Mineral inclusions in zircon from diamond-bearing marble in the Kokchetav massif, northern Kazakhstan

Ikuo KATAYAMA[1,*], Masahito OHTA[2] and Yoshihide OGASAWARA[2]

[1]Department of Earth and Planetary Sciences, Tokyo Institute of Technology, O-okayama, meguro-ku,
Tokyo 152-8551, Japan.
[2]Department of Earth Sciences, Waseda University, Tokyo 169-8050, Japan

Abstract: In order to constrain the metamorphic evolution of deeply subducted impure marble from the Kokchetav massif, we investigated mineral inclusions in zircon, which is known to protect ultrahigh-pressure (UHP) phases from late-stage overprinting. Consequently, diamond, coesite, diopside, garnet, phlogopite, calcite, dolomite, graphite and apatite were identified as inclusion in the zircons. Silica phases were absent in the matrix, indicating they were completely consumed by the following prograde reaction: Dolomite + 2 SiO_2 = Diopside + 2 CO_2.

The relict of coesite inclusions in zircon indicates that prograde P-T trajectory crossed cut the quartz-coesite transition before the decarbonate reaction. Matrix diopsides contain abundant exsolved phengite lamellae, whereas the exsolution is absent in the inclusions in zircon. The diopside inclusions contain higher amounts of K_2O (up to 0.56 wt%) and CaEskola component (up to 3.5 mol%) than those of the matrix (0.14 wt% and 2.1 mol%, respectively). Thus, phengite exsolution occurs in matrix pyroxene with low K_2O and CaEskola components compared to inclusions in zircon. This observation indicates that decreasing K_2O and CaEskola components during decompression resulted in the phengite exsolution in diopside. A trace of hydroxyl in phengite needles was perhaps initially incorporated within the precursor clinopyroxene under high-pressure conditions. The peak metamorphic P-T conditions of the impure marble are estimated to 60-80 kbar and 960-1050°C, derived from K_2O solubility in diopside buffered by phlogopite and from the garnet-clinopyroxene geothermometer.

Key-words: ultrahigh-pressure metamorphism, marble, zircon, coesite, high-K_2O diopside.

Introduction

Recent findings of metacarbonate rocks in ultrahigh-pressure (UHP) metamorphic terranes have indicated that significant amounts of carbon in subducting plates are carried to depths over 100 km (Becker & Altherr, 1992; Schertl & Okay, 1994; Zhang & Liou, 1996; Omori *et al.*, 1998; Ogasawara *et al.*, 2000). This has a major influence on arc magmatism, mantle metasomatism and the global carbon cycle. Metamorphic diamonds have been found in impure marbles from the Kokchetav massif, northern Kazakhstan (Sobolev & Shatsky, 1990; Ogasawara *et al.*, 2000). Evidence of the prograde and peak metamorphic histories of the marbles are mostly obliterated by extensive hydration during a late-stage amphibolite facies overprint related to exhumation. However, it is well known that refractory minerals such as garnet and zircon can preserve relicts of the early history of UHP metamorphic rocks as inclusions (Chopin *et al.*, 1991; Schertl *et al.*, 1991; Schertl & Schreyer, 1996; Zhang *et al.*, 1997; Parkinson, 2000; Katayama *et al.*, 2001a). Zircon is a common accessory mineral in metacarbonate rocks from the Kokchetav UHP terrane, and is considered to be the best UHP metamorphic mineral container due to its extreme resistance and stability over large pressure-temperature conditions (Chopin & Sobolev, 1995). In this study, we investigated mineral inclusions in zircons of a diamond-bearing marble from the Kokchetav massif. Discrete inclusions in zircons were analyzed at the Tokyo Institute of Technology with a laser Raman spectroscopy (JASCO NRS-2000) using the 514.5 nm line of Ar-ion laser, and with a electron microprobe analyzer (JEOL JXA 8800) with a 15 kV accelerating voltage and 12 nA beam current.

Geological setting

The Kokchetav massif is situated in the central domain of the composite Eurasian craton, and was formed during Cambrian collisional orogenic events (Dobretsov *et al.*, 1995). This massif is composed of several Precambrian rock series, Cambro-Ordovician

Table 1. Mineral parageneses in matrix and zircon.

Sample	Dia	Grp	Coe	Di	Grt	Phn	Phl	Tlc	Amp	Cal	Dol	Ap
N21 marble (Kumdy−kol)												
Matrix		△		+		+	△	△	△	△	+	+
Inclusion in zircon	+	△	+	+	+		+			+	+	+

△ : secondary mineral. Mineral abbreviations: Dia=diamond, Grp=graphite, Coe=coesite, Di=diopside
Grt=garnet, Phn=phengite, Phl=phlogopite, Tlc=talc, Amp=amphibole, Cal=calcite, Dol=dolomite, Ap=apatite

volcanic and sedimentary rocks, Devonian volcanic molasse, and Carboniferous-Triassic shallow-water and lacustrine sediments; these rocks were intruded by multi-stage granitoids (Dobretsov *et al.*, 1995). The UHP-HP metamorphic part of the massif is a thin (1-2 km), more or less coherent, subhorizontal sheet, which is structurally overlain by a weakly metamorphosed unit, and underlain by the Daulet Suite (Kaneko *et al.*, 2000). The UHP-HP unit mainly consists of para- and ortho-gneiss, marble, eclogite and amphibolite. Eclogites occur as lenticular masses within diamond-bearing gneiss and marble, and yield P-T conditions of P > 60 kbar and T > 1000°C based on the K_2O-in-augite geobarometer and Grt-Cpx geothermometer (Okamoto *et al.*, 2000). Metamorphic diamonds have been identified in pelitic gneisses, marbles and garnet pyroxenites from the Kumdy-Kol region (Sobolev & Shatsky, 1990; Zhang *et al.*, 1997; Ogasawara *et al.*, 2000; Katayama *et al.*, 2001a), which is located in the central part of the massif. Coesites also widely occur in eclogite, mica schist and whiteschist as inclusions in zircon and garnet from the Kumdy-Kol, Barchi-Kol and Kulet regions (Shatsky *et al.*, 1995 and 1998; Korsakov *et al.*, 1998; Parkinson, 2000). Other mineralogical and textural indicators of UHP metamorphism, such as exsolved silica rods in omphacite, K-rich pyroxene, Si-rich phengite, and aluminous titanite are also present in the Kokchetav UHP-HP part of the massif (Shatsky *et al.*, 1995; Zhang *et al.*, 1997; Okamoto *et al.*, 2000; Katayama *et al.*, 2000). Metamorphism of the diamond-bearing and associated rocks took place in the Middle Cambrian, as indicated by Sm-Nd and U-Pb zircon ages between 530 and 540 Ma
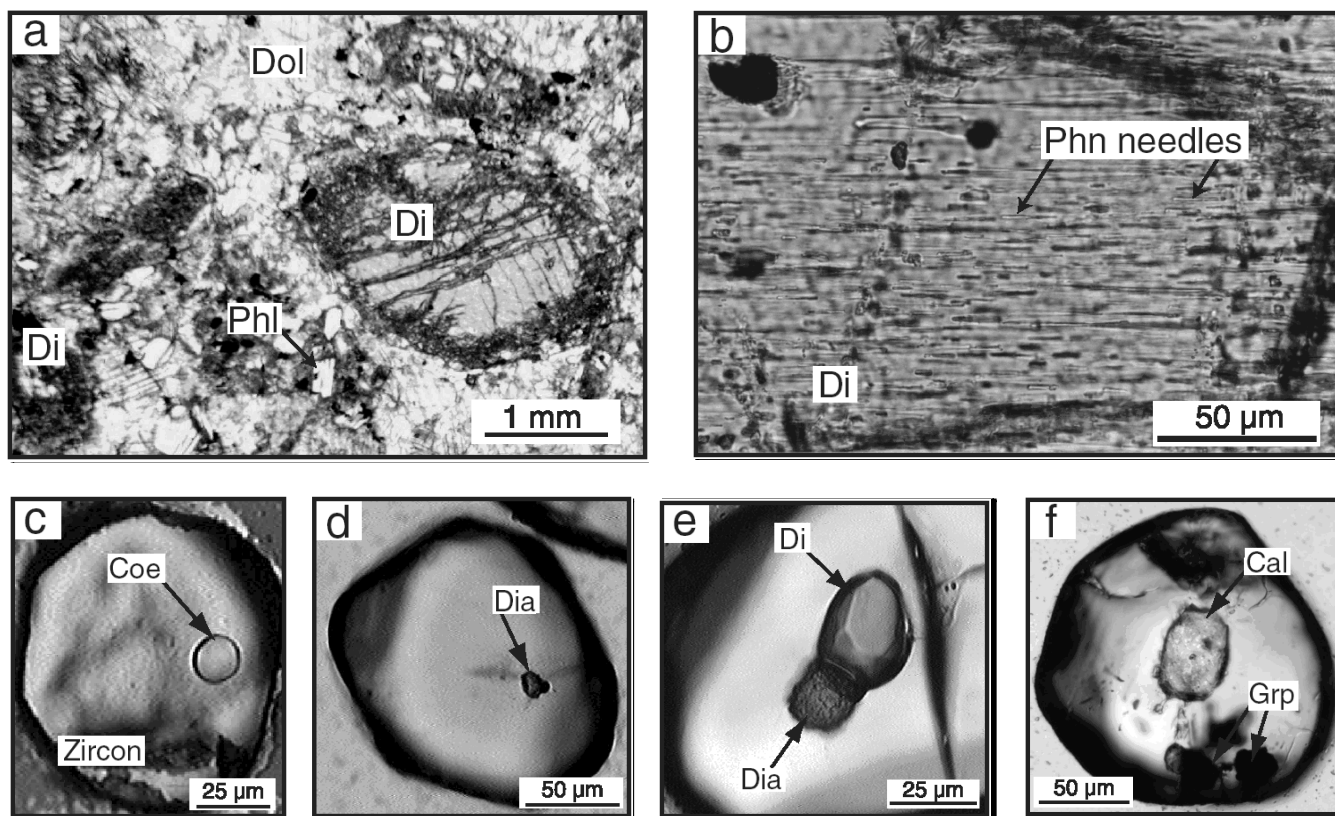

Fig. 1. Photomicrographs of mineral assemblages from the matrix and inclusions in zircon from impure marble (plane-polarized light). (a) Matrix mineral assemblage. Di, diopside; Phl, phlogopite; Dol, dolomite. (b) Phengite needles in diopside. The needles show a preferred orientation. (c) Coesite inclusion (Coe) in zircon. (d) Diamond inclusion (Dia) in zircon. (e) Diopside and diamond inclusions coexisting in zircon. This type of diopside contains high amounts of K_2O. (f) Calcite (Cal) and graphite (Grp) inclusions in zircon.

(Shatsky *et al*., 1999; Claoué-Long *et al*., 1991). Muscovite and biotite in diamond-bearing gneiss yielded ^{40}Ar-^{39}Ar ages of 517 ± 5 Ma and 516 ± 5 Ma, respectively, which have been interpreted as a cooling age (Shatsky *et al*., 1999). Recent SHRIMP U-Pb dating of UHP mineral-bearing zircon cores and sub-UHP mineral-bearing rims (representing peak UHP and retrograde metamorphism) yielded 537 ± 9 Ma and 507 ± 8 Ma, respectively (Katayama *et al.*, 2001a).

Petrography and mineral chemistry

The marble sample (N21) from the Kumdy-Kol region is intercalated within diamond-bearing gneisses and eclogites. It mainly consists of dolomite + diopside + phlogopite + talc with minor amounts of amphibole, calcite, zircon and apatite (Table 1). The matrix diopside contains abundant exsolved phengite lamellae, which are a few μm in diameter and approximately 10 μm in length (Fig. 1). The amphibole, phlogopite and talc occur as retrograde phases, surrounding diopside. The most characteristic feature of this rock is the abundance of diamond inclusions in clinopyroxene and zircon. Zircon contains inclusions of diamond, coesite, garnet, diopside, phlogopite, calcite, dolomite, apatite and graphite. Whereas zircons in pelitic gneisses from this massif usually show a zonal texture in secondary electron microscope and cathodoluminescence images (Katayama *et al*., 2001a), those in the marbles are mostly homogeneous.

Inclusions in zircon

Abundant microdiamond inclusions were identified in zircons. The average diameter of the diamond crystals is 10 μm, and their morphological forms comprise both octahedral and polycrystalline aggregates (Fig. 1). The diamonds were confirmed by the characteristic peak on the Raman spectrum at 1333 ± 2 cm^{-1}. Some graphite also occurrs as inclusions in zircon along cracks and in outer margins. Coesite inclusions are very rare in the zircon, and they usually show an oval texture (Fig. 1). They are about 10 μm in size and were confirmed by characteristic Raman spectra with a dominant peak at 523 cm^{-1} and weaker ones at 271 cm^{-1}, 181 cm^{-1} and 149 cm^{-1}. However, quartz inclusions were absent in zircon. It is important to note that SiO_2 phases (both coesite and quartz) are absent in matrix assemblages (Table 1).

Diopside inclusions exhibit significantly high K_2O and Ca-Eskola components, up to 0.56 wt% and 3.5 mol%, respectively (Table 2). These amounts are higher than those of matrix diopside (0.14 wt% K_2O and 2.1 mol% CaEs on average). Recalculated composition of the matrix diopside involving 2.16 wt% phengite lamellae, based on back-scattered electron images of a 200 x 100 μm area, leads to 0.4 wt% K_2O and 2.7 mol% Ca-Eskola components for the primary diopside, which is mostly consistent with compositions of diopside-forming inclusions in zircon. The recalculated diopside contains approximately 1000 ppm H_2O. This hydroxyl should be incorporated within the precursor clinopyroxene as part of its structure.

Table 2. Representative mineral compositions of inclusions in zircon and matrix minerals.

Mineral	Diopside			Garnet	Phlogopite		Calcite	
	In zircon	In zircon	Matrix	In zircon	In zircon	Matrix	In zircon	Matrix
Wt% oxides								
SiO_2	54.83	56.04	54.97	39.83	41.17	41.01	0.00	0.00
TiO_2	0.03	0.00	0.00	0.18	0.97	1.16	0.00	0.00
Al_2O_3	2.76	2.21	1.41	23.35	16.30	15.59	0.03	0.00
Cr_2O_3	0.03	0.01	0.00	0.02	0.03	0.00	0.00	0.02
FeO*	2.03	2.02	1.61	9.53	4.13	4.40	0.10	0.08
MnO	0.02	0.14	0.03	1.39	0.00	0.00	0.37	0.26
MgO	15.56	15.64	17.00	8.82	22.40	23.60	0.18	0.64
CaO	23.26	23.69	24.69	16.18	0.02	0.08	56.34	56.35
Na_2O	0.66	0.57	0.39	0.01	0.12	0.16	0.00	0.00
K_2O	0.56	0.41	0.09	0.00	9.47	9.63	0.00	0.00
Total	99.73	100.72	100.19	99.32	94.60	95.63	57.01	57.35
Cations	O=6	O=6	O=6	O=12	O=22	O=22	Σ cat.=1	Σ cat.=1
Si	1.989	2.010	1.986	2.971	5.82	5.76	0.000	0.000
Ti	0.001	0.000	0.000	0.010	0.10	0.12	0.000	0.000
Al	0.118	0.093	0.060	2.052	2.72	2.58	0.000	0.000
Cr	0.001	0.000	0.000	0.001	0.00	0.00	0.000	0.000
Fe^{2-}	0.061	0.060	0.049	0.595	0.49	0.52	0.001	0.001
Mn	0.001	0.004	0.001	0.088	0.00	0.00	0.005	0.004
Mg	0.841	0.836	0.916	0.981	4.72	4.94	0.004	0.015
Ca	0.904	0.910	0.956	1.293	0.00	0.01	0.989	0.980
Na	0.046	0.039	0.027	0.001	0.03	0.04	0.000	0.000
K	0.026	0.019	0.004	0.000	1.71	1.73	0.000	0.000
CaEs (mol%)**	2.5	3.5	0.1					

* Total Fe was calculated as FeO. ** CaEskola component was calculated from excess 6-fold coordinated Al.
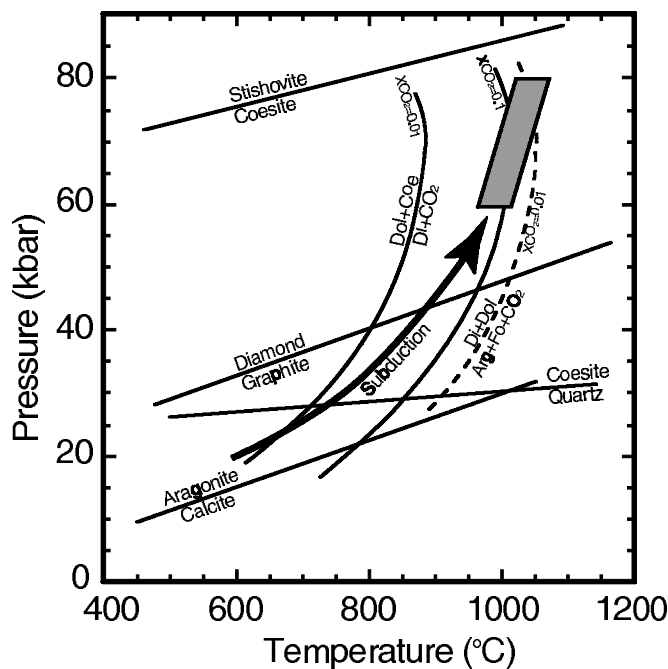
Fig. 2. Pressure-temperature diagram showing metamorphic peak conditions of the marble (shaded square), estimated from K_2O solubility in diopside inclusions in zircon buffered by phlogopite (Luth, 1997) and from the garnet-clinopyroxene geothermometer (Ellis & Green, 1979) for inclusion pairs in zircon. The reaction curves of dolomite + coesite (quartz) = diopside + CO_2, at X_{CO_2} = 0.1 and 0.01, and diopside + dolomite = aragonite + forsterite + CO_2, at X_{CO_2} = 0.01 are from Ogasawara et al., (1995). These decarbonate reactions applied to the peak mineral assemblage of this marble restrict X_{CO_2} to between 0.01 and 0.1. Stability fields for diamond (Bundy, 1980), stishovite (Zhang et al., 1996), coesite (Bohlen & Boettcher, 1982) and aragonite (Hacker et al., 1992) are also shown.

Rare garnet inclusions were identified in zircon. They coexist with diamond inclusions, and show high Grs (44 %) and Prp (33 %) components (Table 2). Garnet is absent in the matrix. Garnets in eclogites and pelitic gneisses from the Kumdy-Kol region contain relatively high amounts of Na_2O (up to 0.15 wt%), which is negligible in the studied marble.

Phlogopite inclusions occur together with microdiamond in a single zircon grain. They have higher Si content, 5.82-84 per 22 oxygens, and a slightly higher Fe/(Fe+Mg) ratio of 0.09-0.10 than those of matrix phlogopite (5.68-5.82 Si value and 0.08-0.10 Fe/(Fe+Mg) ratio). The Al/(Al+Si) ratio of inclusion phlogopite is higher than that of the matrix. The decreasing Al/(Al+Si) in phlogopite can be attributed to decreasing pressure at constant temperature (Arai, 1984).

Calcite and dolomite inclusions occur as inclusions in zircon. The calcite inclusions contain very low $MgCO_3$ (0.1-1.1 mol%). In the matrix, calcite occurs as a secondary mineral replacing dolomite. This type of calcite shows a relatively wide range of $MgCO_3$ component (0.5-2.5 mol%), which is higher than that of the inclusions

(Table 2). Similar low-$MgCO_3$ calcites were also formed as inclusions in garnet (Ogasawara et al., 2000). These calcites probably represent former aragonite, which coexisted with dolomite and diamond at high pressures, whereas Mg-calcite in the matrix was formed during retrogression.

Discussion

Constraints on prograde reactions

The prograde P-T path of UHP metamorphic rocks is mostly obliterated; rare evidence was found in mineral inclusion studies on zoned porphyroblasts (Harley & Carswell, 1995). In the Kokchetav UHP metamorphic rocks, prograde conditions were reported to temperatures of 460-580°C and pressures of 8-19 kbar, based on inclusion assemblages in zoned garnet from coesite-bearing whiteschist in the Kulet region (Zhang et al., 1997; Parkinson, 2000). They observed inclusions of Chl + Ky + Zo + Mrg + Qtz in cores, and Tlc + Ky + Rt + Coe in rims. However, this evidence is absent in the diamond-grade rocks. In this study, we found coesite inclusions in zircon from the diamond-bearing marble, whereas silica phases were absence in the matrix. Those evidences suggest that the zircon has preserved relict of prograde metamorphism as mineral inclusions, and silica phases in the matrix were consumed by the following prograde reaction:
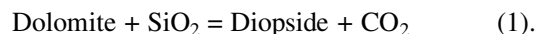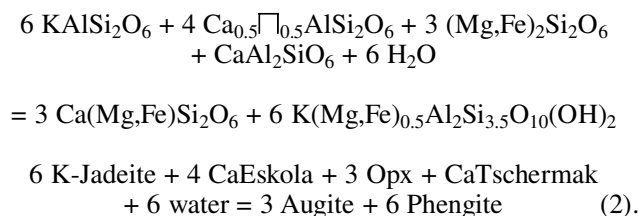
$$Dolomite + SiO_2 = Diopside + CO_2 \qquad (1).$$

Figure 2 shows this reaction curve, which was calculated in the model system MgO-CaO-SiO_2-H_2O-CO_2 by Ogasawara et al. (1995). The prograde P-T trajectory crossed cut the quartz-coesite transition at less temperature than the reaction (1). However, this decarbonate reaction highly depends on X_{CO_2}. Fluid inclusions in diamond were reported from garnet pyroxenite in the Kokchetav massif (De Corte et al., 1998), but their precise composition is still uncertain. If we take account of P-T conditions of the coesite-grade rocks (27-38 kbar, 750-800°C), the X_{CO_2} could be higher than 0.01. On the other hand, the presence of diopside at the peak metamorphic stage restricted $X_{CO_2} < 0.1$ by the reaction (1).

Phengite exsolution in diopside

Exsolution textures are common in UHP metamorphic minerals; these include ilmenite rods in olivine and clinopyroxene, magnetite plates or rods in olivine and clinohumite, quartz rods in omphacite, monazite lamellae in apatite, and clinopyroxene needles in garnet (see compilation of Liou et al., 1998). These textures are believed to form during decompression; however, the mechanisms for the exsolution in UHP phases are mostly unclear. Zircon is a key to ascertain the pre-exsolution mineral composition, because it can protect peak UHP metamorphic phases in inclusion. Quartz exsolution in omphacite from a Kokchetav eclogite was correlated with breakdown of

CaEskola component by Katayama *et al.* (2000) who compared the chemical composition of omphacites in the matrix with that in inclusions in zircon. In this study, phengite needles occur in matrix diopside and show a preferred orientation (Fig. 1b). Diopside inclusions in zircon contain a higher K_2O content and CaEskola component than those in the matrix, and yield a similar composition of recalculated matrix diopside when the phengite exsolutions are included. These observations suggest that phengite lamellae were formed by the following reaction:

$$6\ KAlSi_2O_6 + 4\ Ca_{0.5}\square_{0.5}AlSi_2O_6 + 3\ (Mg,Fe)_2Si_2O_6 + CaAl_2SiO_6 + 6\ H_2O$$

$$= 3\ Ca(Mg,Fe)Si_2O_6 + 6\ K(Mg,Fe)_{0.5}Al_2Si_{3.5}O_{10}(OH)_2$$

$$6\ \text{K-Jadeite} + 4\ \text{CaEskola} + 3\ \text{Opx} + \text{CaTschermak} + 6\ \text{water} = 3\ \text{Augite} + 6\ \text{Phengite} \qquad (2).$$

During decompression, K-jadeite and CaEskola components became unstable. As a result, reaction (2) was promoted resulting in exsolution of phengite needles in the matrix clinopyroxene. However, zircon has preserved precursor pyroxene, which contains high K_2O and a vacancy (CaEskola component) in the structure. An increase of the augite component in matrix diopside (91-96 mol%) also points to the retrograde reaction. Hydroxyl included in phengite may have been initially incorporated within the precursor clinopyroxene under high-pressure conditions. According to volume of the phengite exsolution (2.6 volume%), the precursor diopside contains approximately 1000 ppm H_2O. Smyth *et al.* (1991) reported that mantle-derived pyroxene from Roberts Victor kimberlite pipe contains up to 1800 ppm OH, and that the hydroxyl is associated with cation vacancies. Recently, infrared spectra of omphacites in UHP eclogites from the Kokchetav massif yielded significant amount of hydroxyl, up to 3020 ppm (Katayama *et al.*, 2001b). These hydrated clinopyroxenes in UHP metamorphic rocks indicate that significant amounts of water can be carried into the upper mantle by the subducted crust.

Peak P-T conditions

The occurrence of metamorphic diamonds constrains the minimum pressure of the peak metamorphic assemblage of the Kokchetav UHP rocks; however precise peak-pressure conditions are still debated. K_2O solubility in clinopyroxene is an important indicator of UHP conditions (*e.g.*, Schmidt, 1996; Luth, 1997; Okamoto & Maruyama, 1998); high-K_2O clinopyroxene has been reported for diamond-grade eclogite in the Kumdy-Kol region (Shatsky *et al.*, 1995; Zhang *et al.*, 1997; Okamoto *et al.*, 2000). In the investigated impure marble, the clinopyroxene inclusions in zircon also contain high K_2O (up to 0.56 wt%), and the zircon contains diamond and phlogopite (Fig. 1c). Luth (1997) performed experiments in the diopside + phlogopite system, and reported that the K_2O content in clinopyroxene buffered with phlogopite increases with pressure, from 0.18 wt% at 30 kbar to 0.54 wt% at 75 kbar, at temperatures of 1250-1400°C. Our sample shows lower temperature than in the experiments, but temperature has a less effect compared with pressure. The results of Luth (1997) applied to our investigations on diopsides from the Kokchetav massif require metamorphic pressures in the range of 60-80 kbar. The recent finding of coesite exsolutions in titanite also indicates a peak pressure of over 60 kbar (Ogasawara *et al.*, 2002). Absence of stishovite and magnesite in the marble yields an upper pressure limit (P < 80 kbar). The peak metamorphic temperature was calculated using Fe-Mg partitioning between garnet and clinopyroxene inclusion pairs in zircon. The geothermometer of Ellis & Green (1979) yields temperatures of 960-1000°C at 60 kbar and 1010-1050°C at 80 kbar (Fig. 2). The calculated temperatures are generally consistent with those obtained from eclogite and biotite gneiss in this region (Shatsky *et al.*, 1995; Zhang *et al.*, 1997; Okamoto *et al.*, 2000). These estimates reveal approximately the same metamorphic conditions for the different lithologies of the Kumdy-Kol region, suggesting that coherent units of supracrustal rocks were subjected to UHP metamorphism at mantle depths and subsequently exhumed to the surface.

References

Arai, S. (1984): Pressure-temperature dependent compositional variation of phlogopitic micas in upper mantle peridotites. *Contrib. Mineral. Petrol.*, **87**, 260-264.

Becker, H. & Altherr, R. (1992): Evidence from ultrahigh-pressure marbles for recycling of sediments into the mantle. *Nature*, **358**, 745-748.

Bohlen, S.R. & Boettcher, A.L. (1982): The quartz-coesite transformation: A pressure determination and the effect of other components. *J. Geophy. Res.*, **87**, 7073-7078.

Bundy, F.P. (1980): The P, T phase and reaction diagram for elemental carbon. *J. Geophy. Res.*, **85**, 6930-6936.

Chopin, C. & Sobolev, N.V. (1995): Principal mineralogic indicators of UHP in crustal rocks. *in* "Ultrahigh-Pressure Metamorphism", Coleman, R.G. & Wang, X. eds. Cambridge Univ. Press, 96-133.

Chopin, C., Henry, C., Michard, A. (1991): Geology and petrology of the coesite-bearing terrain, Dora Maira massif, Western Alps. *Eur. J. Mineral.*, **3**, 263-291.

Claoué-Long, J.C., Sobolev, N.V., Shatsky, V.S., Sobolev, A.V. (1991): Zircon response to diamond pressure metamorphism in the Kokchetav massif, USSR. *Geology*, **19**, 710-713.

De Corte, K., Cartigny, P., Shatsky, V.S., Sobolev, N.V., Javoy, M. (1998): Evidence of fluid inclusions in metamorphic microdiamonds from the Kokchetav massif, northern Kazakhstan. *Geochim. Cosmochim. Acta*, **62**, 3765-3773.

Dobretsov, N.L., Sobolev, N.V., Shatsky, V.S., Coleman, R.G., Ernst, W.G. (1995): Geotectonic evolution of diamondiferous paragneisses, Kokchetav Complex, Northern Kazakhstan: The geologic enigma of ultrahigh-pressure crustal rocks within a Paleozoic foldbelt. *The Island Arc*, **4**, 267-279.

Ellis, D.J. & Green, D.H. (1979): An experimental study of the effect of Ca upon garnet-clinopyroxene Fe-Mg exchange equilibria. *Contrib. Mineral. Petrol.*, **71**, 13-22.

Hacker, B.R., Kirby, S.H., Bohlem, S.R. (1992): Metamorphic petrology: Calcite = aragonite experiments. *Science*, **258**, 110-112.

Harley, S.L. & Carswell, D.A. (1995): Ultradeep crustal metamorphism: A prospective view. *J. Geophy. Res.*, **100**, 8367-80.

Kaneko, Y., Maruyama, S., Terabayashi, M., Yamamoto, H., Ishikawa, M., Anma, R., Parkinson, C.D., Ohta, T., Nakajima, Y., Katayama, I., Yamamoto, J., Yamauchi, K. (2000): Geology of the Kokchetav UHP-HP metamorphic belt, northern Kazakhstan. *The Island Arc*, **9**, 264-283.

Katayama, I., Parkinson, C.D., Okamoto, K., Nakajima, Y., Maruyama, S. (2000): Supersilicic clinopyroxene and silica exsolution in UHPM eclogite and pelitic gneiss from the Kokchetav massif, Kazakhstan. *Am. Mineral.*, **85**, 1368-1374.

Katayama, I., Maruyama, S., Parkinson, C. D., Terada, K., Sano, Y. (2001a): Ion micro-probe U-Pb zircon geochronology of peak and retrograde stages of ultrahigh-pressure metamorphic rocks from the Kokchetav massif, northern. *Earth Planet. Sci. Lett.*, **188**, 185-198.

Katayama, I., Nakashima, S., Maruyama, S. (2001b): Hydrated clinopyroxene in ultrahigh-pressure metamorphic rocks from the Kokchetav massif: Implication for water transportation into the mantle. *in* 11th Goldschmidt Conference, Virginia, USA, 3486.

Korsakov, A.V., Shatsky, V.S., Sobolev, N.V. (1998): The first finding of coesite in the eclogites of the Kokchetav massif. *Dok. Earth Sci.*, **360**, 469-473.

Liou, J.G., Zhang, R.Y., Ernst, W.G., Rumble, D., Maruyama, S. (1998): High-pressure minerals from deeply subducted metamorphic rocks. *in* "Ultrahigh-pressure mineralogy: physics and chemistry of the Earth's deep interior". *Rev. Mineral.*, **37**, 33-96.

Luth, R.W. (1997): Experimental study of the system phlogopite-diopside from 3.5 to 17 GPa. *Am. Mineral.*, **82**, 1198-1209.

Ogasawara, Y., Liou, J.G., Zhang, R.Y. (1995): Petrogenetic grid for ultrahigh-pressure metamorphism in the model system $CaO-MgO-SiO_2-CO_2-H_2O$. *The Island Arc*, **4**, 240-253.

Ogasawara, Y., Ohta, M., Fukasawa, K., Katayama, I., Maruyama, S. (2000): Diamond-bearing and diamond-free metacarbonate rocks from Kumdykol in the Kokchetav Massif, northern Kazakhstan. *The Island Arc*, **9**, 400-416.

Ogasawara, Y., Fukasawa, K., Maruyama, S. (2002): Coesite exsolution from titanite in UHP marble from the Kokchetav Massif. *Am. Mineral.*, **87**, 452-461.

Okamoto, K. & Maruyama, S. (1998): Multi-anvil re-equilibration experiments of a Dabie Shan ultrahigh-pressure eclogites within the diamond-stability fields. *The Island Arc*, **7**, 52-69.

Okamoto, K., Liou, J.G., Ogasawara, Y. (2000): Petrology of the diamond-grade eclogite in the Kokchetav Massif, northern Kazakhstan. *The Island Arc*, **9**, 379-399.

Omori, S., Liou, J.G., Zhang, R.Y., Ogasawara, Y. (1998): Petrogenesis of impure dolomitic marble from the Dabie Mountains, central China. *The Island Arc*, **7**, 98-114.

Parkinson, C.D. (2000): Coesite inclusions and prograde compositional zonation of garnets in whiteschists of the Kokchetav UHP-HP massif, Kazakhstan: a unique record of progressive UHP metamorphism. *Lithos*, **52**, 215-233.

Schertl, H.P. & Okay, A.I. (1994): A coesite inclusion in dolomite in Dabie Shan, China: Petrological and rheological significance. *Eur. J. Mineral.*, **6**, 995-1000.

Schertl, H.P., Schreyer, W., 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. *Contrib. Mineral. Petrol.*, **108**, 1-21.

Schertl, H.P. & Schreyer, W. (1996): Mineral inclusions in heavy minerals of the ultrahigh-pressure metamorphic rocks of the Dora-Maira massif and their bearing on the relative timing of the petrological events. *in* "Earth Processes: Reading the Isotopic Code", Basu, A. & Hart, S. eds. Geophysical Monograph Series 95, American Geophysical Union, 331-342.

Schmidt, M.W. (1996): Experimental constraints on recycling of potassium from subducted oceanic crust. *Science*, **272**, 1927-1930.

Shatsky, V.S., Sobolev, N.V., Vavilov, M.A. (1995): Diamond-bearing metamorphic rocks of the Kokchetav Massif (northern Kazakhstan). *in* "Ultrahigh-Pressure Metamorphism", Coleman, R.G. & Wang, X. eds. Cambridge Univ. Press, 427-455.

Shatsky, V.S., Theunissen, K., Dobretsov, N.L., Sobolev, N.V. (1998): New indication of ultrahigh-pressure metamorphism in the mica schist of the Kulet site of the Kokchetav massif. *Russ. Geol. Geophy.*, **39**, 1041-1046.

Shatsky, V.S., Jagoutz, E., Sobolev, N.V., Kozmenko, O.A., Parkhomento, V.S., Troesch, M. (1999): Geochemistry and age of ultra-high pressure rocks from the Kokchetav massif, northern Kazakhstan. *Contrib. Mineral. Petrol.*, **137**, 185-205.

Smyth, J.R., Bell, D.R., Rossman, G.R. (1991): Incorporation of hydroxyl in upper-mantle clinopyroxenes. *Nature*, **351**, 732-735.

Sobolev, N.V. & Shatsky, V.S. (1990): Diamond inclusion in garnets from metamorphic rocks. *Nature*, **343**, 742-746.

Zhang, J., Li, B., Utsumi, W., Liebermann, R. C. (1996): In situ X-ray observations of coesite-stishovite transition: reversed phase boundary and kinetics. *Phys. Chem. Minerals*, **23**, 1-10.

Zhang, R.Y. & Liou, J.G. (1996): Coesite inclusions in dolomite from eclogite in the southern Dabie Mountains, China: The significance of carbonate minerals in UHPM rocks. *Am. Mineral.*, **81**, 181-186.

Zhang, R.Y., Liou, J.G., Ernst, W.G., Coleman, R.G., Sobolev, N.V., Shatsky, V.S. (1997): Metamorphic evolution of diamond-bearing and associated rocks from the Kokchetav massif, northern Kazakhstan. *J. metamorphic Geol.*, **15**, 479-496.