Coesite inclusions and prograde compositional zonation of garnet in eclogite from Zekou in the Su–Lu ultrahigh–pressure terrane, eastern China

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In the Su–Lu UHP terrane, eastern China, coesite-bearing eclogites have been reported in five areas (Weihai, Yangkou, Rizhao, Donghai and Rongcheng). The presence of a coesite inclusion (70 μm) in garnet in a strongly retrograded eclogite at Zekou (about 40 km southwest of Rongcheng) shows for the first time that this region also underwent coesite–eclogite facies metamorphism. In addition, the garnet of the Zekou eclogite preserves a distinct compositional zonation. The eclogite consists of garnet (20%), symplectite (70%: amphibole + plagioclase) and other accessory minerals (amphibole, rutile, quartz and ilmenite). Garnet porphyroclasts (0.5–1 mm in diameter) show compositional zonation that can be divided into three parts: core ($\text{Alm}_{58-59} \text{Sp}_{0.7-0.9} \text{Prp}_{15-17} \text{Adr}_{0.1-0.2} \text{Grs}_{23-24}$), mantle ($\text{Alm}_{55-58} \text{Sp}_{0.5-0.8} \text{Prp}_{14-15} \text{Adr}_{0.1-0.2} \text{Grs}_{25-28}$), and rim ($\text{Alm}_{53-56} \text{Sp}_{0.4-0.6} \text{Prp}_{17-18} \text{Adr}_{0.1-0.2} \text{Grs}_{25-27}$). Each part has a characteristic inclusion mineralogy: the core part contains rutile, quartz and no coesite, the mantle part contains coesite, quartz–pseudomorphs after coesite, rutile, omphacite and zircon, and the rim part contains rutile. The coesite inclusion (70 μm) is located in the outer mantle part and is associated with radial fractures in the surrounding garnet. The different inclusion assemblages and the chemical zonation from core to rim in garnet porphyroclasts suggest that the Zekou eclogite preserves the information of the prograde stage during UHP metamorphism.

Introduction

Ultrahigh–pressure (UHP) metamorphic terranes are recognized in several collisional zones in the Eurasian and African continents. UHP index minerals (e.g., coesite and diamond) occur as inclusions in garnet, omphacite, kyanite, zircon, and epidote/zoisite (e.g., Chopin, 1984; Smith, 1984, 1995; Dobrzhinetskaya et al., 1993; Eide, 1994). In the Dabie–Sulu UHP terrane, the largest UHP belt in the world, coesite occurs in eclogite in five areas; Weihai, Yangkou, Rizhao, Donghai, and Rongcheng (e.g., Okay, 1993; Hirajima et al., 1990; Zhang and Liou, 1998; Nakamura and Hira-

jima, 2000). Coesite is also widespread in the Dabie Mountains. In addition, Xu et al. (1992) and Okay (1993) also report the presence of microdiamond inclusions in garnet from eclogite in the Dabie Mountains. In this paper, we report a new occurrence of coarse-grained coesite found as inclusions in garnet of a strongly retrograded eclogite from the Zekou area (about 40 km southwest from Rongcheng). It is generally difficult to analyze the prograde P–T history for strongly retrograded rocks, because the minerals formed during the prograde stages are commonly completely replaced by peak and retrograde assemblages. Despite the pervasive strong retrogression, the Zekou eclogite preserves information on the prograde metamorphic history, as demonstrated by the inclusion mineralogy in the garnet and its chemical zonation. This paper describes the inclusion mineralogy and chemical zonation of garnet of the Zekou eclogite and discusses the implication for the metamorphic evolution of this area. Abbreviations for

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minerals and end-members hereafter follow those of Kretz (1983); additionally, Amp, amphibole; Coe, coesite.

Mineral compositions of all samples were analyzed with a JEOL JXA-8900 electron probe microanalyzer at the Department of Earth Sciences, Waseda University. Inclusions were identified by a JASCO NRS-2000 laser Raman spectrophotometer at Tokyo Institute of Technology.

Geologic background

The Su-Lu terrane is located in the eastern Shandong and northern Jiangsu Provinces. This terrane is the eastern extension of the Qinling-Dabie collision zone developed between the Yangtze and Sino-Korean cratons. It is bounded by the Yantai-Qingdao-Wulian fault (YQWF) on the northwest and the Xiangshui-Jiashan fault (XJF) on the south, and it has been displaced about 530 km by the left-lateral Tanlu fault. The Su-Lu terrane consists of the ultrahigh-pressure (UHP) and high-pressure (HP) belts (Zhang and Liou, 1998). Figure 1 shows a geological sketch map of the Su-Lu region.

The UHP belt in the Su-Lu terrane consists mainly of amphibolite-granulite facies granitic gneiss with minor amphibolite layers and minor marble lenses as well as widespread but rare metamorphosed garnet

peridotite and pyroxenite. Eclogite bodies occur as isolated lenses and discontinuous layers in gneiss, in ultramafic bodies and in marble (Zhang and Liou, 1998). In the HP belt, quartz-mica schist, chloritoid-kyanite-mica-quartz schist, marble, and rare blueschist are discontinuously exposed, but no eclogite has been identified (Zhang and Liou, 1998). Both HP and UHP belts have similar protoliths, and they were intruded by post-orogenic Mesozoic granite (Zhang et al., 1994).

Many independent geochronologic studies demonstrate that the peak of the UHP and HP metamorphism occurred during the collision of the Yangtze and Sino-Korean cratons during the late Triassic, e.g. Sm-Nd isochron ages give 210 to 230 Ma (Li et al., 1993; Jahn et al., 1996), and $^{40}\text{Ar}/^{39}\text{Ar}$ ages give 220 Ma (Cong et al., 1992). The Dabie-Sulu UHP metamorphic belt has also attracted attention as one of the sites for the Continental Drilling Project by China and ICDP (International Scientific Continental Drilling Program).

Petrography of Zekou eclogite

The Zekou eclogite mainly consists of porphyroclastic garnet (20%) and amphibole (barroisite)+sodic oligoclase symplectite (70%). Accessory minerals are amphibole (magnesirotamite), rutile, quartz, and ilmenite (Fig. 2a). The grain size of garnet is 0.5–1 mm in diameter and each grain is surrounded by a thin corona of amphibole (taramite, 50–80 μm in width). Matrix amphibole (magnesirotamite, 0.5–1 mm in diameter), which locally has a plagioclase corona (10–20 μm in width), is subhedral to anhedral (Fig. 2b). Rutile occur both as discrete grains in the matrix and as inclusions in garnet (Fig. 2a, c). Matrix grains show an oval or rounded shaped (0.1–0.25 mm in diameter). Rutile inclusions show both oval (5–80 μm in diameter) and needle-shapes (10–50 μm in length, 3–5 μm in width).

Silica minerals occur as 1) coarse-grained quartz (0.5–0.8 mm in diameter) in the matrix, 2) fine-grained inclusions (10–30 μm in diameter) in garnet (Fig. 2c) and 3) coesite inclusions in garnet (Fig. 2d, e). Quartz and coesite inclusions are described in more detail later. Zircon, which has a rounded shape, rarely occurs as inclusions in garnet (Fig. 2e). Ilmenite (100–200 μm in diameter), which shows a subhedral to anhedral form, occurs only in the matrix. Many grains of ilmenite are intergrown with rutile. Symplectite, which is probably after omphacite, consists of amphibole (barroisite)+sodic oligoclase ($\text{Ab}_{88-90}\text{An}_{10-12}$).

Figure 1. Geological sketch map of the Su-Lu region, eastern China, showing major tectonic units, distribution of coesite/quartz pseudomorphs after coesite-bearing eclogites and ultramafic rocks. Abbreviations: XJF, Jiaoshan-Xianshui fault; YQWF, Yantai-Qingdao-Wulian fault.

Figure 2. Photomicrographs showing parageneses and textures of the eclogite from the Zekou area (sample no. 96ZK2Yc). All photomicrographs were taken using plane polarized light. (a) Garnet porphyroclast sets in a symplectite in matrix: Amp (barroisite)+sodic oligoclase. Garnet is rimmed by a corona of Amp (taramite), and contains numerous dusty inclusions of Rt and Qtz in the core part, and quartz-pseudomorphs after coesite with radial fractures and Rt in the mantle part. (b) Matrix amphibole and symplectite. (c) Abundant Rt and euhedral grains of single Qtz crystals in the core part of Grt. (d) Coesite inclusion (see Figure 2e for details) in garnet porphyroclast. The host garnet exhibits well-developed radial fractures around coesite. (e) Coesite inclusion partly replaced by quartz in garnet. Zircon occurs near coesite. (f) Omphacite inclusion in the inner mantle part of garnet porphyroclast.

Figure 3. Compositional maps of garnet porphyroclasts in the Zekou eclogite (sample no. 96ZK2Yc). (a)–(d) maps show Ca, Mg, Fe and Mn distributions in the garnet porphyroclast of Figure 2a, respectively. Oxide wt% is also shown. Scale bar is 0.2 mm. (a)–(b) Euhedral zonation of garnet, which has core, mantle, and rim parts separated by sharp compositional boundaries. (e)–(h) Grt compositional zonation around coesite inclusion (Fig. 2e). Scale bar is 50 μ m.

Table 1. Distribution of inclusions of garnet

	Qtz	Coe/Qtz-ps	Rt	Omp	Zr
core	+		+		
mantle		+	+	+	+
rim			+		

Inclusion mineralogy of garnet

Garnet includes rutile, quartz, coesite, quartz-pseudomorphs after coesite, omphacite and zircon (Fig. 2a, c, e, f). The garnet displays compositional zonation, which can be divided into three parts; core, mantle and rim. These are described in the next chapter and shown in Figures 3 and 4. The inclusion assemblages in the garnet are clearly related to the compositional zonation. Table 1 shows the distribution of mineral inclusions in each part of the garnet.

Core part of garnet: Dusty inclusions of rutile and quartz are scattered in the core of garnet (Fig. 2a, c). 10–100 grains of rutile inclusions are contained in this part of one garnet. Oval or rounded grains are 5 to 80 μm in diameter, and needle-shaped grains are 10–50 μm in length and 1–3 μm in width. 5–20 grains of quartz are present in this part of one garnet. They occur as euhedral and single crystal inclusions, which range from 10 to 30 μm in diameter. Garnet shows no fracturing or deformation around them.

Mantle part of garnet: This part of garnet includes coesite, quartz-pseudomorphs, omphacite, rutile and zircon. The outer mantle part of the garnet contains coesite (70 μm in diameter) (Fig. 2d, e) and quartz-

pseudomorphs after coesite (100–200 μm in diameter) (Fig. 2a). Silica inclusions in the mantle part of the garnet are generally larger than those in the core part. The numbers of silica inclusions in this part are less than those in the core. The presence of coesite and quartz-pseudomorphs after coesite suggest that the mantle part of the garnet formed in the coesite-stability field. Nearly all the silica is present as quartz-pseudomorphs, but two coesite grains are preserved in one thin section (sample no. 96ZK2Yc). Coesite (70 μm) is subhedral, and occurs with a rim of palisade polycrystalline quartz aggregates (about 20 μm in width) that is characteristic for pseudomorphs after coesite. Quartz-pseudomorphs after coesite display oval or rounded shape. Coesite and quartz-pseudomorphs are preferentially included in the outermost mantle of garnet near the boundary with rim part (Figs. 2a, d and 3). The host garnet exhibits radial fractures around both coesite with quartz-pseudomorphs and quartz-pseudomorphs. Similar occurrence of silica inclusions of garnet is also shown in rocks from other region, such as whiteschist from the Kokchetav massif, Kazakhstan (Parkinson, 2000).

In addition to the textural difference under microscope, coesite and quartz were also positively identified and distinguished by laser Raman spectroscopy. The coesite inclusion in garnet shows the Raman band at 520 cm^{-1} (Fig. 5), which closely corresponds to the main Raman band for coesite 521–526 cm^{-1} (Boyer et al., 1985).

Omphacite inclusions (60–90 μm in diameter) are restricted to the inner mantle part of garnet near the boundary with the core part (Fig. 2f). Rutile shows an oval or rounded shape and ranges from 15 to 50 μm in diameter. Zircon (50–80 μm in diameter) has an oval or rounded form (Fig. 2e). Rutile inclusions in the mantle part are much less than in the core.

Figure 4. Sketch of core, mantle and rim distribution in garnet porphyroblast of Figure 3a–d.

Figure 5. Representative laser Raman spectra for coesite in garnet porphyroblast.

Rim part of garnet: This part is thinner than the core and mantle (Figs. 3 and 4), and could have been partially replaced by the amphibole (taramite) corona. This part contains only a few inclusions of rutile (50–200 μm in diameter), and no silica inclusion is present. Rutile displays an oval or rounded shape, and it is larger than that preserved in the core and mantle parts.

Chemical zonation of garnet

Representative microprobe analyses of garnet and other minerals are listed in Table 2. Chemical compositions of different parts of garnet porphyroclast are; core (Alm₅₈₋₅₉ Sps_{0.7-0.9} Prp₁₅₋₁₇ Adr_{0.1-0.2} Grs₂₃₋₂₄), mantle (Alm₅₃₋₅₈ Sps_{0.5-0.8} Prp₁₄₋₁₅ Adr_{0.1-0.2} Grs₂₅₋₂₈), and rim (Alm₅₃₋₅₆ Sps_{0.4-0.6} Prp₁₇₋₁₈ Adr_{0.1-0.2} Grs₂₅₋₂₇). Figure 3 shows compositional zonation patterns of two garnet grains, and Figure 6 gives a typical compositional profile (Alm, Sps, Prp, Adr and Grs) across garnet. The boundaries between these parts can be defined by the changes in the Mg and Ca contents. The contents

Figure 6. Compositional profile of garnet porphyroclast (Alm, Grs, Prp, Sps, Adr). A–A' is shown in Figure 4.

Table 2. Representative microprobe analysis of principal minerals from the Zekou eclogite

mineral	Grt			Cpx		Amp		Pl	
	O=12			O=6		O=23		O=5	
point	core	mantle	rim	inclusion	matrix	corona	sym	corona	sym
SiO ₂	38.799	39.682	39.630	55.100	43.995	40.132	48.795	64.776	65.128
TiO ₂	0.074	0.029	0.058	0.003	0.499	0.100	0.363	0.020	0.000
Al ₂ O ₃	21.948	22.009	22.034	10.044	13.279	17.189	7.385	21.685	21.253
Cr ₂ O ₃	0.000	0.000	0.003	0.000	0.025	0.001	0.010	0.000	0.000
FeO*	26.802	25.583	24.972	8.040	13.993	16.931	11.814	0.361	0.273
MnO	0.370	0.328	0.193	0.000	0.056	0.135	0.048	0.000	0.000
MgO	4.150	3.596	4.294	6.905	12.709	9.031	12.757	0.002	0.011
CaO	8.588	9.447	9.402	11.517	8.651	10.305	14.941	2.622	2.587
Na ₂ O	0.011	0.035	0.016	7.418	3.435	3.289	1.952	10.361	10.437
K ₂ O	0.000	0.000	0.000	0.000	0.403	0.114	0.034	0.019	0.026
total	100.742	100.709	100.602	99.027	97.045	97.227	98.099	99.846	99.715
Si	3.011	3.062	3.052	2.010	6.495	6.039	7.100	2.862	2.879
Ti	0.004	0.002	0.003	0.000	0.055	0.011	0.040	0.001	0.000
Al	2.008	2.002	2.000	0.432	2.311	3.049	1.267	1.129	1.107
Cr	0.000	0.000	0.000	0.000	0.003	0.000	0.001	0.000	0.000
Fe	1.739	1.651	1.608	0.245	1.728	2.131	1.438	0.013	0.010
Mn	0.024	0.021	0.013	0.000	0.007	0.017	0.006	0.000	0.000
Mg	0.480	0.414	0.493	0.375	2.797	2.026	2.767	0.000	0.001
Ca	0.714	0.781	0.776	0.450	1.368	1.662	2.330	0.124	0.123
Na	0.002	0.005	0.002	0.525	0.983	0.960	0.551	0.888	0.895
K	0.000	0.000	0.000	0.000	0.076	0.022	0.006	0.001	0.001
total	7.982	7.938	7.946	4.037	15.823	15.916	15.505	5.018	5.016
Alm	58.8	57.6	55.7					Ab	88
Sps	0.8	0.7	0.4					An	12
Pyp	16.2	14.4	17.1						
Adr	0.2	0.1	0.2						
Grs	23.9	27.2	26.7						

*Total Fe expressed as FeO.

of Na₂O and TiO₂ in whole garnet are less than 0.04 wt% and 0.1 wt%, respectively.

Core part of garnet: The core part of garnet shows almost euhedral growth zoning (Fig. 3a). The contents of CaO and MgO in this part are heterogeneous. The content of CaO decreases from inside (9.7 wt%) to outside (8.9 wt%) and is lowest at the boundary with the mantle part. The MgO content varies in the opposite sense to the CaO distribution. The average MgO content is 4.0 wt% in the inner core, and 4.2 wt% in the outer core. FeO and MnO in the core part are homogeneous, and are higher than those in both the mantle and rim parts. The average composition of this part is Alm_{58.8} Sp_{8.8} Prp_{16.2} Adr_{0.2} Grs_{23.9}. The boundary between the core and mantle parts is generally sharp showing a sudden change in chemical composition.

Mantle and rim parts of garnet: The mantle part is compositionally heterogeneous (Fig. 3b). The contents of FeO and MnO gradually decrease toward outer mantle part. The average composition of the mantle part is Alm_{57.6} Sp_{8.7} Prp_{14.4} Adr_{0.1} Grs_{27.2}.

The shape of the boundary between the mantle and rim parts is a little obscure in comparison with that between the core and mantle parts. The rim part of the garnet is CaO-poor and highly MgO-rich relative to the mantle part (the average composition: Alm_{55.7} Sp_{8.4} Prp_{17.1} Adr_{0.2} Grs_{26.7}). The average content of MgO in the rim part is 4.3 wt%.

According to compositional analysis, maps, and chemical profiles of the garnet, there is a general decrease in FeO and MnO from the core to rim parts, and an increase in MgO in the same direction, clearly suggesting prograde growth of garnet. In Figure 3e, a coesite inclusion is shown, the CaO content is heterogeneous around the coesite, and the CaO pattern in the rim part is divided into two zones; low CaO (9.4 wt%) at inner rim part and little high CaO (9.7 wt%) at outer rim part.

Garnet formation and metamorphic evolution

The characteristics of the inclusion assemblages and the chemical zonation of the garnet porphyroclasts suggest that garnet porphyroclasts in the Zekou eclogite preserve records of prograde and UHP metamorphic stages. The core part of garnet records lower P–T conditions attained during the prograde stage as suggested by; 1) the numerous dusty rutile and quartz inclusions (Fig. 2a, c), 2) the decreasing content of MnO from inner core to outer core (Fig. 3d). The characteristics of the core part inclusion mineralogy are similar to those of quartz inclusions in garnet in whiteschist from the Kokchetav massif, Kazakhstan (Parkinson, 2000). Parkinson

(2000) interpreted quartz inclusions as follows; the single crystal quartz inclusions must have been present during a relatively low-grade part of the prograde stage. Subsequent transition from quartz to coesite was prevented by overgrowth by garnet and inclusion within the core part of garnet. In the Zekou eclogite, we suggest that the single crystal quartz inclusions in the core part of garnet also never transformed to coesite during deep burial.

The occurrence of coesite and quartz-pseudomorphs after coesite at the outer mantle part of garnet indicates that the outer mantle grew in the coesite-stability field. Gradual decrease of FeO and MnO contents from core to rim also suggests the formation during the prograde history. Thus, the studied garnet records the prograde growth history with the core part formed in the quartz-stability field (low P–T stage), and the outer mantle part formed in the coesite-stability field.

Omphacite inclusions occur only in the inner mantle part of garnet. We estimated the equilibrium temperature using Fe–Mg exchange geothermometers between garnet and clinopyroxene (Ellis and Green, 1979; Powell, 1985; Krogh, 1988). Temperature estimates at the inner mantle part that contains omphacite inclusions gives results ranging from 750–880°C (Krogh), 760–880°C (Powell), and 780–890°C (Ellis and Green) at assumed pressures of 2.0–2.5 Gpa, respectively. These pressure values are inferred on the base that the outer mantle part contains coesite inclusions and inner mantle grew at pressures below the quartz-coesite transition. The results are consistent with the estimated temperature in other areas in the Su–Lu region (Zhang and Liou, 1998; Kurahashi, 2000).

As garnet porphyroclasts in the Zekou eclogite contain no hydrous minerals as inclusions, the Zekou eclogite was locally SiO₂ oversaturated in its prograde history, and garnet included either quartz or coesite as a result of pressure and temperature changes.

Seventy volume percent of the eclogite consists of amphibole (barroisite)+sodic oligoclase symplectite, which probably formed after omphacite due to fluid infiltration during retrograde metamorphism. Garnet in the Zekou eclogite contains coesite and its quartz-pseudomorphs as inclusions and shows radial fractures around coesite and quartz-pseudomorphs (Fig. 2a, e). If the radial fractures of garnet caused by the volume-increase associated with the coesite-quartz transition had formed before fluid infiltration, all coesite is likely to have been transformed to quartz due to the presence of fluid as a catalyzer. The preservation of coesite, therefore, suggests that the radial fractures of garnet around coesite and quartz-pseudomorphs may have formed

Figure 7. Highly schematic P-T diagram for the Zekou eclogite by the garnet growth history on the basis of inclusion mineralogy, garnet zoning and geothermometric estimates in the inner mantle. Stage 1: core part of garnet formed in the quartz stability field, and contains euhedral single quartz inclusions. Stage 2: inner mantle part formed at estimated P-T conditions (750–890°C at 2.0–2.5 GPa) in the quartz-stability field. Stage 3: outer mantle part formed within the coesite stability field. Stage 4: rim part possibly formed at peak UHP stage. Stage 5: garnet rimmed by a corona of retrograded amphibole, and symplectite (Amp+Pl) formed after omphacite by the fluid infiltration during retrograde metamorphism. Stage 6: garnet has radial fractures around coesite and quartz-pseudomorphs after the formation of symplectite.

after the formation of symplectite.

Figure 7 is a schematic P-T diagram showing the prograde growth of garnet in the Zekou eclogite during UHP metamorphism on the basis of inclusion mineralogy and chemical zonation of garnet as mentioned above.

Conclusions

Coesite inclusions (maximum 70 μm) are well preserved in garnet porphyroclasts in a strongly retrograded eclogite from the Zekou area of the Su-Lu UHP terrane. Garnet porphyroclasts have a clear compositional zonation, which can be divided into three parts: core, mantle and rim. Each zone has a characteristic inclusion mineralogy: the core part contains rutile, quartz and no coesite, the mantle part contains coesite, quartz-pseudomorphs after coesite, rutile, omphacite and zircon, and the rim part contains rutile.

These observations indicate that the core part formed in the quartz-stability field, whereas the mantle part formed in the coesite-stability field. Characteristics of the chemical zonation of garnet porphyroclasts are consistent with such a prograde growth history. Thus, the Zekou eclogite preserves information concerning both the prograde and peak UHP stages of metamorphism.

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