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# *Hydroxyl in diopside of diamond-free ultrahigh-pressure dolomitic marble from the Kokchetav Massif, Kazakhstan*

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## ABSTRACT

**Hydroxyl (OH) content in diopside of one diamond-free ultrahigh-pressure (UHP) marble from the Kokchetav Massif, Kazakhstan, was estimated by a micro–Fourier transform infrared (FTIR) spectrometer. Two intrinsic diopside OH bands of FTIR absorption spectra were identified at 3645 and 3465 cm$^{-1}$, with the former band dominating the spectra. Another band occurred at 3685 cm$^{-1}$, which seemed to be accompanied by trivial bands at 3750, 3730, 3585, and 3565 cm$^{-1}$. Intensity variation of the 3685 cm$^{-1}$ band within a single diopside crystal and its location may suggest that the cause of this band was submicroscopic amphibole lamellae. The OH concentration of diopside was estimated to be no less than 850 ppm by weight. Using the previously published experimental data, this OH content indicates that diopside formed at pressures >5 GPa and in a high water activity ($a$H$_2$O) environment.**

**Keywords:** diamond-free UHP dolomitic marble, hydroxyl in diopside, FTIR, Kokchetav Massif.

## INTRODUCTION

The Kokchetav Massif has been well known as one of the most abundant occurrences of microdiamonds in world ultrahigh-pressure (UHP) terranes. Diamond-bearing dolomite marble with an extremely high concentration of microdiamonds at Kumdy-Kol is a representative UHP carbonate rock in this massif (Ogasawara et al., 2000; Yoshioka et al., 2001). A unique UHP calcite marble at Kumdy-Kol contains titanite with coesite exsolution needles/lamellae (Ogasawara et al., 2002); minor amounts of microdiamonds have recently been identified in limited domains or layers (Ogasawara et al., 2004). Moreover, diopsides with $K_2O$-bearing exsolved lamellae (phengite or phlogopite in dolomite marble and phengite and K-feldspar in calcite marble) also occur in these two types of marbles. This texture indicates that precursor diopsides incorporated significant $K_2O$ under UHP conditions, corresponding to experimentally determined $K_2O$ solubility in clinopyroxenes (e.g., Harlow, 1997; Luth, 1997; Okamoto and Maruyama, 1998). The peak metamorphic pressure condition has been estimated at >6 GPa (Ogasawara et al., 2000, 2002).

The third carbonate from Kumdy-Kol is a Ti-clinohumite–bearing dolomitic marble that lacks microdiamond, and has been regarded as a product of extremely low-$X_{CO_2}$ fluid conditions during UHP metamorphism (Ogasawara et al., 2000). Recently, one dolomitic marble sample with a thin layer of dolomite marble, containing diopside with phlogopite lamellae, was reported as evidence for the local heterogeneity of fluid conditions during UHP metamorphism (Ogasawara and Aoki, 2005). Ti-clinohumite–bearing diamond-free dolomitic marble contains a remarkable amount of diopside that lacks $K_2O$ lamellae. Because diopside incorporates significant hydroxyl under UHP conditions (Locke

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et al., 2000), Ogasawara and Aoki (2005) speculated that hydroxyl may be present in the lamella-free diopside in this marble.

Fourier transform infrared (FTIR) studies on clinopyroxene (Cpx) reveal significant amounts of OH (>1000 ppm by weight) in mantle-derived omphacites (e.g., Skogby et al., 1990; Smyth et al., 1991). OH content varies in different geological settings and shows a positive correlation with pressure (e.g., Katayama and Nakashima, 2003). The purpose of this paper is to estimate hydroxyl content of lamella-free diopside in diamond-free dolomitic marble using micro-FTIR spectra and to discuss the formation conditions of dolomitic marble.

## PETROLOGY OF DIAMOND-FREE DOLOMITIC MARBLE

### Geological Outline

In the Kokchetav Massif, northern Kazakhstan, the high-pressure and UHP rocks occur in a large area (10–15 × 150 km$^2$) along a NW-SE direction (e.g., Dobretsov et al., 1995; Kaneko et al., 2000; Maruyama and Parkinson, 2000). Four metamorphic units (I, II, III, and IV) have been identified for the high-pressure–UHP rocks on the basis of their geological structures and lithology, and are fault-bounded by lower-pressure units (unit V and Daulet suite) (Kaneko et al., 2000). At Kumdy-Kol, the highest metamorphic unit in the Kokchetav Massif, unit II, consists predominantly of pelitic and psammitic gneisses, white schist, eclogite, and small amounts of orthogneiss, Ti-clinohumite-garnet ultramafic rocks, and metacarbonate rocks, including diamond-free dolomitic marble (Kaneko et al., 2000; Ogasawara et al., 2000; Muko et al., 2002; Katayama et al., 2003).

The minimum peak pressure condition has been estimated at >6 GPa, based on excess silica content of the precursor titanite in calcite marble (Ogasawara et al., 2002). The temperature condition has been determined to be 1000–1250 °C, based on the mineral assemblages in diamond-bearing dolomite marble and diamond-free dolomitic marble (Ogasawara et al., 2000). These *P-T* estimates are consistent with those of coherent blocks, such as eclogite and metapelites, in the Kumdy-Kol region (e.g., Okamoto et al., 2000; Katayama et al., 2002). The Kokchetav UHP rocks have an age of ca. 530 Ma (e.g., Claoue-Long et al., 1991; Katayama et al., 2001).

### Characteristic Features of Diamond-Free Dolomitic Marble

Significant contrasts between diamond-bearing dolomite marble and diamond-free dolomite marble at Kumdy-Kol have been described previously (Ogasawara et al., 2000). Dolomitic marble lacks microdiamond and exsolution lamellae in diopside; however, this rock is useful for constraining the fluid composition under UHP conditions (Ogasawara et al., 2000). The presence of Ti-clinohumite with $CaCO_3$ phase in this rock requires extremely low-$X_{CO_2}$ conditions ($X_{CO_2}$ < 0.01) under UHP compared with $X_{CO_2}$ ~ 0.1 based on coexisting diopside-dolomite pairs in diamond-bearing dolomite marble.

Although diopside in the diamond-bearing dolomite marble has phengite (rarely phlogopite) exsolution lamellae, diopside in the diamond-free dolomitic marble lacks such lamellae. Ogasawara and Aoki (2005) interpreted this by leaching of $K_2O$ component through extremely low-$X_{CO_2}$ ($H_2O$-rich) fluid.

Ohta et al. (2003) carried out C, O, and Sr isotope studies on constituent carbonates in the Kokchetav UHP marbles. The diamond-free dolomitic marble had a limited range of variation in $\delta^{18}O$ (+10.6 to +13.3‰) and $\delta^{13}C$ (–2.2 to –1.5‰) values. Conversely, the diamond-bearing dolomite marble had a wider range of variation in $\delta^{18}O$ (+9.1 to +20.5‰) and $\delta^{13}C$ (–9.4 to –1.0‰) values. The $^{87}Sr/^{86}Sr$ values of dolomitic marble (0.7259–0.7273) were lower than those of dolomite marble (0.7500–0.8050). Based on these results, they concluded that the dolomitic marble escaped later-stage hydrothermal alteration, whereas alteration was rather strong in the diamond-bearing dolomite marble.

Diopside in the diamond-free dolomitic marble was unaltered. In contrast, diopside in the diamond-bearing dolomite marble was often partly replaced by tremolite. Therefore, it has been suggested that the diamond-free dolomitic marble may preserve a significant amount of OH as evidence of fluid-rock interaction under UHP conditions (Ogasawara and Aoki, 2005).

### Petrography of Diamond-Free Dolomitic Marble

The diamond-free dolomitic marble sample used for the present study is no. Y676. This marble exhibits granoblastic texture and consists mainly of Mg-calcite (30% by volume), dolomite (20%), forsterite (15%), diopside (10%), Ti-clinohumite (<10%), and symplectite (10%) (diopside + spinel + Mg-calcite) after garnet (Fig. 1). Diopside shows granular form and has an

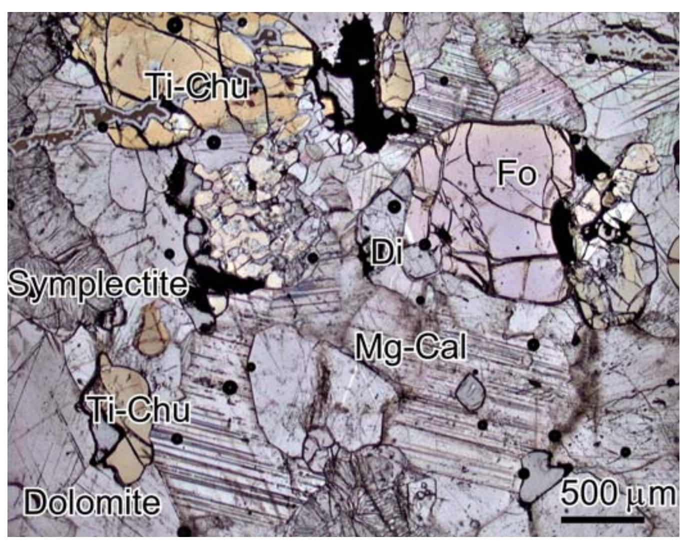


Figure 1. Photomicrograph of diamond-free dolomitic marble (sample no. Y676). Mineral abbreviations: Mg-Cal—Mg-calcite, Di—diopside, Dol—dolomite, Fo—forsterite, Ti-Chu—Ti-clinohumite.

average grain size of ~0.5 mm in longer dimension. All diopside grains in this marble are fresh and lack lamellae. No microdiamond has been identified. No later-stage alteration has been found by microscopic observation. Ogasawara and Aoki (2005) demonstrated that the peak-stage mineral assemblage was dolomite + aragonite + diopside + garnet + Ti-clinohumite (+ forsterite?) (see also Ogasawara et al., 1998, 2000).

Chemical compositions of diopside in sample no. Y676 were analyzed with a JEOL JXA-8900 electron microprobe using wavelength-dispersive mode with an accelerating voltage of 15 kV, beam current of 20 nA, and beam diameter of 10 µm. Five representative analyses are listed in Table 1. Diopside shows no chemical zoning and contains 0.6–0.9 wt% of FeO and 1.2–2.0 wt% of $Al_2O_3$. $K_2O$ was below the detection limit.

TABLE 1. REPRESENTATIVE CHEMICAL COMPOSITIONS OF DIOPSIDE

| | | | | | |
|---|---|---|---|---|---|
| Oxides (wt%) | | | | | |
| $SiO_2$ | 53.95 | 54.01 | 54.36 | 53.91 | 54.07 |
| $TiO_2$ | 0.12 | 0.22 | 0.11 | 0.17 | 0.15 |
| $Al_2O_3$ | 1.88 | 1.71 | 1.20 | 1.77 | 1.56 |
| $Cr_2O_3$ | 0.02 | 0.01 | 0.00 | 0.00 | 0.07 |
| FeO | 0.65 | 0.88 | 0.80 | 0.80 | 0.86 |
| MnO | 0.04 | 0.05 | 0.05 | 0.05 | 0.05 |
| MgO | 17.68 | 17.83 | 18.00 | 17.69 | 17.62 |
| CaO | 25.61 | 25.28 | 25.32 | 25.67 | 25.61 |
| $K_2O$ | BDL | BDL | BDL | BDL | BDL |
| $Na_2O$ | BDL | BDL | 0.02 | 0.03 | BDL |
| Total | 99.95 | 99.99 | 99.86 | 100.09 | 99.99 |
| Cations per 6 oxygen atoms | | | | | |
| Si | 1.9523 | 1.9543 | 1.9683 | 1.9508 | 1.9583 |
| Ti | 0.0034 | 0.0059 | 0.0030 | 0.0047 | 0.0041 |
| Al | 0.0800 | 0.0728 | 0.0513 | 0.0753 | 0.0666 |
| Cr | 0.0005 | 0.0003 | 0.0000 | 0.0000 | 0.0020 |
| Fe | 0.0197 | 0.0268 | 0.0243 | 0.0241 | 0.0260 |
| Mn | 0.0012 | 0.0014 | 0.0017 | 0.0015 | 0.0017 |
| Mg | 0.9538 | 0.9615 | 0.9715 | 0.9540 | 0.9513 |
| Ca | 0.9933 | 0.9803 | 0.9825 | 0.9955 | 0.9938 |
| K | BDL | BDL | BDL | BDL | BDL |
| Na | BDL | BDL | 0.0015 | 0.0020 | BDL |

*Note*: Total Fe calculated as FeO. BDL: below detection limit.

## METHODS OF STUDY

### Sample Preparation

For micro-FTIR spectrometry, a 150-µm-thick section was prepared. In order to polish the section, an adhesive (Toagosei Co., Tokyo) was used to fix the sample on a deck glass. Both sides of the section were polished with diamond abrasives (grain size: 1 µm). After polishing with diamond paste, the sample was immersed in acetone to dissolve the glue. The thickness of the section was measured with a digital caliper. We confirmed that these chemicals, the glue, and acetone used in sample preparation, did not interfere with FTIR spectra.

### Micro-FTIR Spectrometer

FTIR absorption spectra of diopside were acquired with a Thermo Nicolet Continuµm microscope with Avatar 370 Fourier transform IR spectrometer equipped with IR light source, KBr beam-splitter, and MCT-A detector. An aperture of 30 µm in diameter was used. Unpolarized light was used in the measurements. Each FTIR spectrum of unoriented diopside grains was accumulated from 100 scans. The wavenumber resolution of spectrum was 4 $cm^{-1}$. In order to avoid the effect of inclusions and/or cracks, optically clear parts of diopside were selected. We calculated the peak intensities with the software OMNIC, correcting the base line linearly around the objective bands.

### Estimation of OH Content in Diopside

Ideally, polarized spectra in the three principal optical directions ($x$, $y$, and $z$) are necessary to determine the OH amount in diopside. However, since we used a randomly oriented thin section sample, we took the following method to reduce the absorption anisotropic effect. Unpolarized light, which brings spectra resulting from two perpendicular directions of each grain, was utilized, and 30 spectra were averaged. Water contents in clinopyroxenes have been determined from FTIR spectra using both peak heights (Skogby et al., 1990) and peak integration (Bell et al., 1995). Katayama and Nakashima (2003) compared both methods and found the results differed by <5%. The peak height method was utilized in the present study. The calculation method for unoriented samples, modified after Katayama and Nakashima (2003), is as follows: $C_{OH}$ (wt%) = 1.8 {Abs /(ρ × ε × ζ × $t$)}, where $C_{OH}$, Abs, ρ, ε, ζ, and $t$ are OH concentration, total sum of absorbances of intrinsic OH of diopside, the density of diopside, molar absorptivity, the correction coefficient for unoriented samples, and thickness of the sample (path length), respectively. The molar absorptivity of 150(L/[mol × cm]) calibrated by Skogby et al. (1990) was used. The value 1/3 is generally applied as the correction coefficient for unoriented samples. We used the pure diopside density of 3.22 from Deer et al. (1992).

## RESULTS

Optically clear diopside grains were selected for acquisition of FTIR spectra. Fifty FTIR spectra were obtained from 35 diopside grains. Eight representative spectra that were normalized to 1 mm thick are shown in Figure 2. Two apparent bands, 3645 and 3685 $cm^{-1}$, were detected in the range 4000–3200 $cm^{-1}$; their intensities are listed in Table 2. The former band appears in every spectrum, and usually is the strongest. Some spectra have a strong peak at 3685 $cm^{-1}$ (e.g., spectra E, F, G, H of Fig. 2), but others have no band at 3685 $cm^{-1}$ (e.g., spectra A, B, C of Fig. 2). In addition to the two bands, spectra exhibit some subtle bands at 3750, 3730, 3585, 3565, and rarely 3465 $cm^{-1}$ (especially in spectra H and G in Fig. 2).

The peak intensity of the band at 3645 $cm^{-1}$ is homogeneous in a single diopside grain, but varies between distinct

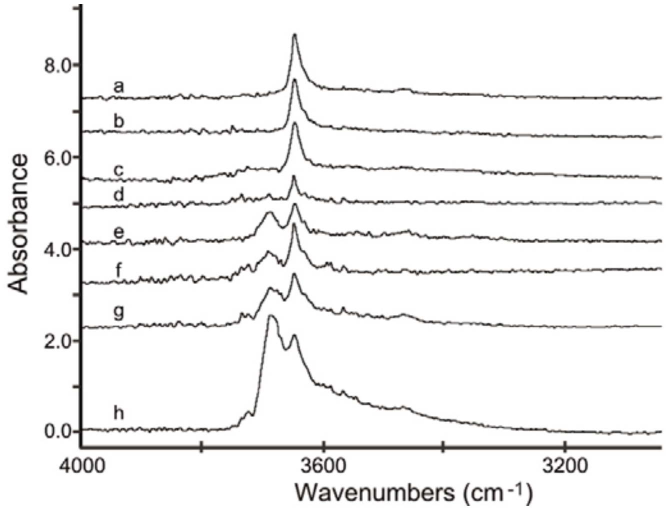


Figure 2. Representative unpolarized Fourier transform infrared (FTIR) spectra of diopsides in diamond-free dolomitic marble. Diopsides were unoriented; optically clear parts without inclusions or cracks were selected for analyses. Spectra were normalized to a thickness of 1-mm thickness and were on the same absorbance scale for comparison. Two obvious bands were found in the FTIR spectra: 3645 and 3685 cm$^{-1}$.

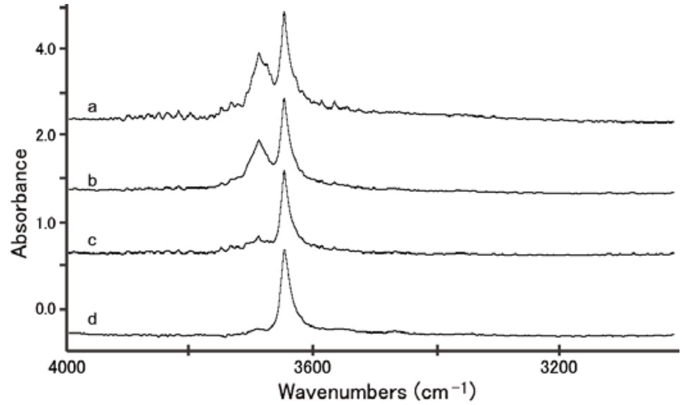


Figure 3. Unpolarized Fourier transform infrared (FTIR) spectra obtained within a single diopside grain, which were normalized to 1 mm thickness. Peak intensity of the 3645 cm$^{-1}$ band is homogeneous, whereas that of the 3685 cm$^{-1}$ band varies. Other bands at 3750, 3730, 3585, and 3565 cm$^{-1}$ seem to be associated with the 3685 cm$^{-1}$ band.

TABLE 2. INTENSITIES OF THE BANDS AT 3685 AND 3645 CM$^{-1}$ IN 8 SPECTRA OF FIGURE 2

| | 3685 cm$^{-1}$ | 3645 cm$^{-1}$ |
|---|---|---|
| a | 0.000 | 1.236 |
| b | 0.000 | 1.008 |
| c | 0.000 | 0.993 |
| d | 0.141 | 0.503 |
| e | 0.275 | 0.460 |
| f | 0.300 | 0.987 |
| g | 0.468 | 0.639 |
| h | 1.414 | 0.573 |

*Note*: The peak intensities were calculated with the software OMNIC, correcting the background linearly.

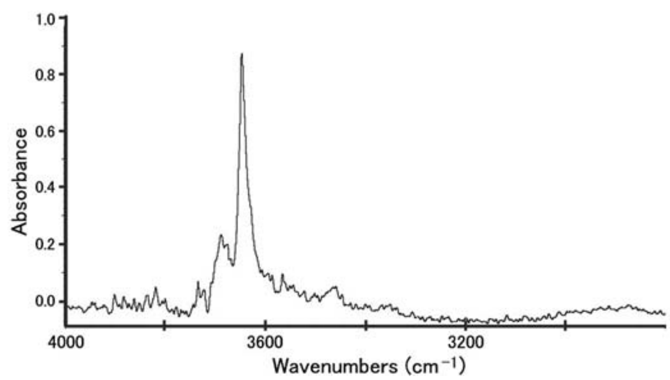


Figure 4. Averaged Fourier transform infrared (FTIR) spectrum calculated using 30 spectra of diopsides with relatively weak band at 3685 cm$^{-1}$. The spectrum was normalized to 1 mm thickness.

grains from 0.41 to 1.51 (avg. 0.83). This variation of the peak intensities is caused by the absorption anisotropic effect. Johnson et al. (2002) used diopside from a marble xenolith to demonstrate that the peak intensity of the 3645 cm$^{-1}$ band varies in three optical directions with $x = y >> z$. On the other hand, the peak intensity of the band at 3685 cm$^{-1}$ varies even within a single diopside grain (Fig. 3). Figure 3 also indicates that the bands at 3750, 3730, 3585, and 3565 cm$^{-1}$ seem to be associated with the 3685 cm$^{-1}$ band.

Because only the 3645 and 3465 cm$^{-1}$ bands have been reported as intrinsic OH bands of diopside (e.g., Skogby et al., 1990; Johnson et al., 2002), an average spectrum was calculated using 30 spectra that have a relatively weak band at 3685 cm$^{-1}$ and other related bands in order to estimate the amount of OH in our diopside (Fig. 4). In the resultant spectrum, we could not recognize the 3465 cm$^{-1}$ band, because this band rarely appeared in spectra of our diopside sample. Therefore, OH amount in our diopside was estimated with only the 3645 cm$^{-1}$ band; the peak intensity of this band was 0.788 in the averaged spectrum. The resultant OH content was >850 ppm.

## DISCUSSION

### Evaluation of Micro-FTIR Spectra

Previous studies have demonstrated that diopside generally exhibits four intrinsic OH bands: 3645, 3530, 3450, and 3350 cm$^{-1}$ (e.g., Skogby and Rossman, 1989; Skogby et al., 1990; Skogby, 1994; Johnson et al., 2002). These four bands are classified into two groups on the basis of their pleochroic behavior: group I (3645 cm$^{-1}$) and group II (3530, 3450, and 3350 cm$^{-1}$) (for review, see Ingrin and Skogby, 2000). Johnson et al. (2002), however, reported only one major OH band at 3645 cm$^{-1}$ from a marble xenolith. Based on these previous studies and the homogeneity of the peak intensity in a single grain, the 3645 $cm^{-1}$ band obtained in our sample can be regarded as an intrinsic OH vibration of diopside. A weak band at 3465 $cm^{-1}$ sometimes occurs (e.g., spectra G and H in Fig. 2) and is also an intrinsic diopside OH band.

The 3685 $cm^{-1}$ band shows a different behavior compared with the 3645 $cm^{-1}$ band. The peak intensity of the 3685 $cm^{-1}$ band varies even within a single diopside grain (Fig. 3), indicating that this band is not intrinsic. Figure 3 also indicates that the 3685 $cm^{-1}$ band seems to be accompanied by trivial bands at 3750, 3730, 3585, and 3565 $cm^{-1}$. Koch-Müller et al. (2004) described a band at 3624–3600 $cm^{-1}$ in omphacite that showed strong variation in a single grain; they concluded that this band was caused by nanometer-sized inclusions of sheet silicates. Usually, a sharp band at 3675 $cm^{-1}$ accompanies four intrinsic OH bands of diopside and is thought to result from submicroscopic amphibole lamellae and/or disordered pyribole layers (Ingrin et al., 1989; Skogby et al., 1990). Some amphiboles show OH bands in the range 3690–3680 $cm^{-1}$ (Kodama, 1985). Based on these previous studies, the 3685 $cm^{-1}$ band in our diopside can be attributed to submicroscopic amphibole lamellae in diopside. The broadness of the 3685 $cm^{-1}$ band may be related to disorder in the submicroscopic lamellae. These inferences can be tested by transmission-electron microscope (TEM) study.

### Source of the OH Associated with Nonintrinsic Diopside Band

Ohta et al. (2003) demonstrated that C, O, and Sr isotopic composition of Mg-calcite and dolomite in the diamond-free dolomitic marble was homogeneous, whereas the diamond-bearing dolomite marble exhibited isotopic heterogeneity and disequilibrium. They concluded that the diamond-free dolomitic marble was isolated from retrograde fluids. Therefore, diopside in diamond-free dolomitic marble had no chance to incorporate OH from fluids during the retrograde stage. The only possible source of OH in submicroscopic amphibole is the host precursor diopside, because the precursor diopside could contain much higher concentrations of OH than the estimated value in this study. Submicroscopic amphibole lamellae were exsolved from diopside during the exhumation stage due to decompression. Conclusively, the source of the OH detected as the amphibole band (3685 $cm^{-1}$) was originally OH in diopside.

### Estimated OH Content in Diopside and its Geological Implications

Locke et al. (2000) showed that the amount of OH in diopside increased with pressure, <120 ppm at 5 GPa and 1150 °C and ~1500 ppm at 7.5 GPa and 1200 °C, and their results indicated that OH content in diopside greatly increases from 5 to 7 GPa. Other previous studies have shown that several factors control the OH concentration in clinopyroxenes, these include pressure, oxygen fugacity, water activity, and chemical compositions (e.g., Skogby et al., 1990; Johnson et al., 2002; Bromiley et al., 2004). Among these, water contents in clinopyroxenes are proportional to pressure conditions if other variables are constant. Clinopyroxenes in mantle-derived rocks usually contain larger amounts of OH than those of crustal origin (e.g., Skogby et al., 1990; Smyth et al., 1991). Katayama and Nakashima (2003) reported that the OH content of omphacite from the Kokchetav Massif increases with the peak pressure conditions: ~1000 ppm in quartz eclogite; ~2000 ppm in coesite eclogite; and ~3000 ppm in diamond-grade eclogite. Bromiley et al. (2004) performed annealing experiments on natural chromian diopside and found that the hydrogen solubility increased with pressure at a controlled oxygen fugacity with Ni-NiO buffer. Based on experimental results by Locke et al. (2000), the diopside analyzed in our study has preserved a pressure condition >5 GPa.

Considering the presence of submicroscopic amphibole and the effect of hydrogen loss from OH-bearing diopside, the OH content of diopside in diamond-free dolomitic marble might have been much larger than the estimated value. Since we ignored the OH content of submicroscopic amphibole lamellae, precursor diopside could have incorporated much greater OH content. In addition, the effect of hydrogen loss in OH-bearing diopside during the exhumation stage cannot be ruled out. Skogby and Rossman (1989) found that the intensity of OH band at 3645 $cm^{-1}$ was controlled by the following reduction-oxidation reaction in Fe-bearing systems:

$$Fe^{2+} + OH^{-} = Fe^{3+} + O^{2-} + 1/2H_2. \quad (1)$$

They demonstrated that the hydrogen diffusion rate in diopside is so large that hydrogen loss could occur in the order of hours. Johnson et al. (2002) conducted Mössbauer analyses of diopsides and showed that the diopside in the marble xenolith having one major OH band at 3645 $cm^{-1}$ contained a high ratio of $Fe^{3+}$:$Fe^{total}$ (~50%). They suggested that, if all the Fe had been originally $Fe^{2+}$, their diopside could have originally incorporated >1300 ppm OH, which is 10 times greater than the detected value.

The other important factor that controls the quantity of OH in diopside is $H_2O$ activity, $aH_2O$. Johnson et al. (2002) compared OH content of diopside in various marbles and demonstrated that OH contents increased with increasing $aH_2O$. Koch-Müller et al. (2004), however, found an OH-poor (<30 ppm) omphacite in a diamond-bearing eclogite xenolith from the Mir kimberlite pipe, which formed under sufficient pressure to incorporate a significant amount of OH. They attributed the low water content in the omphacite to formation of the host eclogite under low $aH_2O$. Therefore, the significant amount of OH in diopside of diamond-free dolomitic marble from the Kokchetav Massif is evidence for the high $aH_2O$ conditions during UHP metamorphism. Such results are consistent with previous studies that indicated diamond-free dolomitic marble had formed under extremely low-$X_{CO_2}$ conditions (Ogasawara et al., 2000; Ogasawara and Aoki, 2005; Kikuchi and Ogasawara, 2003).

## CONCLUSIONS

A major intrinsic OH band of diopside was found at 3645 $cm^{-1}$ in the FTIR spectra of diopside in diamond-free dolomitic marble from the Kokchetav UHP Massif using micro-FTIR. The other OH band occurred at 3685 $cm^{-1}$, intensity varied even within a single grain, and this band was caused by submicroscopic amphibole lamellae exsolved from diopside during the exhumation stage.

The estimated OH content in diopside is >850 ppm by weight, and this value corresponds to a pressure condition of >5 GPa based on the experimental study by Locke et al. (2000). The OH content in diopside under peak metamorphic conditions was probably much larger for the following reasons: (1) OH in submicroscopic amphibole lamellae was originally in diopside, and (2) hydrogen loss from OH-bearing diopside could occur during decompression. The significant quantity of OH in diopside in the diamond-free dolomitic marble also indicates the high $H_2O$ activity under UHP metamorphism. These results are consistent with previous studies (e.g., Ogasawara et al., 2000), which infer that the diamond-free dolomitic marble formed under extremely low-$X_{CO_2}$ conditions at pressures >6 GPa.

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## REFERENCES CITED

Bell, D.R., Ihinger, P.D., and Rossman, G.R., 1995, Quantitative analysis of trace OH in garnet and pyroxenes: The American Mineralogist, v. 80, p. 465–474.

Bromiley, G.D., Keppler, H., McCammon, C., Bromiley, F.A., and Jacobsen, S.D., 2004, Hydrogen solubility and speciation in natural, gem-quality chromian diopside: The American Mineralogist, v. 89, p. 941–949.

Claoue-Long, J.C., Sobolev, N.V., Shatsky, V.S., and Sobolev, A.V., 1991, Zircon response to diamond-pressure metamorphism in the Kokchetav Massif, USSR: Geology, v. 19, p. 710–713, doi: 10.1130/0091-7613(1991)019<0710:ZRTDPM>2.3.CO;2.

Deer, W.A., Howie, R.A., and Zussman, J., 1992, An introduction to the rock-forming minerals (second edition): London, Pearson Prentice Hall, p. 143–154.

Dobretsov, N.L., Sobolev, N.V., Shatsky, V.S., Coleman, R.G., and 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, v. 4, p. 267–279.

Harlow, G.E., 1997, K in clinopyroxene at high pressure and temperature: An experimental study: The American Mineralogist, v. 82, p. 259–269.

Ingrin, J., and Skogby, H., 2000, Hydrogen in nominally anhydrous upper-mantle minerals: Concentration levels and implications: European Journal of Mineralogy, v. 12, p. 543–570.

Ingrin, J., Latrous, K., Doukhan, J.C., and Doukhan, N., 1989, Water in diopside: An electron microscopy and infrared spectroscopy study: European Journal of Mineralogy, v. 1, p. 327–341.

Johnson, E.A., Rossman, G.R., Dyar, M.D., and Valley, J.W., 2002, Correlation between OH concentration and oxygen isotope diffusion rate in diopsides from the Adirondack Mountains, New York: The American Mineralogist, v. 87, p. 899–908.

Kaneko, Y., Maruyama, S., Terabayashi, M., Yamamoto, H., Ishikawa, M., Anma, R., Parkinson, C.D., Ota, T., Nakajima, Y., Katayama, I., Yamamoto, J., and Yamauchi, K., 2000, Geology of the Kokchetav UHP-HP metamorphic belt, northern Kazakhstan: The Island Arc, v. 9, p. 264–283, doi: 10.1046/j.1440-1738.2000.00278.x.

Katayama, I., and Nakashima, S., 2003, Hydroxyl in clinopyroxene from the deep subducted crust: Evidence for $H_2O$ transport into mantle: The American Mineralogist, v. 88, p. 229–234.

Katayama, I., Maruyama, S., Parkinson, C.D., Terada, K., and Sano, Y., 2001, Ion micro-probe U-Pb zircon geochronology of peak and retrograde stages of ultrahigh-pressure metamorphic rocks from the Kokchetav Massif, northern Kazakhstan: Earth and Planetary Science Letters, v. 188, p. 185–198, doi: 10.1016/S0012-821X(01)00319-3.

Katayama, I., Ohta, M., and Ogasawara, Y., 2002, Mineral inclusions in zircon from diamond-bearing marble in the Kokchetav Massif, northern Kazakhstan: European Journal of Mineralogy, v. 14, p. 1103–1108, doi: 10.1127/0935-1221/2002/0014-1103.

Katayama, I., Muko, M., Iizuka, T., Maruyama, S., Terada, K., Tsutsumi, Y., Sano, Y., Zhang, R.Y., and Liou, J.G., 2003, Dating of zircon from Ti-clinohumite–bearing garnet peridotite: Implication for timing of mantle metasomatism: Geology, v. 31, p. 713–716, doi: 10.1130/G19525.1.

Kikuchi, M., and Ogasawara, Y., 2003, Stability relations in Ti-bearing assemblages in the Kokchetav UHP marbles: Eos (Transactions, American Geophysical Union), v. 84, no. 46, p. V22D–0619.

Koch-Müller, M., Matsyuk, S.S., and Wirth, R., 2004, Hydroxyl in omphacites and omphacitic clinopyroxenes of upper mantle to lower crustal origin beneath the Siberian platform: The American Mineralogist, v. 89, p. 921–931.

Kodama, H., 1985, Infrared spectra of minerals: Reference guide to identification and characterization of minerals for the study of soils: Agriculture Canada Research Establishments, Technical Bulletin 1985–1E, 197 p.

Locke, D.L., Holloway, J.R., and Hervig, R., 2000, Experimental determination of $H_2O$ solubility in mantle clinopyroxene at 5 GPa and 7.5 GPa [abs.]: Eos (Transactions, American Geophysical Union), v. 81, no. 19, p. V52D–05.

Luth, R.W., 1997, Experimental study of the system phlogopite-diopside from 3.5 to 17 GPa: The American Mineralogist, v. 82, p. 1198–1209.

Maruyama, S., and Parkinson, C.D., 2000, Overview of the geology, petrology and tectonic framework of the high-pressure–ultrahigh-pressure metamorphic belt of the Kokchetav Massif, Kazakhstan: The Island Arc, v. 9, p. 439–455, doi: 10.1046/j.1440-1738.2000.00288.x.

Muko, A., Okamoto, K., Yoshioka, N., Zhang, R.Y., Parkinson, C.D., Ogasawara, Y., and Liou, J.G., 2002, Petrogenesis of Ti-clinohumite–bearing garnetiferous ultramafic rocks from Kumdy-Kol, *in* Parkinson, C.D., et al., eds., The diamond-bearing Kokchetav Massif, Kazakhstan: Tokyo, Universal Academy Press, Inc., p. 343–359.

Ogasawara, Y., and Aoki, K., 2005, The role of fluid for diamond-free dolomitic marble from the Kokchetav Massif: International Geological Review, v. 47, p. 1178–1193.

Ogasawara, Y., Zhang, R.Y., and Liou, J.G., 1998, Petrogenesis of dolomitic marbles from Rongcheng in the Su-Lu ultrahigh-pressure metamorphic terrane, eastern China: The Island Arc, v. 7, p. 82–97, doi: 10.1046/j.1440-1738.1998.00177.x.

Ogasawara, Y., Ohta, M., Fukasawa, K., Katayama, I., and Maruyama, S., 2000, Diamond-bearing and diamond-free metacarbonate rocks from Kumdy-Kol in the Kokchetav Massif, northern Kazakhstan: The Island Arc, v. 9, p. 400–416, doi: 10.1046/j.1440-1738.2000.00285.x.

Ogasawara, Y., Fukasawa, K., and Maruyama, S., 2002, Coesite exsolution from supersilicic titanite in UHP marble from the Kokchetav Massif, northern Kazakhstan: The American Mineralogist, v. 87, p. 454–461.

Ogasawara, Y., Adachi, A., and Aoki, K., 2004, Occurrence of microdiamond in UHP calcite marble from the Kokchetav Massif: Eos (Transactions, American Geophysical Union), v. 85, no. 47, p. T21A–0503.

Ohta, M., Mock, T., Ogasawara, Y., and Rumble, D., 2003, Oxygen, carbon, and strontium isotope geochemistry of diamond-bearing carbonate rocks from Kumdy-Kol, Kokchetav Massif: Kazakhstan: Lithos, v. 70, p. 77–90, doi: 10.1016/S0024-4937(03)00093-8.

Okamoto, K., and Maruyama, S., 1998, Multi-anvil re-equilibration experiments of Dabie Shan ultrahigh-pressure eclogite within the diamond-stability fields: The Island Arc, v. 7, p. 52–69, doi: 10.1046/j.1440-1738.1998.00179.x.

Okamoto, K., Liou, J.G., and Ogasawara, Y., 2000, Petrology of diamond-grade eclogite in the Kokchetav Massif, northern Kazakhstan: The Island Arc, v. 9, p. 379–399, doi: 10.1046/j.1440-1738.2000.00284.x.

Skogby, H., 1994, OH incorporation in synthetic clinopyroxene: The American Mineralogist, v. 79, p. 240–249.

Skogby, H., and Rossman, G.R., 1989, $OH^-$ in pyroxene: An experimental study of incorporation mechanisms and stability: The American Mineralogist, v. 74, p. 1059–1069.

Skogby, H., Bell, D.R., and Rossman, G.R., 1990, Hydroxide in pyroxene: Variations in the natural environment: The American Mineralogist, v. 75, p. 764–774.

Smyth, J.R., Bell, D.R., and Rossman, G.R., 1991, Incorporation of hydroxyl in upper-mantle clinopyroxenes: Nature, v. 351, p. 732–735, doi: 10.1038/351732a0.

Yoshioka, N., Muko, A., and Ogasawara, Y., 2001, Extremely high diamond concentration in dolomite marble: UHPM Workshop 2001—Fluid/slab/mantle interactions and ultrahigh-*P* minerals (extended abstract): Tokyo, Waseda University, p. 51–55.

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