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Coesite inclusions in garnet from eclogitic rocks in western Tianshan, northwest China: Convincing proof of UHP metamorphism

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Abstract

Coesite inclusions in garnet have been recognized in eclogitic rocks from western Tianshan, northwest China. The coesite grains exhibit distinct radial cracks in host porphyroblastic garnet; some coesite relics are well preserved, whereas others are partially replaced by quartz. Coesite has been identified optically and then confirmed by in situ Raman spectroscopy, showing the characteristic band at 522 cm^{-1} and subsidiary bands at 428, 326, 271, 178, 151, and 121 cm^{-1}. The eclogitic rocks contain garnet, omphacite, and Na-Ca-amphibole, and they are rich in white mica (>30%) and graphite. Peak conditions of 570–630 °C and 2.7–3.3 GPa are constrained by garnet-clinopyroxene geothermometry and the occurrence of coesite. The presence of coesite and widespread quartz inclusions in garnet with radial cracks indicative of former coesite in these unique graphitic rocks confirms the previous suggestion of the UHP terrane for the western Tianshan, China.

Keywords: Coesite, UHP metamorphism, Raman spectroscopy, western Tianshan, China

Introduction

Since coesite was first discovered in metamorphic rocks from Dora Maira (Chopin 1984) and in Caledonian eclogites (Smith 1984), more than 20 UHP metamorphic terranes have been reported worldwide (Carswell and Compagnoni 2003; Liou et al. 2004). In eclogite from western Tianshan, China, Zhang et al. (2002a, 2002b) first reported inclusions of coesite pseudomorphs in garnet, quartz exsolution in omphacite, and relics of metamorphic magnesite. In spite of these findings, the existence of UHP metamorphism in western Tianshan has remained suspect (see Klemd 2003; Zhang et al. 2003b); such doubts were raised mainly because no well-preserved coesite relics had been recognized in this terrane. However, UHP metamorphic conditions for eclogites and associated metasediments are indicated by the coexistence of magnesite and aragonite as HP breakdown products of dolomite in metapelites (Zhang et al. 2003a) and relict coesite exsolution in porphyroblastic omphacite in western Tianshan eclogite (Zhang et al. 2005). In this paper, we report well-preserved coesite inclusions in garnet from some eclogitic rocks and thus prove that some tectonic units of the western Tianshan, China, indeed experienced UHP metamorphism.

Geological setting and occurrences

The Chinese western Tianshan HP-UHP belt extends for about 200 km between the Central Tianshan-Yili plate and the Tarim plate (Figs. 1a and 1b). This HP-UHP metamorphic belt continues westward to the Atbashy eclogite-blueschist belt, where inclusions of coesite pseudomorphs in eclogitic garnet have been reported in Kazakstan and Kyrghyzstan (Dobretsov et al. 1987; Tagiri et al. 1995) (Fig. 1a). It consists mainly of eclogites, blueschists, and garnet-mica schists. So far, three types of eclogite have been recognized in western Tianshan, China: (1) eclogite with pillow structure; (2) eclogite lenses in blueschists and garnet-phengite schists; and (3) banded eclogite interlayered with marble (Zhang et al. 2002a, 2005). This HP-UHP belt is in fault contact with a low-*P* and high-*T* metamorphic belt to the north, which consists of cordierite-bearing garnet + sillimanite gneiss and two-pyroxene granulite (Li and Zhang 2004), and to the south with a unit of intercalated marble and chlorite muscovite schists (Fig. 1b). The HP-UHP belt formed by the northward subduction of the Tarim plate beneath the Central Tianshan-Yili plate during the closure of the Paleo-Tianshan ocean (Gao et al. 1999; Zhang et al. 2001, 2005). Recent SHRIMP zircon U-Pb dating shows that the HP-UHP metamorphic age is Triassic (220–230 Ma) and the formation ages of the eclogite protoliths are older than 310 Ma (Zhang et al. 2007).

The foliated coesite-bearing eclogitic rocks are lenticular, and are surrounded by garnet-mica schists along the Habutengsu River, in the northern part of the HP-UHP belt (Fig.1c).

Petrography and mineral chemistry

Electron-microprobe analyses of minerals in this paper were performed on a Jeol 8100 super probe at Peking University, operated at 15 kV acceleration voltage, 20 nA beam current, and 20 s counting time. Synthetic silica (Si) and spessartine (Mn), and natural pyrope (Mg), andradite (Fe, Ca), albite (Na, Al), rutile (Ti), and sanidine (K) were used as standards. Final results were reduced by a ZAF correction program.

The coesite-bearing eclogitic schists investigated are mainly composed of garnet (15%), omphacite (20%), white mica (40%), Na-Ca-amphibole (20%), and retrograde albite (15%) (Fig. 2a). Accessory minerals include dolomite/calcite, graphite, rutile, and titanite. No quartz was found in the matrix probably owing to extensive retrograde consumption during the growth of albite.

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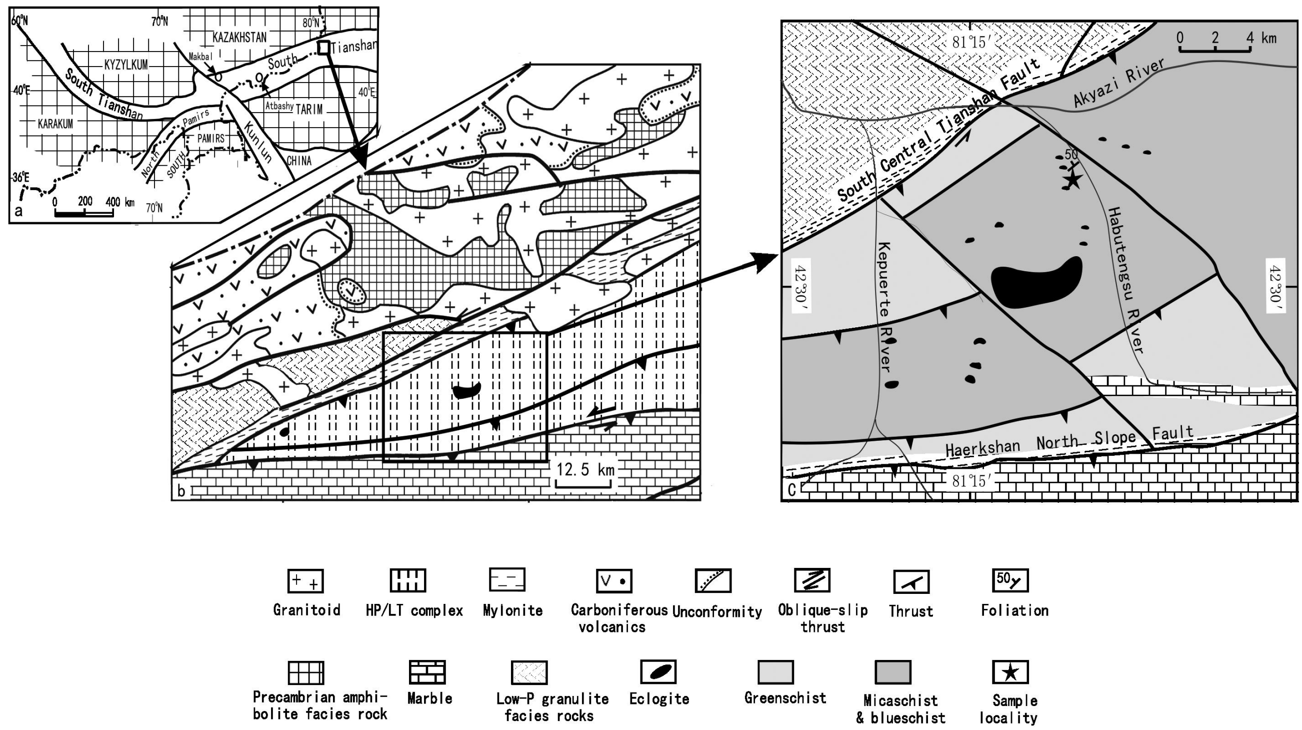

FIGURE 1. Geological map of the western Tianshan orogenic belt (modified after Zhang et al. 2002a, 2007; Klemd 2003), showing (**a**) the distribution of South Tianshan orogenic belt in the middle Asia, (**b**) HP-UHP/LT belt of the Chinese Tianshan, and (**c**) distribution of HP-UHP rocks and sample localities.

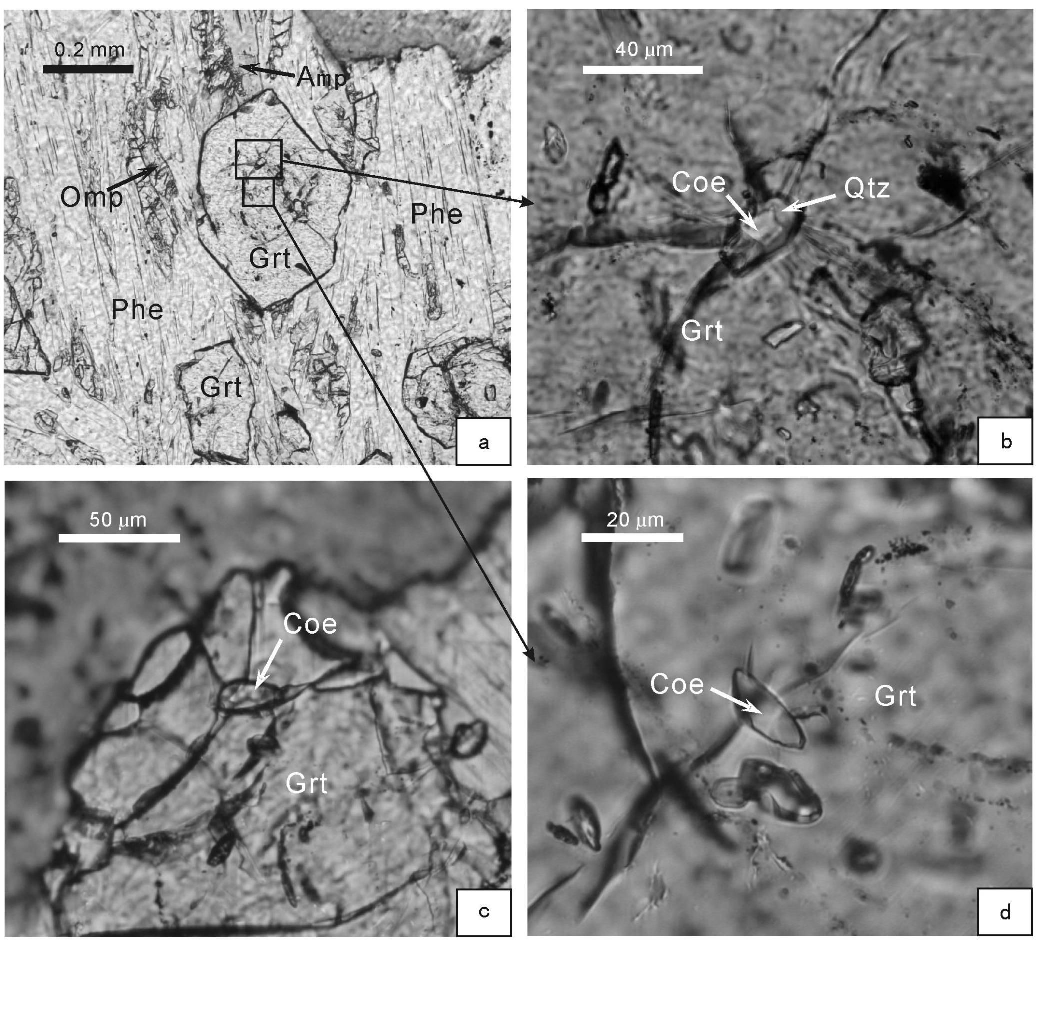

FIGURE 2. Photomicrographs of major minerals and coesite inclusions embedded in garnet from western Tianshan eclogitic rocks (sample H601-9). (**a**) Major minerals of the coesite-bearing eclogitic rocks (plane-polarized light); (**b** and **c**) coesite with radial fractures, with its rim partly transformed into quartz (plane-polarized light); (**d**) monomineralic coesite (plane-polarized light).

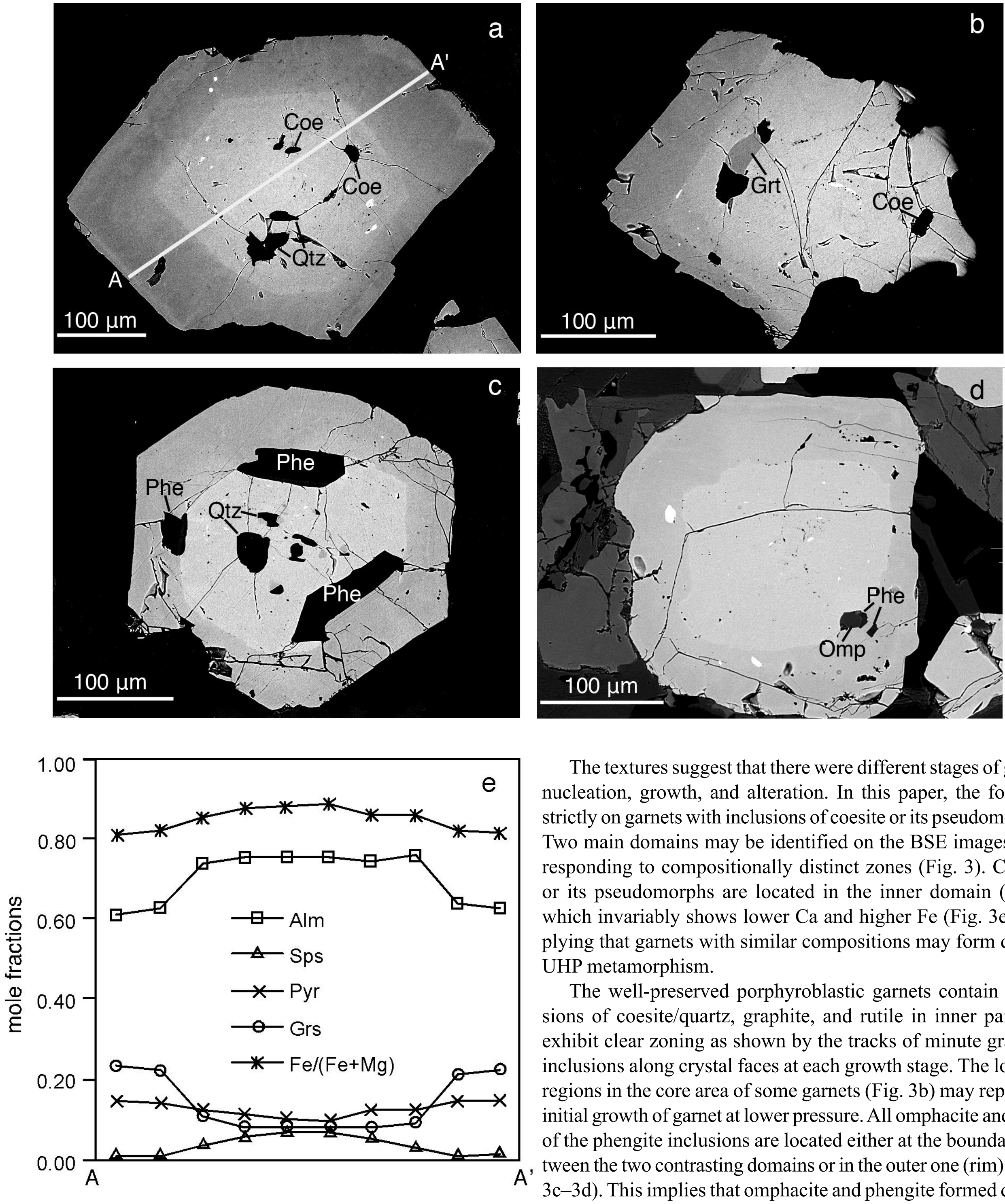

FIGURE 3. BSE images and compositional profile showing the distinct domains of porphyroblastic garnet and the distribution of inclusions. (**a**) Euhedral garnet with coesite and/or its pseudomorphs. (**b**) Irregular-shaped garnet with coesite and a Ca-rich and Mg-poor region in the core area. (**c**) Euhedral garnet showing large phengite grains along the rim of the core. (**d**) Garnet with omphacite and phengite inclusions, exhibiting an irregular rim of the core. (**e**) Compositional zoning of the garnet in **a**.

The textures suggest that there were different stages of garnet nucleation, growth, and alteration. In this paper, the focus is strictly on garnets with inclusions of coesite or its pseudomorphs. Two main domains may be identified on the BSE images, corresponding to compositionally distinct zones (Fig. 3). Coesite or its pseudomorphs are located in the inner domain (core), which invariably shows lower Ca and higher Fe (Fig. 3e), implying that garnets with similar compositions may form during UHP metamorphism.

The well-preserved porphyroblastic garnets contain inclusions of coesite/quartz, graphite, and rutile in inner part and exhibit clear zoning as shown by the tracks of minute graphite inclusions along crystal faces at each growth stage. The low-Ca regions in the core area of some garnets (Fig. 3b) may represent initial growth of garnet at lower pressure. All omphacite and most of the phengite inclusions are located either at the boundary between the two contrasting domains or in the outer one (rim) (Figs. 3c–3d). This implies that omphacite and phengite formed during the overgrowth of Ca-rich garnet on the Ca-poor UHP core, i.e., they are later than the UHP stage. The irregular but sharp rim of the inner domain (Fig. 3d) and the change of inclusion minerals may indicate a discontinuous overgrowth of garnet related to an associated change in rock composition.

There is also another type of garnet that occurs as atoll-shaped, i.e., it has an irregular shell structure and is characterized by a core partially or entirely replaced by phengite, epidote, and quartz, indicating alteration after the UHP stage. With the progress of retrogression, some shells were completely replaced by the product minerals, whereas others survived as ring-shaped garnet "islands." No coesite inclusions have been found in this atoll-shaped garnet.

Parallel white micas, including both phengite and paragonite, define a strong foliation in the matrix. Most of the white mica is phengitic with Si contents from 3.36 for that included in garnet to 3.40 for phengite in the matrix. The presence of phengite and paragonite implies that the rock may have originated from pelitic sediments. Phengite inclusions in garnet are replaced by chlorite.

Omphacite in the eclogitic schists occurs primarily as matrix aggregates. Fine-grained omphacite inclusions in garnet have been identified using the microprobe. The composition is similar to that of matrix omphacite (Table 1). Na-Ca-amphibole occurs either as porphyroblastic crystals with inclusions of relict omphacite and garnet, or as fine, euhedral needles coexisting with albite. According to the amphibole classification of Leake et al. (1997), the Na-Ca-amphibole is barroisite (Table 1). Tiny graphite grains occur as dark bands in the matrix and as inclusions in most minerals. The presence of graphite buffers the oxygen fugacity during the entire metamorphic evolution to relatively low values.

Two types of coesite inclusions in garnet were identified: composite coesite-quartz (Figs. 2b–2c) and single coesite (Fig. 2d) inclusions. Microprobe analyses reveal that all coesite inclusions are pure SiO_2. The bi-mineralic inclusion of relict coesite rimmed by retrograde quartz aggregates is surrounded by radial fractures in the host garnet. The maximum grain size of relict coesite is 30 μm (Figs. 2b–2c). Quartz, with lower relief than coesite, comprises approximately 30% of the inclusion (Fig. 2b). No palisade or mosaic texture of quartz has been discerned due to small grain size.

Single-grain coesite inclusions are oval-shaped, about 10 μm long and 4 μm wide, and exhibit very faint radial fractures in the garnet host. The inclusions (Fig. 2d) have been identified using Raman spectroscopy (discussed below). It is speculated that similar, but larger, quartz inclusions with radial fractures may have been originally coesite.

Table 1. Representative compositions of garnet, omphacite, phengite, and amphibole of sample H601-9 from western Tianshan, China

Mineral	Grt core	Grt rim	Omp matrix	Omp in	Phe matrix	Phe in	Amp core	Amp rim
SiO_2	36.97	37.15	56.31	56.44	52.90	51.23	48.08	48.78
TiO_2	0.10	0.07	0.01	0.06	0.38	0.32	0.20	0.16
Al_2O_3	20.72	21.00	10.92	11.33	29.71	28.78	11.12	9.45
Cr_2O_3	0.04	0.00	0.04	0.00	0.05	0.00	0.10	0.08
FeO*	33.81	29.50	4.26	4.65	1.68	2.48	13.05	11.93
MnO	2.95	0.34	0.03	0.00	0.00	0.02	0.06	0.06
MgO	2.40	3.53	7.99	7.80	3.13	3.08	11.77	13.57
CaO	2.75	7.64	13.46	13.17	0.00	0.08	8.60	10.17
Na_2O	0.14	0.06	7.27	7.19	0.79	0.63	3.30	2.44
K_2O	0.01	0.00	0.00	0.03	7.14	8.60	0.27	0.21
Total	99.88	99.29	100.29	100.67	95.78	95.27	96.55	96.84
Si	2.985	2.958	1.989	1.990	3.406	3.366	6.990	7.054
Ti	0.006	0.004	0.000	0.002	0.018	0.016	0.022	0.017
Al	1.972	1.971	0.455	0.471	2.255	2.229	1.906	1.611
Cr	0.003	0.000	0.001	0.000	0.003	0.000	0.011	0.009
Fe^{3+}	0.066	0.114	0.063	0.039	0.000	0.000	0.255	0.231
Fe^{2+}	2.217	1.850	0.062	0.098	0.090	0.136	1.332	1.212
Mn	0.202	0.023	0.001	0.000	0.000	0.001	0.007	0.007
Mg	0.289	0.419	0.421	0.410	0.300	0.302	2.550	2.924
Ca	0.238	0.652	0.509	0.498	0.000	0.006	1.340	1.576
Na	0.022	0.009	0.498	0.492	0.099	0.080	0.930	0.684
K	0.001	0.000	0.000	0.001	0.587	0.722	0.050	0.039
Cation	8.00	8.00	4.00	4.00	6.758	6.857	15.395	15.365

Notes: Formula proportions based on 8 cations and 12 oxygen atoms for garnet, 4 cations and 6 oxygen atoms for omphacite, and 11 oxygen atoms for phengite, amphibole normalized after Holland and Blundy (1994). in = inclusion in garnet.
* Total iron as FeO, Fe^{3+} calculated from charge balance.

Micro-Raman analyses

Raman analyses were conducted at the School of Earth and Space Sciences, Peking University. The operating conditions are described in Zhang et al. (2005) and are not repeated here. The characteristic bands of coesite match the corresponding positions of the reference coesite Raman spectra (Figs. 4a–4d). The strongest band of coesite is at ~522 cm^{-1} with subsidiary bands at 428, 326, 271, 178, 151, and 121 cm^{-1} (Liu et al. 1997). All spectra of coesite include diagnostic bands of quartz at 466–470 cm^{-1}.

Figure 4a coesite shows two strong bands at 523 and 470 cm^{-1}, which may be attributed to the difficulty in simultaneous focus and overlap of the laser beam onto both silica phases (Fig. 2b). Figure 4b coesite shows the characteristic coesite band at 521 cm^{-1}. The band is remarkably strong, even near the rim of coesite. Variable quartz band intensity (Figs. 4b and 4d) may reflect the different degree of replacement of coesite by quartz resulting in the intergrowth of both phases. Figure 2d coesite is nearly monomineralic. The quartz band seen at 468 cm^{-1} is very weak due to the small amount of coesite transformed to quartz (Fig. 4c). Furthermore, this coesite grain lacks the distinguishing characteristic of radial fractures in the surrounding host garnet. Small coesite grains may be well preserved because they are too small to fracture garnet upon decompression. The confining pressure of the rigid host mineral inhibits brittle deformation and hence any fluid infiltration (Mosenfelder and Bohlen 1997; O'Brien et al. 2001; Mosenfelder et al. 2005).

P-T estimates

Phengite and omphacite have not been observed as inclusions within the same domain as coesite, so it is impossible to estimate the exact UHP conditions directly from traditional geothermobarometry. Although graphite accompanied the entire UHP growth of garnet, it does not show any characteristics suggesting the former presence of diamond. Therefore, the pressure of formation of garnet cores lies between the pressure of the coesite/quartz and the diamond/graphite phase transitions, respectively.

On the other hand, *P-T* conditions for the outer garnet domain can be observed from well-preserved and isolated phengite and omphacite inclusions. All Fe was taken as divalent owing to the invariably low content of total Fe and the uncertainty associated with estimating the Fe^{3+} content of omphacite inclusions from charge balance. The Grt-Cpx geothermometer of Powell (1985), the Grt-Cpx-Phe geobarometer of Waters and Martin (1993) with the garnet activity model from Berman (1990), and the Grt-Cpx-Phe geobarometer of Ravna and Terry (2004) provided the *P-T* estimates. Using the compositions of the outer domain of garnet and its omphacite and phengite inclusions (Fig. 3d) the calculated pressures range from 2.0 to 2.5 GPa and the temperatures from

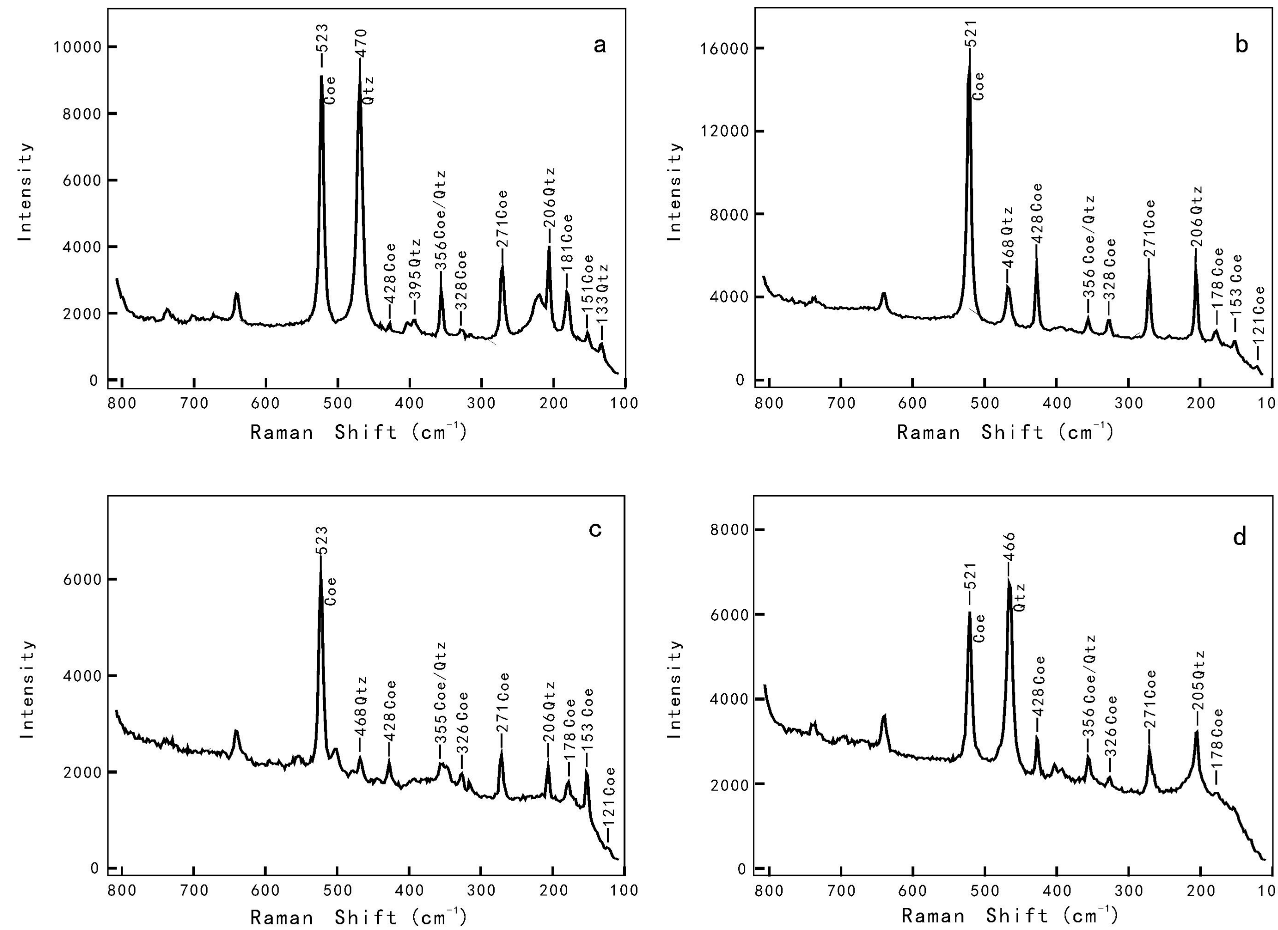

FIGURE 4. Representative Raman spectra in the range 100–800 cm^{-1} for coesite inclusions in garnet (unlabeled bands belong to garnet or section resin mount). (**a**) Raman spectrum of coesite in Figure 2b showing the same intensive bands of 523 and 470 cm^{-1}; (**b** and **d**) comparison of Raman spectra of the core and rim of coesite in Figure 2c (see the relative intensity at ~467 cm^{-1}), indicating the different degree of replacement by quartz of the same grain; (**c**) Raman spectrum of monomineralic coesite in Figure 2d, with most of the characteristic bands of coesite.

570 to 630 °C, which represent the retrograde *P-T* conditions after UHP stage. The revised Grt-Phe geothermometer of Wu and Zhao (2002) suggests that the temperature of formation of the outer domain ranges between 580 and 620 °C.

The grossular component of garnet increases toward the rim and Fe/(Fe + Mg) decreases slightly in the same direction (Fig. 3e), indicating that the outer domain grew during a period of decreasing pressure. Therefore, we conclude that the equilibrium conditions of UHP stage would be 570–630 °C and 2.7–3.3 GPa, the latter of which is inferred by the coexistence of coesite and graphite. This is consistent with the results of previous studies (Zhang et al. 2002a, 2002b).

DISCUSSION AND CONCLUDING REMARKS

Along the southern Tianshan orogenic belt, Tagiri et al. (1995) and Zhang et al. (2002a) reported inclusions of polycrystalline quartz aggregates after coesite in garnets with radial fractures. Klemd (2003) rejected that such inclusions of mosaic quartz aggregates with radial fractures were relict coesite and concluded that no convincing evidence of UHP metamorphism for this blueschist-eclogite belt has been provided.

Zhang et al. (2005) identified relic coesite exsolution lamellae in porphyroblastic omphacite in Chinese western Tianshan. Although the characteristic bands of coesite were recognized by Raman spectra, the diagnostic coesite band at 520–521 cm^{-1} had a much lower intensity compared to that of quartz, indicating significant back reaction during decompression (see Fig. 2 of Zhang et al. 2005). The coesite inclusions in porphyroblastic garnet described in this study suggest that the inclusions of polycrystalline quartz aggregates in garnet reported by Zhang et al. (2002a, 2002b) are indeed coesite replacement structures.

Eclogite-facies rocks associated with blueschists from western Tianshan, China, belong to the Group C eclogite (Coleman et al. 1965; Gao et al. 1999; Zhang et al. 2001; Klemd et al. 2002). Most rocks contain abundant hydrous minerals and are thus susceptible to retrogression upon decompression. Aqueous fluid associated with hydrous solids will catalyze the retrograde reaction during decompression and erase peak-pressure phases by recrystallization. In addition, deformation during the decompression stage is often accompanied by fluid infiltration and resultant recrystallization (Mosenfelder et al. 2005; Ghiribelli et al. 2002). However, in rocks with the fluid composition partially buffered by the presence of graphite, H_2O-poor fluids would facilitate the preservation of coesite to relatively low pressures.

Index minerals, diagnostic assemblages, and characteristic UHP-related textures are rare. Their scarcity provoked some doubts as to the existence of UHP-conditions in this orogenic belt (Klemd 2003), even though additional evidence of UHP metamorphism had been previously reported (Zhang et al. 2002b, 2003a). The detailed petrologic investigation presented in this paper further confirms the presence of preserved coesite in Tianshan eclogite. The HP units of the Chinese western Tianshan belt had, in fact, experienced pervasive Triassic UHP metamorphism and intense amphibolite-facies overprint upon exhumation.

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