## Occurrences of intergranular coesite in ultrahigh-P rocks from the Sulu region, eastern China: Implications for lack of fluid during exhumation

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### ABSTRACT

Several coesite grains along garnet-omphacite grain boundaries were discovered in eclogites from Yangkou Beach of the Sulu region, eastern China. These grains exhibit variable extents of conversion of coesite to palisade- through mosaic- to granoblastic-quartz aggregates. The rare occurrence of intergranular and matrix coesite in ultrahigh-pressure (UHP) crustal rocks is related to the fast rate of exhumation and the low amount of fluid infiltration required during retrograde recrystallization. Sluggish reactions due to the lack of fluid in both UHP and retrograde metamorphism resulted in the occurrence of intergranular coesite in these eclogites, the preservation of gabbroic texture and relict igneous minerals, and the metastable persistence of low-P assemblages in the coesite-stability field.

### INTRODUCTION

When C. Chopin discovered inclusions of relict coesite in pyrope porphyroblasts of quartzite from the western Alpine Dora Maira Massif in 1984, it was assumed that the matrix quartz of the rock was also once coesite (e.g., Chopin et al. 1991; Schreyer 1988). During the return from mantle depths to crustal levels, the matrix coesite recrystallized completely under amphibolite-facies conditions to intergranular polygonal quartz aggregates with undulatory extinction (e.g., Schertl et al. 1991; Michard et al. 1995). Subsequent studies of other ultrahigh-pressure (UHP) regions have revealed accumulating evidence of UHP metamorphism of supracrustal rocks that had been taken to mantle depths. These include the occurrence of microdiamond and coesite inclusions in garnet and zircon from pelitic gneiss and carbonate from the Kokchetav Massif, northern Kazakhstan (e.g., Sobolev and Shatsky 1990; Shatsky et al. 1995) and inclusions of coesite or coesite pseudomorphs in zircon, garnet, jadeite, and dolomite of calc-silicate rocks and jadeite quartzite from the Sulu-Dabie region of east-central China (e.g., Schertl and Okay 1994; Sobolev et al. 1994; Wang et al. 1995; Zhang and Liou 1996a; Liou et al. 1996). The preservation of coesite and microdiamond in UHP crustal rocks depends on many petrochemical and tectonic factors, including rate of exhumation, fluid content, and P-Tconditions of superimposed retrograded metamorphism, and possibly other unknown factors. Rigid minerals such as zircon, garnet, and omphacite are the most common containers preserving these UHP minerals. However, to our knowledge, intergranular coesite or matrix coesite has not been described in rocks from any recognized UHP terranes. Employing elastic calculations, Gillet et al. (1984) and Van der Molen and Van Roermund (1986) concluded that coesite can be preserved as inclusions only if T is <200 °C. All recognized UHP minerals such as coesite and microdiamond occur only as inclusions in rigid minerals such as zircon, garnet, omphacite, and kyanite (e.g., Chopin and Sobolev 1995), inasmuch as rapid exhumation invariably converted coesite to quartz aggregates. The pressure-vessel effect restricts the coesite-quartz retrogression to only moderate amounts ( $\sim 25-30$  vol%) of the large-volume polymorph before the host garnet fractures, allowing ingress of fluid and more complete conversion.

In our on-going study of UHP rocks from the Dabie-Sulu region, we have found several intergranular coesite crystals in some eclogites from the Sulu UHP region, easternmost China. This short paper describes their occurrence and P-T condition of formation as well as implications for the role of fluid and the rate of exhumation of the UHP metamorphic region.

# DESCRIPTION OF INTERGRANULAR COESITE IN UHP ECLOGITE

Intergranular coesite crystals occur in eclogitic rocks from a UHP metamorphic slab at Yangkou Beach near Qingdao in the Sulu region (Zhang and Liou 1996c). The UHP rocks are blocks of metagabbro, metagranitoid, ultramafic rock, and mylonitic orthogneisses of variable bulk composition enclosed in granitic gneiss; the latter consists of plagioclase + potassium feldspar + quartz + epidote + muscovite, with minor garnet and titanite. Metagranitoid with relict igneous microcline and granitic texture contains high-P minerals, including omphacite and garnet (Hirajima et al. 1993). Similarly, various stages of recrystallization from metagabbro with relict igneous textures and minerals (augite, bronzite, biotite, and ilmenite) to weakly eclogitized gabbro containing neoblastic omphacite + zoisite + kyanite + garnet, to the assemblage

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Transformation of gabbro to coesite eclogite

**FIGURE 1.** Schematic of steps and summarized P-T estimates for transformation of gabbroic to coesite eclogite assemblages from Yangkou Beach, eastern China.

sodium plagioclase + muscovite + kyanite  $\pm$  zoisite  $\pm$ garnet, and to coesite-bearing eclogite were identified in a single mafic block 20 m long; details of this mineralogic transformation are described by Zhang and Liou (1996c). Igneous augite of the metagabbro is rimmed by sodic augite or omphacite, and orthopyroxene is rimmed by a corona of cummingtonite  $\pm$  actinolite and omphacite +quartz layers. Coarse plagioclase grains (>75 vol%) are replaced by very fine-grained skeletal aggregates of albite + zoisite + muscovite, primary biotite by an aggregate of neoblastic muscovite flakes + fine-grained relict biotite, and ilmenite grains by irregularly shaped rutile aggregates. Thin coronas of fine-grained garnet developed at interfaces between plagioclase and other phases. In transitional rocks, augite and orthopyroxene are totally replaced by omphacite (Jd70); the lower pressure assemblage albite + kyanite + phengite + zoisite + garnet coexists with domains of omphacite (Jd<sub>70-73</sub>) + kyanite + phengite  $(Si_{3,3})$  in plagioclase pseudomorphs. Both massive and weakly deformed coesite-bearing eclogites at the margins of the block contain omphacite  $(Jd_{56-73})$  +



**FIGURE 2.** Plane-light photomicrograph of an intergranular coesite grain at the contact between garnet (Grt) and omphacite (Omp) crystals of eclogite (95YK-4E) from Yangkou Beach. Note the thin rim of palisade quartz around the coesite crystal and the well-developed cleavage of the relict coesite crystal. Width of view = 0.37 mm.



**FIGURE 3.** Plane-light photomicrograph of an intergranular coesite grain at the contact between garnet (Grt) and omphacite (Omp) crystals of eclogite (95YK-4E) from Yangkou Beach. Note advanced conversion of coesite to quartz aggregates around the rim and along cleavages, with a few relict coesite strips. Width of view = 0.37 mm.

kyanite + garnet + phengite  $(Si_{3,4-3,5}) \pm zoisite + coesite$ or quartz + rutile and preserve a faint gabbroic texture. Abundant coesite relics occur as inclusions in garnet and omphacite and exhibit limited conversion to palisade quartz aggregates. Some were also identified as intergranular grains in the matrix as described below. Eclogites do not show distinct retrogression. Figure 1 summarizes the stages and the estimated *P*-*T* conditions for the transformation from recognized corona metagabbro through transitional to coesite eclogite assemblages.

Figure 2 shows an oval-shaped coesite grain 0.06 mm in diameter at the boundary between garnet and two omphacite grains in eclogite sample 95YK-4E; a rutile grain occurs nearby. The coesite shows a thin palisade of quartz aggregates around its rim, with sharp contacts against both garnet and omphacite. This texture is similar to other recognized coesite inclusions in UHP rocks, including the one in dolomite from eclogite enclosed within impure marble (see Fig. 2B of Zhang and Liou 1996a). Another intergranular coesite crystal displaying advanced conversion to quartz aggregates (Fig. 3) occurs along a garnetomphacite grain boundary in the same eclogite sample. More than 60% of the coesite has been converted to quartz aggregates around the margin and along the cleavage of the original coesite crystal; several minute coesite stringers are preserved. The radial texture of quartz aggregates replacing intergranular coesite is illustrated in Figures 4 and 5. In another eclogitic sample (92SL-1D), the initial growth of quartz aggregates at the boundary between garnet and omphacite exhibits a radiating palisade texture (Fig. 4); later-grown quartz aggregates at the center of the pseudomorph show mosaic or patchy textures similar to those generated in the laboratory during the experimental transformation of a synthetic coesite rock to quartz aggregates (Bohlen and Mosenfelder 1995). Figure 5 shows quartz aggregates after coesite included in garnet and as an intergranular grain along a garnet-omphacite bound-



**FIGURE 4.** Cross-polarized photomicrograph of polycrystalline aggregates of quartz after intergranular coesite at the contact between garnet (Grt) and omphacite (Omp) crystals of eclogite (92SL-1D) from Yangkou Beach. Note the characteristic radial growth texture at the rim and the mosaic texture at the center. Width of view = 0.37 mm.

ary (95YK-4E). Several domains of quartz aggregates occur; those at the contact with garnet and omphacite show palisade growth texture, whereas those at the center exhibit a fine-grained mosaic intergrowth.

Very similar intergranular coesite rimmed with thin palisade-quartz aggregates occurs at the grain boundary of a grospydite xenolith from the Roberts-Victor kimberlite, South Africa (Smyth 1977). In these rocks, coarsegrained coesite occurs as a primary phase as inclusions or along grain boundaries of kyanite, garnet, sanidine, and clinopyroxene; polycrystalline quartz aggregates are well developed around the rim and along internal fractures. An example is shown in Figure 6.

The two eclogite samples from China with intergranular coesite also contain medium-grained garnet + omphacite + kyanite + phengite + rutile with abundant inclusions of both coesite and coesite pseudomorphs in garnet and omphacite. Garnet from the coesite eclogites is rich in almandine and grossular components (Alm<sub>40-50</sub>-Sps<sub>0.9-1.2</sub>Grs<sub>30-37</sub>Prp<sub>16-19</sub>), whereas the jadeite component in omphacite varies from 56 to 73 mol%. Phengite has 3.4-3.5 Si atoms pfu. Peak *P-T* conditions of the coesite eclogites range from 790 °C (95-YK-4E) to 850 °C (92SL-1D) at P > 28 kbar. These eclogites show very minor retrogression; omphacite grains are not bordered by symplectic intergrowths of amphibole + plagioclase as is common in other UHP rocks, and only rare garnet crystals are rimmed by taramitic amphiboles.

### DISCUSSION

The kinetics of the coesite  $\rightarrow$  quartz transformation and the preservation of coesite during exhumation of UHP rocks have attracted a great deal of attention in terms of both natural observation and experimental investigation (e.g., Rubie 1990; Mosenfelder et al. 1994; Hacker and Peacock 1995; Bohlen and Mosenfelder 1995). Our previous petrologic studies of many inclusions of coesite and



**FIGURE 5.** Cross-polarized photomicrograph of polycrystalline aggregates of quartz after intergranular coesite at the contact between garnet (Grt) and omphacite (Omp) crystals of eclogite (95YK-4E) from Yangkou Beach. Note an inclusion of quartz aggregates after coesite in garnet. Phn = phengite. Width of view = 0.37 mm.

coesite pseudomorphs in garnet and omphacite have delineated the following steps for the conversion: (1) growth of fine-grained, thin, palisade-quartz aggregates from the grain boundary inward (Figs. 2 and 6); (2) coarsening and coalescing of palisade-quartz to mosaic-quartz aggregates and progressive conversion of coesite to quartz along cleavages of coesite, preserving relict coesite islands (Fig. 3); (3) total replacement of coesite by fibrous quartz aggregates with mosaic-quartz boundaries (Fig. 4); (4) polygonal coarser grained quartz aggregates resulting from prolonged annealing; (5) recrystallization of quartz aggregates to a few coarser quartz crystals with a granoblastic texture; and (6) formation of a single quartz grain with either homogeneous or undulatory extinction. This trans-



**FIGURE 6.** Cross-polarized photomicrograph of several intergranular coesite grains (Coe) in grospydite from the Roberts-Victor kimberlite, South Africa (Smyth 1977). Note the coarsegrained size of these coesite crystals and the polycrystalline quartz aggregates around the rim and along internal fractures, as well as an inclusion of coesite and quartz aggregates after coesite in garnet (Grt). Cpx = clinopyroxene, Ky = kyanite. Width of view = 0.74 mm.

formation process suggests that conversion of coesite to quartz aggregates does not take place by epitaxial growth but is due to a reconstructive, interface-controlled mechanism (Bohlen and Mosenfelder 1995). Photomicrographs of these stages have been published (e.g., Zhang and Liou 1996b); various stages of the conversion process of coesite  $\rightarrow$  quartz aggregates can be observed in a single thin section. The rate of the transformation has not been well determined, but it must depend on factors such as the exhumation rate and the P-T path of a UHP slab, the availability of fluid during retrogression, and the grain size of precursor coesite. Similar textures for different extents of transformation of synthetic coesite rock to quartzite have been documented in the experimental kinetic studies (Mosenfelder et al. 1994; Bohlen and Mosenfelder 1995).

The finding of intergranular coesite and coesite pseudomorphs described above in Yangkou Beach is unique. Metagabbro and metagranitic rocks with preserved relict igneous minerals and textures occur at this locality; they represent the early stages of a progressive conversion of metagabbro to coesite-bearing eclogites (Zhang and Liou 1996c). Moreover, most of these UHP eclogites show only incipient retrogression, with only minor late-stage amphibole. These petrologic features together with the occurrence of intergranular coesite grains suggest slow reaction kinetics. Lack of fluids during and after the UHP metamorphism may be the key to such sluggish prograde and retrograde reactions; reconnaissance experiments by Dachille et al. (1963) indicate that the coesite  $\rightarrow$  quartz reaction is sluggish in the absence of H<sub>2</sub>O. This suggestion is consistent with the occurrence of similar intergranular coesite grains (Fig. 6) from a mantle-derived grospydite xenolith in a kimberlite pipe in South Africa and with the extremely negative  $\delta^{18}$ O values for garnet, omphacite, phengite, and quartz from nearby eclogites and quartzites of the Sulu region (Yui et al. 1995).

Minor hydrous and carbonate phases, including talc, epidote-zoisite, phengite, nyböite, magnesite, and dolomite, have been identified as matrix phases or as mineral inclusions in some UHP rocks from the Dabie-Sulu terranes, and it has been suggested that they are important carriers of minor amounts of fluid to mantle depths (e.g., Liou et al. 1995). Petrologic and geochemical data indicate that most of the  $H_2O$  and  $CO_2$  is bound within these phases in cold subduction zones during UHP metamorphism of sialic continental materials; a separate UHP fluid phase is not likely. The very limited devolatilization from a cold subducting slab at mantle depths may fail to induce large-scale partial melting, accounting for the absence of a typical calc-alkaline magmatic arc.

In comparison with typical crustal and mantle  $\delta^{18}$ O values of +2 to +7‰, some eclogites and interlayered quartzites from the Sulu UHP terrane have the most negative  $\delta^{18}$ O values ever recorded for high-*T* silicates such as garnet, omphacite, quartz, and phengitic mica, ranging from -10.4 to -7.3‰ (Yui et al. 1995). Near isotopic equilibrium among minerals and host rocks suggests that

these rock types must have acquired such low negative  $\delta^{18}$ O compositions before the UHP metamorphism, apparently through near-surface meteoric water-rock interactions. The rocks were then subducted to mantle depths during continent-continent collision, forming UHP minerals with concomitant O-isotope redistribution. Such a hypothesis suggests that fragments of old continental materials with strongly negative  $\delta^{18}$ O compositions were isolated from fluid interaction during their descent to mantle depths and later returned to the surface.

The extremely rare occurrence of intergranular or matrix coesite and coesite pseudomorphs suggests that the lack of fluid during exhumation of UHP rocks may play a more important role than the pressure-vessel effect on the preservation of coesite described by previous investigators. Except for mantle-derived eclogitic rocks such as the one from the Roberts Victor kimberlite (Fig. 6; Smyth 1977), mosaic and granoblastic quartz aggregates in the matrix have been documented in pyrope quartzite (e.g., Chopin 1984), calc-silicate country rock of eclogitebearing unit (Zhang and Liou 1996a), and jadeite quartzite and its adjacent quartz-rich eclogitic layer (Liou et al. 1996). Therefore, positive identification of intergranular or matrix coesite in UHP rocks strongly indicates the lack of fluids during rapid exhumation.

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### **References cited**

- Bohlen, S.R., and Mosenfelder, J. (1995) The coesite to quartz transformation: Nature vs. experiment. Eos, 76, F531.
- Chopin, C. (1984) Coesite and pure pyrope in high-grade blueschists of the western Alps: A first record and some consequences. Contributions to Mineralogy and Petrology, 86, 107–118.
- Chopin, C., Henry, C., and Michard, A. (1991) Geology and petrology of the coesite-bearing terrain, Dora Maira massif, Western Alps. European Journal of Mineralogy, 3, 263–291.
- Chopin, C., and Sobolev, N. (1995) Principal mineralogic indicators of UHP in crustal rocks. In R.G. Coleman and X. Wang, Eds., Ultrahighpressure metamorphism, p. 96-131. Cambridge University Press, Cambridge.
- Dachille, F., Zeto, R.J., and Roy, R. (1963) Coesite and stishovite: Stepwise reversal transformations. Science, 140, 991–993.
- Gillet, P., Ingrin, J., and Chopin, C. (1984) Coesite in subducted continental crust: P-T history deduced from an elastic model. Earth and Planetary Science Letters, 70, 426-436.
- Hacker, B.R., and Peacock, S.M. (1995) Creation, preservation, and exhumation of UHPM rocks. In R.G. Coleman and X. Wang, Eds., Ultrahigh-pressure metamorphism, p. 159–181. Cambridge University Press, Cambridge.
- Hirajima, T., Wallis, S.R., Zhai, M., and Ye, K. (1993) Eclogitized metagranitoid from the Sulu ultrahigh-pressure (UHP) province, eastern China. Proceedings of Japan Academy, 69, 249–254.

- Liou, J.G., Zhang, R.Y., and Ernst, W.G. (1995) Occurrences of hydrous and carbonate phases in ultrahigh-pressure rocks from east-central China: Implications for the role of volatiles deep in cold subduction zones. Island Arc, 4, 362–375.
- Liou, J.G., Zhang, R.Y., and Jahn, B.M. (1996) Petrogenesis of ultrahighpressure jadeite quartzite from the Dabie region, east-central China. In W. Schreyer, Ed., High-P metamorphism in nature and in laboratory, Lithos, in press.
- Michard, A., Henry, C., and Chopin, C. (1995) Structures in UHPM rocks: A case study from the Alps. In R.G. Coleman and X. Wang, Eds., Ultrahigh-pressure metamorphism, p. 132–158. Cambridge University Press, Cambridge.
- Mosenfelder, J.L., Bohlen, S.R., and Hankins, W.B. (1994) Kinetics of the coesite to quartz transformation. Eos, 75, 702.
- Rubie, D.C. (1990) Role of kinetics in the formation and preservation of eclogite. In D.A. Carswell, Ed., Eclogite facies rocks, p. 111-140. Chapman and Hall, New York.
- Schertl, H., Schreyer, W., and Chopin, C. (1991) The pyrope-coesite rocks and their country rocks at Parigi, Dora Maira massif, western Alps: Detailed petrography, mineral chemistry and *PT*-path. Contributions to Mineralogy and Petrology, 108, 1–21.
- Schertl, H., and Okay, A.I. (1994) Coesite inclusion in dolomite of Dabie Shan, China: Petrological and geological significance. European Journal of Mineralogy, 6, 995-1000.
- Schreyer, W. (1988) Subduction of continental crust to mantle depths: Petrological evidence. Episodes, 11, 97–104.
- Shatsky, V.S., Sobolev, N.V., and Vavilov, M.A. (1995) Diamond-bearing metamorphic rocks of the Kokchetav massif (Northern Kazakhstan). In R.G. Coleman and X. Wang, Eds., Ultrahigh-pressure metamorphism, p. 427–455. Cambridge University Press, Cambridge.

- Smyth, J.R. (1977) Quartz pseudomorphs after coesite. American Mineralogist, 62, 828-830.
- Sobolev, N.V., and Shatsky, V.S. (1990) Diamond inclusions in garnets from metamorphic rocks. Nature, 343, 742-746.
- Sobolev, N.V., Shatsky, V.S., Vavilov, M.A., and Goryainov, S.V. (1994) Zircon from ultrahigh-pressure metamorphic rocks of folded regions as a unique container of inclusions of diamond, coesite and coexisting minerals. Doklady Akademii Nauk, 334, 488-492.
- Van der Molen, I., and Van Roermund, H.L.M. (1986) The pressure path of solid inclusions in minerals: The retention of coesite inclusions during uplift. Lithos, 19, 317–324.
- Wang, X., Zhang, R.Y., and Liou, J.G. (1995) Ultrahigh-pressure metamorphic terrane in eastern central China. In R.G. Coleman and X. Wang, Eds., Ultrahigh-pressure metamorphism, p. 356–390. Cambridge University Press, Cambridge.
- Yui, T.F., Rumble, D., and Lo, C.H. (1995) Unusually low <sup>18</sup>O ultrahighpressure metamorphic rocks from the Sulu terrain, eastern China. Geochimica et Cosmochimica Acta, 59, 2859–2864.
- Zhang, R.Y., and Liou, J.G. (1996a) Coesite inclusions in dolomite from eclogite in the southern Dabie mountains, China: The significance of carbonate minerals in UHPM rocks. American Mineralogist, 81, 181– 186.
- (1996b) Mineralogy of UHP Rocks. In B. Cong, Ed., Ultrahighpressure metamorphism in Dabieshan and Sulu region, China. China Publishing House and Science Press, Beijing, in press.
- (1996c) Transformation of gabbro to coesite-bearing eclogite facies rocks from Yangkou, the Sulu region, eastern China. Journal of Metamorphic Geology, in press.

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