

Discovery of super-silicic and super-titanic garnets in garnet-pyroxenite in Zhaheba and its geological significance

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Super-silicic garnet which exists stably at more than 5 GPa is a typical ultra-high pressure mineral. The super-silicic garnet and super-titanic garnet were discovered for the first time in garnet-pyroxenite of early Paleozoic Zhaheba-Aermantai orogenic belt in north Xinjiang. Our study indicates that these super-silicic garnets as well as super-titanic garnets were formed at a depth of at least 300 km. Their host rock—garnet-pyroxenite is one kind of ultra-pressure metamorphic rocks which is related to the ultra-deep subduction of the oceanic crust. Thus, the early Paleozoic Zhaheba-Aermantai orogenic belt is related to the ultra-deep subduction of the Paleo-Asian oceanic crust.

Zhaheba ophiolite, garnet-pyroxenite, super-silicic garnet, super-titanic garnet, ultra-high pressure metamorphism

Super-silicic garnet is chemically characterized by an excess of silicon (> 3.0 Si per formula unit (pfu))^[1–3]. Si (pfu) > 3.05 is considered as a criterion of super-silicic garnet^[4]. Ringwood and Major^[5–7] experimentally synthesized the end member of super-silicic garnet and majorite ($\text{Mg}_4\text{Si}_4\text{O}_{12}$). Subsequently, Smith and Mason^[1] found majorite in aerolite. Experimental studies have indicated that pyroxene dissolves into garnet at ultra-high pressures, with the solubility of pyroxene increasing as pressure increases^[2,8,9]. Since Si:O ratios in garnet and pyroxene are 1:4 and 1:3, respectively, some Si^{4+} may substitute for Al^{3+} , Cr^{3+} , Fe^{3+} and enter the octahedral sites to form super-silicic garnet (Si (pfu) > 3.0) when pyroxene dissolves into garnet. The super-silicic garnet stably exists at more than 5 GPa and is a typical ultra-high pressure mineral.

Van Roermund et al.^[10] found garnets with ilmenite and rutile exsolutions, in addition to super-silicic garnet, in garnet-peridotite of Norway Caledonian orogenic belt. They proposed that the original mineral of the garnet with ilmenite and rutile exsolutions is a typical ultra-high pressure mineral and similar to super-silicic garnet, named super-titanic garnet. The garnet with il-

menite exsolutions was found in mantle inclusions of deep source and has been considered to be the decomposition products of super-titanic garnet at low pressures^[11]. Up to now, no super-titanic garnet has been reported as an individual mineral in the natural orogenic belt.

Recently, we found the super-silicic garnet and super-titanic garnet in the garnet-pyroxenite of early Paleozoic Zhaheba-Aermantai orogenic belt. It is the first time to report the super-silicic garnet and super-titanic garnet as individual minerals in orogenic belt. The existence of residual super-silicic garnet and super-titanic garnet not only indicates that ultra-high pressure blocks exist in Zhaheba ophiolite, but also provides a unique “window” for studying on the dynamics of early Paleozoic orogenic belt generation in north Xinjiang.

1 Geological background and samples

Zhaheba-Aermantai ophiolite belt is the main part of

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Central Asian Orogenic Belt and is located on the northeastern edge of Junggar Basin (Figure 1)^[12–15]. It is 130 km long and 3–5 km wide. The ophiolitic blocks outcropped spasmodically along NWW. The ophiolite belt consists of serpentinized harzburgite, serpentinized dunite, serpentinized lherzolite, gabbro, diabase, basalt, anorthosite and silicolite, with garnet-pyroxenite and quartz-magnetite lens. The samples in this study are collected from the garnet-pyroxenites of Zhaheba ophiolite.

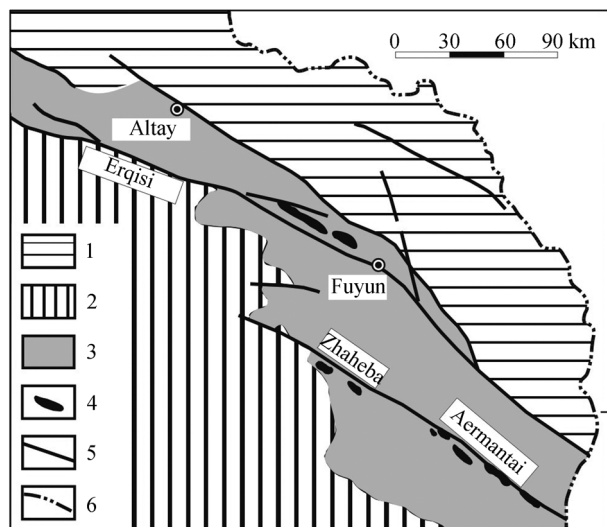


Figure 1 The geological sketch of north Xinjiang. 1, Siberian Plate; 2, Kazakstan-Junggar Plate; 3, Paleozoic orogenic belt; 4, ophiolites; 5, fault; 6, national boundary.

The garnet-pyroxenites occur as lens of 0.3–0.8 m wide and 3–5 m long in serpentinized lherzolites. The lenses are distributed along the faults in serpentinized lherzolites casually. Garnet-pyroxenites are of compact texture and consist of clinopyroxene (35 vol%), garnet (35 vol%), chlorite (27 vol%) and ilmenite (3 vol%),

with chlorite being the alteration product. Clinopyroxene and garnet are hypautomorphic-granular with grain sizes of 0.3–1.0 and 0.2–0.8 mm, respectively. Ilmenites are grains with a size range from 0.1 to 0.5 mm and are distributed in the interstice among the pyroxenes and garnets.

Fine-grained super-silicic garnets distribute within the clinopyroxenes or coexist with fine-grained clinopyroxenes in Zhaheba garnet-pyroxenites (Figure 2). Figure 3 is the Raman spectrum of the super-silicic garnet. Super-titanic garnets in Zhaheba garnet-pyroxenites have two occurrences. One is fine-grained within clinopyroxenes with a grain size of 10–100 μm (Figure 4). The laser Raman spectrum of this super-titanic garnet is shown in Figure 5. Their chemical characteristics are similar to those of super-titanic garnets experimentally synthesized by Zhang et al.^[16] at 5–15 GPa. Another super-titanic garnet is similar to those reported by Van Roermund et al.^[10] and Keshav et al.^[11], and consists of normal garnet and ilmenite exsolutions. The ilmenite exsolutions in the garnet are orientationally distributed and take up a volume of 6% (Figure 6). This kind of super-titanic garnet coexists with clinopyroxene as grand-grains.

2 Chemical compositions of super-silicic and super-titanic garnets

Chemical compositions of super-silicic garnets and super-titanic garnets were obtained by JEOL-JXA 8800M EPMA at State Key Laboratory for Mineral Deposits Research, Nanjing University. The experimental conditions are as follows: Acceleration voltage is 15 kV, current is 20 nA and electron beam diameter is 1 μm . BSE

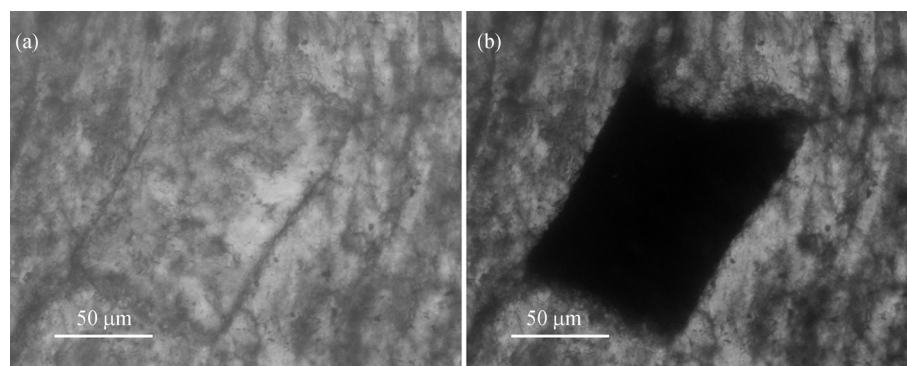


Figure 2 Super-silicic garnets in clinopyroxene. (a) Plane polarized light; (b) cross polarized light.

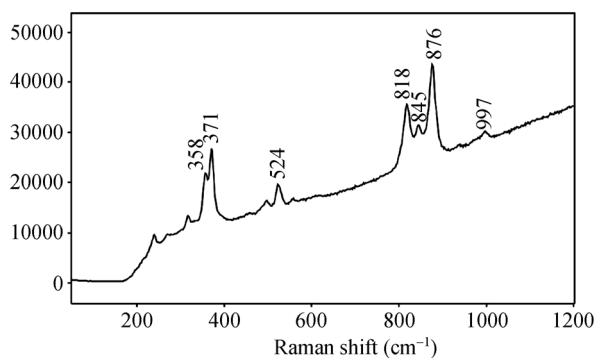


Figure 3 Raman spectra of super-silicic garnet.

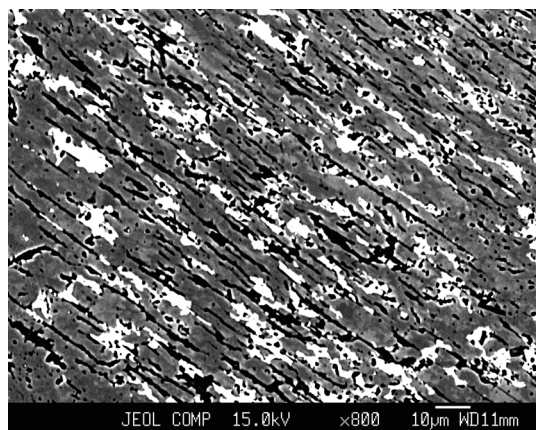


Figure 4 Super-titanic garnets in clinopyroxene (BSE, grayish minerals are super-titanic garnets).

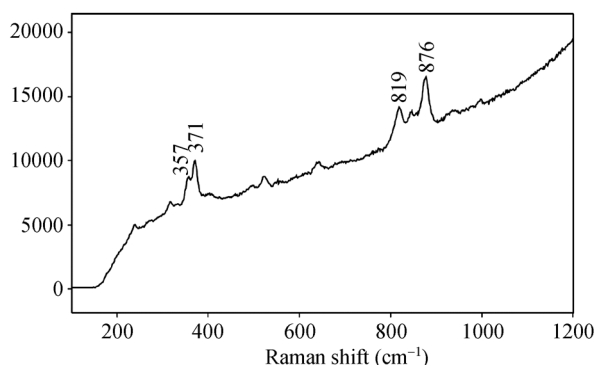


Figure 5 Raman spectra of super-titanic garnet.

image was obtained by JEOL-JXA 8100 EPMA at Guangzhou Institute of Geochemistry, CAS.

2.1 Super-silicic garnet

EPMA results show that the chemical composition of super-silicic garnets from Zhaheba garnet-pyroxenites is characterized by high FeO_T , CaO , SiO_2 , and low Al_2O_3 contents (Table 1). Si (pfu) of Zhaheba super-silicic garnets ranges from 3.19 to 3.29. The amounts of

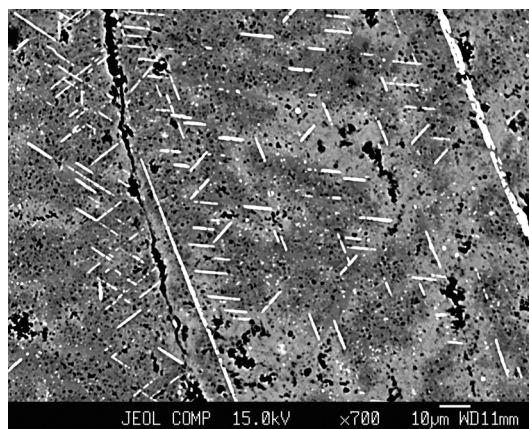


Figure 6 Ilmenite crystals directionally distributing in garnet (BSE, acicular crystals are ilmenite).

$\text{Si}^{4+} + \text{Ti}^{4+}$ and M^{2+} ($\text{M}^{2+} = \text{Ca} + \text{Mg} + \text{Mn} + \text{Fe}^{2+}$) are similar, but all are more than 3, indicating that the amounts of quadrivalent ions in octahedral sites are similar to those of bivalent ions in octahedral sites, characteristic of typical super-silicic garnet.

2.2 Super-titanic garnet

EPMA results show that SiO_2 and TiO_2 contents of super-titanic garnets from Zhaheba garnet-pyroxenites range from 33.50 wt% to 36.54 wt% and 5.66 wt% to 8.21 wt%, respectively. Their FeO_T , CaO and Al_2O_3 contents are similar to those of super-silicic garnets from Zhaheba garnet-pyroxenites (Table 1). The amounts of $\text{Si}^{4+} + \text{Ti}^{4+}$ and M^{2+} ($\text{M}^{2+} = \text{Ca} + \text{Mg} + \text{Mn} + \text{Fe}^{2+}$) are similar, but all are more than 3, indicating that isomorphism between quadrivalent ions and bivalent ions exists in octahedral sites of super-titanic garnets.

3 Discussion

Super-silicic garnets commonly occur in the aerolite, mantle inclusions and diamond inclusions^[1,2,4,17,18]. Van Roermund et al.^[19] found the micro-texture consisting of exsolved clinopyroxenes, enstenites and host garnets in garnet-peridotite of Norway Caledonian orogenic belt. This was the product of decomposition of super-silicic garnet at low pressure. The existence of this micro-texture is the mineral evidence of the ultra-pressure metamorphism. Ye et al.^[20] reported the super-silicic garnet in Su-Lu ultra-pressure metamorphic belt. They considered that continental matters were subducted to a mantle depth of more than 200 km. Song et al.^[21] and Liu et al.^[22] reported super-silicic garnets in garnet-peridotite of north Qaidam ultra-pressure metamor-

Table 1 Chemical compositions of super-silicic garnets and super-titanic garnets

	Super-silicic garnets					Super-titanic garnets					
	21-20	21-21	21-22	21-30	21-35	21-1	21-2	21-3	21-4	21-5	21-6
SiO ₂	39.96	40.96	40.52	41.24	40.33	36.54	35.53	35.14	35.90	35.71	33.50
TiO ₂	0.50	1.01	0.18	0.54	0.85	6.51	6.07	5.66	6.63	6.95	8.21
Al ₂ O ₃	7.45	7.13	8.12	7.25	7.72	7.07	6.82	9.20	7.11	8.30	3.65
Cr ₂ O ₃	0.00	0.35	0.04	0.37	0.02	–	–	–	–	–	–
Fe ₂ O ₃	13.34	9.88	13.34	11.42	13.30	12.98	15.52	12.64	12.79	11.46	18.27
FeO	4.78	8.50	5.26	6.89	5.46	0.00	0.76	1.14	2.72	0.00	0.49
MnO	0.04	0.04	0.02	0.04	0.05	0.05	0.01	0.02	0.00	0.05	0.00
MgO	0.06	0.19	0.05	0.06	0.08	2.74	0.38	0.72	0.44	2.00	0.16
CaO	33.79	32.00	33.78	32.97	33.78	34.76	36.28	34.86	35.45	35.65	36.33
Na ₂ O	0.01	0.01	0.00	0.12	0.02	0.05	0.01	0.01	0.00	0.03	0.03
Total	99.93	100.07	101.31	100.90	101.61	100.70	101.37	99.39	101.04	100.15	100.64
	O=12					O=12					
Si ⁴⁺	3.21	3.29	3.21	3.28	3.19	2.89	2.85	2.84	2.88	2.84	2.75
Ti ⁴⁺	0.03	0.06	0.01	0.03	0.05	0.39	0.37	0.35	0.40	0.40	0.51
Al ³⁺	0.70	0.68	0.76	0.68	0.72	0.66	0.64	0.87	0.67	0.78	0.35
Fe ³⁺	0.81	0.59	0.80	0.68	0.79	0.77	0.94	0.77	0.77	0.69	1.13
Cr ³⁺	0.00	0.02	0.00	0.02	0.00	–	–	–	–	–	–
Fe ²⁺	0.32	0.57	0.35	0.46	0.36	0.00	0.05	0.08	0.18	0.00	0.03
Mg ²⁺	0.01	0.02	0.01	0.00	0.01	0.32	0.05	0.09	0.05	0.24	0.02
Mn ²⁺	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Ca ²⁺	2.91	2.76	2.87	2.81	2.86	2.95	3.11	3.01	3.05	3.04	3.20
Na ⁺	0.00	0.00	0.00	0.02	0.00	0.01	0.00	0.00	0.00	0.01	0.01
Si ⁴⁺ +Ti ⁴⁺	3.24	3.35	3.22	3.31	3.24	3.28	3.22	3.19	3.28	3.24	3.26
Al ³⁺ +Fe ³⁺ +Cr ³⁺	1.51	1.29	1.56	1.38	1.51	1.43	1.58	1.64	1.44	1.47	1.48
M ²⁺	3.24	3.35	3.23	3.27	3.23	3.27	3.21	3.18	3.28	3.28	3.25
Sum	7.99	7.99	8.01	7.98	7.98	7.99	8.01	8.01	8.00	8.00	8.00

phic belt and Altyn gneissoid K-feldspar garnet pyroxenite, respectively. The formation pressures are from 5 to 7 GPa, or even higher. The natural super-silicic garnets have two forms: One is the primary garnet with high Si content (Si (pfu) > 3.0), such as those in the mantle inclusions of Malaita Island and in diamond of Yakutia kimberlite, with the respective Si (pfu) contents of more than 3.20 and 3.07^[23,24], the other contains quartz and pyroxene exsolutions that is the decomposition product of super-silicic garnet, and has been found in the garnet peridotite and eclogite of some orogenic belts^[12–15]. Previous studies indicated that super-silicic garnet is a typical ultra-pressure mineral, the formation pressure of which is higher than that of coesite and diamond. Super-silicic garnet exists stably at more than 5 GPa^[4,12,25].

Ti and Si contents in super-silicic garnets show obviously negative correlation. Dingwell et al.^[26] considered that Ti⁴⁺ preferentially entered into the tetrahedral sites

and substituted for Si⁴⁺. Superfluous Ti⁴⁺ together with bivalent ions enters the octahedral sites and substitute for trivalent ions. Yang and Liu^[27] suggested that the coupled substitutions of Si⁴⁺+M²⁺→Al³⁺+Al³⁺ or Ti⁴⁺+M²⁺→Al³⁺+Al³⁺ exist in the garnet under ultra-pressure conditions (M = bivalent ions of Ca, Mg, Mn, Fe, and Al³⁺ may be substituted by Cr³⁺, Fe³⁺). Zhang et al.^[16] experimentally demonstrated that Ti⁴⁺+M²⁺→Al³⁺+Al³⁺ exists in high-Ti garnet under ultra-pressure conditions (M = bivalent ions of Ca, Mg, Mn, Fe, and Al³⁺ may be substituted for by Cr³⁺, Fe³⁺).

Since super-silicic garnets exist stably at more than 5 GPa, the discovery of super-silicic garnets and super-titanic garnets indicates that Zhaheba garnet-pyroxenites underwent metamorphism of more than 5 GPa. Super-silicic garnets and super-titanic garnets would decompose at low pressure to form garnet + pyroxene and garnet + ilmenite (rutile), respectively. Therefore, the individual minerals of super-silicic garnets and super-titanic

garnets are the residuals after retrogressive metamorphism, while the garnets with ilmenite exsolution in the Zhaheba garnet-pyroxenites are the decomposition products of super-titanic garnet at low pressure.

Si content in the octahedral site of super-silicic garnet increases as pressure increases, based on which Van Roermund et al. [19] considered that Si content in garnet might be a potential geo-manometer. Collerson et al. [23] proposed two empiristic formulas for estimating the generation pressure of super-silicic garnet based on experimental petrology. Tappert et al. [4] discussed the depth of diamond formation in Jagersfontein kimberlite of southern Africa by super-silicic garnet compositions. In Tappert's diagram, super-silicic garnets from Zhaheba might be formed at depth of 340–420 km (Figure 7). Since Fe and Ti are rich in the super-titanic garnets of Zhaheba garnet-pyroxenites, we add Fe^{3+} in y -axis and Ti^{4+} in x -axis to amend Tappert's diagram. It was found that super-titanic garnet of Zhaheba garnet-pyroxenites might be formed at depth of 300–390 km (Figure 7). Because Ti solubility in garnet is mainly controlled by pressure and just slightly influenced by temperature, the estimated depth for the formation of Zhaheba super-titanic garnets is a good approximation.

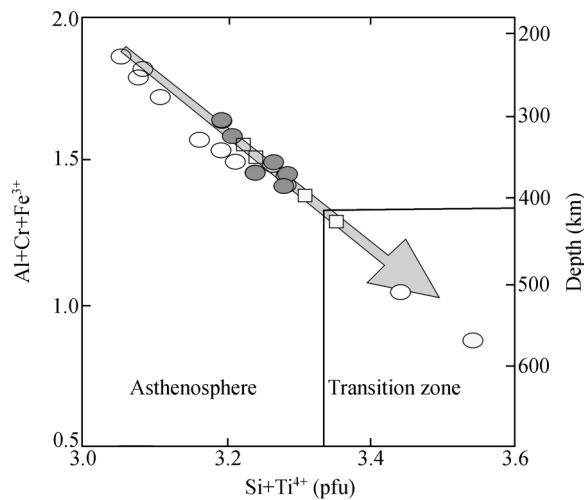


Figure 7 $\text{Al}+\text{Cr}+\text{Fe}^{3+}$ - $\text{Si}+\text{Ti}^{4+}$ diagram of super-silicic and super-titanic garnets (after Tappert et al. [4]). Blank circle represents the super-silicic garnet in diamond, solid circle represents the super-silicic garnets from Zhaheba, square represents the super-titanic garnets from Zhaheba.

The Zhaheba garnet-pyroxenite is enriched in Ca and poor in Si, Al, Mg, with an average composition of SiO_2 36.20 wt%, TiO_2 1.92 wt%, Al_2O_3 9.12 wt%, CaO 29.40 wt%, Fe_2O_3 14.09 wt%, MgO 6.63 wt%, MnO 0.16 wt%,

CO_2 0.65 wt%, and H_2O 1.95 wt%. Compositionally, the garnet-pyroxenite is quite different from pyrolite. Therefore, Zhaheba garnet-pyroxenites might not be the ultra-pressure pyrolite from the deep. Joswig et al. [28] found Ca-enriched silicate inclusions consisting of perovskite (CaSiO_3), β -larnite (Ca_2SiO_4) and CaSi_2O_5 -titanite in diamond. They suggested that there was a Ca-enriched unhomogeneous source in the lower mantle. Brenker et al. [29] confirmed that a Ca-enriched source existed at a depth of more than 300 km. It might result from ultra-deep subduction of Ca-metasomatic oceanic lithosphere or the overlying carbonate.

The total REE content, $(\text{LREE}/\text{HREE})_N$ and δEu of Zhaheba garnet-pyroxenites are 10.08 $\mu\text{g}/\text{g}$, 0.66 and 1.60, respectively. They are similar to those of MORB. The initial $^{143}\text{Nd}/^{144}\text{Nd}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of Zhaheba garnet-pyroxenites are 0.5133 and 0.7020, respectively, showing the characteristics of depleted mantle.

Major elements, trace elements and isotopic characteristics indicate that Zhaheba garnet-pyroxenites are the products of Ca-metasomatic oceanic crust or/and overlying sediments which subducted to the mantle and return to the surface. Although we can not speculate that serpentinized lherzolites underwent ultra-pressure metamorphism because ultra-pressure garnet-pyroxenites contact serpentinized lherzolites via faults, Fe-enriched mentillic mineral exsolution in the olivine of some serpentinized lherzolites were found. Olivine with magnetite exsolution was reported in Dabie ultra-pressure belt and was considered to form at ultra-high pressure [30]. Therefore, it is possible that the olivine with Fe-enriched mentillic mineral exsolution might be formed at ultra-high pressure, but its chemical composition and the spatial relation between the Fe-enriched mentillic mineral exsolution and host olivine need further study.

In sum, the discovery of ultra-pressure garnet-pyroxenites indicates that ultra-pressure rock blocks existed in the early Paleozoic Zhaheba-Aermantai orogenic belt. They are related with ultra-deep subduction of oceanic crust.

4 Conclusions

In this study, super-silicic garnets and super-titanic garnets were found in the garnet-pyroxenites of Zhaheba ophiolite, which may be formed at depth of more than 300 km. The host garnet-pyroxenites of super-silicic garnets and super-titanic garnets are the ultra-pressure

metamorphic rocks related to ultra-deep subduction of oceanic crust. The discovery of ultra-high pressure garnet-pyroxenites in Zhaheba ophiolite indicates that ultra-high pressure rocks existed in the early Paleozoic Zhaheba-Aermantai orogenic belt. It might be related with the ultra-deep subduction of Ca-metasomatic oceanic lithosphere or the overlying carbonate. This study

provides a unique “window” for studying on the generation dynamics of the early Paleozoic orogenic belt in north Xinjiang.

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