xinyang) Group and the Luzhanguan (or Guishan) complex, whereas Zones (2), (3), (4) and (5) belong to the subducted South China Block (Xu et al., 2003, 2005; Liu et al., 2005, 2007a, 2010b, 2011a; Liu and Li, 2008).

A variety of UHP metamorphic rocks, including eclogite, gneiss, quartz jadeitite, schist and impure marble with eclogite nodules, occur in the CDZ and SDZ (e.g., Xu et al., 1992; Okay, 1993; Okay et al., 1993; Rolfo et al., 2004; Li et al., 2004). The occurrence of diamond and coesite in the metamorphic rocks from the CDZ indicates that the UHP metamorphism occurred at 700–850 °C and > 2.8 GPa (e.g., Okay et al., 1989; Wang et al., 1989; Xu et al., 1992; Okay, 1993; Rolfo et al., 2004), whereas the peak *P–T* conditions of the eclogites in the SDZ were estimated at 670 °C and 3.3 GPa (Li et al., 2004). In both the CDZ and SDZ units the UHP eclogite-facies stage was followed by HP eclogite- and amphibolite-facies retrograde metamorphism (e.g., Xu et al., 1992; Rolfo et al., 2004; Li et al., 2004).

The NDZ mainly consists of tonalitic and granitic orthogneisses and post-collisional intrusions with subordinate meta-peridotite (including dunite, harzburgite and lherzolite), garnet pyroxenite, garnet-bearing amphibolite, granulite and eclogite. The oriented mineral exsolutions in garnet and clinopyroxene, and the

1 175 occurrence of micro-diamond imply that the NDZ eclogites underwent UHP  
2 176 metamorphism at  $P > 3.5$  GPa (Xu et al., 2003, 2005; Liu et al., 2005; Malaspina et al.,  
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4 177 2006). The Triassic zircon U-Pb ages (Liu et al., 2000, 2007a, 2011a; Wang et al.,  
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6 178 2012) and Sm-Nd ages (Liu et al., 2005) of the eclogites from the NDZ suggest that  
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8 179 these rocks formed by the Triassic subduction of the South China Block, similarly to  
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10 180 those from the CDZ and SDZ. The Triassic metamorphic ages (Liu et al., 2000, 2007b;  
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12 181 Xie et al., 2010) and the occurrence of micro-diamond in zircon and garnet (Liu et al.,  
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14 182 2007b) from the NDZ banded gneisses suggest that also the gneisses hosting the  
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16 183 eclogites were involved in the deep subduction of the South China Block, thus  
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18 184 implying that the NDZ experienced UHP metamorphism as a coherent unit. After the  
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20 185 UHP and HP eclogite facies metamorphism, the NDZ eclogites experienced  
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22 186 granulite-facies overprinting and later amphibolite-facies retrogression (e.g., Xu et al.,  
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24 187 2000; Liu et al., 2001, 2005, 2007a). This corroborates the case for a distinct  
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26 188 evolution in the different slices of the Dabie UHP belt. That is, although the three  
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28 189 eclogite-bearing units, *i.e.* the SDZ, CDZ and NDZ, all experienced UHP  
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30 190 metamorphism, they had different exhumation histories, suggesting that they represent  
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32 191 decoupled UHP slices and most probably represent different levels of crustal rocks  
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34 192 (see Liu and Li, 2008 for a review).

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37 193 The Luotian dome in the southwestern segment of the NDZ is a deeply eroded  
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39 194 area with both felsic and mafic granulite lenses (Chen et al., 1998, 2006; Liu et al.,  
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41 195 2007a; Wu et al., 2008). The eclogite occurs as lenses or blocks in garnet-bearing  
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43 196 granitic migmatitic orthogneiss (Liu et al., 2007a). They preserve early  
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45 197 granulite-facies mineral relics and have been overprinted by regionally pervasive HP  
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47 198 granulite-facies metamorphism, followed by penetrative amphibolite-facies  
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49 199 retrogression during exhumation. The eclogite-facies assemblage consists of garnet  
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51 200 and relict omphacite, with rutile, quartz, allanite and fluoro-apatite as common  
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53 201 additional constituents. Although the precise time–temperature cooling history is still  
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55 202 not well-known in detail, the studies by Liu et al. (2007a, 2011b) showed that the  
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57 203 NDZ underwent a complex multistage evolution characterized by a nearly isothermal  
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59 204 decompression during the early stages of exhumation. In particular, five metamorphic  
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1 205 stages have been recognized for the eclogites in the Luotian dome area (Liu et al.,  
2 206 2007a, 2011b): (1) granulite-facies stage, suggested by the occurrence of hypersthene,  
3 207 plagioclase and diopside inclusions within garnet and/or by Neoproterozoic  
4 208 metamorphic zircon (Liu et al., 2007a); (2) UHP coesite/diamond eclogite-facies stage  
5 209 at  $P \sim 4.0$  GPa, suggested by the occurrence of diamond (Xu et al., 2003, 2005; Liu et  
6 210 al., 2007b) and coesite (Liu et al., 2011b); (3) HP quartz eclogite-facies stage,  
7 211 characterized by the coexistence of garnet, jadeite-poor omphacite and rutile with  
8 212 quartz instead of coesite; (4) granulite-facies retrogression stage, indicated by the  
9 213 presence of hypersthene, plagioclase and diopside symplectite after Na-clinopyroxene;  
10 214 (5) amphibolites-facies retrograde stage, documented by the widespread growth of  
11 215 amphibole. However, P–T conditions, especially temperatures for different stages  
12 216 have not been better constrained because of multiple decompression and  
13 217 re-crystallization processes as mentioned above.  
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### 29 219 **3. Sample descriptions**

30 220 The investigated samples were collected from Banchuanshan (samples LT9 and  
31 221 LT10), Luotian (sample 03LT1-1), Jinjiapu (samples 06LT3-2 and 09LT1) and  
32 222 Shiqiaopu (samples 07LT6-1 and 09LT2), respectively (Fig. 1). They can roughly be  
33 223 divided into two groups based on zircon typologies: the first eclogite type (Type 1;  
34 224 samples 03LT1-1, 06LT3-2, 07LT6-1, 09LT1 and 09LT2) contains almost  
35 225 homogeneous Triassic metamorphic zircons with rare or even no Neoproterozoic  
36 226 zircon cores (Liu et al., 2011a; Gu, 2012), whereas the second type (Type 2; samples  
37 227 LT9 and LT10) contains Neoproterozoic igneous and metamorphic zircon cores with  
38 228 rare Triassic metamorphic overgrowth rims (Liu et al., 2007a).

39 229 The detailed ages of the samples LT9, LT10, 03LT1-1, 06LT3-2, 07LT6-1 and  
40 230 09LT2 were reported in Liu et al. (2007a, 2011a) and Gu (2012), respectively (see  
41 231 also Table 2). Based on previous investigations (Liu et al., 2011a; Gu, 2012), by CL  
42 232 images, inclusion assemblages, REE patterns and ages, the  
43 233 metamorphic/metamorphosed zircons from samples of the Type 1 eclogites can be  
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1 234 subdivided into two episodes of mantle domains (called inner- and outer-mantles,  
2 235 named as M1 and M2) with distinct age-records of 230–220 Ma and 220–210 Ma,  
3 236 cluster at  $226 \pm 2$  Ma and  $214 \pm 2$  Ma, respectively. These two zircon domains grew  
4 237 in distinct stages of the eclogites metamorphic evolution because they show UHP and  
5 238 HP eclogite-facies signatures of Ca-rich garnet + omphacite (Jd = 40–50) + coesite +  
6 239 rutile and Mn-rich garnet + omphacite (Jd = 20–30) + quartz + rutile, respectively  
7 240 (Liu et al., 2011a; Gu, 2012). Rare thin overgrowth rims of 209–207 Ma and 200–190  
8 241 Ma, formed at granulite- and amphibolite-facies stages, respectively, are locally  
9 242 observed in zircon.

10 243 Details of the petrography and mineral chemistry of the eclogites were given in  
11 244 Liu et al. (2007a, 2011b) and are only summarized here. Samples LT9 and LT10  
12 245 consist of garnet, omphacite and rutile and retrograde quartz, diopside, hypersthene,  
13 246 hornblende, plagioclase and ilmenite. Sample 03LT1-1 is a strongly retrogressed  
14 247 eclogite, mainly consisting of garnet, rutile, hornblende and plagioclase with minor  
15 248 quartz, diopside, hypersthene and ilmenite. Rare coesite in zircon and its  
16 249 pseudomorphs with radial fractures in garnet were observed (Liu et al., 2011b). The  
17 250 other eclogite samples (06LT3-2, 07LT6-1, 09LT1 and 09LT2) are less retrogressed  
18 251 and are composed of garnet, omphacite, diopside and rutile, with minor hypersthene,  
19 252 hornblende, plagioclase, quartz or its pseudomorphs after coesite and ilmenite. In all  
20 253 the samples, omphacite generally occurs as inclusion in garnet or zircon (Figs. 2a, b  
21 254 and 3). Two generations of omphacite may be distinguished on the basis of their Na<sub>2</sub>O  
22 255 contents, the earlier one being Na richer than the later generation (Fig. 4; Table 1).  
23 256 The later generation often coexists with quartz in zircon (Fig. 3b, f), suggesting a  
24 257 Si-rich precursor omphacite and is locally replaced by clinopyroxene + plagioclase +  
25 258 quartz intergrowths in garnet (Fig. 2d). In samples 07LT6-1 and 09LT2 omphacite  
26 259 inclusions within garnet and zircon are particularly abundant, and coesite  
27 260 pseudomorphs with radial fractures were locally observed within garnet (Figs. 2 and 3;  
28 261 Liu et al., 2011b). Furthermore, low-Na omphacite + quartz and rutile + ilmenite  
29 262 locally occur as coexisting or intergrowth inclusions in zircon (Figs. 3b, d, f, l and 5).  
30 263 This shows that mineral inclusions in zircon and garnet from the eclogites have been

1 264 strongly modified or broken down during multiple decompression and retrogression,  
2 265 also hampering the determination of peak  $P$ - $T$  conditions by conventional  
3 266 thermobarometry. Thus, in order to better constrain the metamorphic temperatures of  
4 267 UHP and HP eclogite-facies stages, the Ti-in-zircon thermometry and Zr-in-rutile  
5 268 thermometry on inclusions within zircon and garnet have been applied.  
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#### 11 270 **4. Analytical methods**

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13 271 Zircons were separated from the samples by crushing and sieving, followed by  
14 272 magnetic and heavy liquid separation and hand-picking under a binocular microscope.  
15 273 Representative zircon crystals were prepared for the CL investigations and in-situ  
16 274 U-Pb dating and trace-element analyses. They, together with a zircon U-Pb standard  
17 275 TEM (417 Ma), were mounted in epoxy, which was then polished until all zircon  
18 276 grains were approximately cut in half. The internal zoning patterns of the crystals  
19 277 were observed by cathodoluminescence (CL) imaging at the Beijing SHRIMP Center  
20 278 and the Institute of Mineral Resources, Chinese Academy of Geological Sciences  
21 279 (CAGS) in Beijing. The representative CL images for the sample 07LT6-1 are  
22 280 presented in Fig. 3, and the remaining CL images were reported in Liu et al. (2007a,  
23 281 2011a) and Gu (2012).  
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38 282 Mineral inclusions in zircon were identified using Raman spectroscopy at the  
39 283 Continental Dynamics Laboratory, CAGS in Beijing and the CAS Key Laboratory of  
40 284 Crust-Mantle Materials and Environments, University of Science and Technology of  
41 285 China in Hefei, and/or identified using the electron probe micro analyzer (EPMA) at  
42 286 the Institute of Mineral Resources, CAGS in Beijing. The analytical conditions of the  
43 287 Raman and EMPA were reported by Liu et al. (2009). Representative Raman spectra  
44 288 and compositions of mineral inclusions in zircon are reported in Fig. 5 and Table 1.  
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52 289 The rutile analyses were performed on a JEOL JXA-8230 EPMA at the Institute  
53 290 of Mineral Resources, CAGS in Beijing. Accelerating voltage was set at 20 kV with  
54 291 100 nA beam current and 3–5  $\mu\text{m}$  beam spot, counting times for Zr, Nb, Cr and Fe  
55 292 were 300, 400, 150 and 60 s, respectively. Spectroscopic crystals for Zr, Nb, Cr and  
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1 293 Fe were PETH, PETJ, LIFJ and LIFJ, respectively (corresponding detection limits: 20,  
2 294 27, 28 and 43 ppm). A ZrO<sub>2</sub> standard was used to calibrate the peak position of Zr,  
3  
4 295 and a synthetic rutile was used to inspect the zero-concentration of Zr at the beginning,  
5  
6 296 middle and at the end of each sequence. Analytical errors were about  $\pm 15$  ppm at  $1\sigma$   
7  
8 297 according to counting statistics (Chen and Li, 2008). Optical and CL-images  
9  
10 298 combined with back-scattered electron (BSE) images were used to select target areas  
11  
12 299 devoid of cracks or inclusions other than rutile in zircon. Also, the BSE images were  
13  
14 300 guided to determine the analyzed domains on rutile inclusions in garnet on the thin  
15  
16 301 sections. Generally, larger rutile grains ( $> 3$   $\mu\text{m}$  in diameter, mostly 5–10  $\mu\text{m}$  or more)  
17  
18 302 were selected for spot analyses. If SiO<sub>2</sub> contents were above 0.3 wt.% the analysis  
19  
20 303 was discarded as these data were probably influenced by nearby zircon grains (Zack et  
21  
22 304 al., 2004). In addition, it has been shown (Boniface et al., 2012) that there are the  
23  
24 305 lower Zr contents in matrix rutile compared to rutile inclusions in garnet, due to  
25  
26 306 re-equilibration of the matrix grains during the late-stage mylonitization that affected  
27  
28 307 the eclogites. So, we analyzed rutile inclusions in garnet and zircon from the samples.

31 308 The Ti contents in zircon from samples LT9, LT10, 03LT1-1, 06LT3-2 and  
32  
33 309 07LT6-1 were measured using laser ablation multi-collector inductively coupled  
34  
35 310 plasma mass spectrometer (LA-MC-ICPMS) at Institute of Geology and Geophysics,  
36  
37 311 the Chinese Academy of Sciences in Beijing. The detailed parameters of the  
38  
39 312 instrument can be found in Jiao et al. (2011), and the analytical procedure was  
40  
41 313 previously reported by Yuan et al. (2004). A Geolas-193 laser-ablation microprobe  
42  
43 314 was attached to a Neptune multi-collector ICPMS. Typical ablation times were 30 to  
44  
45 315 90 s with a 10 Hz repetition rate and laser power of 100 mJ/pulse, resulting in a pit  
46  
47 316 depth of 30 to 50  $\mu\text{m}$ . The spot diameter for zircon was 32  $\mu\text{m}$ .

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## 51 318 **5. Results**

### 52 319 *5.1. Zr contents in rutile and Zr-in-rutile temperature estimates*

53  
54  
55 320 Calculation of Zr-in-rutile temperatures for rutile inclusions within zircon follows  
56  
57 321 the pressure-dependent thermometer of Tomkins et al. (2007) at assumed 4.0 GPa and  
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1 322 2.0 GPa for the UHP ( $M_1$  domains) and HP ( $M_2$  domains) eclogite-facies  
2 323 metamorphism, respectively and at 1.0 GPa for the granulite-facies stage (rim  
3 324 domains) (Liu et al., 2011a; Gu, 2012). The estimation of Zr-in-rutile temperatures for  
4 325 rutile inclusions within garnet was made at  $P = 4.0$  GPa and 2.0 GPa for the UHP and  
5 326 HP eclogite-facies conditions, respectively. The Zr contents and calculated  
6 327 temperatures are listed in Tables 2 and 3 and depicted in Figs. 6 and 7.

7 328 Rutile inclusions in zircon mainly occur within mantle domains  $M_1$  and  $M_2$  of  
8 329 metamorphic/metamorphosed zircons, formed at UHP and HP eclogite-facies  
9 330 conditions, respectively, and a few in overgrowth rims formed at granulite-facies  
10 331 conditions. Zirconium concentrations in rutile within garnet and zircon are  
11 332 characterized by a large spread, varying from less than 900 to more than 4000 ppm,  
12 333 and defining a broad range of calculated temperatures from  $< 700$  to approximately  
13 334  $1100$  °C (Figs. 6, 7). More in detail, the rutile inclusions located in inner-mantle  
14 335 domains ( $M_1$ ) of zircon have the high Zr contents (1030–4310 ppm) and record a  
15 336 relatively narrow range of temperatures of 880–1080 °C, mostly 936–1072 °C with an  
16 337 average value of 982 °C. Rutile grains included in the outer-mantle domains ( $M_2$ ) of  
17 338 zircon contain Zr contents of 800–5800 ppm and define a wide range of temperatures  
18 339 (780–1030 °C), a few 901–1028 °C with an average value of 946 °C. A few rutile  
19 340 grains occurring in the rims of zircon give lower temperatures of *c.* 850 °C (Fig. 6). In  
20 341 contrast, rutile inclusions within garnet have relatively lower Zr contents of 100–800  
21 342 ppm, yielding lower temperatures (600–850 °C at  $P = 4.0$  GPa and 600–800 °C at  $P =$   
22 343 2.0 GPa; Fig. 6a and Table 3).

#### 23 344 24 345 *5.2 Ti contents in zircon and Ti-in-zircon temperatures*

25 346 Ti-in-zircon temperatures were calculated following the experimental calibration  
26 347 of Watson et al. (2006). The results for Ti contents in zircon and calculated  
27 348 temperatures are listed in Tables 3 and 4 and presented in Figs. 8 and 9. Zircon grains  
28 349 in the three Type 1 eclogite samples consist of different domains among which inner  
29 350 ( $M_1$ ) and outer ( $M_2$ ) mantle domains formed at UHP and HP eclogite-facies  
30 351 conditions at ~226 Ma and ~214 Ma, respectively. These UHP and HP domains have

1 352 Ti contents of 2.15–97.8 ppm (Table 4), yielding Ti-in-zircon temperatures of  
2 353 620–990 °C. Ti contents in the zircon rim domains are low (< 7 ppm) and indicate a *T*  
3 354 of 650–700 °C, except for two granulite-facies overgrowth rims which yield a *T* of  
4 355 807–828 °C (Fig. 8). Thus, most of the calculated temperatures for different domains  
5 356 of metamorphic zircons are < 800 °C and generally lie at 650 ± 50 °C. Exceptions are  
6 357 the 934 °C and the 940 °C, 991 °C results from UHP and HP eclogite-facies zircon  
7 358 domains, respectively (Fig. 8). The studied zircons with few igneous cores from the  
8 359 Type 1 samples are mostly metamorphic in origin as suggested by the low Th/U  
9 360 values, mineral inclusions, Hf-isotopes and CL images (Liu et al., 2011a; Gu, 2012)  
10 361 and do not record Ti contents corresponding to earlier magmatic crystallization  
11 362 events.

12 363 In the two samples of the Type 2 eclogites, several Neoproterozoic magmatic and  
13 364 metamorphic zircon cores with thin Triassic overgrowth rims have been observed (Liu  
14 365 et al., 2007a). The cores have Ti contents of 4.3–274 ppm (Table 4), yielding  
15 366 Ti-in-zircon temperatures of 670–1149 °C according to the experimental calibration  
16 367 of Watson et al. (2006) (Fig. 9). Temperatures mostly fall in the range 670–800 °C  
17 368 and a few > 900 °C. The metamorphic overgrowth rims in the Type 2 eclogite zircons  
18 369 are too thin to be analyzed by the LA-MC-ICPMS.

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## 20 371 **6. Discussion**

### 21 372 *6.1. Metamorphic temperatures at peak and post-peak stages*

22 373 The results of this study show that, although all the samples experienced the same  
23 374 metamorphic evolution, only 5–10% of the Triassic peak and post-peak metamorphic  
24 375 zircons from the Type 1 eclogites contain sufficient Ti concentrations to give high-*T*  
25 376 conditions (Fig. 8). Temperatures higher than 900 °C are preserved only in one UHP  
26 377 and two HP eclogite-facies zircon domains (M1 and M2, respectively), whereas the  
27 378 majority of the analyzed zircons give temperatures of 650 ± 50 °C (Fig. 8), probably  
28 379 indicating the amphibolite-facies re-equilibration/re-crystallization temperature of the  
29 380 Ti-in-zircon thermometer.



1 381 The significant variability of Zr in rutile (Tables 2 and 3) and the resulting scatter  
2 382 in calculated temperatures (especially for rutile inclusions in garnet) (Fig. 6) are  
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4 383 probably due to retrograde re-equilibration and/or to local fluid-mediated  
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6 384 re-crystallization during retrogression owing to the occurrence of fractures in garnet  
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8 385 (see Fig. 2c) (Meyer et al., 2011; Kooijman et al., 2012). As a consequence, results of  
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10 386 the Zr-in-rutile thermometry should be treated with caution when dealing with high-*T*  
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12 387 rocks which have undergone pronounced retrogression. In comparison, Zr-in-rutile  
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14 388 thermometry applied on rutile inclusions within zircon, especially those shielded in  
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16 389 the inner- and outer-mantle domains of Triassic zircons, yields 900 to ~1100 °C.

18 390 The high temperature values of 900–1050 °C estimated by both the Ti-in-zircon  
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20 391 and the Zr-in-rutile thermometers for the UHP metamorphic stage are consistent with  
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22 392 the reported peak UHP temperatures of 900–960 °C (at  $P = 4.0$  GPa) calculated using  
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24 393 Grt-Cpx thermometry (Liu et al., 2007a). Only one inclusion of rutile was observed in  
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26 394 the overgrowth rims of zircon and records temperatures of 820–850 °C (Fig. 6),  
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28 395 similar to those estimated by Ti-in-zircon thermometry (granulite-facies overgrowth  
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30 396 rims; Fig. 8).

33 397 The Zr-in-rutile and Ti-in-zircon thermometers combined with conventional  
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35 398 thermometry demonstrate that the eclogites experienced a multistage high-*T* (>  
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37 399 900 °C) metamorphic evolution at UHP and HP eclogite-facies conditions, followed  
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39 400 by granulite-facies overprinting at UHT conditions.

41 401 In addition, as to the two samples of the Type 2 eclogites, their Neoproterozoic  
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43 402 magmatic and metamorphic zircon cores yield Ti-in-zircon temperatures of 670–1149  
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45 403 °C (Fig. 9) with temperatures mostly in the range of 670–800 °C and a few > 900 °C.  
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47 404 The highest temperature values of > 900 °C may be the closest to the real  
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49 405 temperatures (Liu et al., 2010a), thus for the first time documenting a UHT  
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51 406 metamorphism during the Neoproterozoic. In contrast, the lower temperatures might  
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53 407 represent the result of re-equilibration as suggested by Timms et al. (2011).  
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## 58 409 *6.2. Factors affecting Ti-in-zircon and Zr-in-rutile temperature estimates*

### 60 410 *5.2.1. Ti-in-zircon thermometer*

1 411 Pre-existing zircon in rocks may re-equilibrate in response to changing  $P$ - $T$   
2 412 conditions or fluid compositions (Kooijman et al., 2011). Timms et al. (2011) also  
3 413 suggested that the highest Ti-in-zircon temperatures recorded in zircon might  
4 414 represent only minimum estimates for primary zircon crystallization and that the  
5 415 lowest Ti concentrations might record re-equilibration. Our results are in agreement  
6 416 with this interpretation. The analyzed zircons from the NDZ eclogites, in fact, show a  
7 417 large spread of Ti concentrations thus defining a wide range of temperatures. These  
8 418 strongly variable calculated temperatures may result from two main factors: (i) they  
9 419 may correspond to different growth stages of zircon, as suggested by the multiple  
10 420 age-records (Liu et al., 2011a, b; Gu, 2012), and/or (ii) they may be related to  
11 421 significant re-equilibration processes. However, since zircon domains with different  
12 422 ages generally define homogeneous Ti-in-zircon temperatures of  $650 \pm 50$  °C with the  
13 423 exception of few high- $T$  values  $> 900$  °C (Figs. 8 and 9), we suggest that the highest  
14 424 calculated temperatures may represent the  $T$  of zircon growth/crystallization, while  
15 425 the lower temperatures probably represent the re-equilibration temperature at  
16 426 amphibolite-facies conditions, in agreement with those determined by conventional  
17 427 thermobarometry (Liu et al., 2007a) and with the lower temperatures derived from  
18 428 Zr-in-rutile thermometry (this study).

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### 20 430 *6.2.2. Zr-in-rutile thermometer*

21 431 It has been documented that the Zr-in-rutile thermometer is very resistant to  
22 432 diffusion and re-equilibration even under UHT metamorphic conditions and can  
23 433 preserve peak metamorphic temperatures higher than most thermometers (e.g.,  
24 434 Kooijman et al., 2012; Ewing et al., 2013; and references therein). Zack et al. (2004)  
25 435 argued that rutile included in mineral phases in which diffusivities are high (e.g.  
26 436 quartz, kyanite) generally show significant evidence of re-equilibration during cooling,  
27 437 whereas rutile inclusions in garnet generally preserve higher Zr contents than matrix  
28 438 rutile. However, conflicting evidence exists on this argument, since other studies (e.g.,  
29 439 Baldwin et al., 2007) show little correlation between recorded Zr-in-rutile  
30 440 temperatures and the rutile being in the matrix or included in garnet. The diffusion

1 441 data also suggest that Zr signatures of rutiles from UHT systems are likely to be lost  
2 442 except under conditions of extremely rapid cooling (Cherniak et al., 2007). Thus, Zr  
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4 443 in rutile signatures from high-*T* contexts may be only locally retained, depending on  
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6 444 the nature of surrounding materials and the effectiveness of diffusional transport  
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8 445 through them (e.g., Zack et al., 2004; Watson et al., 2006).

10 446 In this study, the highest concentrations of Zr are systematically recorded in well  
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12 447 shielded rutile inclusions within zircon, although numerous grains located in the same  
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14 448 mantle and rim domains of zircon preserve low Zr concentrations as well (Figs. 6 and  
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16 449 7; Tables 2 and 3). Thus, being shielded in zircon is not a prerequisite for rutile to  
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18 450 preserve high temperatures. In contrast, rutile inclusions in garnet have systematically  
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20 451 lower Zr contents than those included in zircon (Fig. 6). Previous investigations (e.g.,  
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22 452 Jiao et al., 2011; Meyer et al., 2011; Triebold et al., 2011; Kooijman et al., 2012)  
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24 453 clearly indicate that rutile grains with lower Zr concentrations have been likely  
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26 454 affected by re-equilibration and/or re-crystallization processes, even if included in  
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28 455 robust minerals such as garnet; in this case, the corresponding calculated temperatures  
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30 456 are not representative of the metamorphic conditions of entrapment (see also Hermann  
31  
32 457 and Rubatto, 2003). Although zircon is probably the best rigid host mineral, this study  
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34 458 demonstrates that some rutile inclusions within zircon were transformed to ilmenite,  
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36 459 thus suggesting that retrogression may affect also zircon and its inclusions (Fig. 3). It  
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38 460 may be thus concluded that rutile grains with higher Zr concentrations (and  
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40 461 corresponding calculated temperatures) should be the least affected by late resetting,  
41  
42 462 most probably revealing rutile formation temperatures (Triebold et al., 2011), whereas  
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44 463 the lower temperatures of 650–750 °C (Fig. 6) probably represent the closure  
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46 464 temperature of the Zr-in-rutile thermometer (Cherniak et al., 2007) and/or  
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48 465 re-equilibration/re-crystallization temperatures at amphibolites-facies conditions (Liu  
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50 466 et al., 2007a).

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### 54 468 *6.2.3. Late re-equilibration processes affecting rutile and zircon*

55  
56 469 The widespread and homogeneous low-*T* estimates of 650–750 °C obtained from  
57  
58 470 both the Zr-in-rutile and Ti-in-zircon thermometers imply that both rutile and zircon

1 471 from the studied NDZ eclogites were significantly affected by re-equilibration or  
2 472 re-crystallization processes during exhumation or decompression, as reported by Liu  
3 473 et al. (2009), Boniface et al. (2012) and Ewing et al. (2013). Moreover, the wide range  
4 474 of calculated temperatures obtained from both thermometers is interpreted to be the  
5 475 result of trace element exchange between rutile/zircon and the matrix, this process  
6 476 likely occurring at the grain-boundary scale or along the fracture and being controlled  
7 477 by fluid-mediated transport within very local domains.

8 478 Furthermore, Lucassen et al. (2010) showed that, in fluid-dominated natural  
9 479 systems, the diffusion coefficients of Zr and Nb in rutile could be higher than those  
10 480 determined experimentally. Luvizotto and Zack (2009) also argued that  
11 481 re-equilibration of Zr in rutile occurs by ion exchange with neighboring minerals in a  
12 482 fluid-present system, whereas in the absence of fluids, volume diffusion of Zr in rutile  
13 483 is limited by grain boundary diffusion. In this regard, the lower Zr contents of rutile  
14 484 inclusions in garnet relative to those in zircon could be due to the effect of fluids,  
15 485 likely introduced in garnet through radial fractures (see Fig. 2c) (e.g., Meyer et al.,  
16 486 2011). In contrast, zircon is better than garnet in preventing fluid infiltration, so that  
17 487 rutile inclusions within zircon may preserve high Zr contents.

18 488 In addition, the high- $T$  ( $> 900$  °C) decompression process during the initial stage  
19 489 of exhumation from UHP eclogite facies to granulite facies has led to significant  
20 490 partial melting of the eclogites in the region (Liu et al., 2011b; Gu, 2012). This partial  
21 491 melting on the zircons might have a marked effect, and only few zircons could survive  
22 492 and record the peak metamorphic temperatures (Liu et al., 2009).

23 493 In summary, rutile and zircon are robust enough to preserve compositions from  
24 494 earlier stages of a complex metamorphic history, and Zr-in-rutile and Ti-in-zircon  
25 495 thermometers have the potential to be very useful tools for estimating crystallization  
26 496 temperatures and peak metamorphic conditions. Furthermore, rutile included in a rigid  
27 497 phase such as zircon is able to retain its original Zr content. Therefore, for  
28 498 (ultra)high- $T$  metamorphic rocks, Zr-in-rutile, especially applied on rutile inclusions  
29 499 within zircon, may yield more reliable peak metamorphic temperatures than most  
30 500 other exchange geothermometers, which tend to partially re-equilibrate during cooling

1 501 (Kooijman et al., 2012).

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4 503 *6.3. Implications for peak metamorphic conditions and high- $T$  exhumation*

5  
6 504 Figure 10 shows the  $P$ - $T$ - $t$  path of the NDZ eclogites as constrained by  
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8 505 Ti-in-zircon and Zr-in-rutile thermometry (this study), conventional thermometry and  
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10 506 SHRIMP U-Pb ages (Liu et al., 2011a; Gu, 2012). A variety of models for exhumation  
11  
12 507 of UHP metamorphic rocks from mantle depths have been proposed (e.g., Ernst, 1971,  
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14 508 2001; Chemenda et al., 1995; Maruyama et al., 1996; Hacker et al., 2000; Liu et al.,  
15  
16 509 2007b). The present and the already published data support a scenario in which the  
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18 510 deeply subducted continental crust of the South China Block did not remain a single  
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20 511 coherent unit, but formed several slices by multiple decoupling during subduction to  
21  
22 512 mantle depths and subsequent exhumation; this decoupling may have been triggered  
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24 513 by the difference in mechanic strength of rocks occurring at different levels of the  
25  
26 514 continental crust (Liu et al., 2007b, 2011a; Liu and Li, 2008). Considering the  
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28 515 weighted mean ages of UHP metamorphism (226 Ma) and HP eclogite-facies  
29  
30 516 retrogression (214 Ma), the exhumation from mantle depths (ca. 4.0 GPa) to crustal  
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32 517 depths of ca. 2.0 GPa must have been completed within about 12 Ma (Fig. 10). This  
33  
34 518 implies that about 60 km of exhumation should have occurred within about 12 Ma,  
35  
36 519 leading to an average exhumation rate of 0.5 cm/y. A comparatively lower exhumation  
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38 520 rate of  $\sim 0.4$  cm/y characterized the following evolution from HP eclogite-facies (214  
39  
40 521 Ma) to granulite-facies (207 Ma) conditions, corresponding to nearly isothermal  
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42 522 exhumation at very high  $T$  ( $> 900^{\circ}\text{C}$ ) from pressures of 2.0 to 1.0 GPa. Therefore, the  
43  
44 523 rapid exhumation rate of the initial stage of exhumation was followed by a  
45  
46 524 comparatively slower exhumation at UHT conditions, which led to significant partial  
47  
48 525 melting (Liu et al., 2011b; Gu, 2012). The protracted high- $T$  evolution experienced by  
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50 526 the NDZ eclogites may explain why UHP relicts are rarely preserved in the eclogites  
51  
52 527 and in the associated rocks from the NDZ. In fact, although a relatively rapid  
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54 528 exhumation is considered to be one of the factors favoring the preservation of UHP  
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56 529 mineral assemblages (e.g., Mosenfelder et al., 2005; Liu et al., 2011b), a long  
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58 530 residence time at high temperatures may have played an opposite role (Katayama and  
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1 531 Maruyama, 2009).

2 532 UHT conditions may be reached in many different tectonic environments  
3  
4 533 (Santosh and Kusky, 2010) whereas the heat source to attain UHT conditions in the  
5  
6 534 lower crust has been ascribed to asthenospheric mantle upwelling in response to  
7  
8 535 delamination or thinning of the continental lithosphere (e.g., Harley, 2008). However,  
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10 536 based on the present study, the high temperatures of > 900 °C estimated by  
11  
12 537 Ti-in-zircon thermometer for the Neoproterozoic magmatism and granulite facies  
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14 538 metamorphism in the NDZ could have been caused by a mantle plume, or an  
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16 539 asthenospheric upwelling in response to large-scale continental rifting, resulting from  
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18 540 the breakup of Rodinia at the Neoproterozoic in the South China Block (Ames et al.,  
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20 541 1996; Rowley et al., 1997; Li et al., 2003; Liu et al., 2007a, 2010b). Recent works  
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22 542 (e.g., Whittington et al., 2009; Santosh and Kusky, 2010) suggest that the lower crust  
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24 543 has a low thermal diffusivity and is therefore able to retain heat for long time and that  
25  
26 544 the underlying mantle has a higher mean temperature. Thus, in the case of extensional  
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28 545 settings such as the continental rift zones, the heat and volatiles supplied by rising  
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30 546 plumes might contribute to the generation of UHT metamorphism in the lower crust  
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32 547 (Santosh and Kusky, 2010). In this context, the underplating and injection of the  
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34 548 high-temperature melts may have triggered extensive crustal anatexis, producing large  
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36 549 volumes of granitoids and associated basaltic rocks (precursors for most of UHP  
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38 550 meta-igneous rocks in the Dabie-Sulu orogenic belt) along the periphery of the South  
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40 551 China Block, and local UHT metamorphism in the Neoproterozoic. Furthermore,  
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42 552 petrological and geochronological studies have demonstrated that the eclogites  
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44 553 described in this study derived from Neoproterozoic mafic granulites (Liu et al.  
45  
46 554 2007a). In other words, the protolith of the eclogite was a mafic granulite that  
47  
48 555 originated from underplating of mantle-derived magma onto the base of lower  
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50 556 continental crust during the mid-Neoproterozoic (ca. 800 Ma) and was then subducted  
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52 557 during the Triassic, experiencing UHP eclogite facies metamorphism at mantle depths.  
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54 558 Therefore, this study provides additional thermometric evidence for the proposed  
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56 559 Neoproterozoic mantle plume that led to the breakup of the supercontinent Rodinia,  
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58 560 especially along the periphery of the South China Block.  
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## 562 **7. Conclusions**

563 The temperatures estimated using zircons and rutile inclusions within zircon from  
564 the NDZ granulitized eclogites reveal a protracted high- $T$  ( $> 900$  °C) metamorphic  
565 history with at least three metamorphic stages, that occurred at significantly different  
566 pressures and ages, during Triassic continental subduction and subsequent exhumation.  
567 The investigated rutiles occur as inclusions in both garnet and zircon, and contain  
568 different Zr concentrations corresponding to different ranges of calculated  
569 temperatures. Rutile inclusions within zircons have the highest Zr concentrations,  
570 corresponding to  $T > 900$  °C. However, only 5–10% of the analyzed zircons record  
571 these high- $T$  conditions. Considering the significantly variable concentrations of Zr in  
572 rutile inclusions within garnet, the resulting broadly scattered calculated temperatures  
573 are probably related to retrograde re-equilibration and/or to local re-crystallization  
574 during retrogression. On the contrary, rutile inclusions within zircon are able to  
575 preserve primary compositions even at high- $T$  conditions ( $> 900$  °C) yielding reliable  
576 temperatures for rutile crystallization and peak metamorphic conditions.

577 The present temperature estimates, combined with petrological observations and  
578 geochronological results, further suggest that the eclogite in the NDZ experienced a  
579 clockwise trajectory with a near-isothermal decompression path under high- $T$   
580 conditions, multistage exhumation and rapid uplift during the early stages of  
581 exhumation. This protracted high- $T$  persistence with slow cooling may explain the  
582 rare preservation of UHP assemblages and compositions in the NDZ.

583 Finally, this study provides robust thermometric evidence in support of the  
584 previously proposed Neoproterozoic mantle plume that led to the breakup of the  
585 supercontinent Rodinia, especially along the northern periphery of the South China  
586 Block.

587

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6  
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9 594 analysis.  
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## Figure captions

907

908 **Figure 1** Schematic geological map of the Dabie orogen, with inset showing its  
909 location within the Triassic Qinling—Dabie—Sulu collision orogen in central China.  
910 Sample localities with sample numbers are described in detail in the text. BZ,  
911 Beihuaiyang zone; NDZ, North Dabie complex zone; CDZ, Central Dabie UHP  
912 metamorphic zone; SDZ, South Dabie low-*T* eclogite zone; SZ, Susong complex zone;  
913 HMZ, Huwan mélangé zone; HZ, Hong'an low-*T* eclogite zone; DC,  
914 amphibolite-facies Dabie complex; XMF, Xiaotian-Mozitan fault; WSF,  
915 Wuhe-Shuihou fault; HMF, Hualiangting-Mituo fault; TSF, Taihu-Shanlong fault; TLF,  
916 Tan-Lu fault; SMF, Shangcheng-Macheng fault.

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918 **Figure 2** Photomicrographs of eclogite (sample 07LT6-1) from the Luotian dome in  
919 the Dabie orogen. a. Omphacite (Omp) and quartz (Qtz) inclusions in garnet with two  
920 generations of symplectites (Hy+Di+Pl and Hbl+Pl+Mt); b. Omphacite, rutile and  
921 quartz inclusions in garnet, rimmed by distinctive double symplectites (Liu et al.  
922 2011b); c. Quartz and rutile inclusions in garnet with well-developed radial cracks  
923 (Liu et al. 2011b); d. Clinopyroxene (Cpx) + plagioclase (Pl) + quartz (Qtz)  
924 intergrowth after omphacite in garnet. Mineral abbreviations are after Whitney and  
925 Evans (2010).

926

927 **Figure 3** Cathodoluminescence (CL) (a, c, e, g and i–k) and Back scattered electron  
928 (BSE) images (b, d, f, h and l) for zircon from sample 07LT6-1. Zircon (a) and (b), (c)  
929 and (d), (e) and (f), (g) and (h), and (k) and (l) are the same grains, respectively. The  
930 open circles are analysis spots with available  $^{206}\text{Pb}/^{238}\text{U}$  ages. Omp represents low-Na  
931 omphacite as mentioned in the text.

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933 **Figure 4** WEF–Jd–Ae diagram (after Morimoto et al. 1988) of clinopyroxenes  
934 occurring as inclusions in garnet and zircon of the eclogite (sample 07LT6-1) from the  
935 Luotian dome.

936

937 **Figure 5** Representative Raman spectra of mineral inclusions in zircon of eclogites  
938 from the Luotian dome. (a) Omphacite and quartz; (b) Rutile; (c) Garnet. These  
939 spectra also contain host zircon peaks at 227–228, 357–359, 440–441, 975–976 and  
940 1009–1010  $\text{cm}^{-1}$ .

941

942 **Figure 6** Calculated Zr temperatures ( $^{\circ}\text{C}$ ) of rutile occurring as inclusions in garnet  
943 (a), in zircon inner mantle (b), in zircon outer mantle (c) and in zircon rim (d) from  
944 the investigated samples in the North Dabie complex zone.

945

946 **Figure 7** Diagram of Zr-in-rutile temperatures ( $^{\circ}\text{C}$ ) estimated at the inferred  
947 metamorphic pressures (GPa) for the eclogites from the Luotian dome. Red circles,  
948 black circles and black triangles represent calculated temperatures from inner mantle  
949 (M1), outer mantle (M2) and rim domains of zircon, respectively (see explanation in  
950 the text).

951

952 **Figure 8** Diagram of zircon U-Pb age (Ma) and corresponding Ti-in-zircon  
953 temperatures ( $^{\circ}\text{C}$ ) for the Type 1 eclogites from the Luotian dome. Square, circle and  
954 triangle symbols represent calculated temperatures from samples 03LT1-1, 06LT3-2  
955 and 07LT6-1, respectively. Blue, red, purple, green and gray symbols denote different  
956 groups of metamorphic zircon domains formed at 230–240 Ma (pre-peak mantle),  
957 220–230 Ma (UHP eclogite-facies inner mantle M1), 210–220 Ma (HP eclogite-facies  
958 outer mantle M2), 200–210 Ma (granulite-facies rim) and 180–200 Ma  
959 (amphibolites-facies rim), respectively (see explanation in the text).

960

961 **Figure 9** Diagram of zircon U-Pb age (Ma) and corresponding Ti-in-zircon  
962 temperatures ( $^{\circ}\text{C}$ ) for the Type 2 eclogites (samples LT9 and LT10) from the Luotian  
963 dome. Black square and red circle symbols refer to the Neoproterozoic magmatic and  
964 metamorphic zircon cores dated by Liu et al. (2007a).

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966 **Figure 10** A schematic  $P$ - $T$ - $t$  path for the eclogites from the Luotian dome in the  
967 Dabie orogen. The equilibrium lines for diamond = graphite (Kennedy and Kennedy,  
968 1976) and coesite = quartz (Hemingway et al., 1998) are shown.

Table 1 Electron microprobe analyses of representative minerals from the eclogite (sample 07LT6-1) in the Luotian dome (wt%)

Mineral	Garnet		High-Na omphacite				Low-Na omphacite			
	No.	Gt1	Gt1a	Omp4	Omp1	Omp2	Omp3	Cpx1	Cpx4	Cpx5
Site	m	iz	ig	ig	ig	ig	iz	iz	iz	iz
<b>SiO<sub>2</sub></b>	38.01	39.44	55.58	55.49	54.34	54.41	55.20	54.93	53.35	56.77
<b>TiO<sub>2</sub></b>	0.10	0.03	0.03	0.06	0.05	0.10	0.04	0.04	0.00	0.00
<b>Al<sub>2</sub>O<sub>3</sub></b>	21.02	22.00	10.07	10.48	10.71	10.26	7.64	6.18	8.90	8.36
<b>FeO</b>	26.89	23.50	7.04	6.71	7.35	7.12	5.74	6.53	5.47	5.74
<b>Cr<sub>2</sub>O<sub>3</sub></b>	0.19	0.00	0.00	0.04	0.10	0.00	0.02	0.05	0.03	0.00
<b>MnO</b>	0.24	0.82	0.01	0.03	0.08	0.06	0.15	0.05	0.03	0.14
<b>MgO</b>	3.82	6.52	7.93	7.84	7.44	8.05	10.43	11.40	10.15	10.63
<b>CaO</b>	9.88	8.12	12.71	12.88	13.14	13.76	17.30	17.81	19.14	15.05
<b>Na<sub>2</sub>O</b>	0.06	0.00	6.62	6.33	6.44	6.09	3.43	2.98	2.41	3.89
<b>K<sub>2</sub>O</b>	0.00	0.00	0.00	0.02	0.00	0.00	0.00	0.00	0.00	0.00
<b>Total</b>	100.02	100.43	99.99	99.88	99.65	99.85	99.95	99.97	99.48	100.62
<b>O</b>	12	12	6	6	6	6	6	6	6	6
<b>Si</b>	2.979	3.030	1.992	1.994	1.959	1.959	2.009	2.004	1.962	2.044
<b>Al<sup>IV</sup></b>	0.021	0.000	0.008	0.006	0.041	0.041	0.000	0.000	0.038	0.000
<b>Al<sup>VI</sup></b>	1.919	1.990	0.416	0.437	0.414	0.393	0.327	0.266	0.347	0.335
<b>Fe<sup>3+</sup></b>	0.088	0.075	0.049	0.005	0.070	0.066	0.000	0.000	0.000	0.000
<b>Ti</b>	0.006	0.002	0.001	0.002	0.001	0.003	0.001	0.001	0.000	0.000
<b>Fe<sup>2+</sup></b>	1.674	1.434	0.162	0.196	0.152	0.147	0.175	0.199	0.168	0.099
<b>Cr</b>	0.012	0.000	0.000	0.001	0.003	0.000	0.001	0.001	0.001	0.000
<b>Mg</b>	0.446	0.747	0.424	0.420	0.400	0.432	0.566	0.620	0.556	0.571
<b>Mn</b>	0.016	0.053	0.000	0.001	0.002	0.002	0.005	0.002	0.001	0.004
<b>Ca</b>	0.830	0.668	0.488	0.496	0.508	0.531	0.675	0.696	0.754	0.581
<b>Na</b>	0.009	0.000	0.460	0.441	0.450	0.425	0.242	0.211	0.172	0.272
<b>K</b>	0.000	0.000	0.000	0.001	0.000	0.000	0.000	0.000	0.000	0.000

Note: m, matrix; ig, inclusion in garnet; iz, inclusion in zircon. Garnet/omphacite stoichiometries and the amount of Fe<sup>3+</sup> and Fe<sup>2+</sup> were estimated on the base of eight/four cations and the charge-balance constraint.

Table 2 Major element compositions and Zr temperatures of rutile inclusions in zircon and zircon U-Pb ages for eclogites from the Luotian dome in the North Dabie complex zone

Analysis No.	Locality	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	TiO <sub>2</sub>	FeO	Cr <sub>2</sub> O <sub>3</sub>	Nb <sub>2</sub> O <sub>5</sub>	ZrO <sub>2</sub>	Total	Zr(ppm)	T(°C)	<sup>206</sup> Pb/ <sup>238</sup> U Age(Ma)
<b>03LT1-1</b>												
03LT1-1Rt1	M2	0.00	0.00	96.65	0.36	0.04	0.06	0.19	97.29	1421	844	214±3
03LT1-1Rt1a	M2	0.00	0.00	97.21	0.35	0.04	0.03	0.16	97.79	1199	825	214±3
03LT1-1Rt4	M1	0.00	0.00	97.41	0.49	0.04	0.05	0.33	98.31	2419	988	
03LT1-1Rt4a	M2	0.00	0.00	97.98	0.52	0.04	0.06	0.35	98.94	2560	915	
03LT1-1Rt4b	M2	0.00	0.00	98.27	0.47	0.03	0.07	0.34	99.19	2538	913	
03LT1-1Rt5	M2	0.00	0.00	98.00	0.25	0.03	0.08	0.31	98.68	2301	901	
03LT1-1Rt1	M2	0.00	0.00	98.33	0.33	0.04	0.07	0.11	98.89	843	788	
03LT1-1Rt6	M2	0.00	0.00	97.56	0.54	0.04	0.08	0.73	98.95	5416	1018	
03LT1-1Rt9	M2	0.00	0.00	98.51	0.47	0.03	0.08	0.14	99.23	1014	807	
03LT1-1Rt6a	M2	0.00	0.00	97.68	0.56	0.03	0.05	0.22	98.53	1591	857	
03LT1-1Rt9	M2	0.00	0.00	96.61	2.60	0.03	0.05	0.11	99.40	814	785	
03LT1-1Rt2	M1	0.07	0.00	98.39	0.45	0.08	0.09	0.34	99.43	2515	993	
03LT1-1Rt3	M1	0.04	0.00	99.35	0.36	0.07	0.06	0.22	100.1	1628	936	
03LT1-1Rt7	M2	0.04	0.00	98.11	0.53	0.07	0.06	0.15	98.96	1110	817	
03LT1-1Rt8	M2	0.05	0.00	98.77	0.53	0.07	0.07	0.37	99.86	2737	923	
03LT1-1Rt7	M2	0.05	0.00	98.36	0.26	0.06	0.07	0.30	99.10	2220	897	
03LT1-1Rt1b	M2	0.05	0.00	98.38	0.44	0.04	0.09	0.15	99.16	1131	819	
03LT1-1ARt2	M1	0.04	0.00	97.98	0.37	0.02	0.07	0.23	98.72	1702	941	
03LT1-1ARt3	M1	0.05	0.00	97.53	0.48	0.04	0.07	0.38	98.55	2800	1008	
03LT1-1ARt1	M2	0.06	0.00	98.18	0.37	0.07	0.09	0.18	98.95	1332	837	
<b>06LT3-2</b>												
06LT3-2Rt2	M2	0.00	0.00	98.19	0.14	0.03	0.01	0.15	98.51	1080	814	
06LT3-2Rt3	M1	0.00	0.00	97.46	0.39	0.02	0.01	0.25	98.13	1864	954	
06LT3-2Rt4	M2	0.00	0.00	97.40	0.22	0.02	0.02	0.78	98.43	5771	1028	
06LT3-2Rt5	rim	0.04	0.00	98.41	0.21	0.02	0.00	0.28	98.97	2098	838	200±18
06LT3-2Rt5a	rim	0.04	0.00	98.09	0.20	0.05	0.01	0.32	98.72	2368	852	200±18
06LT3-2Rt1	M2	0.05	0.00	97.92	0.15	0.06	0.01	0.18	98.37	1332	837	
06LT3-2Rt2a	M2	0.03	0.00	97.89	0.15	0.02	0.01	0.16	98.27	1202	826	
<b>07LT6-1</b>												
07LT6-1Rt1	M1	0.03	0.00	98.69	0.48	0.02	0.04	0.14	99.41	1033	881	221±6
07LT6-1Rt2	M1	0.04	0.00	98.22	0.63	0.01	0.03	0.24	99.17	1790	948	228±5
07LT6-1Rt3	M1	0.05	0.00	98.13	0.48	0.05	0.03	0.33	99.06	2405	987	
07LT6-1Rt4	M1	0.04	0.00	98.57	0.40	0.03	0.04	0.26	99.34	1955	959	
07LT6-1Rt5	M2	0.06	0.00	98.34	0.52	0.02	0.04	0.27	99.25	1978	883	



07LT6-1Rt6	M2	0.06	0.00	98.07	0.47	0.02	0.04	0.40	99.06	2983	934	
07LT6-1Rt7	M2	0.06	0.00	98.50	0.49	0.03	0.04	0.20	99.32	1458	847	
07LT6-1Rt8	M2	0.03	0.00	98.68	0.55	0.02	0.00	0.22	99.51	1627	860	
07LT6-1Rt9	M2	0.07	0.00	98.67	0.52	0.03	0.16	0.29	99.75	2163	894	
07LT6-1Rt10	M2	0.06	0.00	98.56	0.45	0.03	0.04	0.17	99.32	1286	833	
07LT6-1Rt11	M2	0.06	0.00	98.57	0.50	0.03	0.04	0.25	99.44	1876	876	
07LT6-1Rt12	M1	0.05	0.00	98.33	0.46	0.03	0.04	0.25	99.16	1819	950	
07LT6-1Rt13	M2	0.04	0.00	98.59	0.36	0.02	0.01	0.29	99.30	2133	892	
07LT6-1Rt14	M2	0.06	0.00	98.57	0.41	0.02	0.03	0.21	99.30	1520	852	
07LT6-1Rt15	M1	0.07	0.00	98.18	0.46	0.02	0.00	0.26	98.99	1929	957	226±7
07LT6-1Rt16	M1	0.06	0.00	98.17	0.46	0.02	0.00	0.34	99.05	2495	992	228±7
07LT6-1Rt17	M2	0.08	0.00	97.76	0.44	0.04	0.05	0.45	98.82	3297	948	
07LT6-1Rt18	M2	0.07	0.00	98.61	0.11	0.01	0.02	0.25	99.08	1831	873	
07LT6-1Rt19	M2	0.05	0.00	97.65	0.46	0.03	0.04	0.40	98.63	2977	934	
07LT6-1Rt20	M2	0.07	0.00	98.61	0.28	0.03	0.00	0.20	99.18	1447	846	
07LT6-1Rt1a	M1	0.03	0.00	98.46	0.48	0.02	0.00	0.15	99.14	1078	886	221±6
<b>09LT1</b>												
09LT1Rt1	M1	0.03	0.00	98.43	0.41	0.03	0.00	0.33	99.24	2405	987	
09LT1Rt2	M1	0.21	0.00	98.15	0.32	0.02	0.03	0.58	99.32	4310	1072	
<b>09LT2</b>												
09LT2Rt2	M2	0.05	0.00	97.88	0.39	0.05	0.01	0.28	98.66	2072	888	
09LT2Rt1	M1	0.14	0.00	97.45	0.58	0.05	0.00	0.51	98.73	3773	1052	224±3

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Notes: M1, inner mantle; M2, outer mantle. All rutiles in this table are inclusions in zircon, the analysis method was EPMA. Temperatures were calculated by Tomkins *et al.* (2007); the pressures were set to be 4 GPa for M1, 2 GPa for M2 and 1 GPa for rim domains. Age data from Liu *et al.* (2011a) and Gu (2012).

Table 3 Major element compositions and Zr temperatures of rutile inclusions in garnet for eclogites from the Luotian dome in the North Dabie complex zone

Analysis No.	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	FeO	TiO <sub>2</sub>	Cr <sub>2</sub> O <sub>3</sub>	Nb <sub>2</sub> O <sub>5</sub>	ZrO <sub>2</sub>	Total	Zr (ppm)	Tt (°C)/4GPa	Tt (°C)/2GPa
07LT6-1-R1	0.00	0.00	0.31	100.03	0.03	0.03	0.01	100.41	67	633	595
07LT6-1-R3	0.00	0.02	0.27	99.27	0.01	0.06	0.07	99.70	481	799	753
07LT6-1-R2	0.00	0.02	0.32	99.21	0.02	0.05	0.03	99.66	252	738	695
07LT6-1-R5	0.00	0.00	0.30	99.66	0.03	0.03	0.05	100.08	363	772	727
07LT6-1-R6	0.00	0.04	0.23	99.82	0.08	0.04	0.02	100.22	141	690	648
07LT6-1-R7	0.00	0.02	0.23	99.41	0.05	0.04	0.02	99.77	126	681	640
07LT6-1A-R1	0.00	0.00	0.29	98.23	0.06	0.04	0.05	98.66	345	767	723
07LT6-1A-R2	0.00	0.00	0.21	99.35	0.10	0.02	0.03	99.71	215	725	682
07LT6-1A-R3	0.00	0.00	0.43	98.90	0.05	0.04	0.03	99.44	192	715	673
07LT6-1A-R4	0.00	0.00	0.35	99.26	0.03	0.04	0.01	99.69	96	660	620
07LT6-1A-R5	0.00	0.00	0.30	100.52	0.03	0.03	0.10	100.97	710	839	792
07LT6-1A-R6	0.00	0.02	0.15	100.81	0.21	0.05	0.07	101.30	504	804	758
07LT6-1A-R7	0.00	0.00	0.21	100.35	0.07	0.11	0.11	100.85	777	849	801
07LT6-1-R4	0.00	0.01	0.30	101.11	0.03	0.04	0.08	101.56	561	815	710
09LT2-1-R1	0.00	0.01	0.36	101.36	0.05	0.03	0.04	101.88	298	754	776
09LT2-1-R2	0.00	0.01	0.50	101.52	0.03	0.07	0.08	102.20	608	823	625
09LT2-1-R3	0.00	0.00	0.46	100.88	0.04	0.03	0.01	101.42	102	665	782
09LT2-1-R4	0.06	0.00	0.36	96.97	0.05	0.03	0.09	97.56	645	829	770
03LT1-1H-R1	0.00	0.00	0.36	101.55	0.03	0.07	0.08	102.09	573	817	789
03LT1-1H-R2	0.00	0.00	0.37	101.93	0.09	0.07	0.10	102.54	693	837	768
03LT1-1Ru1	0.07	0.03	1.01	99.29	0.04	0.08	0.04	101.08	296	753	709
03LT1-1Ru2	0.03	0.02	0.51	96.94	0.06	0.07	0.06	98.01	466	796	750
03LT1-1Ru3	0.08	0.04	1.23	98.47	0.06	0.07	0.04	100.58	311	758	713
06LT3-2Ru1	0.01	0.01	0.30	98.57	0.10	0.02	0.08	99.14	607	823	776
06LT3-2Ru2	0.03	0.05	0.53	98.33	0.10	0.01	0.03	99.28	229	730	688

Temperatures were calculated using the equation given by Tomkins *et al.* (2007), the pressures were set to be 4 GPa and 2 GPa, respectively. The Zr contents were analyzed by EPMA.

Table 4 Ti-in-zircon temperatures and zircon U-Pb ages for eclogites from the Luotian dome in the North Dabie complex zone

Type	Sample No.	Domain	Nature	Ti (ppm)	T (°C)	$^{206}\text{Pb}/^{238}\text{U}$ Age (Ma)
<b>Type 1</b>	<b>03LT1-1</b>					
	03LT1-1-1-1	m	me	3.4	654	226±4
	03LT1-1-3-1	m	me	3.6	659	231±4
	03LT1-1-8-1	m	me	4.8	680	224±3
	03LT1-1-10-1	m	me	3.1	647	216±3
	03LT1-1-17-1	m	me	4.4	673	217±4
	03LT1-1-16-1	m	me	3.4	654	234±3
	03LT1-1-18-1	m	me	2.2	622	217±4
	03LT1-1-20-1	m	me	8.5	726	225±3
	03LT1-1-22-1	m	me	4.7	678	229±3
	03LT1-1-26-1	m	me	4	667	213±3
	03LT1-1-24-1	m	me	26.9	836	220±3
	<b>06LT3-2</b>					
	06LT3-2-1-1	r	me	4.6	678	180±12
	06LT3-2-3-1	r	me	3.4	653	191±10
	06LT3-2-7-1	m	me	2.9	643	220±3
	06LT3-2-6-1	m	me	63.1	934	225±14
	06LT3-2-11-1	m	me	6.8	709	207±5
	06LT3-2-15-1	m	me	13.9	771	230±25
	06LT3-2-18-1	m	me	20.3	807	215±18
	06LT3-2-19-1	m	me	97.8	991	211±3
	06LT3-2-21-1	r	me	25	828	207±4
	06LT3-2-20-1	r	me	16.2	785	200±18
	<b>07LT6-1</b>					
	07LT6-1-1-1	m	me	4.8	680	221±6
	07LT6-1-3-1	m	me	5.2	688	225±5
	07LT6-1-5-1	r	me	3.1	647	189±6
	07LT6-1-8-2	m	me	20.5	808	218±5
	07LT6-1-9-1	r	me	3.3	652	197±5
	07LT6-1-10-2	m	me	4	667	227±5
	07LT6-1-17-1	r	me	3.3	652	208±6
	07LT6-1-13-1	m	me	66.3	940	218±5
	07LT6-1-15-1	m	me	2.9	644	238±7
07LT6-1-14-1	m	me	3.2	649	215±7	
07LT6-1-16-1	m	me	2.4	630	225±5	
<b>LT10</b>						
LT10-2-1	c	ma	6.9	709	783±13	
LT10-2-2	c	ma	8.8	730	737±15	

<b>Type 2</b>	LT10-3-2	c	me	6.4	703	822±17	
	LT10-4-1	c	ma	7.7	718	638±11	
	LT10-1-1	c	me	274	1149	788±13	
	LT10-1-2	c	me	9.3	734	766±13	
	LT10-4-2	c	me	4.3	672	788±14	
	LT10-3-5	c	ma	47.2	898	799±15	
	LT10-3-9	c	ma	6.3	702	642±14	
	LT10-1-4	c	me	48.5	902	791±13	
	LT10-4-5	c	ma	14.1	772	798±16	
	LT10-4-4	c	ma	17.7	794	784±16	
	LT10-4-7	c	ma	6.3	702	791±16	
	LT10-4-3	c	me	12.6	762	335±7	
	LT10-1-8	c	me	21.4	812	783±13	
	LT10-1-11	c	me	5.5	691	799±14	
	LT10-1-9	c	me	33.7	860	730±12	
	LT10-3-6	c	me	6	698	696±14	
	LT10-3-7	c	me	11.5	753	726±15	
	<b><i>LT9</i></b>						
	LT9-2-1	c	ma	17.6	793	802±16	
	LT9-3-1	c	me	236.1	1124	830±18	
LT9-2-2	c	ma	136.2	1038	736±14		
LT9-1-6	c	me	94.4	986	375±6		
LT9-1-7	c	me	68.8	945	707±12		

Notes: c, core; m, mantle; r, rim; ma, magmatic; me, metamorphic. Temperatures were calculated by Watson *et al.* (2006). The Ti contents in zircons were analyzed by LA-MC-ICPMS.

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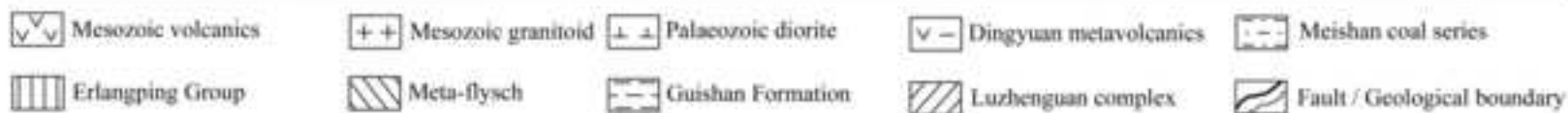
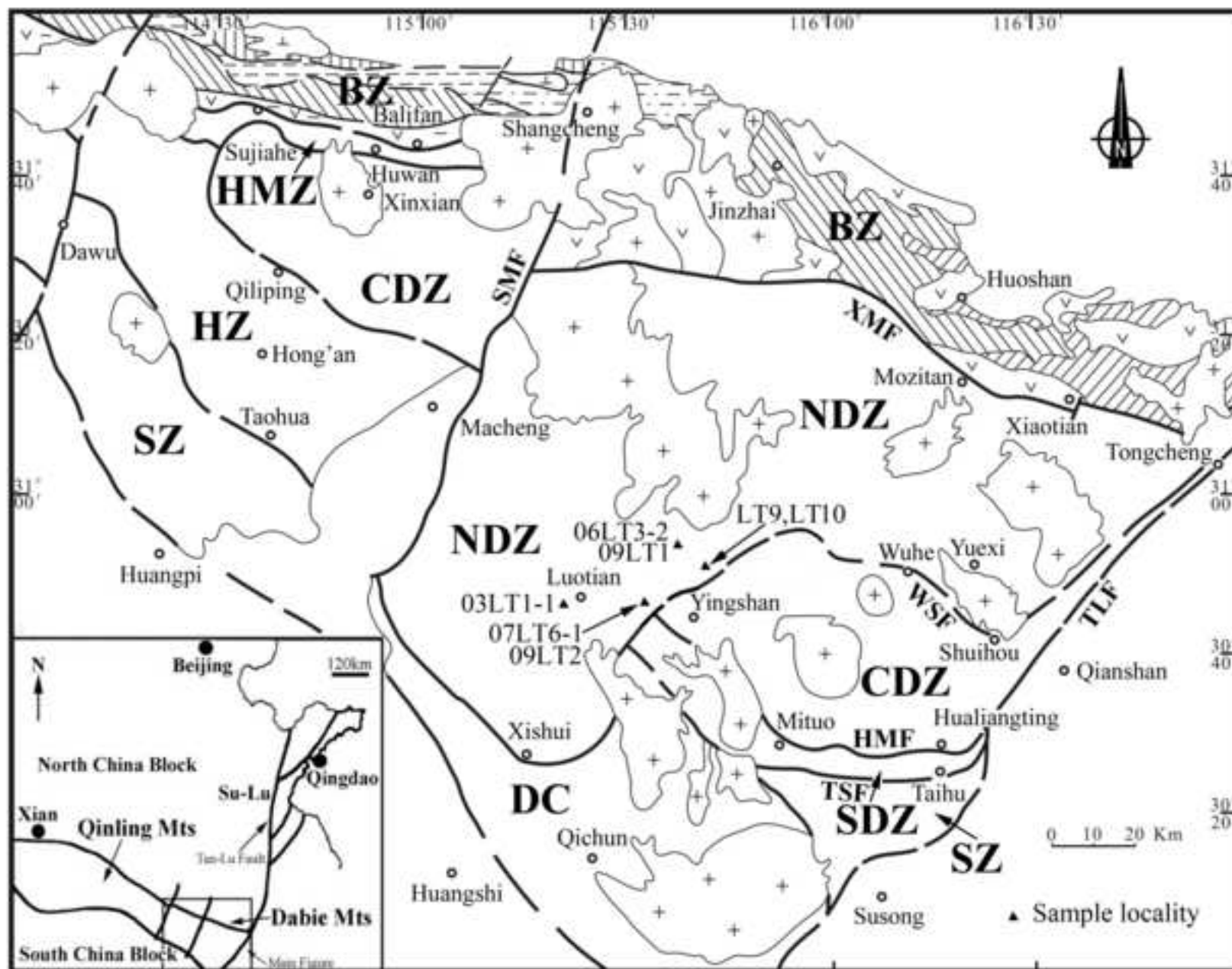


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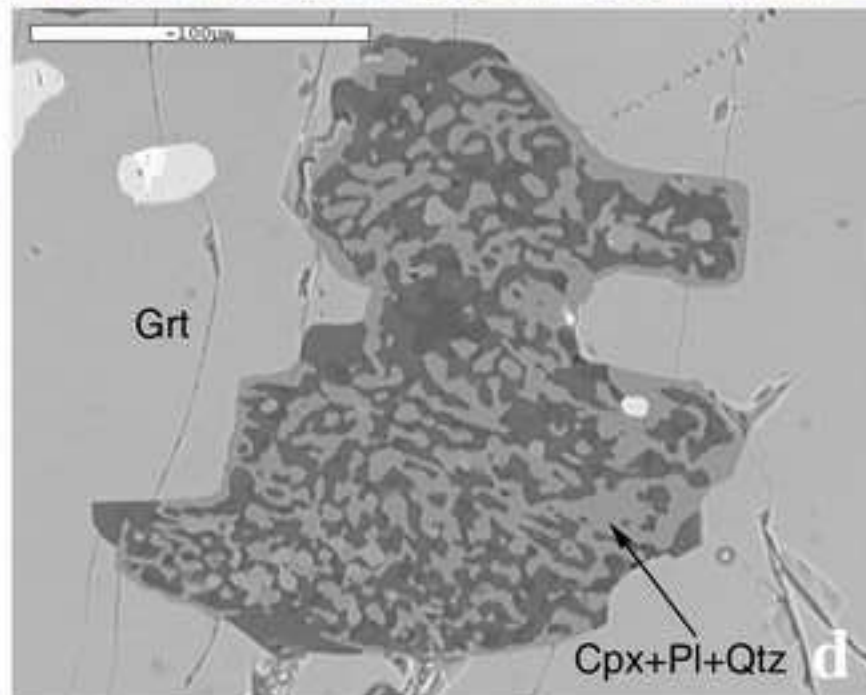
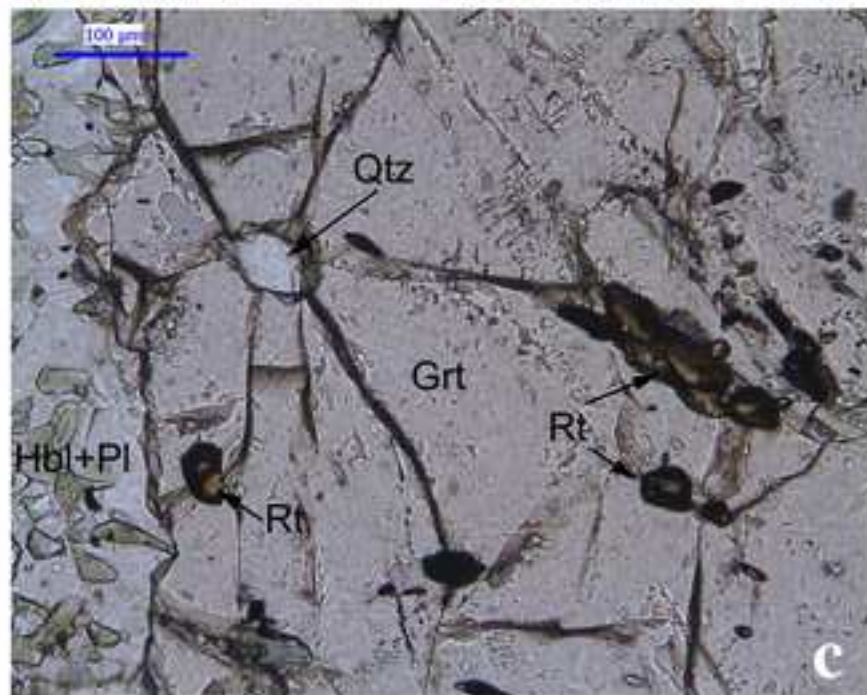
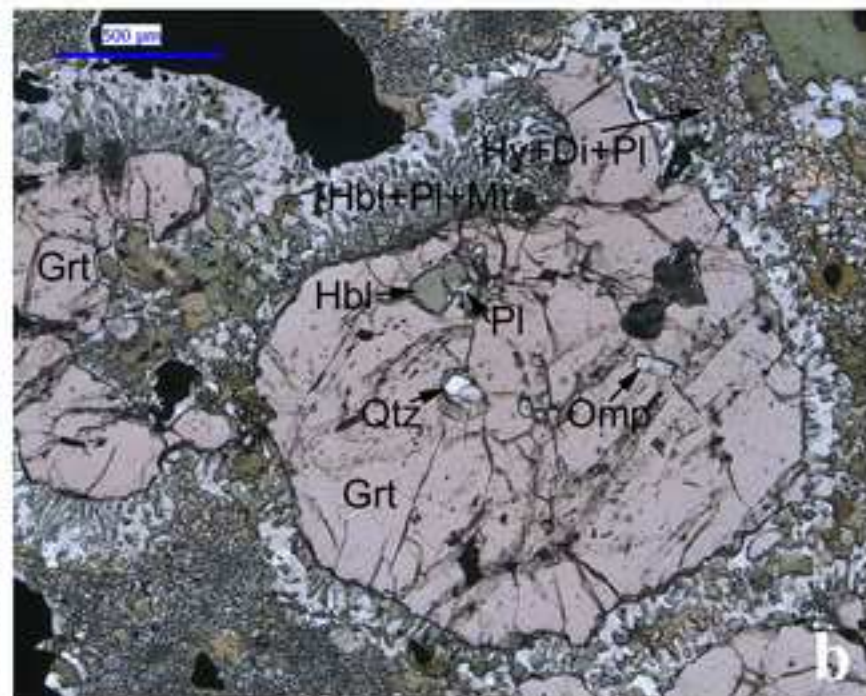
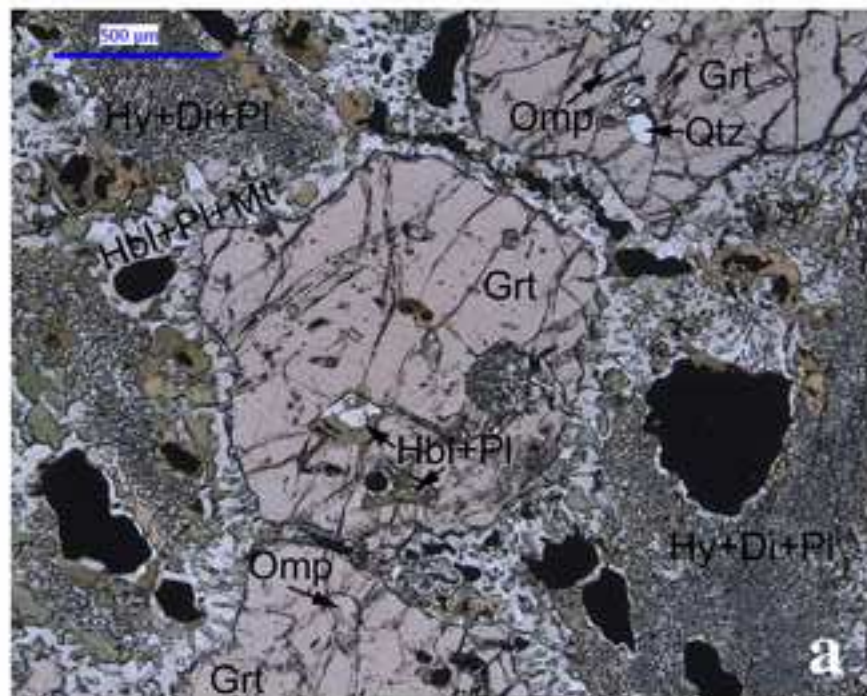


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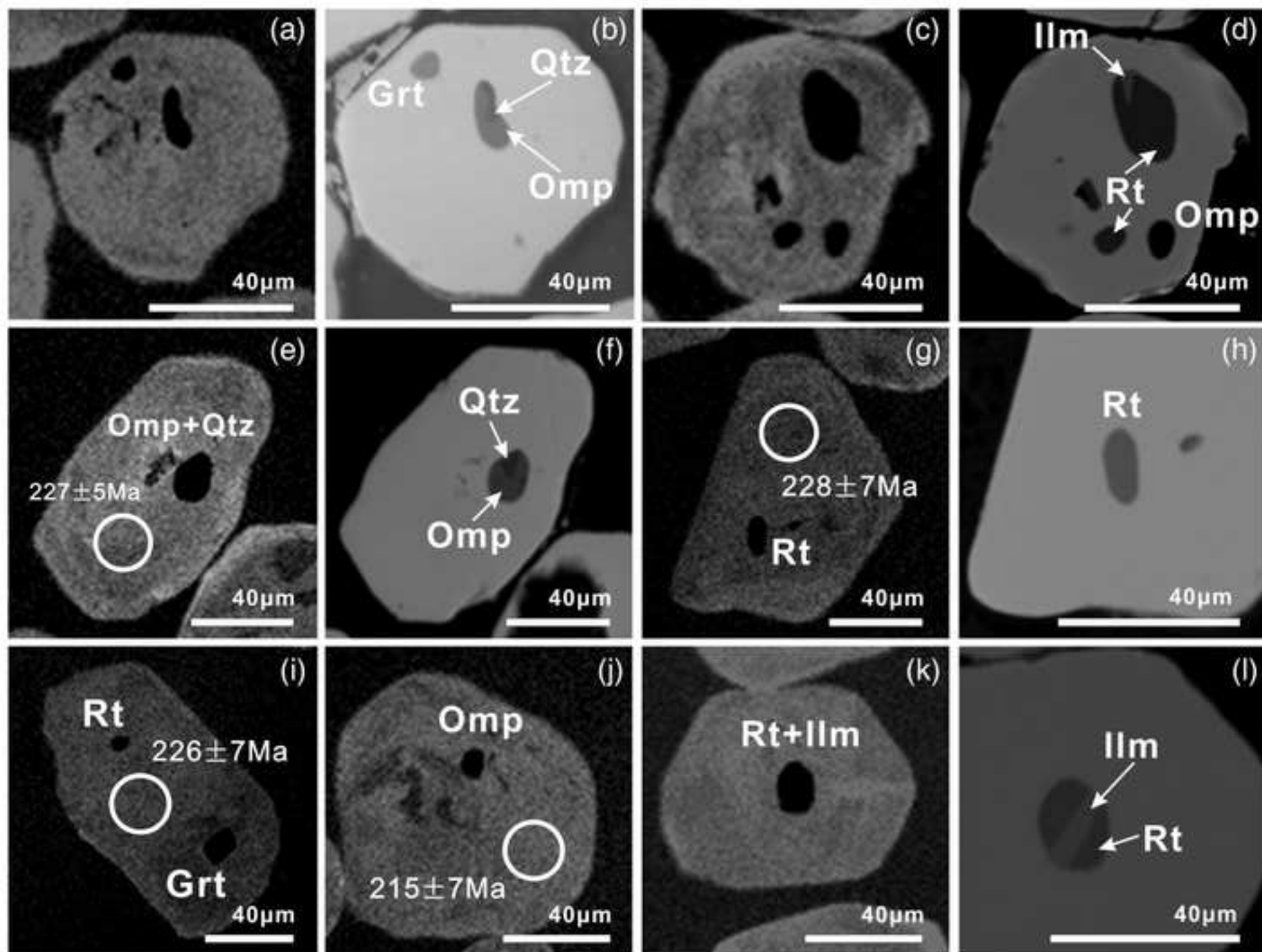


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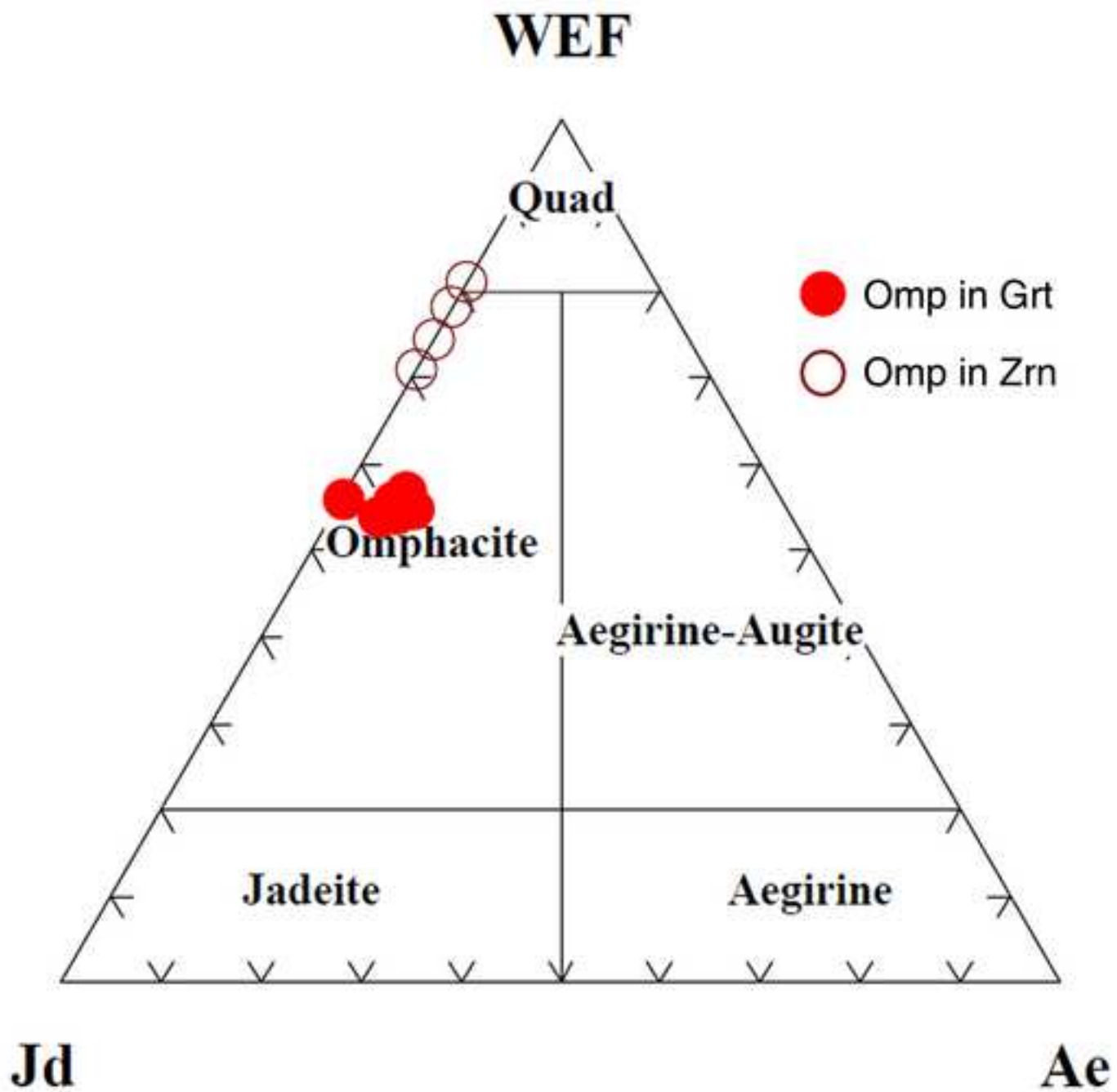




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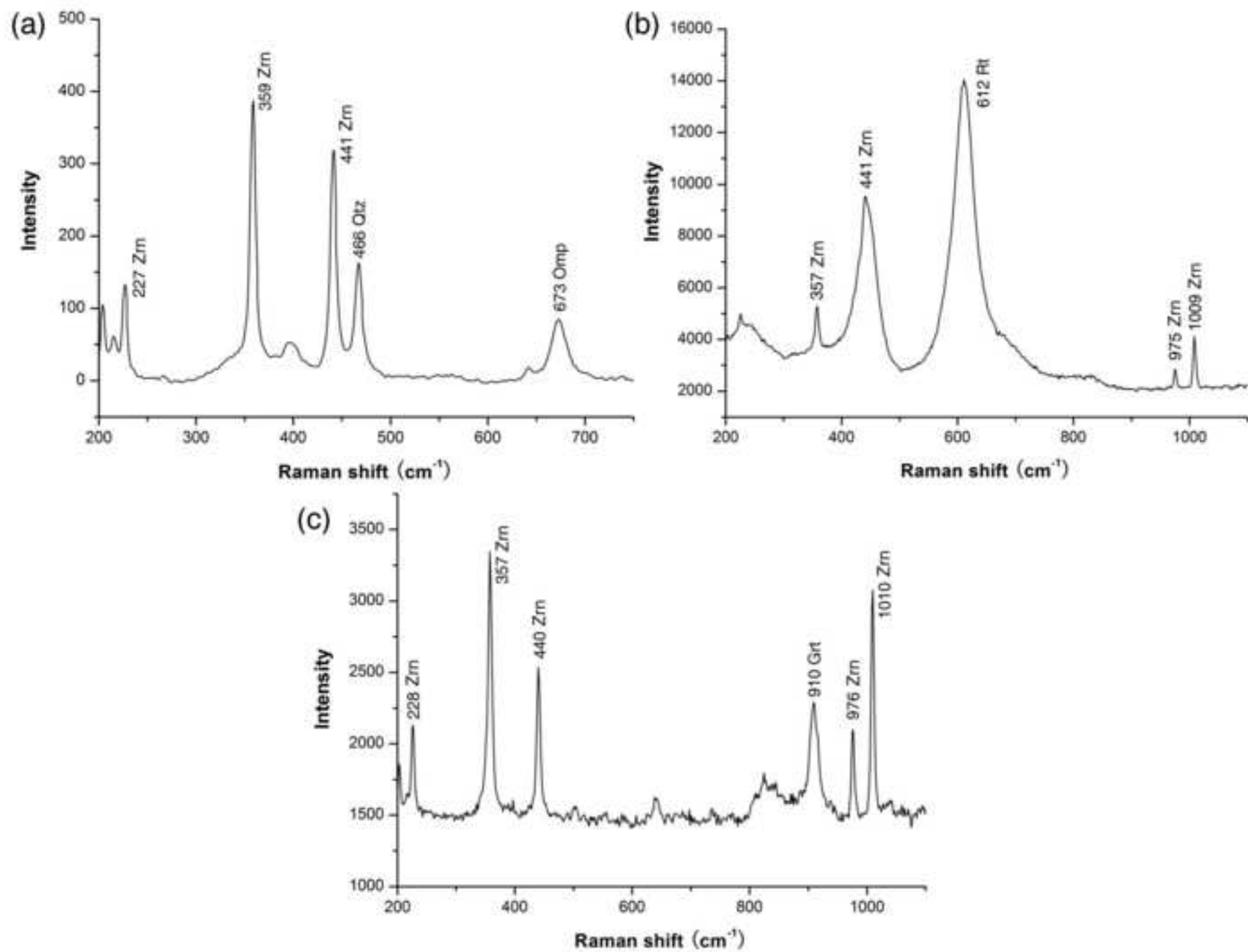


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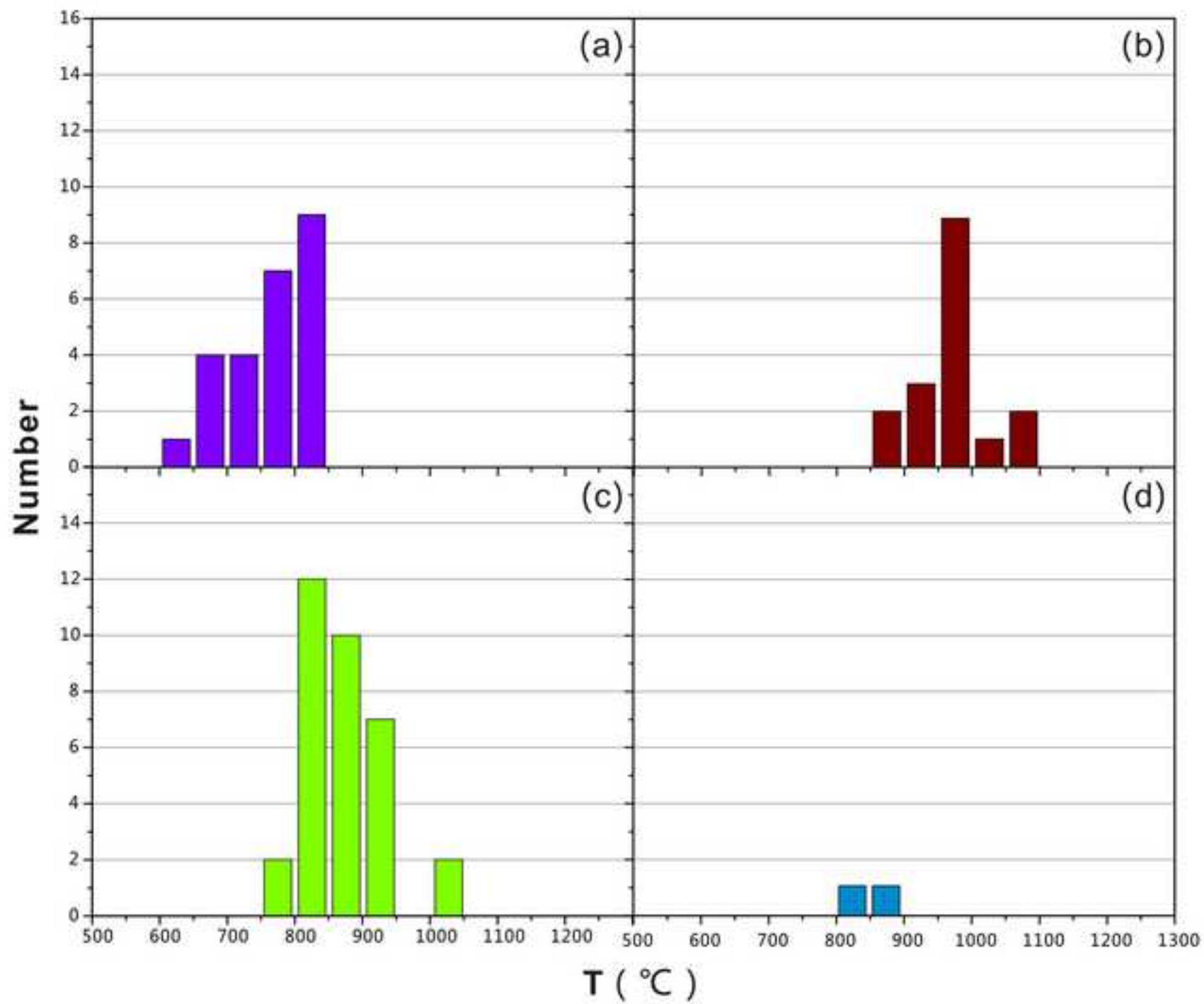


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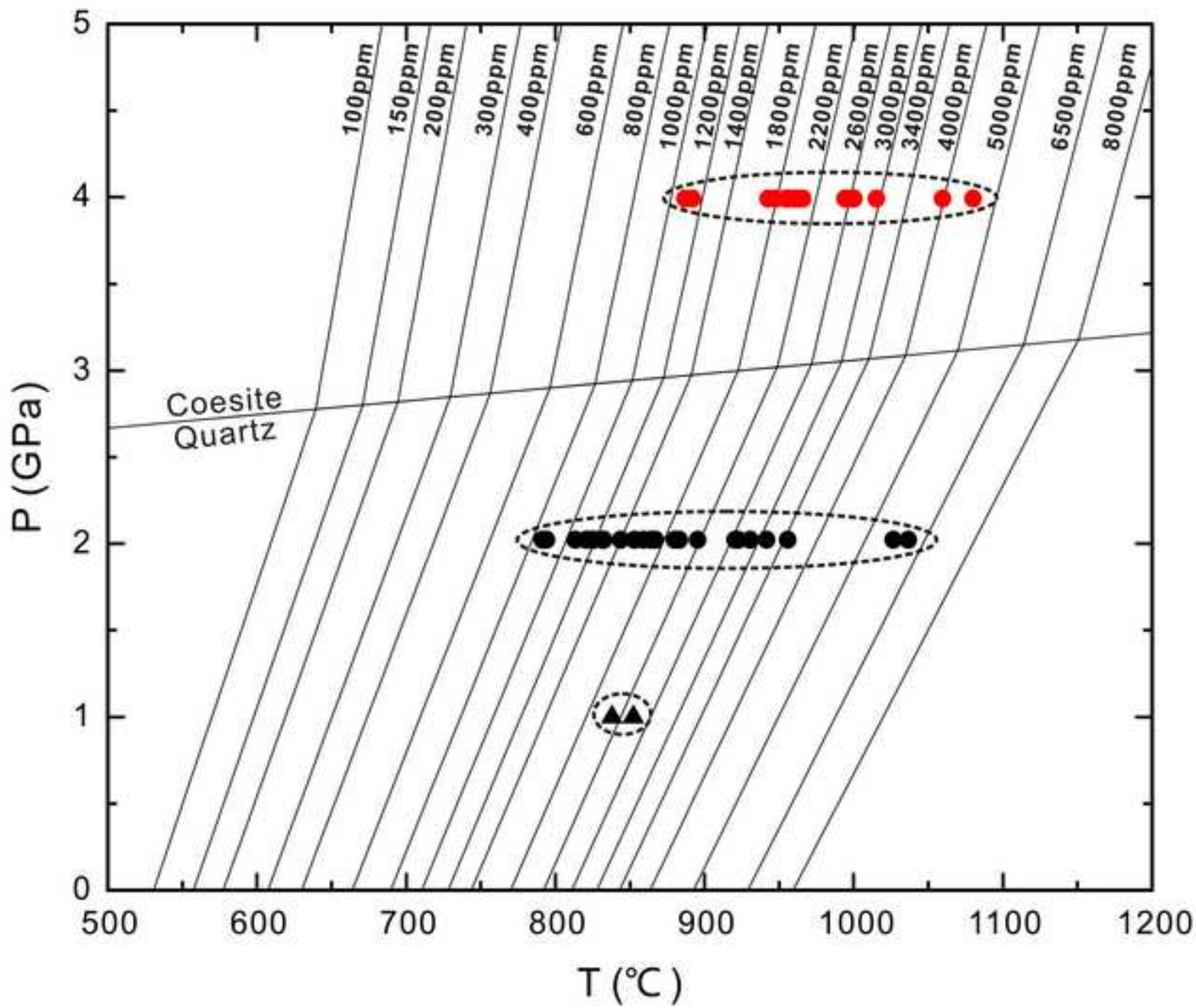


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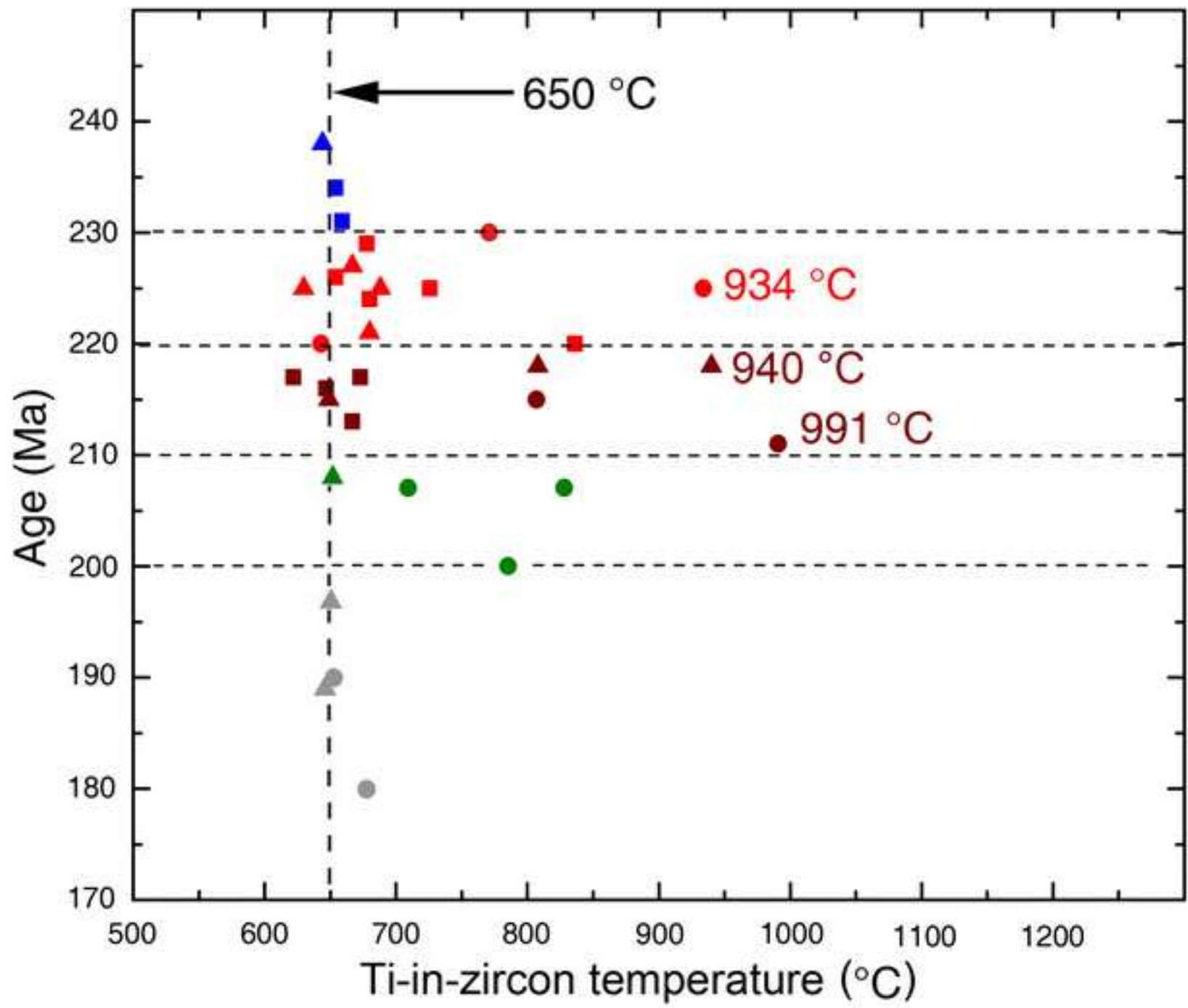


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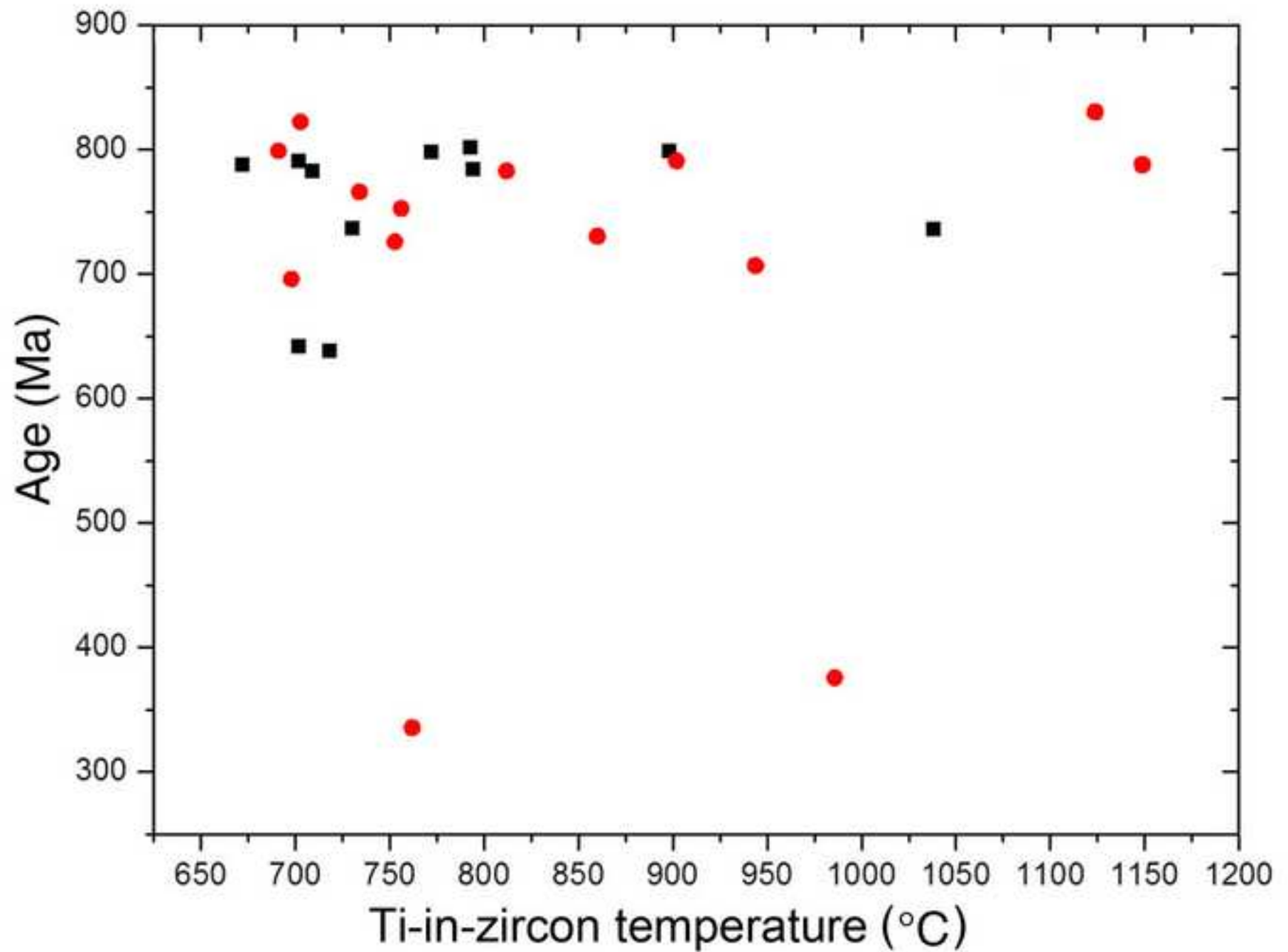


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