Article

Ultra-High Pressure Metamorphism and Geochronology of Garnet Clinopyroxenite in the Paleozoic Dunhuang Orogenic Belt, Northwestern China

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Abstract: Ultra-high pressure (UHP) metamorphism is recorded by garnet clinopyroxenite enclaves enclosed in an undeformed, unmetamorphosed granitic pluton, northeastern Paleozoic Dunhuang orogenic belt, northwestern China. The protoliths of the garnet clinopyroxenite might be basic or ultrabasic volcanic rocks. Three to four stages of metamorphic mineral assemblages have been found in the garnet clinopyroxenite, and clockwise metamorphic pressure–temperature (*P*–*T*) paths were retrieved, indicative of metamorphism in a subduction environment. Peak metamorphic *P*–*T* conditions (790–920 °C/28–41 kbar) of garnet clinopyroxenite suggest they experienced UHP metamorphism in the coesite- or diamond-stability field. The UHP metamorphic event is also confirmed by the occurrence of high-Al titanite enclosed in the garnet, along with at least three groups of aligned rutile lamellae exsolved from the garnet. Secondary ion mass spectrometry (SIMS) U–Pb dating of metamorphic titanite indicates that the post-peak, subsequent tectonic exhumation of the UHP rocks occurred in the Devonian period (~389–370 Ma). These data suggest that part of the Paleozoic Dunhuang orogenic belt experienced UHP metamorphism, and diverse metamorphic facies series prevailed in this Paleozoic orogen. It can be further inferred that most of the UHP rocks in this orogen remain buried.

Keywords: Dunhuang Orogenic Belt; garnet clinopyroxenite; geochronology; high-Al titanite; rutile lamellae; *P*–*T* path; ultra-high pressure metamorphism

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1. Introduction

It is well known that the ultra-high pressure (UHP) metamorphism is anticipated to be formed during subduction at very low thermal gradient, usually less than 10 °C/km, or even as low as ~5 °C/km, which refers to metamorphic pressure high enough to stabilize coesite [1,2]. Together with coesite, other diagnostic minerals such as coesite, diamond [3,4], Na–Ti–P-bearing garnet [5], or pseudomorph of stishovite [6,7] also certify UHP metamorphism, which usually requires ultra-deep subduction and subsequent rapid exhumation. However, these diagnostic minerals do not appear in some orogenic belts, which in turn brings people some doubts if such orogenic belts experienced UHP metamorphism.

The Dunhuang area has long been considered as an ancient stable block formed in the Precambrian [8,9]. Until recently, clockwise metamorphic pressure–temperature (*P*–*T*) paths of eclogite, mafic granulite, amphibolite, and metapelite, typical metamorphic products of subduction setting, were retrieved elsewhere in this region [9–19], and the metamorphic event was dated to occur from Silurian to Devonian periods [10,11,14–19]. These enabled people to believe that this area was a Paleozoic orogenic belt [13,15–19]. Eclogite [15] and high-pressure (HP) mafic granulite [10,11,14–16,18,19] have been found in this orogen, but

UHP rocks have not been discovered before, which in turn limits our understanding of the orogenic process as a whole. The recognition of UHP metamorphism is challenging because the presence of minerals formed under such conditions in some orogenic belts is possible but requires appropriate physical–chemical conditions for their formation and preservation and a mechanism(s) for their exhumation.

In this contribution, we present a comprehensive study of field investigation, petrology, geothermobarometric computation, and secondary ion mass spectrometry (SIMS) U-Pb dating of titanite for garnet clinopyroxenite in the Daquan area, northeastern Dunhuang orogenic belt, to obtain their *P-T* paths and certify UHP metamorphism in this Paleozoic orogenic belt.

2. Regional Geology

The Dunhuang orogenic belt strikes WSW-ENE and covers an area of approximately 440 km long and 100 km wide (Figure 1A,B). It is tectonically bordered by the Paleozoic Beishan orogenic belt to the north, the Precambrian Tarim Craton to the west, the Precambrian Alexa Block to the east, and the Paleozoic Altyn Tagh-Qilian orogenic belt to the south [20] (Figure 1A). The Dunhuang orogenic belt was dismembered by sinistral strike-slip faults to several tectonic blocks [20,21] (Figure 1B), possibly in the late Cenozoic [22]. The prominent characteristics of the Dunhuang orogenic belt are that at least in the Hongliuxia, Qingshigou, Kalatashitage, and Mogutai-Dongbatu tectonic blocks, eclogite, high- and medium-pressure mafic granulite, and amphibolite occur as rootless tectonic lenses or puddings enclosed within the metapelite and metasandstone matrix [14,15,17–19], indicative of typical block-in-matrix features of tectonic mélanges [23]. Some closely amalgamated tectono-metamorphic slices can also be found in the northwestern Dunhuang orogenic belt, which were metamorphosed at different depths and were later juxtaposed in the same crustal level during tectonic exhumation [19].

Recently, we found high-Al titanite-bearing garnet clinopyroxenite and obtained UHP *P-T* conditions of such rocks in the Daquan area, northeastern Dunhuang orogenic belt (Figure 1C). Garnet clinopyroxenite occurs as enclaves enclosed in an undeformed, unmetamorphosed granitic body, or as enclaves within paragneiss, which themselves are also enclosed in the granitic body (Figure 1D). The boundary between these metamorphic rocks and the host granitic body is clear and sharp (Figure 1D–F). However, the crystallization age of the granitic body cannot be determined due to severe decrystallization of magmatic zircon of this granitic body caused by radioactive damage.

Figure 1. (A) Tectonic sketch of the Dunhuang orogenic belt and its surrounding tectonic units (modified after Zhang et al. [20]). (B) Tectonic sketch of the Dunhuang orogenic belt (modified after Zhang et al. [20] and Lu et al. [21]). (C) Geological map of the Sanweishan area (modified after 1:1,000,000 geological map of Gansu Province). (D) Geological map of the study area (based on our fieldwork). (E,F) Field images of the garnet clinopyroxenite puddings enclosed in the granitic body. (G) Hand specimen of garnet clinopyroxenite with garnet porphyroblasts.

3. Petrography

In this study, we target garnet clinopyroxene puddings enclosed in the granitoids (Figure 1D). Retrograde symplectite rimming the embayed, relict garnet of the garnet clinopyroxene can be easily seen in the outcrop (Figure 1G). Micropetrographic features of the garnet clinopyroxene are depicted in Figures 2 and 3. Three to four stages of metamorphic mineral assemblages were found in the four representative samples. The mineral abbreviations are from Whitney and Evans [24], and the subscripts of the minerals 1, 2, 3, and 4 refer to the corresponding minerals formed at the sequential four metamorphic stages, respectively, throughout this paper.

All four samples are mainly biminerally, consisting of garnet and clinopyroxene. The prograde assemblage (M1) is represented by the fine-grained ilmenite (Ilm₁) + plagioclase (Pl₁) ± hornblende (Hbl₁) ± clinopyroxene (Cpx₁) ± rutile (Rt₁) inclusions enclosed in the garnet (Grt₂) (Figure 2A–D). High-Al titanite (Ttn₂) also appears as inclusion within garnet (Figure 2E and Figure 3A,B). The peak metamorphic assemblage (M2) consists of garnet (Grt₂) and clinopyroxene (Cpx₂), plus matrix minerals including minor rutile (Rt₂), high-Al titanite (Ttn₂), and apatite (Ap₂). The matrix rutile (Rt₂) is rare and was severely retrograded to ilmenite (Figure 2F,G). The retrograde assemblage (M3) is mainly the worm-like symplectite, consisting of fine-grained plagioclase (Pl₃), hornblende (Hbl₃), and ilmenite (Ilm₃) intergrowth, rimming the garnet (Figure 2A,C,H). Similar decomposition textures in mafic granulite can be found elsewhere in this orogen and are repeatedly demonstrated to be formed by nearly isothermal decompression (ITD) during tectonic exhumation [14–16,18,19]. Other retrograde assemblages (M3) include fine-grained ilmenite (Ilm₃) ± plagioclase (Pl₃) ± hornblende (Hbl₃) ± titanite (Ttn₃) lamellae exsolved from within the clinopyroxene (Cpx₂) (Figure 2I,J), hornblende (Hbl₃) retrograded from clinopyroxene (Cpx₂) (Figure 2K), ilmenite (Ilm₃) retrograded from rutile (Rt₂) (Figure 2F,G), ilmenite (Ilm₃) retrograded from high-Al titanite (Ttn₂) (Figure 3B), and ilmenite (Ilm₃) + hornblende (Hbl₃) symplectite formed from an unknown precursor (might be high-Al titanite or rutile, Figure 2L), as well as aligned rutile lamellae (Rt₃) exsolved from within the garnet in three different directions (Figure 3C,D). Occasionally, the final retrograde assemblage (M4) can be found, i.e., actinolite (Act₄) and chlorite (Chl₄) retrograded from hornblende (Hbl₃) (Figure 2H). In sample 17D95, minor spinel (Spl₃) can be found, and it mainly coexists with tremolite (Tr₃) ± rutile (Rt₃) as idiomorphic retrograded phases within the garnet (Figure 3E). It was possibly exsolved from within garnet, similar to the clinopyroxene exsolved from within the garnet in eclogite from Sulu orogenic belt, eastern China [5]. Such inclusion-like minerals were in fact decomposed from garnet [25]. In sample 17D80, there is idiomorphic hexagon ilmenite (Ilm₃) in garnet and is separated by high-Al titanite (Ttn₂) from centerline (Figure 3F). Such reaction textures are similar to those in granulite facies metapelite and may represent extremely high-*P* or high-*T* conditions [26].

Figure 2. Micropetrography of the garnet clinopyroxenite. Subscripts 1, 2, 3, and 4 refer to the prograde (M1), metamorphic peak (M2), first retrograde (M3), and final retrograde (M4) minerals, respectively. The dashed red arrow refers to the electron microprobe analytical profile of garnet. Mineral abbreviations are after Whitney and Evans [24]. (A) The prograde assemblage (M1) is the tiny inclusions $Pl_1 + Hbl_1 + Ilm_1$ preserved in the garnet interior. The peak metamorphic assemblage (M2) consists of $Grt_2 + Cpx_2$. The first retrograde assemblage (M3) is the symplectic $Hbl_3 + Pl_3$ intergrowth formed in between the matrix Grt_2 and Cpx_2 . (B) Besides the M1, M2, and M3 assemblages similar to that in (A), the Cpx_2 rim partially retrograded to Hbl_3 . (C) The symplectic assemblage (M3) $Hbl_3 + Pl_3$ formed between the matrix Grt_2 and Cpx_2 . (D) Rutile (Rt_1) inclusions enclosed in garnet (Grt_2). (E) The retrograde assemblage (M3) $Hbl_3 + Pl_3 + Bt_3$ formed both in the Grt_2 interior and in between the matrix Grt_2 and Cpx_2 , and the retrograde Chl_4 formed from the Hbl_3 rim. (F) Relict rutile (Rt_2) within Ilmenite (Ilm_3). (G) Most of the Rt_2 retrograded to Ilm_3 . (H) The Grt_2 was almost completely retrograded to $Hbl_3 + Pl_3$, and Act_4 formed from the Hbl_3 rim. (I) The Hbl_3 and Ilm_3 lamellae (M3) exsolved from within the Cpx_2 . (J) The retrograde minerals Pl_3 , Ilm_3 , and Ttn_3 lamellae (M3) exsolved from within the Cpx_2 . (K) The Cpx_2 rim retrograded to Hbl_3 . (L) Ilmenite (Ilm_3) + hornblende (Hbl_3) symplectite was possibly retrograded from rutile or high-Al titanite.

Figure 3. Micropetrographic evidence of ultra-high pressure (UHP) metamorphism. (A) High-Al titanite enclosed in garnet porphyroblast. (B) High-Al titanite rimmed by ilmenite and hornblende within garnet porphyroblast. (C,D) At least three groups of rutile lamellae (the needles) exsolved from within the garnet. (E) Idiomorphic multiple-phase inclusion of spinel (Spl) + tremolite (Tr) ± rutile (Rt) within garnet. (F) Idiomorphic hexagon ilmenite separated by high-Al titanite from centerline in garnet.

4. Analytical Methods and Geothermobarometry

4.1. Major and Trace Elements Analysis

Compositional analyses of major elements, backscattered electron (BSE) images, as well as X-ray compositional mapping of minerals were determined by electron microprobe analysis (EMPA) using a JOEL JXA-8230 analyzer at the School of Resource and Environmental Engineering, Hefei University of Technology, China. The analytical conditions were 15 kV accelerating voltage and 20 nA beam current and the counting time was 10–20 s. Usually, 3–5 μm electron beam diameter was used, while 3 μm electron beam size was only adopted in analyzing the tiny minerals. Natural minerals were used as standards, and the ZAF program was utilized for matrix corrections. Generally, at least 3–5 grains were analyzed for any representative mineral, and 1–60 spots of each grain were probed. Ferric iron contents of both clinopyroxene and garnet were determined by stoichiometric and charge balance criteria [27], while ferric iron content of hornblende was evaluated by the method of Holland and Blundy [28].

Zirconium concentration in titanite was obtained using Agilent 7900 ICP-MS connected to a resolution LR laser system at the Tianjin Institute of Geology and Mineral

Resources, Chinese Academy of Geological Sciences, China. Laser spot size and frequency were 43 μm in diameter and 6 Hz, respectively. Laser energy density was 3 J/cm². The trace element content of the titanite was calibrated externally by the glass standard SRM 610, and ⁴³Ca (19.25%) was used for the internal standard. Meanwhile, the data quality was monitored by the glass standard SRM 612, the titanite MKED-1 and the titanite OLT-1. Two sets of calibration and monitoring standards were inserted every 8 sample points. The data was processed by ICPMSDATA version 10.9.

Zirconium concentration in rutile was analyzed by a JEOL JXA-8230 electron microprobe analyzer (EMPA) at the Institute of Mineral Resources, Chinese Academy of Geological Sciences, Beijing, China. Accelerating voltage was set at 15 kV with 100 nA beam current and 1–5 μm beam spot. Counting times for Zr, Nb, Cr, and Fe were 200, 200, 100, and 60 s, respectively. Spectroscopic crystals for Zr, Nb, Cr, and Fe were PETH, PETJ, LIFJ, and LIFJ, respectively (corresponding detection limits: 13, 18, 21, and 18 ppm). A ZrO₂ standard was used to calibrate the peak position of Zr, and synthetic rutile was used to inspect the zero-concentration of Zr at the beginning, the middle, and the end of each sequence. Analytical errors were about ± 15 ppm at 1 σ level according to counting statistics [29].

The whole rock major and trace element analyses were performed at the Australian Laboratory Services (ALS), Guangzhou, China, with their analytical method codes of ME-XRF26d and ME-MS81, respectively.

4.2. SIMS U-Pb Dating of Titanite

No zircon was found in these samples, possibly due to SiO₂-undersaturated bulk composition of these rocks. Therefore, SIMS U-Th-Pb dating of metamorphic titanite was conducted to determine the age of metamorphism. The SIMS U-Th-Pb analyses of titanite were performed using a Cameca IMS-1280HR SIMS at the Institute of Geology and Geophysics, Chinese Academy of Sciences, Beijing, China. The instrument description and analytical procedure for titanite dating are identical to that of dating perovskite [30] and have been described in detail in Li et al. [31] and Ling et al. [32], thus only a brief summary is described here. The O^{2−} primary ion beam was accelerated at ~13 kV, with an intensity of ~9 nA. The ellipsoidal spot is about 20 μm $\times$ 30 μm in size. The ⁴⁰Ca⁴⁸Ti²¹⁶O₄⁺ peak is used as a reference peak for centering the secondary ion beam, energy, and mass adjustments. A mass resolution of ~7000 (defined at 50% peak height) was used. A single electron multiplier was used in ion-counting mode to measure secondary-ion beam intensities by a peak jumping sequence, including isotopes of Pb⁺, Th⁺, U⁺, ThO⁺, UO⁺, and ⁴⁰Ca⁴⁸Ti²¹⁶O₄⁺ to produce one set of data. Analyses of the standard YQ82 titanite were interspersed with unknown grains. Each measurement consists of 15 cycles, and the total analytical time is ~19 min. Pb/U calibration was performed relative to YQ82 titanite standard (²⁰⁶Pb/²³⁸U age = 1837.6 Ma, Li et al. [33]). U and Th concentrations were calibrated against titanite BLR-1 [34]. A long-term uncertainty of 1.5% (1 σ RSD) for ²⁰⁶Pb/²³⁸U measurements of the standard titanite was propagated to the unknowns, despite that the measured ²⁰⁶Pb/²³⁸U error in a specific session is generally $\leq 1\%$ (1 σ RSD). A Tera-Wasserburg [35] plot was constructed with common lead uncorrected data to deduce the common lead composition, and then a ²⁰⁷Pb-based common lead correction method was conducted to single analysis. Data reduction was carried out using the Isoplot/Ex v. 2.49 program [36]. Uncertainties on individual analysis in data table are reported at 1 σ level. The final U-Pb age result is quoted with 95% confidence level.

4.3. Geothermobarometry

Metamorphic *P-T* conditions of the peak metamorphism (M2) were determined by the garnet-clinopyroxene geothermometer [37] coupled with the garnet-clinopyroxene geobarometer [38], using the averaged chemical composition of garnet (plateau cores) and reintegrated (Samples 17D78 and 17D80)/averaged (Samples 17D90 and 17D95) chemical composition of clinopyroxene. Although this geobarometer was experimentally calibrated

for mantle eclogite, the chemical compositions of the natural rocks reported in this work are similar to those of the experimental run products [38]. The accuracy of this geobarometer is estimated to be ± 4 kbar [38]. The prograde (M1) and retrograde (M3) assemblages mainly consist of plagioclase and hornblende but without quartz, therefore, P - T conditions of the M1 and M3 assemblages were estimated by the monomineralogic hornblende geothermobarometers, with P - T uncertainties of ± 37 °C and ± 1.2 kbar, respectively [39].

For comparison, Zr-in-titanite [40] and Zr-in-rutile [41] geothermometers were employed to determine the temperature conditions. Because the activity of the SiO_2 and ZrO_2 components cannot be determined due to the absence of quartz/coesite and zircon in these samples, we assumed a series of activities of SiO_2 (i.e., 0.01, 0.05, 0.1, and 0.2). Meanwhile, we set the activity of TiO_2 component to be unity because of the existence of rutile. Jiao et al. [42] concluded that if the assumed activity of SiO_2 and pressure are appropriate, the geothermometers of Watson et al. [43], Ferry and Watson [41] and Tomkins et al. [44] can yield similar temperatures, but the geothermometer of Zack et al. [45] usually yields higher temperatures of ~ 125 °C than others. In our case, due to severe retrogradation of matrix rutile and the marked differences of Zr concentration between rutile in the inclusion and matrix, we do not assure if the zirconium in rutile records temperatures corresponding to which pressure conditions (prograde, peak, or retrograde). It is noted that the rutile of UHP eclogite in the Dabie-Sulu orogenic belt usually records much lower peak temperatures than other geothermometers even if the pressure effects were considered. This possibly indicates zirconium content in rutile might only represent a buffering state of rutile after retrograde metamorphism in the amphibolite facies [29]. Therefore, we preferred the Zr-in-rutile geothermometer of Ferry and Watson [41], which includes the activity of SiO_2 and is unrelated to pressure. While applying the Zr-in-titanite thermometer [40], there are two possibilities. One possibility is that if titanite was formed during the retrograde stage, the input pressure for Zr-in-titanite geothermometer calculation should be that of retrograde metamorphism. Another possibility is that the titanite was retrograded from high-Al titanite, in this case, the input pressure for Zr-in-titanite geothermometer calculation should be corresponding to peak metamorphism. Due to varying zirconium concentrations in rutile, it is uncertain to what geological process the temperatures recorded by zirconium in rutile correspond. Therefore, we cannot combine these two geothermometers as suggested by Hayden et al. [40]. Instead, we input pressures of both the peak metamorphic conditions (if titanite was retrograded from high-Al titanite) and the retrograde metamorphic conditions (if titanite was newly crystallized in retrograde stage) to calculate the temperature conditions recorded by zirconium in titanite.

5. Results

5.1. Mineral Chemistry

The representative major elements of minerals are listed in Tables S1–S4, and the trace element concentrations of rutile and titanite as well as the calculated temperatures are listed in Tables S5 and S6, respectively. The garnet (Gr_2) is chemically homogeneous in each sample and is mainly consisting of almandine [$X_{\text{Alm}} = \text{Fe}^{2+}/(\text{Ca} + \text{Fe}^{2+} + \text{Mg} + \text{Mn}) = 0.34\sim 0.54$], pyrope [$X_{\text{Prp}} = \text{Mg}/(\text{Ca} + \text{Fe}^{2+} + \text{Mg} + \text{Mn}) = 0.19\sim 0.48$], and grossular [$X_{\text{Grs}} = \text{Ca}/(\text{Ca} + \text{Fe}^{2+} + \text{Mg} + \text{Mn}) = 0.18\sim 0.32$] but negligible spessartine [$X_{\text{Sprs}} = \text{Mn}/(\text{Ca} + \text{Fe}^{2+} + \text{Mg} + \text{Mn})$] components. Such garnet is chemically different from those in mantle xenolith or eclogite, which have a much higher MgO/FeO ratio and higher Cr content. Negligible chemical zonation of the garnet was found. In the very rim of the garnet, the $\text{Fe}\#$ [$= \text{Fe}/(\text{Fe} + \text{Mg})$] value increases slightly (Table S7; Figure 4 and Figure S1), indicative of post-peak Fe-Mg diffusion between the garnet rim and adjacent clinopyroxene and/or decomposition of the garnet rim [46]. This is also demonstrated by micropetrograph, in which the garnet rim was consumed and replaced by retrograde assemblages (Figure 2A,B,E).

Chemical analytical profiles (Table S8) suggest that the clinopyroxene (Cpx_2) is almost chemically homogeneous in each sample and is essentially diopside based on the classification of Morimoto [47] (Figure 5) with negligible jadeite fraction. Due to exsolution, however,

the chemical composition of individual Cpx₂ shows some variations. Although the Mg²⁺ and Fe²⁺ cations of the Cpx₂ grains are generally homogeneous, Al³⁺ and Ca²⁺ cations show somewhat variations (Figures S2–S5), thus the reintegrated chemical composition of clinopyroxene was used to estimate peak *P-T* conditions.

Figure 4. Chemical compositional profiles of the garnet porphyroblast in samples 17D78, 17D80, 17D90, and 17D95.

Figure 5. Classification of clinopyroxene in different samples (classification of Morimoto [47]).

High-Al titanite contains remarkable Al₂O₃ (8.2–10.2 wt%) and F contents (1.3–2.8 wt%) as listed in Table S4, which possibly imply high pressure to UHP metamorphism [48–51]. The titanite selected for dating and trace element analysis contains relatively lower Al₂O₃ contents (1.09–2.86%). The rutile enclosed in garnet contains much higher zirconium contents (~3003 to ~3338 ppm) than those in the matrix (which usually retrograde to ilmenite, ~13 to ~160 ppm), this phenomenon might be related to severe retrograde in matrix, which caused rutile to release the vast majority of zirconium [29].

5.2. U-Pb Dating Results of Titanite

The SIMS U-Th-Pb analytical data of titanite separated from garnet clinopyroxenite are listed in Table S9 and the BSE images of titanite are shown in Figure S6. The titanite images are homogeneous in sample 17D78, while in samples 17D90 and 17D95 titanite shows some textural variations. The resulted U-Pb ages of the metamorphic titanite from samples 17D78 and 17D95 are $\sim 370 \pm 9$ Ma and $\sim 389 \pm 8$ Ma (Figure 6), respectively, while sample 17D95 records a younger age of $\sim 362 \pm 7$ Ma. The ages of titanite of sample 17D90 are scattered and younger and have an age peak of $\sim 253 \pm 14$ Ma.

Figure 6. U-Pb concordia diagram of analyzed titanite separated from the garnet clinopyroxenite samples 17D78, 17D95, and 17D90. Data are plotted at 2σ level, and uncertainties on lower intercept ages are on the 95% confidence.

5.3. Metamorphic P-T Paths

The obtained *P-T* results are listed in Table S10. Metamorphic *P-T* path of sample 17D78 passes from 662 °C/5.4 kbar (M1) through 789 °C/28 kbar (M2) to 621 °C/4.6 kbar (M3). As for the other three samples, metamorphic *P-T* paths were estimated as follows, respectively: sample 17D80, 902 °C/38.2 kbar (M2) → 656 °C/5.4 kbar (M3); sample 17D90, 695 °C/7.2 kbar (M1) → 868 °C/31.8 kbar (M2) → 669 °C/6.0 kbar (M3); and sample 17D95, 918 °C/41.3 kbar (M2) → 631 °C/5.6 kbar (M3). The retrieved metamorphic *P-T* paths of the garnet clinopyroxenite enclaves are all clockwise (Figure 7) [52–55]. It should be stated that the peak metamorphism (except for sample 17D78) lies in the coesite or even the diamond stability field (Figure 7), implying UHP metamorphism. The UHP conditions are further supported by the occurrence of at least three groups of aligned rutile lamellae (Rt3) exsolved from within the garnet (Figure 3C,D) and chemically homogeneous high-Al titanite (Ttn₂) enclosed in the garnet (Figure 3A,B), being characterized by $X_{Al} [= Al/(Al + Fe^{3+} + Ti)] = 0.25\sim 0.29$. These two mineralogical characteristics together indicate UHP metamorphism [26,56,57].

Figure 7. Metamorphic *P-T* paths of the four garnet clinopyroxenite samples. (A) Sample 17D78. (B) Sample 17D80. (C) Sample 17D90. (D) Sample 17D95. In each figure, M1, M2, and M3 represent the prograde, peak, and retrograde metamorphism, respectively. The red dotted arrows, and their neighboring annotations and different colored ellipses represent the temperature results obtained by Zr-in-titanite geothermometer [40] with variable activities of SiO₂ (0.01, 0.05, 0.1, and 0.2). *P* = 28 kbar means that the pressure for Zr-in-titanite calculation was set as 28 kbar. The grey thick and black thin boundaries of metamorphic facies are taken from O'Brien and Rötzler [52] and Winter [53], respectively. The diamond = graphite and quartz = coesite polymorph transition curves are taken from Kennedy and Kennedy [54] and Bose and Ganguly [55], respectively.

6. Discussion

Although no coesite or diamond was found in the Dunhuang orogenic belt, UHP metamorphism of the orogen is evidenced by the garnet clinopyroxenite enclaves from the Daquan area. However, problems concerning protolith, micropetrography, *P-T* computation, and geochronology should be discussed in detail in order to assess the validity of UHP metamorphism.

6.1. Protolith of Garnet Clinopyroxenite

The Al-rich titanite was usually reported in skarn, calcsilicate, or impure marble [49,58,59], which are all calcic rocks. However, skarn or calcsilicate always consists of Ca-rich minerals including garnet, diopside, wollastonite, scapolite, vesuvianite, calcite, quartz, and the garnet is mainly consisting of andradite and grossular components [60,61]. Therefore, the garnet clinopyroxenite reported in this work is obviously not skarn or calcsilicate because both the mineral assemblages and chemical composition of the garnet undoubtedly do not match that of skarn or calcsilicate.

The geochemical features can be used to discuss the protoliths and possible tectonic setting of garnet clinopyroxenite. The geochemical properties of the four representative samples (Table S11) suggest that their protoliths were possibly sub-alkaline basalt, according to the classification diagram of Pearce [62] (Figure 8A). In the Zr versus Ti discrimination diagram (Figure 8B) of Pearce [63], two samples (17D80 and 17D90) are classified as island arc basalt (IAB) and the other two samples (17D78 and 17D95) as mid-ocean ridge basalt (MORB) in origin. From the chondrite-normalized rare earth element (REE) pattern and primitive mantle-normalized spidergram [64], two groups of different characteristics can also be seen (Figure 9). One group is represented by samples 17D78 and 17D95, another is shown by samples 17D80 and 17D90, which are consistent with the discrimination diagrams. Therefore, the garnet clinopyroxenites are possibly different in origin. However, it is noted that SiO₂ contents of the rocks are 42.2 wt% (sample 17D78), 44.2 wt% (sample 17D80), 43.6 wt% (sample 17D90), and to 47.7 wt% (sample 17D95), respectively. Consequently, we inferred that the bulk rock compositions had possibly been modified in the metamorphism, or alternatively, the rocks experienced chemical weathering or metasomatism prior to metamorphism. Meanwhile, the inclusion assemblage (M1) suggests the prograde metamorphism [65,66], in this case probably indicating early stages in the subduction process.

Figure 8. Classification of protoliths of garnet clinopyroxenite. (A) Nb/Y vs. Zr/TiO₂ plot (after Pearce [62]); and (B) Zr vs. Ti discrimination diagram (after Pearce [63]).

Figure 9. Chondrite-normalized REE patterns (A) and primitive mantle-normalized spidergrams (B) for garnet clinopyroxenites. The chondrite and primitive mantle values are from Sun and McDonough [64].

The clinopyroxene of this work is essentially Na_2O - Al_2O_3 -deficient ($\text{Na}_2\text{O} < 0.35$ wt%, $\text{Al}_2\text{O}_3 < 3.0$ wt%) and the jadeite phase component of clinopyroxene is negligible. Therefore, although the chemical compositions of the garnet and clinopyroxene somewhat overlap that of mantle xenolith and eclogite, the present garnet clinopyroxenite is neither mantle xenolith nor mantle eclogite or crustal eclogite. Instead, the protoliths might be basic or ultrabasic volcanics of different origin, which were subducted into great depths and experienced UHP metamorphism, then amalgamated into the same crustal level and captured by the granitic pluton.

6.2. UHP Metamorphism Evidenced by Reaction Textures

The rocks contain high-Al titanite enclosed in the garnet and preserve three groups of aligned rutile lamellae exsolved from within the garnet (Figure 3). However, it is noted that high-Al titanite also appears in low- P metamorphic rocks [58,59], and the activity of F and bulk-rock composition also affect the Al and F contents of titanite [49,51,58]. However, the reported low- P rocks are essentially skarn, which contains considerable calcite and also contains negligible pyrope component in garnet. Furthermore, no aligned rutile lamellae in the garnet of skarn were found. Castelli and Rubatto [59] suggested that if there are appropriate bulk compositions with high fluorine activities, high-Al titanite could also be formed at high- T rather than high- P conditions. However, their modeling is based on the carbonate (CaO - TiO_2 - SiO_2 - H_2O - CO_2) system, differently from our samples.

Actually, Frost et al. [67] suggested that the stability of titanite in metabasites is limited in certain P - T conditions, which are constrained by several reactions. Our high-Al titanite are obviously out of their prediction, and the reasons may be as follows: (1) the reactions they supposed would not occur in our bulk rock composition; (2) the P - T diagram they represented was restricted to $P < 12$ kbar and $T < 700$ °C, which show no trend in high- T and high- P domains; and (3) they only considered common titanite in metabasites but excluding high-Al titanite.

Oberti et al. [68] suggested that the An-rich plagioclase could impede the stabilization of high-Al titanite, thus the occurrence of anorthite in prograde and retrograde assemblages indicates that high-Al titanite formed during peak metamorphism, coexisting with garnet which exsolved rutile lamellae. However, except for UHP metamorphism, the rutile lamellae exsolved from within the garnet could also be formed at high- T conditions (>900 °C, especially in high- P granulite) [69]. Actually, experiments show that the Al content of titanite increases with P and decreases with T [48,70,71]. In this regard, in spite of the peak high- T condition, the effect of P should still play a major role, otherwise, Al-rich titanite should not exist in the peak assemblages.

6.3. UHP Metamorphism Confirmed by Geothermobarometers

For estimating metamorphic P - T conditions of garnet clinopyroxenite, the garnet-clinopyroxene geothermometer and the garnet-clinopyroxene geobarometer are quite irreplaceable. At least 30 versions of the garnet-clinopyroxene Fe-Mg exchange geothermometer have been calibrated in the past five decades. The most recent version of this geothermometer [37] was calibrated based on data of phase equilibrium experiments in mafic and ultramafic systems, and the standard error is relatively small (± 74 °C) in reproducing all the available experimental data, in the wide experimental P - T ranges of 800–1820 °C/15–75 kbar [37]. It is noted that previous formulations of the garnet-clinopyroxene geothermometer are inconsistent with the experimental data set, i.e., they either underestimate T s by about 100 °C when $T > 1300$ °C or overestimate T s by 100–200 °C when $T < 1300$ °C [37]. Furthermore, former garnet-clinopyroxene geothermometers tend to overestimate T s for high-Ca garnet ($X_{\text{GrS}} = 0.30\text{--}0.50$), as found by Nakamura [37]. Because chemical compositions of garnet and clinopyroxene of this work fall within the calibration range of this geothermometer [37] and because of its relatively high accuracy, Nakamura's geothermometer [37] was adopted in this work.

In order to estimate metamorphic P s of the garnet-clinopyroxene and mantle eclogite, several versions of the garnet-clinopyroxene geobarometer [38,72–75] have been calibrated. The widely used garnet-clinopyroxene geobarometer was calibrated in the mafic or ultramafic system and is applicable to mantle eclogite with high-Na-Al clinopyroxene, or garnet clinopyroxenite with low-Na-Al clinopyroxene [38], which is the case for rocks reported in this work. In the computation, activities of jadeite and aegirine phase components in clinopyroxene are not needed and, therefore, errors of chemical compositions of low-Na-Al clinopyroxene do not translate to larger pressure errors. Among different versions of the garnet-clinopyroxene geobarometer, the geobarometer of Beyer et al. [38] was calibrated based on phase equilibrium experimental data in the wide P - T ranges of 2–7 GPa/900–1550 °C. Standard error of this barometer is approximately ± 4 kbar [38], and it is the most accurate version at present. Chemical compositions of our minerals are similar to the experimental run products in calibrating this geobarometer and, therefore, this barometer was applied to our samples. It should be stated that the Cr_2O_3 components are negligible for our garnet and clinopyroxene, and thus the Cr_2O_3 -based garnet-clinopyroxene geobarometers [76–78] cannot be applied.

The yielded P - T conditions of peak metamorphism lie in the UHP metamorphic region for samples 17D95, 17D90, and 17D80, or high- P region for sample 17D78, which lies slightly lower than the coesite-quartz transition curve (Figure 7). However, when considering standard error (± 4 kbar) of the present garnet-clinopyroxene geobarometer [38], it can be concluded that peak metamorphism occurred at UHP conditions for all the samples.

In addition, trace element geothermometers were also applied to garnet clinopyroxenite. However, the zirconium component in matrix rutile records much lower temperature (< 500 °C, Table S5); even if the activity of SiO_2 is assumed to be unity, the yielded temperatures are also lower than 600 °C, far below from either the peak or retrograde metamorphic temperatures. The rutile inclusions contain much higher zirconium content, and records ~ 590 °C to ~ 710 °C temperature conditions when the activity of SiO_2 was assumed to be 0.05–0.2, possibly corresponding to prograde metamorphism (if no zirconium was released from rutile). On the other hand, the results of Zr-in-titanite geothermometer are consistent with the P - T conditions obtained by garnet-clinopyroxene geothermobarometers [37,38] or monomineralogic hornblende geothermobarometers [39] when the activities of SiO_2 are appropriately set to be 0.01–0.2 (Table S6; Figure 7). If the analyzed titanite was altered from high-Al titanite when inputting lower pressures (e.g., 15 kbar) to the Zr-in-titanite geothermometer [40], the retrieved temperatures are lower than 850 °C when assuming the activity of SiO_2 to be 0.2, but this result is in conflict with the rutile exsolution in garnet and high-Al titanite. Therefore, we used the pressures resulted from garnet-clinopyroxene geobarometer [38] to compute temperatures using the Zr-in-titanite geothermometer [40] and obtained nearly similar temperature results (Table S6; Figure 7) to the garnet-clinopyroxene

geothermometer [37]. This possibly indicates that titanite (altered high-Al titanite) was once at equilibration with garnet and clinopyroxene. If the analyzed titanite was recrystallized during retrograde, it might be equilibrated with the retrograde assemblages, thus we input the pressures obtained by monomineralogic hornblende geothermobarometers [39], and obtained similar temperature results (Table S6; Figure 7) with the monomineralogic hornblende geothermobarometers [39]. Actually, we may see large temperature variations obtained by Zr-in-titanite geothermometer (Figure 7), even if the activity of SiO₂ and pressure are fixed. This is possible because that titanite was altered and zirconium was removed partially from titanite [79], leading to variable Zr concentrations in titanite.

6.4. Significance of Titanite U-Pb Ages

The closure temperature of U-Pb system in titanite is about 660–700 °C [80] or 750–790 °C [81], and Pb diffusion in titanite seems to be negligible even at about 800 °C [82], which are somewhat lower than the peak metamorphic temperatures (790–920 °C). Furthermore, the dated titanite is not Al-rich, suggesting that the dated titanite might be recrystallized or altered during cooling/retrograde. Therefore, the U-Pb ages of the titanite (~389–370 Ma) possibly record the recrystallization or resetting during the cooling/retrograde period after the peak UHP metamorphic event, i.e., timing of tectonic exhumation, postdating but possibly close to the peak metamorphism.

6.5. Possible Fast Exhumation of the UHP Metamorphic Rocks

It is generally believed that UHP rocks should experience fast tectonic exhumation from great depth, otherwise the UHP assemblages may be replaced by lower-*P* assemblages. In fact, the metamorphic *P-T* paths of the garnet clinopyroxenite (Figure 7) also suggest relatively rapid uplift, albeit the retrograde *P-T* paths are hybrid of the western Alpine and Franciscan types [83]. Furthermore, large differences in the peak metamorphic pressures among these samples suggest that these rocks were subducted to different depths and were later amalgamated at the same crustal level during tectonic exhumation.

Although the UHP rocks analyzed here were found within a single granitic pluton, it is reasonable to infer that other UHP rocks are likely buried in the deep root of the Dunhuang orogenic belt. Furthermore, it is found that both medium and high *P/T* metamorphism occurred in this orogen in the Silurian to Devonian periods [15–19]. The UHP garnet clinopyroxenite reported in this contribution further demonstrates that different metamorphic *P/T* facies series may prevail in the same orogenic belt.

7. Conclusions

Three to four stages of metamorphic mineral assemblages are preserved in the garnet clinopyroxenite enclaves within a granitic pluton in the northeastern Paleozoic Dunhuang orogenic belt, northwestern China. The protoliths of the garnet clinopyroxenite are inferred to be basic or ultrabasic volcanic rocks. The peak metamorphism (870–920 °C/32–41 kbar) occurred in the coesite or even the diamond stability field, and the concurrence of the high-Al titanite and at least three groups of aligned rutile lamellae exsolved from the garnet further confirm the UHP metamorphic event. Clockwise metamorphic *P-T* paths of the garnet clinopyroxenite were retrieved, indicative of subduction process. SIMS U-Pb dating of metamorphic titanite indicates that the tectonic exhumation of the ultra-high pressure metamorphic rocks might have occurred in the Devonian period (~389–370 Ma), postdating but possibly approaching very near the peak UHP metamorphism. It should be noted that both medium- and high-*P/T* facies series metamorphism occurred in this Paleozoic orogen. Furthermore, it is reasonable to infer that most of the UHP rocks are buried in depth, possibly in the deep root of this orogen.

Supplementary Materials: The following are available online at <https://www.mdpi.com/2075-163X/11/2/117/s1>, Figure S1: X-ray compositional mapping of MnO, MgO, FeO, and CaO components of representative garnet porphyroblast in samples 17D80, 17D90, and 17D95, Figure S2: EMPA analytical transverses of clinopyroxene (sample 17D78), Figure S3: EMPA analytical transverses of clinopyroxene (sample 17D80), Figure S4: EMPA analytical transverses of clinopyroxene (sample 17D90), Figure S5: EMPA analytical transverses of clinopyroxene (sample 17D95), Figure S6: Backscattered electron images of titanite separated from garnet clinopyroxenite samples for SIMS U-Pb dating. (a) Sample 17D78. (b) Sample 17D95. (c) Sample 17D90. The circles with red figures represent analytical spots. The yellow numbers are the respective ^{207}Pb -based common lead corrected ages involved in the calculation for samples 17D78 and 17D90, while the white and yellow numbers are the respective ^{207}Pb -based common lead corrected ages both involved in the calculation for sample 17D95, and obtained the younger and older mean ages, respectively, Table S1: Chemical compositions of the representative minerals in sample 17D78, Table S2: Chemical compositions of the representative minerals in sample 17D80, Table S3: Chemical compositions of the representative minerals in sample 17D90, Table S4: Chemical compositions of the representative minerals in sample 17D95, Table S5: EMPA analysis of rutile and temperature calculation results with different aSiO_2 , Table S6: Zr contents in titanite and calculated temperatures with various aSiO_2 , Table S7: Chemical compositional profiles of the garnet, Table S8: Chemical compositional profiles of the clinopyroxene, Table S9: SIMS U-Th-Pb analytical data for titanite from garnet clinopyroxenite, Table S10: Pressure-temperature (P - T) conditions retrieved for the different metamorphic stages of garnet clinopyroxenite, Table S11: Bulk-rock compositions for both major and trace elements of garnet clinopyroxenite.

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