American Mineralogist, Volume 88, pages 1157–1160, 2003

Ultrahigh-pressure metamorphism in eclogites from the western Tianshan, China—Reply

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INTRODUCTION

We thank Dr. Klemd for his comments on our recent papers about ultrahigh-pressure metamorphism in Western Tianshan, China (Zhang et al. 2002a, 2002b). It is good to have this opportunity to respond to his comments and to clarify some of our statements in detail. First of all, we wish to point out that we have never concluded that "all rocks from Chinese western Tianshan have undergone ultrahigh-pressure metamorphism" as claimed by Dr. Klemd, but rather "some eclogites of studied samples have undergone ultrahigh-pressure metamorphism (UHPM)". It should be noted that samples we studied were collected from different outcrops and localities from those considered by Klemd and Gao, although we worked in the same area of Western Tianshan, China.

His comments are mainly related to three aspects of mineralogic evidence for UHP in the eclogites from Western Tianshan (Zhang et al. 2002a, 2002b): (1) coesite pseudomorphs as inclusions in garnet; (2) quartz exsolution lamellae in omphacite; and (3) metamorphic magnesite in eclogite. Our responses are as follows.

COESITE PSEUDOMORPHS

The characteristics of quartz pseudomorphs after coesite as inclusions in garnet with radial fractures in eclogites from Western Tianshan are quite different from those described by Wendt et al. (1993) in metapelites from the southeastern Saih Hatat tectonic window, Northeastern Oman Mountains. In contrast to the Oman metapelites, there are no apatite inclusions surrounded by radial cracks in garnet, and no separation between core and rim of the garnet after radial cracking in the Tianshan eclogites. The most important difference between the Oman and Tianshan eclogites is that, in the latter, the quartz inclusions surrounded by radial cracks are fine-grained polycrystalline aggregates of quartz with a "palisade" texture, i.e., the fine quartz grains are elongated perpendicular to the center in Tianshan eclogites (Figs. 3c and 3d in Zhang et al. 2002a), whereas quartz inclusions in the Oman metapelites are single crystals. Therefore, the Tianshan eclogite case cannot be interpreted in terms of the different elastic behaviors of low-quartz and garnet during decompression as proposed by Wendt et al. (1993).

In recent years, more and more occurrences of fine-grained polycrystalline aggregates of quartz as pseudomorphs after coesite have been reported in several UHPM belts and confirmed by co-existing coesites or other UHP minerals (see summary by Liou et al. 1998). Experimental studies have clearly demonstrated that sequential changes from coesite through palisaded quartz aggregates and mosaic intergrowth of quartz to single-crystal quartz depends on the extent of retrogression (Mosenfelder 1997). Supported by the existence of other UHP minerals, it is reasonable to interpret polycrystalline aggregates of quartz with radial cracks in host garnet from Tianshan eclogites as former coesites formed at peak *P*-*T* conditions.

QUARTZ EXSOLUTION LAMELLAE

Besides quartz needles identified in the core of some omphacites grain (Fig. 4b in Zhang et al. 2002a), we also found quartz exsolution lamellae in some whole omphacite grains in Tianshan eclogites, i.e., quartz exsolution lamellae appear in both core and rim of some omphacite grains (Fig. 1). Chemical compositions of the latter omphacite are similar to those with quartz needles in the core (sample 105-304 in Table 1; Omp-Q1 and Omp-Q2 in Table 1 of Zhang et al. 2002a). Abundant, strongly oriented, fine quartz lamellae up to 100 um long and 1-2 um wide exsolved extensively in the cleavage direction of the host omphacites (Fig. 1a). Some quartz rods occur in bundles that are more than 20 um wide (Fig. 1c). Yes, it is hard to estimate the amount of quartz exsolution lamellae within host omphacites precisely. But it is easy to distinguish them from fluid/fluid-solid and random rutile inclusions under the microscope (as shown in Fig. 1). Figure 2 in the Comment of Klemd is not relevant, because it is a fluid-solid inclusion only. In situ micro-Laser Raman spectrum analyses show that quartz exsolution lamellae have the characteristic peak ($468\ cm^{-1}$) of quartz within host omphacites (Fig.1d). Based on the estimated volume of 5% quartz needles within the host omphacite (Fig. 1b), which are interpreted as having been formed from the decomposition of a Ca-Eskola component, it could be concluded that such supersilicic clinopyroxenes must be stable at pressures >25 kbar according to experimental studies in the Na_2O-CaO-Al_2O_3-SiO_2 system (Gasparik 1985).

Supersilicic clinopyroxene is defined by the expression: $(Si + Ti - 2Na) > (Ca + Mg + Fe^{2+} + Mn + Ni)$ (Smith and Cheeney – 1980). Unfortunately, there was a typing error for this formula in our paper (Zhang et al. 2002a). Using the original mineral data (Omp-Q1 and Omp-Q2 in Table 1 of Zhang et al. 2002a), recalculation of these two quartz needle-bearing omphacites using the correct formula with excess silica (Omp-Q1: 2.6 wt% and Omp-Q2: 3.8 wt%) shows that they are indeed supersilicic clinopyroxene (X > Z in Table 1).

Previous experimental studies have clearly demonstrated that the existence of supersilicic clinopyroxene requires high-pressure conditions (see summary by Liou et al. 1998). Smyth (1980) suggested that the deviations of supersilicic Cpx from

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TABLE 1. The recalculation of supersilisic omphacites in eclogites (sample 9630-4) and quartz needle bearing omphacite in eclogite (sample 105-304) from Western Tianshan, China*

	Omp-Q1	Omp-Q2	105-304
SiO_2	57.70	58.06	55.62
TiO_2	0.00	0.03	0.05
Al_2O_3	9.91	9.74	10.73
FeO*	3.94	4.19	3.31
MgO	8.30	8.36	8.30
MnO	0.00	0.00	0.07
CaO	13.36	13.11	13.87
Na_2O	6.80	6.52	6.85
K_2O	0.00	0.00	0.03
Total	100.01	100.01	99.53
Formula proportions cations based on 6 oxygen atoms			
Si^{4+}	2.05	2.07	1.98
Ti^{4+}	0.00	0.00	0.00
Al^{3+}	0.41	0.41	0.45
Fe^{3+}	0.01	0.01	0.04
Fe^{2+}	0.12	0.13	0.06
Mg^{2+}	0.44	0.44	0.44
Ca^{2+}	0.51	0.50	0.53
Na^{+}	0.47	0.45	0.47
K+	0.00	0.00	0.00
X	1.11	1.17	
Z	1.07	1.07	

Note: X = Si^{4+} + Ti – 2Na; Z = Ca + Mg + Fe^{2+} + Mn + Ni (Smith and Cheeney 1980).
* The original mineral analyses data of Omp-Q1 and Omp-Q2 were shown in Table 1 of Zhang et al. (2002a).

stoichiometry are reconciled by allowing up to 9% vacancy in the M2 site, and that the vacancies are stabilized by pressure in excess of 3 GPa but are highly unstable at lower pressure. Up to now, almost all reported quartz exsolution lamellae or rods within clinopyroxenes from eclogites are located in UHP terranes such as Dabie-Sulu belt (Zhang and Liou 1998; Tsai and Liou 2000), Kokchetav massif (Katayama et al. 2000), Alpe Arami, Switzerland (Dobrzhinetskaya et al. 2002) and North Qaidam, China (Song et al. 2003). Gayk et al. (1995) had reported quartz exsolution in clinopyroxene from a high-pressure granulite of the Munchberg Massif, Germany, which also has undergone UHP metamorphism as coesite had been identified in a retrograde eclogite there by O'Brien (1993). As concluded by Liou (1998, p. 80) "the topotaxial growth of quartz lamellae in eclogitic Ca-Na clinopyroxene are best explained by exsolution from a former supersilicic Cpx stabilized at ultrahigh pressure conditions."

METAMORPHIC MAGNESITE

The metamorphic textures of the samples we studied (519-1, 519-2, and 508) clearly show the possible retrograde reaction: magnesite + omphacite + garnet + coesite + H_2O = dolomite + glaucophane + clinozoisite in Chinese Western Tianshan eclogites (Fig. 1, Zhang et al. 2002b), i.e., rounded to

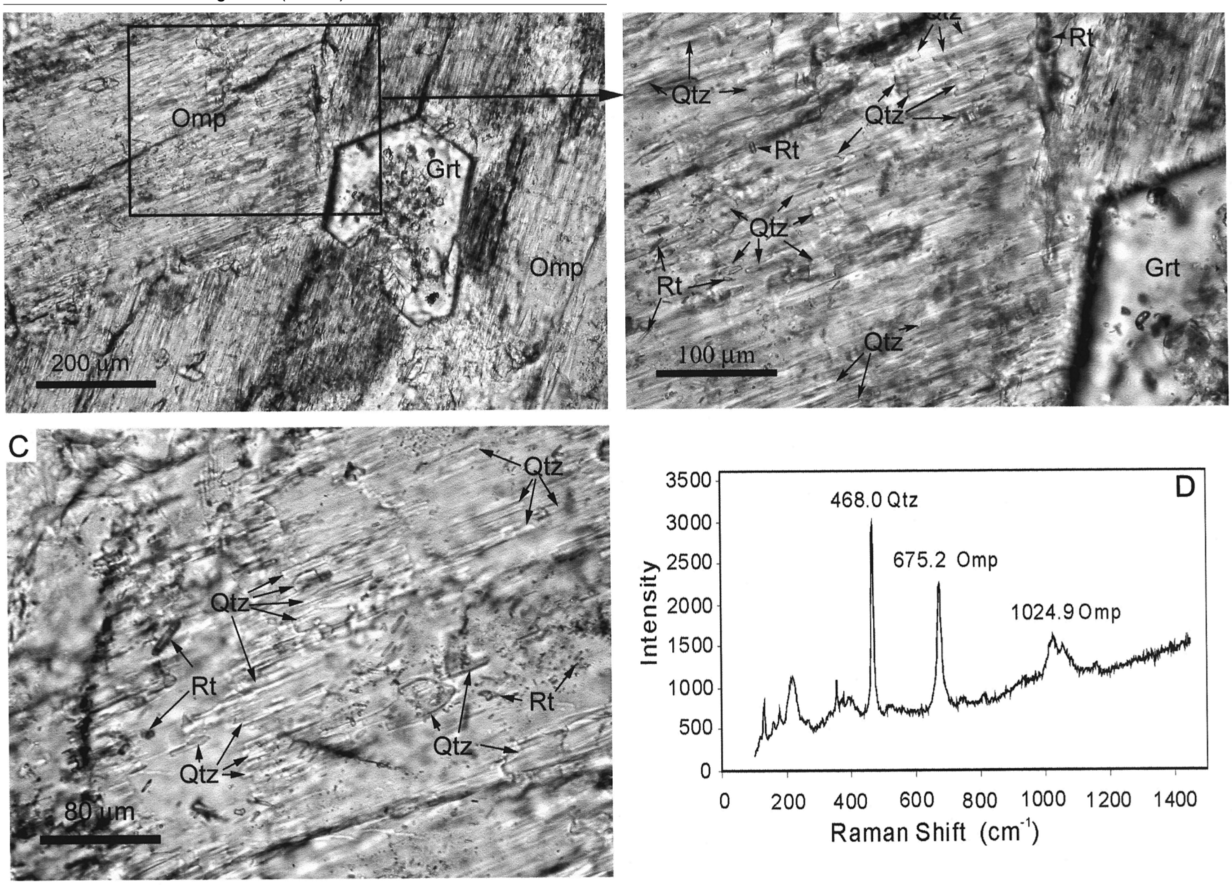

FIGURE 1. Photomicrographs of quartz exsolution lamellae in omphacites from eclogites in Western Tianshan, China (sample 105-34). **(A)** the strongly oriented quartz exsolution lamellae in omphacites (plane-polarized light). **(B-C)** close-up photomicrograph showing quartz exsolution lamellae and random rutile inclusions in omphacite (plane-polarized light). **(D)** Representative Micro-Laser Raman spectrum of quartz exsolution lamellae in omphacites, performed on the Renishaw-RM1000 Laser Raman spectroscopy with 514 nm line of a Ar-ion laser at the Department of Geology, Peking university.

TABLE 2. The representative compositions of garnet, omphacite and phengite for Grt-Omp-Phe geobarometer calculations of magnesite-bearing eclogites from Western Tianshan, China

	302			303			305		
mineral	Grt	Omp	Phen	Grt	Omp	Phen	Grt	Omp	Phen
SiO_2	38.01	55.05	51.16	37.63	55.63	52.66	37.35	55.79	52.25
TiO_2	0.00	0.03	0.47	0.07	0.04	0.09	0.01	0.03	0.22
Al_2O_3	21.13	8.48	24.12	21.51	11.43	23.66	21.99	10.27	23.66
Cr_2O_3	0.00	0.07	0.03	0.00	0.00	0.06	0.02	0.02	0.03
FeO*	29.37	11.33	4.88	29.17	10.93	4.83	29.73	10.43	4.63
MnO	0.39	0.00	0.05	0.41	0.03	0.00	0.21	0.00	0.04
NiO	0.00	0.03	0.00	0.00	0.07	0.00	0.00	0.01	0.00
MgO	2.50	5.28	4.73	2.42	3.96	4.60	2.60	4.47	4.32
CaO	7.98	10.00	0.04	7.86	7.15	0.01	7.57	7.99	0.03
Na_2O	0.00	8.61	0.56	0.02	10.19	0.37	0.06	9.92	0.36
K_2O	0.00	0.03	9.68	0.00	0.03	9.87	0.00	0.03	8.54
Total	99.38	98.91	95.72	99.09	99.46	96.15	99.52	98.96	94.08
Si^{4+}	3.04	1.99	6.88	3.02	2.00	7.02	3.01	1.99	7.06
Al^{IV}	0.00	0.01	1.12	0.00	0.00	0.98	0.00	0.01	0.94
Al^{VI}	1.99	0.35	2.70	2.03	0.49	2.74	1.99	0.43	2.82
Ti^{4+}	0.00	0.00	0.05	0.00	0.00	0.01	0.00	0.00	0.02
Fe^{3+}	0.00	0.27	0.00	0.00	0.23	0.00	0.00	0.28	0.00
Cr^{3+}	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00
Fe^{2+}	1.96	0.07	0.55	1.96	0.07	0.54	2.00	0.04	0.52
Mg^{2+}	0.30	0.29	0.95	0.29	0.21	0.92	0.31	0.24	0.87
Mn^{2+}	0.03	0.00	0.01	0.03	0.00	0.00	0.01	0.00	0.01
Ca^{2+}	0.68	0.39	0.01	0.68	0.28	0.00	0.65	0.31	0.00
Na^{+}	0.00	0.61	0.15	0.00	0.72	0.10	0.01	0.70	0.09
K^{+}	0.00	0.00	1.66	0.00	0.00	1.68	0.00	0.00	1.47
Cation	8.00	4.00	14.06	8.00	4.00	13.99	8.00	4.00	13.81
$P_{omp-gt-phe}$ (T=525 °C) (GPa)		2.46			2.65			2.51	
$P_{omp-gt-phe}$ (T=607 °C) (GPa)		2.61			2.89			2.72	

Note: Formula proportions based on 6 oxygen atoms for omphacite, 12 oxygen atoms for garnet and 24 oxygen atoms for phengite.
*Total iron as FeO, Fe^{3+} calculated from charge balance. Electron microprobe analyses of minerals were performed on a Jeol 6400 at the Australian National University, operated at 15kV acceleration voltage, 20nA beam current, and 20s counting time. Synthetic silica (Si), natural pyrope (Mg), natural andradite (Fe, Ca), natural albite (Na, Al), natural rutile (Ti), synthetic spessartine (Mn) and natural sanidine (K) served as standards. Final results were reduced by a ZAF correction program. $P_{omp-gt-phe}$ calculated by the geobarometer of omphacite-garnet-phengite (Waters and Martin 1993).

subidiomorphic magnesites and omphacites occur as relic inclusions within dolomite, whereas garnet with coesite pseudomorph inclusions was replaced by secondary glaucophanes. There is no paragonite within dolomite in our studied samples. It is a fact, however, that some phengites occur as inclusions in dolomites.

The garnet-omphacite-phengite geobarometer is generally accepted as the most reliable method to estimate metamorphic pressures of eclogites, and has been applied successfully to several studies of UHP eclogites, such as those at Dabie (Caswell et al. 1997), Dora-Maira (Nowlan et al. 2000) and the Himalayas (O'Brien 2001). Using the garnet-clinopyroxene-phengite barometer of Waters and Martin (1993) and Carswell et al. (1997) [$P = 26.9 + 0.0159\ T(\mathrm{K}) - 0.00249T(\mathrm{K})^{*}\ln K \pm 1$ (kbar), $\ln K = 6\ln a_{\mathrm{di}} - \ln a_{\mathrm{prp}} - 2\ln a_{\mathrm{grs}} + 3\ln a_{\mathrm{invphe}}$], calculated pressures for magnesite-bearing Tianshan eclogites (Table 2) at T = 525 ~ 607 °C range from 24.6 ± 1 to 28.9 ± 1 kbar. These results and the P-T calculations (27-28 kbar) on the reaction of magnesite + omphacite + garnet + coesite + H_2O = dolomite + glaucophane + clinozoisite (Zhang et al. 2002b) suggest undoubtedly that the peak metamorphic pressure of magnesite-bearing eclogites had reached the UHP field.

Many magnesites occurrences have been positively identified in UHP eclogites and mantle rocks. Geological occurrences and experimental studies clearly confirm that magnesite is a stable phase under mantle conditions (see the summary by Liou et al. 1998). Our phase equilibria of end-member reactions and activity models for the minerals of magnesite-bearing eclogites from Chinese Tianshan (Zhang et al. 2002b) were calculated by the THERMALCALC and WINAX programs of Holland and Powell (1998), respectively, using the updated internally consistent thermodynamic database (Holland and Powell 1998). In contrast, the P-T conditions (480 to 600 °C and 18~21 kbar) calculated using P-T pseudosections in the NCFMASH system by Klemd et al. (2001) are definitely not suitable for magnesite-bearing eclogites in Western Tianshan, China. This is because so many carbonate minerals, not considered in the NCFMASH system, exist in Tianshan eclogites (Zhang et al. 2002b, and Fig. 3 in the Comment of Klemd).

Some paragonites associated with glaucophanes occur as secondary minerals replacing porphyroblastic garnets or dolomites in magnesite-bearing eclogites. It is most likely that the few small paragonites and glaucophanes found within dolomites (see Fig. 3 of Klemd) are secondary minerals replacing precursors in the micro-cracks of porphyroblastic dolomites and were produced by fluid flow during the blueschist-facies retrograde metamorphism. Furthermore, the textural relations shown in Figure 3b in the comment of Klemd indicate that both glaucophane and dolomite formed in the same retrograde stage as the second minerals after magnesite and garnet, i.e., rounded magnesites appeared as precursor inclusions within dolomites only and euhedral glaucophanes appeared between different dolomite grains, which is consistent with the suggested reaction 4 in our paper (Zhang et al. 2002b). Yes, the experimental studies show that the UHP glaucophane has a significant substitution of Si by ^{IV}Al and excess Mg on the M4 site (Tropper et al. 2000). The present compositions of glaucophanes may be affected by the latest blueschist-facies retrograde metamorphism. Thus, the values of peak metamorphic pressures (27–28 kbar) calculated in our paper (Zhang et al. 2002b) should be the minimum stable pressures for the peak UHP stage. Even with the addition of paragonite and quartz (instead of coesite), the calculation of phase relations also shows that the invariant point is intersected at a pressure of ~25 kbar with 600 ^{O}C and X_{CO_2}=0.006 for activity corrected end-member reactions in Western Tianshan eclogites using the THERMACALC program. This is because the maximum temperature for western Tianshan eclogites is ~607 ^{O}C (Zhang et al. 2002b) not as low as 470 ^{O}C used in the Comment of Klemd.

FURTHER CONSIDERATIONS

We have identified lawsonite pseudomorphs within porphyroblastic garnets in type I eclogites from Western Tianshan, China (Fig. 2a in Zhang et al. 2001). The Chinese western Tianshan blueschist-eclogite metamorphic belt extends westward to connect with the Atbashy high *P*/*T* metamorphic belt in Kazakhstan, which contains coesite pseudomorphs (Tagiri et al. 1995), and the Markabl belt in Kyrgyzstan (Volkava and Budanov, 1999) where coesite has been reported recently by Tagiri et al. (2001) in talc-chloritoid-glaucophane-phengite schists. We have also found magnesite-bearing, chloritoid-glaucophane schists in Western Tianshan, China, that are interlayered with garnet-phengite schists and blueschists associated with magnesite-bearing eclogites. The metamorphic reaction of magnesite + aragonite = dolomite has been recognized in these magnesite-bearing chloritoid-glaucophane schists, which indicates that the peak pressures of UHPM in the Tianshan eclogites facies rocks may reach ~5.0 Gpa (Zhang et al. 2003). Those pressure values suggest that some UHPM eclogites in the Chinese western Tianshan are likely to have an "in situ" origin, i.e., eclogites and their associated country rocks have undergone UHPM together.

In summary, all the discoveries in the Western Tianshan, inlcuding coesite pseudomorphs within garnets, quartz exsolution lamellae in omphacites, and metamorphic magnesite in eclogites (Zhang et al. 2002a, 2002b), as well as magnesite in chloritoid-glaucophane schists (Zhang et al. 2003) support the conclusion that some of these eclogite-facies rocks have definitely experienced ultra-high pressure metamorphism.

ACKNOWLEDGMENT

We give our thanks to S-S Sun for his critical comments on the manuscript. We are grateful to Shuguang Song for his help on the *P-T* calculations of garnet-omphacite-phengite barometer program and the analyses by Laser Raman spectrum at Department of Geology, Peking University. This study was sponsored by the Major State Basic Research Development Program (G1999075508), TRAPOYT of MOE, China and National Nature Science Foundation of China (Grants 49972028, 40228003) to the first author.

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MANUSCRIPT RECEIVED FEBRUARY 18, 2003
MANUSCRIPT ACCEPTED MARCH 9, 2003
MANUSCRIPT HANDLED BY ROBERT DYMEK