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**First report of ultra-high pressure metamorphism in the Paleozoic
Dunhuang orogenic belt (NW China): Constrains from *P-T* paths of
garnet clinopyroxenite and SIMS U-Pb dating of titanite**

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25 **Abstract**

26 Ultra-high pressure (UHP) metamorphism is recorded by garnet clinopyroxenite
27 enclaves enclosed in an undeformed, unmetamorphosed granitic pluton, northeastern
28 Paleozoic Dunhuang orogenic belt, northwest China. Three to four stages of metamorphic
29 mineral assemblages have been found in the garnet clinopyroxenite, and clockwise
30 metamorphic pressure-temperature (P - T) paths were retrieved, indicative of metamorphism
31 of a possible subduction environment. Peak metamorphic P - T conditions (790~920 °C /
32 28~41 kbar) of garnet clinopyroxenite suggest that they experienced high pressure to UHP
33 metamorphism, and the UHP metamorphism occurred in the coesite- or diamond-stability
34 field. The UHP metamorphic event is further confirmed by the occurrence of high-Al
35 titanite enclosed in the garnet, along with at least three groups of aligned rutile lamellae
36 exsolved from within the garnet. SIMS U-Pb dating of metamorphic titanite indicates that
37 the post peak, subsequent tectonic exhumation of the UHP rocks occurred in the Devonian
38 (~389~370 Ma). These data suggest that part of the Paleozoic Dunhuang orogenic belt
39 experienced UHP metamorphism, and diverse metamorphic facies series prevailed in this
40 orogen in the Paleozoic. It can be further inferred that most of the UHP rocks of this orogen
41 are now buried in the depth.

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49 **Introduction**

50 It is well known that ultra-high pressure (UHP) metamorphism refers
51 to metamorphic pressure high enough to stabilize coesite, i.e., pressure reaches at least ~2.7
52 GPa if temperature reaches ~700 °C. The UHP metamorphism is anticipated to be formed
53 in the subduction process at very low thermal gradient of usually less than 10 °C / km, or
54 even as low as ~5 °C / km. In orogenic belts, UHP metamorphism can be validly certified
55 by presence of diagnostic minerals such as coesite (e.g., Chopin, 1984; Smith, 1984),
56 diamond (e.g., Sobolev and Shatsky, 1990; Xu et al., 1992), Na-Ti-P-bearing garnet (e.g.,
57 Ye et al., 2000) or even pseudomorph of stishovite (e.g., Liu et al., 2007, 2018). But
58 unfortunately, in some orogenic belts these diagnostic minerals cannot be found, which in
59 turn, brings people some uncertainties in recognizing UHP metamorphism. In this
60 contribution, we present UHP metamorphism recorded in garnet clinopyroxenite enclaves
61 within an undeformed, unmetamorphosed granitic pluton, northeast Paleozoic Dunhuang
62 orogenic belt, northwest China.

63 The Dunhuang area has long been considered as an ancient stable block formed in the
64 Precambrian. Until recently, clockwise metamorphic *P-T* paths of eclogite, mafic granulite,
65 amphibolite and metapelite, typical metamorphic products of subduction background, were
66 retrieved elsewhere in this region (Zhang et al., 2012; Zong et al., 2012; He et al., 2014;
67 Peng et al., 2014; Zhao et al., 2016; Wang et al., 2016, 2017a, b, 2018a, b; Zhang et al.,
68 2020). The metamorphic event was dated to have occurred in the Silurian to Devonian era
69 (Zong et al., 2012; He et al., 2014; Wang et al., 2016, 2017a, b, 2018a, b; Zhang et al.,
70 2020). These enabled people to believe that this area was a Paleozoic orogenic belt (Zhao
71 et al., 2016; Wang et al., 2017a, b; 2018a, b; Zhang et al., 2020), albeit the subduction



72 polarity remains ambiguous. Eclogite (Wang et al., 2017a) and high-pressure mafic
73 granulite (Zong et al., 2012; He et al., 2014; Wang et al., 2016, 2017a, b, 2018b; Zhang et
74 al., 2020) have been found in this orogen, but UHP rocks have not been discovered before,
75 which in turn, limits our understanding of the orogenic process as a whole.

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77 **Regional geology**

78 The Dunhuang orogenic belt strikes SWW-NEE and covers an area of approximately
79 440 km long and 100 km wide. It is tectonically bordered by the Paleozoic Beishan
80 orogenic belt to the north, the Precambrian Tarim craton to the west, the Precambrian Alexa
81 block to the east, and the Paleozoic Altyn Tagh-Qilian orogenic belt to the south (Fig. 1).
82 The Dunhuang orogenic belt was dismembered by sinistral strike-slip faults to several
83 tectonic blocks (Fig. 2), possibly in the Tertiary. The prominent characteristics of the
84 Dunhuang orogenic belt is that at least in the Hongliuxia, Qingshigou, Kalatashitage and
85 Mogutai-Dongbatu blocks, eclogite, high- and medium-pressure mafic granulite, and
86 amphibolite occur as rootless tectonic lenses or puddings enclosed within the metapelite
87 and metasandstone matrix (Wang et al., 2016, 2017a, 2018a, b), indicative of typical block-
88 in-matrix feature of tectonic mélange (Festa et al., 2012). Some closely amalgamated
89 tectonic-metamorphic slices can also be found in northwest Dunhuang orogenic belt
90 (Zhang et al., 2020), which were metamorphosed in obviously different depths and were
91 later juxtaposed in the same crustal level in the tectonic exhumation.

92 Unfortunately, coesite or diamond, either as inclusion or inter-granular minerals, have
93 not been found from the eclogite, mafic granulite, amphibolite or metapelite, therefore,
94 UHP metamorphism of this orogen has not been found before. Recently, we found high-Al



95 titanite-bearing garnet clinopyroxenite and obtained UHP *P-T* conditions of such rocks in
96 the Daquan area, northeast Dunhuang orogenic belt (Fig. 3). Garnet clinopyroxenite occurs
97 as enclaves enclosed in an undeformed, unmetamorphosed granite body (Figs. 3B, 4A-B),
98 but crystallization age of the granite cannot be determined due to severe decrystallization
99 of magmatic zircon caused by radioactive damage.

100

101 **Petrography**

102 Retrograde symplectite rimming the embayed, relict garnet of the garnet
103 clinopyroxenite can be easily seen in the outcrop (Fig. 4C). Micropetrographic features of
104 the garnet clinopyroxenite are depicted in Figures 5 and 6. Three to four stages of
105 metamorphic mineral assemblages were found in the four representative samples. The
106 mineral abbreviations are from Whitney and Evans (2010) hereafter, and subscripts of the
107 minerals 1, 2, 3, and 4 refer to the corresponding minerals formed at the sequential four
108 metamorphic stages, respectively, throughout this paper.

109 All the four samples are mainly biminerally, consisting of garnet and clinopyroxene.
110 The prograde assemblage (M1) is represented by the fine-grained ilmenite (Ilm₁) +
111 hornblende (Hbl₁) + plagioclase (Pl₁) ± clinopyroxene (Cpx₁) inclusions enclosed in the
112 garnet (Grt₂) (Figs. 5A, B, C). High-Al titanite (Ttn₁) also appears as inclusion within
113 garnet (Figs. 6A-B). The peak metamorphic assemblage (M2) consists of garnet (Grt₂) and
114 clinopyroxene (Cpx₂), plus matrix minerals including minor rutile (Rt₂), magnetite (Mag₂),
115 high-Al titanite (Ttn₂) and apatite (Ap₂), as shown in Figures. 5A-C. The matrix rutile (Rt₂)
116 is rare (Fig. 5G). The retrograde assemblage (M3) is mainly the warm-like symplectite,
117 consisting of fine-grained plagioclase (Pl₃), hornblende (Hbl₃) and ilmenite (Ilm₃)



118 intergrowth, riming the garnet (Figs. 5A-C, H). Similar decomposition textures in mafic
119 granulites can be found elsewhere and are repeatedly demonstrated to be formed under
120 severe decompression during tectonic exhumation (e.g., Wang et al., 2016, 2017a, b;
121 Petrakakis et al., 2018; Zhang et al., 2020). Other retrograde assemblages include fine-
122 grained ilmenite (Ilm_3) \pm plagioclase (Pl_3) \pm hornblende (Hbl_3) \pm titanite (Ttn_3) lamellae
123 exsolved from within the clinopyroxene (Cpx_2) (Fig. 5I), hornblende (Hbl_3) retrograded
124 from clinopyroxene (Cpx_2) (Fig. 5F), ilmenite (Ilm_3) retrograded from rutile (Rt_2) (Fig. 5G),
125 and ilmenite (Ilm_3) retrograded from high-Al titanite (Ttn_2) (Fig. 6B), as well as aligned
126 rutile lamellae (Rt_3) exsolved from within the garnet in three different directions (Figs. 6C-
127 D). Occasionally, the final retrograde assemblage (M_4) can be found, i.e., actinolite (Act_4)
128 and chlorite (Chl_4) retrograded from hornblende (Hbl_3) (Fig. 5H). In sample 17D95,
129 especially, minor spinel (Spl_3) can be found, and it mainly coexists with tremolite (Tr_3) \pm
130 rutile (Rt_3) as idiomorphic retrograded phases within the garnet (Fig. 6E), possibly
131 exsolved from within garnet, similar to the clinopyroxene exsolved from within the garnet
132 in eclogite in Sulu orogenic belt, eastern China (Ye et al., 2000). Such inclusion-like
133 minerals were in fact decomposed from garnet (Hwang et al., 2019). In sample 17D80,
134 there is idiomorphic hexagon ilmenite (Ilm_3) in garnet, and separated by high-Al titanite
135 (Ttn_2) from midcourt line (Fig. 6F), and such reaction textures are similar to those in
136 granulite facies metapelite and may represent extremely high P or T conditions (e.g., Ague
137 and Eckert, 2012).

138

139 **Metamorphic P - T paths**

140 *Mineral chemistry*



141 Compositional analyses, backscattered electron (BSE) images, as well as X-ray
142 compositional mapping of minerals were determined by electron probe microanalysis
143 (EPMA) using a JOEL JXA-8230 analyzer at the School of Resource and Environmental
144 Engineering, Hefei University of Technology, China. The analytical conditions were 15
145 kV accelerating voltage and 20 nA beam current and the counting time was 10–20 s.
146 Usually, 3~5 μm electron beam diameter was used, while 3 μm electron beam size was
147 only adopted in analyzing the tiny minerals. Natural minerals were used as standards, and
148 the ZAF program was utilized for matrix corrections. Generally, at least 3~5 grains were
149 analyzed for any representative mineral, and 1~60 spots of each grain were probed. The
150 representative mineral compositions are listed in Table S1 and the computed P - T conditions
151 are listed in Table 1. Ferric iron content of both clinopyroxene and garnet was determined
152 by stoichiometric and charge balance criteria (Droop, 1987), while ferric iron content of
153 hornblende was evaluated by the method of Holland and Blundy (1994).

154 The garnet (Gr_2) is chemically homogeneous in each sample and is mainly consisting
155 of almandine ($X_{\text{Alm}}=0.34\sim 0.54$), pyrope ($X_{\text{Prp}}=0.19\sim 0.48$) and grossular ($X_{\text{Grs}}=0.18\sim 0.32$)
156 but negligible spessartine components. Such garnet is chemically different from those in
157 mantle xenolith or eclogite. Negligible chemical zonation of the garnet was found. In the
158 very rim of the garnet, the $\text{Fe}\#$ [$=\text{Fe}/(\text{Fe}+\text{Mg})$] value increases slightly (Table S2; Figs. 7,
159 8), indicative of post-peak Fe-Mg diffusion between the garnet rim and adjacent
160 clinopyroxene and / or decomposition of the garnet rim (Spear and Florence, 1992). This
161 is also demonstrated by micropetrography (Figs. 5 and 6). Chemical analytical profiles
162 (Table S3) suggest that the clinopyroxene (Cpx_2) is almost chemically homogeneous in
163 each sample and is essentially diopside based on the classification of Morimoto (1988) (Fig.



164 S1) with negligible jadeite fraction. Due to exsolution, however, chemical composition of
165 most of the Cpx₂ was altered to different extent. Although the Mg²⁺ and Fe²⁺ cations of the
166 Cpx₂ grains are generally homogeneous, but Al³⁺ and Ca²⁺ cations show somewhat
167 variations (Figs. S2, S3, S4, S5), thus the reintegrated chemical composition of
168 clinopyroxene was used to estimate peak *P-T* conditions. High-Al titanite contains
169 remarkable Al₂O₃ (8.2~10.2 wt%) and F contents (1.3~2.8 wt%), which signify HP / UHP
170 pressure metamorphism (e.g., Smith, 1981; Franz and Spear, 1985).

171 ***Geothermobarometry***

172 Metamorphic *P-T* conditions of the peak metamorphism (M2) were determined by the
173 garnet-clinopyroxene geothermometer (Nakamura, 2009) coupled with the garnet-
174 clinopyroxene geobarometer (Beyer et al., 2015), using averaged chemical composition of
175 garnet and reintegrated chemical composition of clinopyroxene. Although this
176 geobarometer was experimentally calibrated for mantle eclogite, however, chemical
177 compositions of the natural rocks reported in this work are similar to those of the
178 experimental run products (Beyer et al., 2015). Accuracy of this geobarometer is estimated
179 to be ±4 kbar (Beyer et al., 2015). The prograde (M1) and retrograde (M3) assemblages are
180 mainly consisting of plagioclase and hornblende but without quartz, therefore, *P-T*
181 conditions of the M1 and M3 assemblages were estimated by the monomineralogic
182 hornblende geothermobarometers (Gerya et al., 1997).

183 ***Metamorphic P-T paths***

184 Metamorphic *P-T* path of sample 17D78 passes from 662 °C / 5.4 kbar (M1) through
185 789 °C / 28 kbar (M2) to 621 °C / 4.6 kbar (M3). As for the other three samples,
186 metamorphic *P-T* paths were estimated respectively as the follows: sample 17D80, 902 °C



187 / 38.2 kbar (M2) → 656 °C / 5.4 kbar (M3); sample 17D90, 695 °C / 7.2 kbar (M1) → 868°C
188 / 31.8 kbar (M2) → 669 °C / 6.0 kbar (M3); sample 17D95, 918°C / 41.3 kbar (M2) →
189 631 °C / 5.6 kbar (M3). The retrieved metamorphic *P-T* paths of the garnet clinopyroxenite
190 enclaves are all clockwise (Fig. 9), indicative of subduction zone setting (c.f., Ernst, 1988;
191 Harley, 1989). It should be stated that the peak metamorphism (except for sample 17D78)
192 lies in the coesite or diamond stability field (Fig. 9), certifying UHP metamorphism. The
193 UHP conditions is further evidenced by the occurrence of at least three groups of aligned
194 rutile lamellae (Rt₃) exsolved from within the garnet (Figs. 6C-D) and chemically
195 homogeneous high-Al titanite (Ttn₂) enclosed in the garnet (Figs. 6A-B), being
196 characterized by $X_{Al} [=Al/(Al+Fe^{3+}+Ti)]=0.25\sim0.29$. These two mineralogical
197 characteristics together indicate UHP metamorphism (c.f., Ye and Ye, 1996; Tropper et al.,
198 2002; Ague and Eckert, 2012).

199

200 **Dating metamorphism**

201 No zircon was found in these samples, possibly due to SiO₂-undersaturated bulk
202 composition of these rocks. Therefore, SIMS U-Th-Pb dating of metamorphic titanite
203 scenario was chosen to determine the age of metamorphism (in this case, the cooling age).
204 The SIMS U-Th-Pb analyses of titanite were performed using a Cameca IMS-1280HR
205 SIMS at Institute of Geology and Geophysics, Chinese Academy of Sciences, Beijing,
206 China. The instrument description and analytical procedure for titanite dating is identical
207 to that of dating perovskite (Li et al., 2010) and has been described in detail in Li et al.
208 (2014) and Ling et al. (2015), thus only a brief summary is described here. The O₂⁻ primary
209 ion beam was accelerated at ~13 kV, with an intensity of ~9 nA. The ellipsoidal spot is



210 about $20\ \mu\text{m} \times 30\ \mu\text{m}$ in size. The $^{40}\text{Ca}^{48}\text{Ti}_2^{16}\text{O}_4^+$ peak is used as a reference peak for
211 centering the secondary ion beam, energy and mass adjustments. A mass resolution of
212 ~ 7000 (defined at 50% peak height) was used. A single electron multiplier was used in ion-
213 counting mode to measure secondary-ion beam intensities by a peak jumping sequence,
214 including isotopes of Pb^+ , Th^+ , U^+ , ThO^+ , UO^+ , and $^{40}\text{Ca}^{48}\text{Ti}_2^{16}\text{O}_4^+$ to produce one set of
215 data. Analyses of the standard YQ82 titanite were interspersed with unknown grains. Each
216 measurement consists of 15 cycles, and the total analytical time is ~ 19 min. Pb/U
217 calibration was performed relative to YQ82 titanite standard ($^{206}\text{Pb}/^{238}\text{U}$ age = 1837.6 Ma,
218 Li et al., 2016). U and Th concentrations were calibrated against titanite BLR-1 (Aleinikoff,
219 et al., 2007). A long-term uncertainty of 1.5% (1σ RSD) for $^{206}\text{Pb}/^{238}\text{U}$ measurements of
220 the standard titanite was propagated to the unknowns, despite that the measured $^{206}\text{Pb}/^{238}\text{U}$
221 error in a specific session is generally $\leq 1\%$ (1σ RSD). A Tera-Wasserburg (Tera and
222 Wasserburg, 1972) plot was constructed with common lead uncorrected data to deduce the
223 common lead composition, then a ^{207}Pb -based common lead correction method was
224 conducted to single analysis. Data reduction was carried out using the Isoplot/Ex v. 2.49
225 program (Ludwig, 2001). Uncertainties on individual analysis in data tables are reported at
226 1σ level. The final U-Pb age result is quoted with 95% confidence interval (Table S4).

227 The BSE images of titanite are shown in Figure S6. The titanite images are
228 homogeneous in sample 17D78, while in samples 17D90 and 17D95 they are altered to
229 different extent. The resulted U-Pb ages of the metamorphic titanite from samples 17D78
230 and 17D95 are $\sim 370 \pm 9$ Ma and $\sim 389 \pm 8$ Ma (Table S4; Fig. 10), respectively, while sample
231 17D95 records a younger age of $\sim 362 \pm 7$ Ma. However, the ages of titanite of sample 17D90
232 are scattered and younger, and have an age spectrum peak of $\sim 253 \pm 14$ Ma. When



233 considering that the U-Pb closure temperature of titanite is about 660~700 °C (Scott and
234 St-Onge, 1995) or 750~790 °C (Sun et al., 2012), the U-Pb age of the titanite (~389-370
235 Ma) possibly records the cooling / retrograde period after the peak UHP metamorphic event,
236 i.e., timing of (earlier) tectonic exhumation.

237

238 **Discussion**

239 Although no coesite or diamond was found in the Dunhuang orogenic belt, UHP
240 metamorphism of the orogen is evidenced by the garnet clinopyroxenite enclaves in a
241 limited location. However, problems concerning rock type, micropetrography and *P-T*
242 computation should be discussed in detail, in order to trustfully demonstrate the UHP
243 metamorphism.

244 *About the rock type*

245 It is well known that skarn or calcsilicate always consists of Ca-rich minerals
246 including garnet, diopside, wollastonite, scapolite, vesuvianite, calcite, quartz, and the
247 garnet is mainly consisting of andradite and grossular components (e.g., Ryan-Davis et al.,
248 2019; Alaminia et al., 2020). However, the garnet clinopyroxenite reported in this work is
249 obviously not skarn or calcsilicate, because both the mineral assemblages and chemical
250 composition of the garnet undoubtedly do not match that of skarn or calcsilicate.

251 The clinopyroxene of this work is essentially Na₂O-Al₂O₃-deficient (Na₂O < 0.35
252 wt%, Al₂O₃ < 3.0 wt%) and the jadeite phase component of clinopyroxene is negligible.
253 Therefore, although chemical compositions of the garnet and clinopyroxene somewhat
254 overlap that of mantle xenolith and eclogite, the present garnet clinopyroxenite is neither
255 mantle xenolith nor mantle eclogite or crustal eclogite. Furthermore, the prograde



256 assemblage (M1) clearly indicates the subduction process. It is therefore suggested that the
257 protolith of the garnet clinopyroxenite might be subducted to very deep but different depths
258 and thus record clockwise P - T paths (Fig. 9).

259 *UHP metamorphism evidenced by reaction textures*

260 The rocks contain high-Al titanite enclosed in the garnet and preserve three groups of
261 aligned rutile lamellae exsolved from within the garnet (Fig. 6). But, it is noted that high-
262 Al titanite also appears in low- P metamorphic rocks (e.g., Enami et al., 1993; Castelli and
263 Rubatto, 2002), and the activity of F and bulk-rock composition also affect the Al and F
264 contents of titanite (Franz and Spear, 1985; Enami et al., 1993; Carswell et al., 1996).
265 However, the low- P rocks they reported are essentially skarn, which contains considerable
266 calcite, and contains negligible pyrope in garnet. Furthermore, there are no aligned rutile
267 lamellae in the garnet of their skarn. Castelli and Rubatto (2002) suggest that if there are
268 appropriate bulk compositions with high fluorine activities, high-Al titanite could also be
269 formed at high- T rather than high- P conditions. However, their modeling is based on the
270 carbonate (CaO-TiO₂-SiO₂-H₂O-CO₂) system, quite different from our samples. In
271 addition, the An-rich plagioclase can impede the stabilization of high-Al titanite (Oberti et
272 al., 1991), thus the occurrence of anorthite in prograde assemblages indicates that high-Al
273 titanite formed during peak metamorphism, coexisting with garnet.

274 However, except for UHP metamorphism, the rutile lamellae exsolved from within
275 the garnet could also be formed at high- T conditions (>900 °C, especially in high- P
276 granulite) (e.g., Snoeyenbos et al., 1995), actually the Al content of titanite increases with
277 P and decreases with T (Smith, 1980, 1981, 1988). In this regard, in spite of the peak high-
278 T condition, the effect of P should still play a major role.



279 ***UHP metamorphism confirmed by valid geothermobarometers***

280 For estimating metamorphic P - T conditions of garnet clinopyroxenite, the garnet-
281 clinopyroxene geothermometer and the garnet-clinopyroxene geobarometer are quite
282 necessary and are in fact irreplaceable. As we know, at least 30 versions of the garnet-
283 clinopyroxene Fe-Mg exchange geothermometer have been calibrated in the past five
284 decades. The most recent Nakamura (2009) thermometer was calibrated based on data
285 collected from the literature of phase equilibrium experiments in mafic and ultramafic
286 systems, and the standard error is relatively small (± 74 °C) in reproducing all the available
287 experimental data, in the experimental P - T ranges 800~1820 °C / 15~75 kbar (Nakamura,
288 2009). On the contrary, previous formulations of the garnet-clinopyroxene geothermometer
289 are inconsistent with the compiled experimental data set, and they either underestimate T_s
290 by about 100 °C when $T > 1300$ °C or overestimate T_s by 100~200 °C when $T < 1300$ °C
291 (Nakamura, 2009). Furthermore, former garnet-clinopyroxene geothermometers tend to
292 overestimate T_s for high-Ca garnet ($X_{grs} = 0.30\sim 0.50$), as found by Nakamura (2009).
293 Therefore, because of its wide representative and relatively high accuracy, the Nakamura
294 (2009) geothermometer was adopted in this paper. It should be stated that grossular
295 component of the garnet ranges between 0.17~0.32, and chemical compositions of garnet
296 and clinopyroxene fall within the calibration range of this geothermometer, therefore,
297 certifies its applicability in these samples.

298 As for estimating metamorphic P_s of the samples, except for one garnet-
299 clinopyroxene geobarometer calibrated based on Ca-Mg exchange between garnet and
300 clinopyroxene (Brey et al., 1986) in the CMAS system for magnesian garnet ($X_{pyr} > 0.8$),
301 all the other garnet-clinopyroxene geobarometers (Mukhopadhyay, 1991; Simakov and



302 Taylor, 2000; Simakov, 2008; Beyer et al., 2015) were calibrated based on net-transfer
303 model reactions between garnet and clinopyroxene, involving grossular and pyrope
304 components in garnet and diopside, as well as Ca-tschermak and enstatite components in
305 clinopyroxene. These garnet-clinopyroxene geobarometers are made in the mafic or
306 ultramafic system, and are applicable to mantle eclogite with high-Na clinopyroxene, or
307 garnet clinopyroxenite with low-Na clinopyroxene which is the case for rocks reported in
308 this work (Na in Cpx < 0.02, based on 6 O basis). In the computation, we don't need
309 activities of either jadeite or acmite phase components in clinopyroxene and therefore,
310 errors of chemical compositions of low-Na clinopyroxene do not translate to larger pressure
311 errors in applying these geobarometers. Among different versions of the garnet-
312 clinopyroxene geobarometers, the Beyer et al. (2015) barometer was calibrated based on
313 phase equilibrium experimental data in the P - T ranges of 2~7 GPa / 900~1550 °C. Standard
314 error of this barometer is approximately ± 4 kbar (Beyer et al., 2015), and this barometer
315 was applied to our samples because it is the most accurate version and chemical
316 compositions of our mineral samples are similar to the experimental run products.

317 It should be stated that for our garnet and clinopyroxene, the Cr_2O_3 components are
318 negligible (garnet, 0.02~0.04 wt%; clinopyroxene, 0.02~0.04 wt%), therefore, the Cr_2O_3 -
319 based garnet-clinopyroxene geobarometers (Mercier, 1980; Taylor and Nimis, 1998; Nimis
320 and Taylor, 2000) cannot be applied.

321 The yielded P - T conditions of peak metamorphism lie in the UHP metamorphic region
322 for samples 17D95, 17D90 and 17D80, or high- P region for sample 17D78 which lies
323 slightly lower than the coesite-quartz transition curve (Fig. 9). However, when considering



324 error (± 4 kbar) of the garnet-clinopyroxene geobarometer (Beyer et al., 2015), it can be
325 concluded that peak metamorphism occurred at UHP conditions for all the samples.

326 *Possible fast exhumation of the UHP metamorphic rocks*

327 It is generally believed that UHP rocks should experience fast tectonic exhumation
328 from the depth, otherwise the UHP assemblages may be replaced by lower- P assemblages.
329 Thus, when considering the closure temperatures (660~700 °C, Scott and St-Onge, 1995;
330 or 750~790 °C, Sun et al., 2012) of the U-Pb system of titanite which are slightly lower
331 than the peak metamorphic temperatures (790~920 °C), SIMS U-Pb dating of metamorphic
332 titanite possibly records the ages (~389-370 Ma) of tectonic exhumation, postdating but
333 very approaching the peak metamorphism. In fact, the metamorphic P - T paths of the garnet
334 clinopyroxenite (Fig. 9) also suggest relatively rapid uplift, albeit the retrograde P - T paths
335 are hybrid of the western Alpine and Franciscan types (Ernst, 1988). Furthermore, large
336 gaps of the peak metamorphic pressures among these samples suggest that these rocks were
337 subducted to different depths and were later amalgamated at the same crustal level during
338 tectonic exhumation.

339 Although the UHP rocks were found within a limited granitic pluton, however, it is
340 reasonable to infer that other UHP rocks, either more or less, are buried in the root of the
341 Dunhuang orogenic belt. Furthermore, it is found both medium and high P / T facies series
342 metamorphism occurred in this orogen in the Silurian to Devonian (Wang et al., 2017a, b,
343 2018a, b; Zhang et al., 2020). The UHP garnet clinopyroxenite reported in this contribution
344 further demonstrates that different metamorphic P / T facies series may prevail in a same
345 orogenic belt, which is neglected to different extent in the past.

346



347 **Conclusion**

348 Three to four stages of metamorphic mineral assemblages are preserved in the garnet
349 clinopyroxenite enclaves within a granitic pluton in the northeast Paleozoic Dunhuang
350 orogenic belt, northwest China. The peak metamorphism (870~920 °C / 32~41 kbar)
351 occurred in the coesite or even the diamond stability field, and the concurrence of the high-
352 Al titanite and at least three groups of aligned rutile lamellae exsolved from within the
353 garnet further confirm the UHP metamorphic event. Clockwise metamorphic *P-T* paths of
354 the garnet clinopyroxenite were retrieved, indicative of subduction process. SIMS U-Pb
355 dating of metamorphic titanite indicates that the tectonic exhumation of the ultra-high
356 pressure metamorphic rocks might occurred in the Devonian (~389-370 Ma), postdating
357 the peak UHP metamorphism. It should be noted that both medium- and high-*P/T* facies
358 series metamorphism occurred in this Paleozoic orogen. Furthermore, it is reasonable to
359 infer that most of the UHP rocks are buried in depth, possibly in the root of this orogen.

360

361 *Data availability.* The data set is given in Supplement.

362

363 *Supplements.* The supplement related to this article is available online at:

364

365 **Figure S1.** Classification of clinopyroxene in different samples (classification of
366 Morimoto, 1988).

367 **Figure S2.** EPMA analytical transverses of clinopyroxene (sample 17D78).

368

369 **Figure S3.** EPMA analytical transverses of clinopyroxene (sample 17D80).|

370

372 **Figure S4.** EPMA analytical transverses of clinopyroxene (sample 17D90).|

373 **Figure S5.** EPMA analytical transverses of clinopyroxene (sample 17D95).



374 **Figure S6.** Backscattered electron images of titanite separated from garnet clinopyroxenite
375 samples for SIMS U-Pb dating. (a) Sample 17D78. (b) Sample 17D95. (c) Sample 17D90.
376 The circles with red figures represent analytical spots. The yellow numbers are the
377 respective ^{207}Pb -based common lead corrected ages involved in the calculation for samples
378 17D78 and 17D90, while the white and yellow numbers are the respective ^{207}Pb -based
379 common lead corrected ages both involved in the calculation for sample 17D95, and
380 obtained the younger and older mean ages, respectively.

381 **Table S1.** Chemical compositions of the representative minerals.

382 **Table S2.** Chemical compositional profiles of the garnet.

383 **Table S3.** Chemical compositional profiles of the clinopyroxene.

384 **Table S4.** SIMS U-Th-Pb analytical data for titanite separated from garnet clinopyroxenite.

385

386 *Author contributions.* Chun-Ming Wu and Hao Y.C. Wang guided the field work, they
387 and Zhen M.G. Li, Qian W.L. Zhang and Meng-Yan Shi did the field investigation. Zhen
388 M.G. Li, Qian W.L. Zhang and Jia-Hui Liu carried all the experiments. Zhen M.G. Li, Jun-
389 Sheng Lu, Qian W.L. Zhang and Jia-Hui Liu processed the data. Zhen M.G. Li drew all
390 the figures. Zhen M.G. Li and Chun-Ming Wu wrote the original manuscript and all the
391 authors revised the manuscript and proved submission of it.

392

393 *Competing interests.* The authors declare that they have no conflict of interest.

394

395 *Acknowledgements.* Professor Yonghong Shi and Dr. Juan Wang guided the authors in
396 electronic microprobe analysis. We thank Professor Qiu-Li Li and Dr. Xiao-Xiao Ling for



397 their assistance in SIMS U-Pb dating of titanite at Institute of Geology and Geophysics,
398 Chinese Academy of Sciences, China.

399

400 *Financial support.* This work was supported by the National Natural Science Foundation
401 of China (41730215) and the Key Research Program of Frontier Sciences from the Chinese
402 Academy of Sciences (QYZDJ-SSW-DQC036).

403

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643 **TABLE 1.** PRESSURE-TEMPERATURE (P-T) CONDITIONS RETRIEVED FOR
644 THE DIFFERENT METAMORPHIC STAGES OF GARNET CLINOPYROXENITE

Sample	Prograde assemblage (M1)			Peak assemblage (M2)			Retrograde assemblage (M3)		
	<i>T</i> (°C)	<i>P</i> (kbar)	Method	<i>T</i> (°C)	<i>P</i> (kbar)	Method	<i>T</i> (°C)	<i>P</i> (kbar)	Method
17D78	662	5.4	Hbl	789	28	GC ₁₂	621	4.6	Hbl
17D80	-	-		902	38.2	GC ₁₂	656	5.4	Hbl
17D90	695	7.2	Hbl	868	31.8	GC ₁₂	669	6	Hbl
17D95	-	-		918	41.3	GC ₁₂	631	5.6	Hbl

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646 Note: Geothermobarometry symbols are given in footnotes.
647 Hbl is the monomineralogic hornblende geothermobarometers (Gerya et al., 1997).
648 GC12 is the garnet-clinopyroxene geothermometer (Nakamura, 2009) coupled with the
649 garnet-clinopyroxene geobarometer (Beyer et al., 2015).

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Figure Captions

665 **Figure 1.** (A) Sketch map showing the Central Asian orogenic belt and adjacent
666 cratons (modified after Han et al., 2015). (B) Tectonic sketch of the Dunhuang orogenic
667 belt and its surrounding tectonic units (modified after Zhang et al., 2017).

668 **Figure 2.** Tectonic sketch of the Dunhuang orogenic belt (modified after Lu et al.,
669 2006; Zhang et al., 2017).

670 **Figure 3.** (A) Geologic map of the Mt. Sanweishan area (modified after 1:1,000,000
671 geological map of Gansu Province). (B) Geological map of the granitic pluton.

672 **Figure 4.** Outcrops of the garnet clinopyroxenite.

673 **Figure 5.** Micropetrography of the garnet clinopyroxenite. Subscripts 1, 2, 3 and 4
674 refer to the prograde (M1), metamorphic peak (M2), first retrograde (M3) and final
675 retrograde (M4) minerals, respectively. The dashed red arrow refers to electron microprobe
676 analytical profile of garnet. Mineral abbreviations are after Whitney and Evans (2010). (A)
677 The prograde assemblage (M1) is the tiny inclusions $Hbl_1 + Ilm_1$ preserved in the garnet
678 interior. The peak metamorphic assemblage (M2) consists of $Grt_2 + Cpx_2 + Ilm_2$. The first
679 retrograde assemblage (M3) is the symplectic $Hbl_3 + Pl_3$ intergrowth formed in between
680 the matrix Grt_2 and Cpx_2 . (B) Besides the M1, M2 and M3 assemblages similar to that in
681 (a), the Cpx_2 rim partially retrograded to Hbl_3 . (C) The symplectic assemblage (M3) Hbl_3
682 + Pl_3 formed in between the matrix Grt_2 and Cpx_2 . (D) The retrograde assemblage (M3)
683 $Hbl_3 + Pl_3 + Bt_3$ formed both in the Grt_2 interior and in between the matrix Grt_2 and Cpx_2 ,
684 and the retrograde Chl_4 formed from the Hbl_3 rim. (E) The retrograde minerals Pl_3 , Ilm_3
685 and Ttn_3 lamellae (M3) exsolved from within the Cpx_2 . (F) The Cpx_2 rim retrograded to
686 Hbl_3 . (G) Most of the Rt_2 retrograded to Ilm_3 . (H) The Grt_2 was almost completely



687 retrograded to $Hbl_3 + Pl_3$, and Act_4 formed from the Hbl_3 rim. (I) The Hbl_3 and Ilm_3
688 lamellae (M3) exsolved from within the Cpx_2 .

689 **Figure 6.** Micropetrographic evidences of UHP metamorphism. (A) High-Al titanite
690 enclosed in garnet porphyroblast. (B) High-Al titanite rimmed by ilmenite and hornblende
691 within garnet porphyroblast. (C-D) At least three groups of rutile lamellae (the needles)
692 exsolved from within the garnet. (E) Idiomorphic multiple-phase inclusion of spinel (Spl)
693 + tremolite (Tr) ± rutile (Rt) within garnet. (F) Idiomorphic hexagon ilmenite separated by
694 high-Al titanite from midcourt line in garnet.

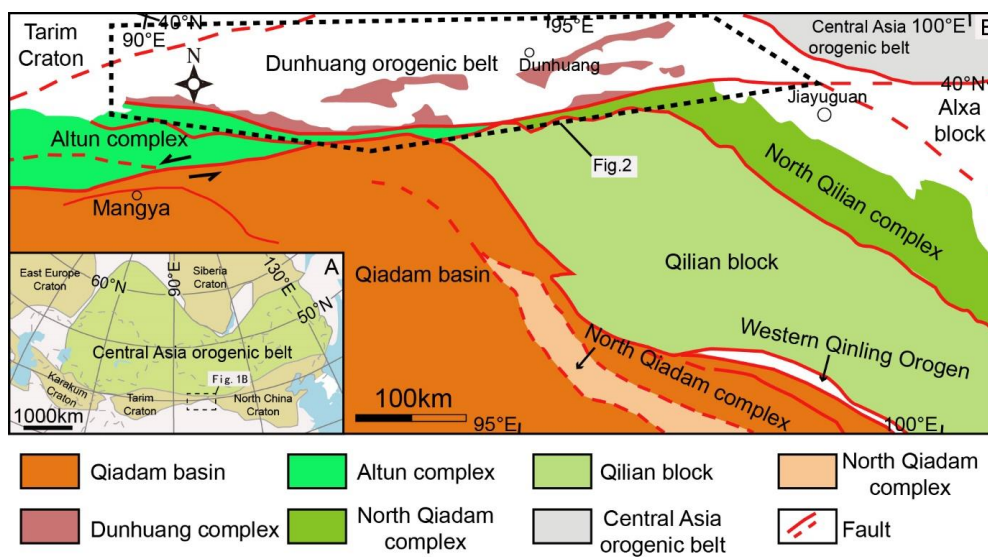
695 **Figure 7.** X-ray compositional mapping of MnO, MgO, FeO, and CaO components
696 of representative garnet porphyroblast in samples 17D80, 17D90, and 17D95.

697 **Figure 8.** Chemical compositional profiles of the garnet porphyroblast in samples
698 17D78, 17D80, 17D90, and 17D95.

699 **Figure 9.** Metamorphic *P-T* paths of the four garnet clinopyroxenite samples. The
700 boundaries of metamorphic facies and metamorphic facies series are taken from O'Brien
701 and Rötzler (2003) and Spear (1993), respectively. The diamond = graphite and quartz =
702 coesite polymorph transition curves are taken from Kennedy and Kennedy (1976) and Bose
703 and Ganguly (1995), respectively.

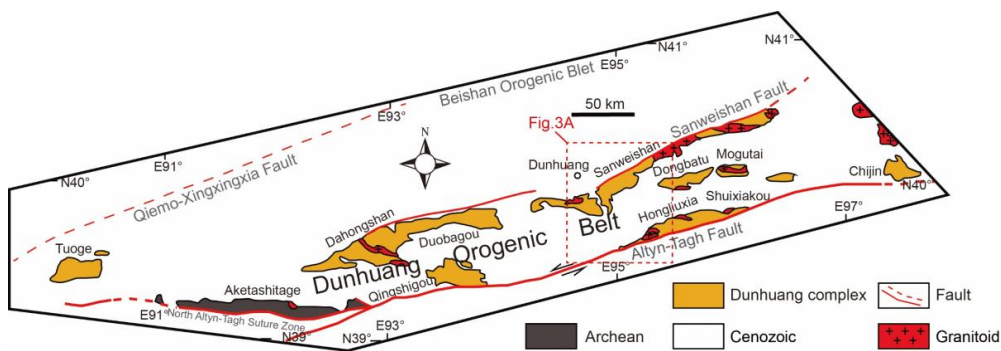
704 **Figure 10.** U-Pb concordia diagram of analyzed titanite separated from the garnet
705 clinopyroxenite samples 17D78, 17D95 and 17D90. Data are plotted at 2σ level, and
706 uncertainties on lower intercept ages are on the 95% confidence.
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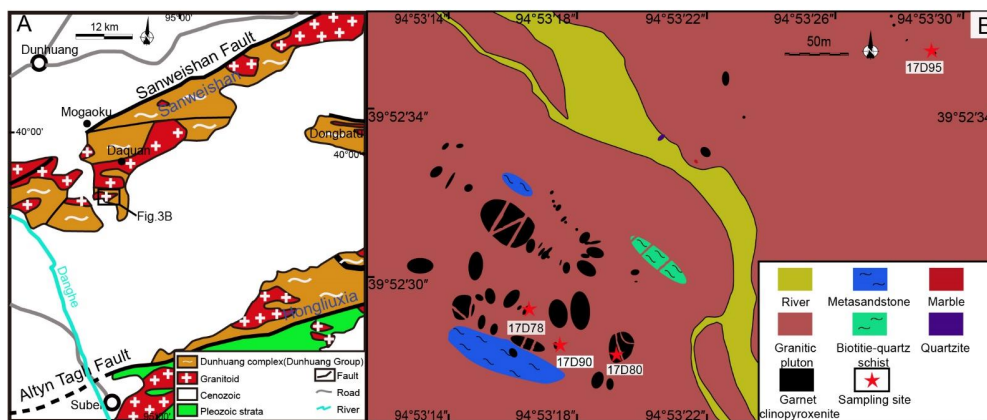
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Figure 1



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Figure 2



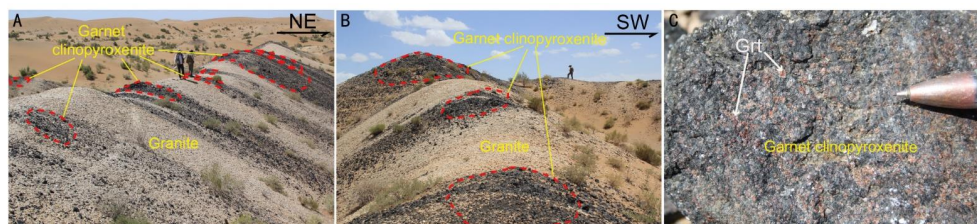
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Figure 3



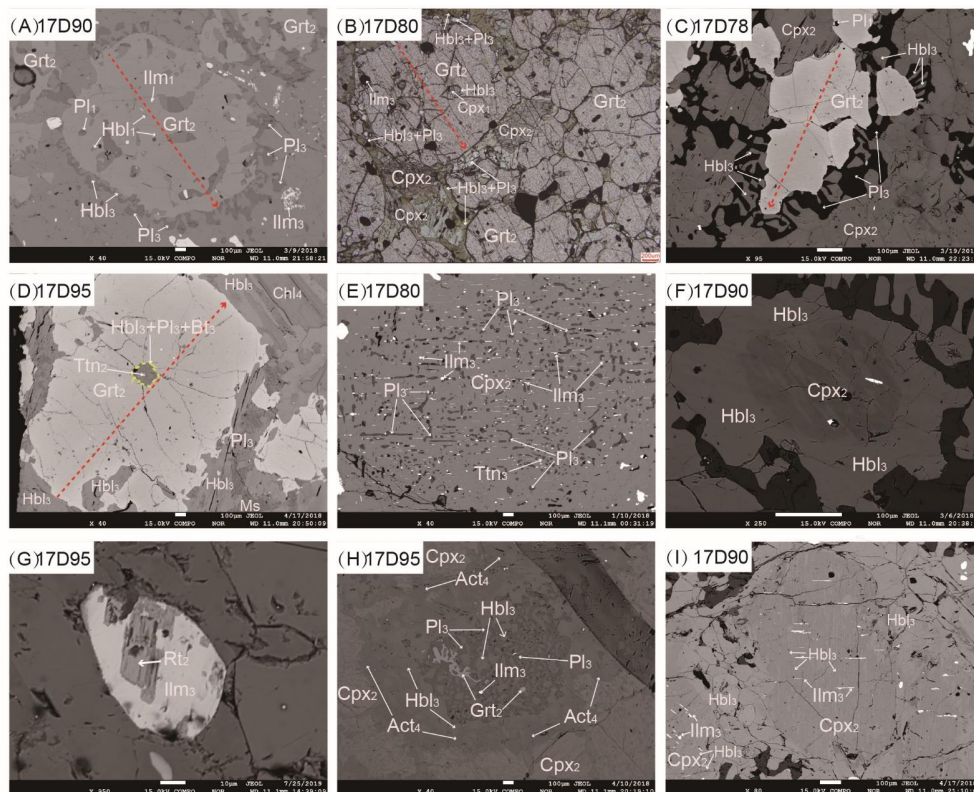
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Figure 4



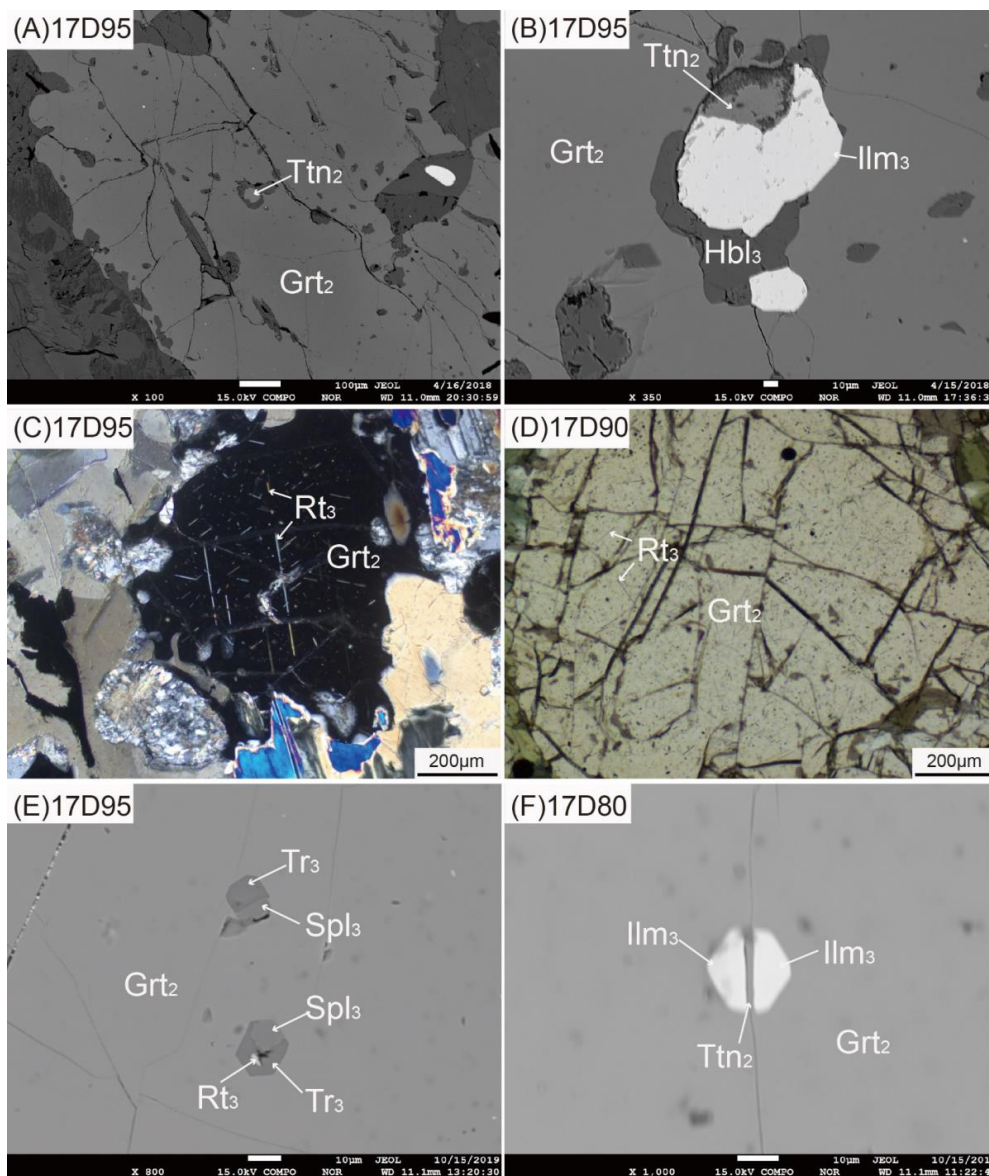
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Figure 5



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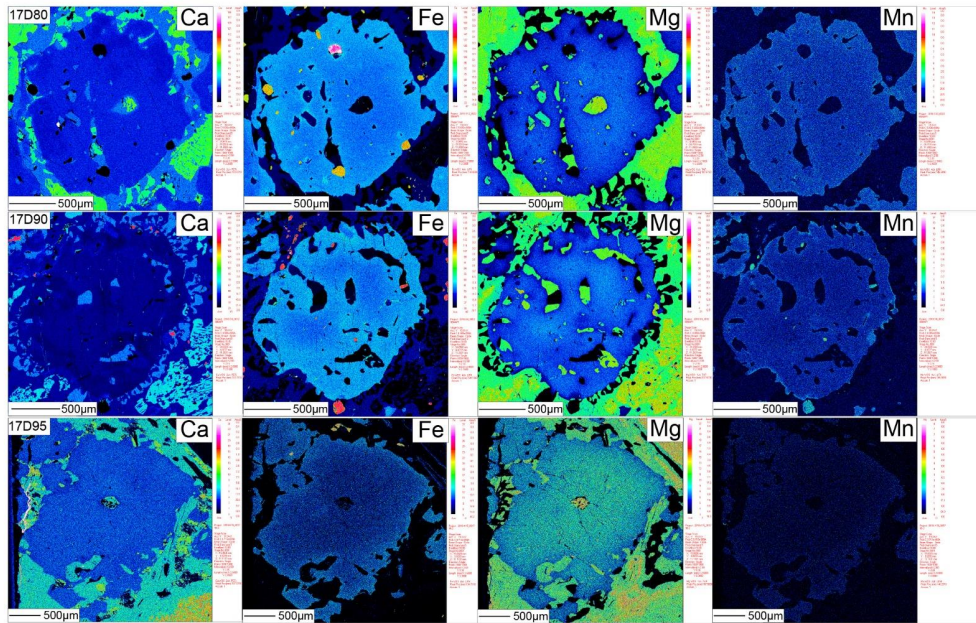
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Figure 6



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Figure 7

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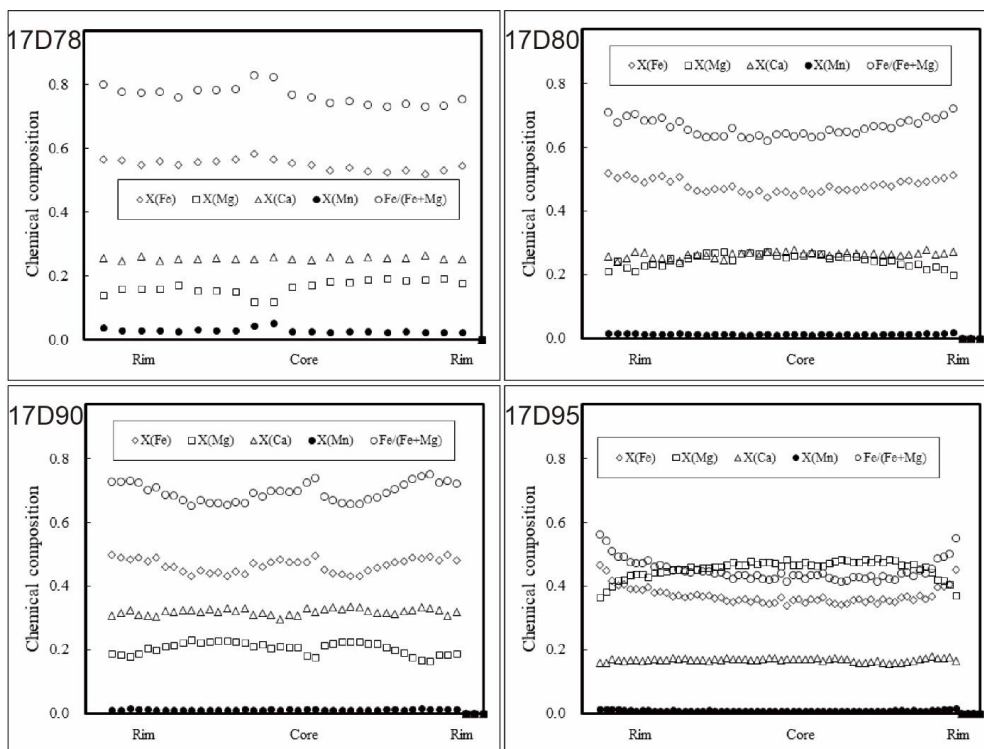
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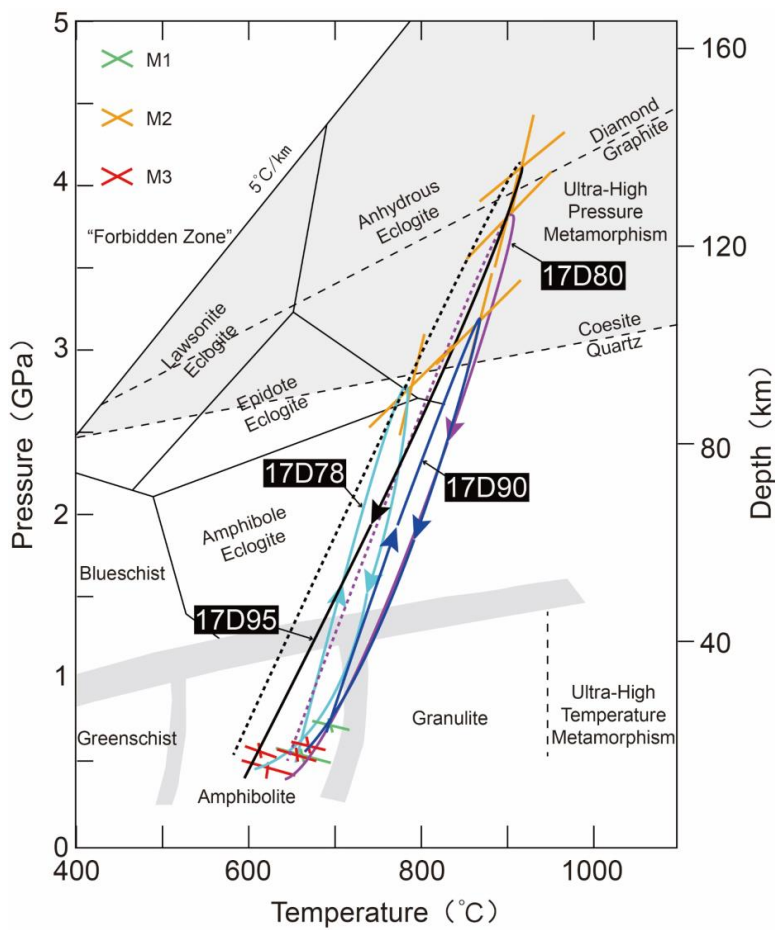
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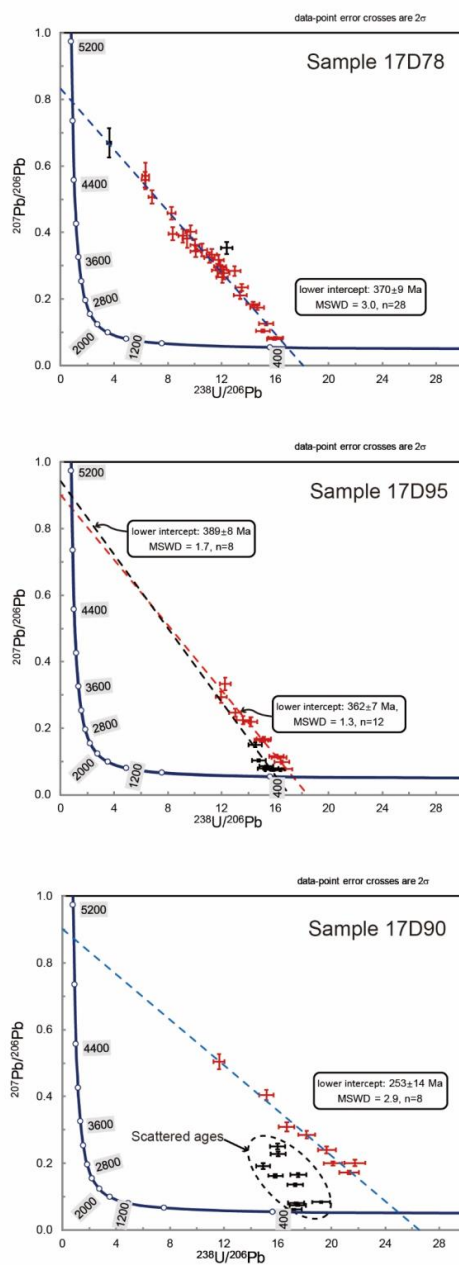
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Figure 8



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Figure 9



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Figure 10