

Hydroxyl in clinopyroxene from the deep subducted crust: Evidence for H₂O transport into the mantle

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ABSTRACT

Clinopyroxenes in eclogites from the deep subducted crust in the Kokchetav, Kazakhstan, ultra-high-pressure metamorphic terrane were found by infrared spectroscopy to contain up to 3020 ppm OH. These rocks were recrystallized at pressures over 60 kbar and temperatures over 1000 °C, where no hydrous minerals are stable. Infrared spectra of the clinopyroxenes show three hydroxyl absorption bands in the regions 3440–3460 cm⁻¹, 3500–3530 cm⁻¹, and 3600–3625 cm⁻¹. The hydroxyl absorbance increases with recrystallization pressure of the eclogites and with vacancy concentration in the pyroxene structure (Ca-Eskola component). Clinopyroxenes represent about 40–50 vol% of eclogites, such that the bulk eclogites contain approximately 1300 ppm hydroxyl at depths greater than 150 km. Thus, subducted oceanic crust can transport trace amounts of H₂O into the upper mantle, even in the absence of nominally hydrous minerals.

INTRODUCTION

H₂O transport into the mantle has attracted the attention of many Earth scientists because water plays an essential role in magma genesis and mantle dynamics. The input of water into the mantle is restricted to subduction zones. For a cold geotherm, lawsonite in a basaltic bulk composition is considered to be a host of water to depths greater than 150 km, according to high-pressure experiments (Schmidt and Poli 1998; Ono 1998; Okamoto and Maruyama 1999). Phengite is also stable up to 330 km depth (Schmidt 1996; Domanik and Holloway 1996), but this phase is rare in the basaltic compositions. However, for conditions involving a relatively hot geotherm, hydrous minerals become unstable. Subduction zone *P-T* paths calculated from natural metamorphic rocks suggest that thermal gradients are usually higher than the stability fields of hydrous minerals at great depth (>100 km) (e.g., Maruyama et al. 1996). Thus, subducted oceanic crust is mostly dehydrated at shallow depth, and then transformed to dry eclogite containing no hydrous minerals at *T* > 700 °C and *P* > 30 kbar. It has therefore been believed that subducted crust cannot carry significant amounts of H₂O into the deep upper mantle.

Recent studies reported that trace amounts of hydroxyl can be contained in nominally anhydrous minerals (NAMs) (e.g., Bell and Rossman 1992). Trace water in these minerals is capable of recycling into the Earth's interior at subduction zones. Clinopyroxene is the most hydrous mineral of the major constituents in deep subducted crust, and contains up to 1840 ppm OH (by weight) in kimberlite xenoliths (Smyth et al. 1991) and up to 2200 ppm OH (by weight) by laboratory experiments (Skogby 1994). However, to date, only a few studies have addressed the hydroxyl content of natural clinopyroxenes in high- to ultrahigh-pressure (HP-UHP) metamorphic rocks that have

been subducted to mantle depths and returned to the surface. Among these, the Kokchetav massif, Kazakhstan, is considered to be the highest-pressure metamorphic terrane because of its abundant microdiamonds, coesites, and other mineralogical evidence (Sobolev and Shatsky 1990; Zhang et al. 1997; Okamoto et al. 2000; Katayama et al. 2000a). The diamond-grade rocks were recrystallized at *P* > 60 kbar and *T* > 1000 °C (Okamoto et al. 2000), and they do not contain hydrous minerals. To estimate how much water is transported into the Earth's interior at deep subduction zones, we investigated the hydroxyl contents of clinopyroxenes in the Kokchetav UHP eclogites using infrared (IR) micro-spectroscopy.

GEOLOGICAL SETTING

The Kokchetav massif is situated in the central domain of the composite Eurasian craton (Fig. 1), the major part of which was amalgamated and stabilized by a series of Paleozoic-Mesozoic collisional events (Dobretsov et al. 1995). This massif is composed of several Precambrian rock series, Cambro-Ordovician volcanic and sedimentary rocks, Devonian volcanic rocks, and Carboniferous-Triassic shallow-water and lacustrine sedimentary rocks (Dobretsov et al. 1995). The HP-UHP massif is considered to be a thin (1–2 km), more-or-less coherent subhorizontal sheet, which is structurally overlain by a weakly metamorphosed unit (Unit V) composed of slate and quartzite, and underlain by the Daulat Suite, composed of quartz and pelitic/psammitic schists (Kaneko et al. 2000).

On the basis of gross lithological variations, the HP-UHP massif is subdivided into four units (Fig. 1). Unit I is composed of amphibolite and quartzofeldspathic gneiss, Unit II mainly of pelitic-psammitic gneiss with locally abundant eclogite boudins, Unit III of alternating orthogneiss and amphibolite with rare eclogite lenses, and Unit IV is composed of quartz schist and siliceous schist (Kaneko et al. 2000). These HP-UHP rocks were intruded by post-orogenic granitoids in

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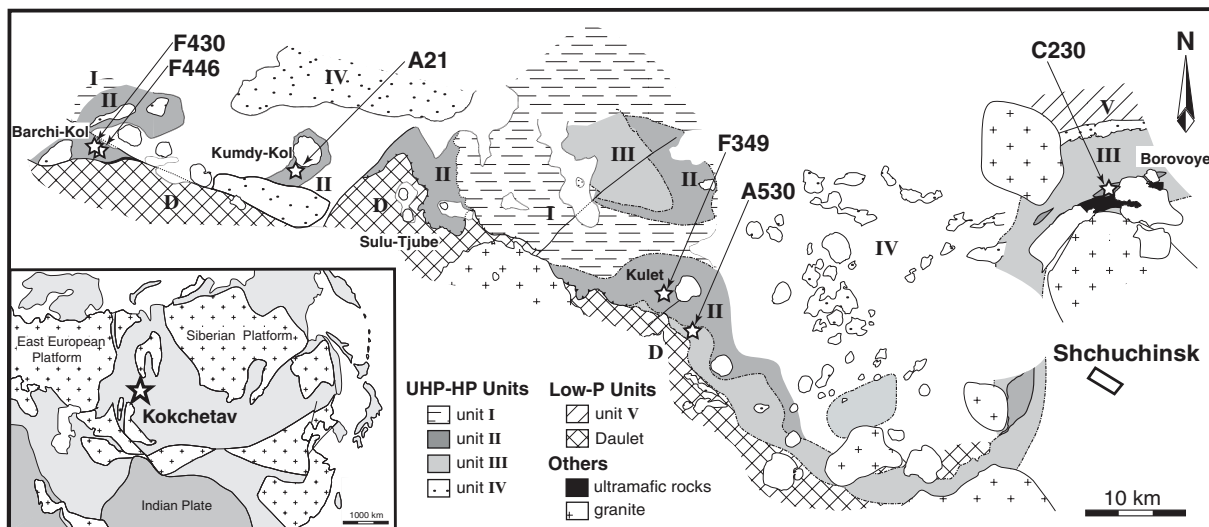


FIGURE 1. Geologic map of the Kokchetav massif, Kazakhstan, modified after Kaneko et al. (2000). Sample localities for this study are also shown with corresponding sample numbers. Inset map is the location of the Kokchetav massif in the Eurasian continent.

Ordovician-Silurian times (Dobretsov et al. 1995).

Metamorphic diamonds have been identified in the Kumdyy-Kol region in the central domain of the massif (Sobolev and Shatsky 1990; Zhang et al. 1997; Katayama et al. 2000a). Eclogites occur as lenticular masses surrounding diamond-bearing rocks, and yield P - T conditions of >60 kbar and >1000 °C based on the K_2O -in-augite geobarometer and the Grt-Cpx geothermometer (Okamoto et al. 2000). Coesite has been identified in eclogite and whiteschist as inclusions in zircon and garnet from the Kumdyy-Kol, Barchi-Kol, and Kulet regions (Korsakov et al. 1998; Shatsky 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 HP-UHP massif (Shatsky et al. 1995; Zhang et al. 1997; Okamoto et al. 2000; Katayama et al. 2000b).

PETROGRAPHY AND MINERAL CHEMISTRY

We chose six eclogite samples of three different P - T conditions from the Kokchetav massif (Fig. 1 and Table 1), in order to investigate an inferred pressure dependence of hydroxyl content in the clinopyroxenes. A diamond-grade eclogite (Dia-Ec) from the Kumdyy-Kol region consists of garnet + omphacite + rutile + quartz with minor amounts of apatite and zircon. Diamond is absent in the eclogite due to unfavorable bulk composition, but is abundant in surrounding pelitic gneisses and dolomitic marble. Coesite occurs as inclusions within refractory minerals such as zircon and clinopyroxene. Metamorphic peak P - T conditions for this eclogite were estimated to be 60–80 kbar and 940–1020 °C. Coesite-eclogites (Coe-Ec) were collected from the Barchi-Kol, and consist of coesite + omphacite + garnet + quartz + rutile ± phengite. Garnet and omphacite of the coesite-eclogites contain inclusions of pseudomorphs after coesite, which consist of polycrystalline quartz aggregates with radial fractures. The coesite-eclogites were

recrystallized at pressures of 28–39 kbar and temperatures of 770–800 °C. Quartz-eclogites (Qtz-Ec) from Kulet and Borovoye regions commonly contain hydrous minerals such as amphibole, zoisite or phengite, which yielded pressures of 20–27 kbar and temperatures of 610–730 °C.

Most matrix clinopyroxene grains in the diamond-grade eclogite contain crystallographically oriented quartz rods, which are a few micrometers in width and about 100 μm in length. The matrix pyroxene grains are nearly homogeneous chemically, and are omphacitic in composition ($X_{\text{Fs}}: 0.38\text{--}0.40$). Conversely, zircon-hosted clinopyroxene inclusions from the same sample contain significant amounts (up to 9.6 mol%) of the Ca-Eskola component ($\text{Ca}_{0.5}\square_{0.5}\text{AlSi}_2\text{O}_6$, where \square is a vacancy on the M_2 site), in contrast to the small amounts (1.3 mol%, on average) in the matrix clinopyroxenes. Because the matrix clinopyroxene contains quartz exsolution lamellae, the original composition was recalculated based on its quartz content. The resulting original pyroxene contains 6.6 mol% Ca-Eskola component (Table 2), which is very similar to those pyroxenes included in zircon. The primary clinopyroxene at peak UHP metamorphism is considered to contain a high Ca-Eskola component and therefore a large number of vacancies on the M_2 site. In the other eclogites, quartz exsolution was not observed in the clinopyroxenes; these have a relatively low Ca-Eskola component (0.3–1.1 mol%), except for one coesite-eclogite (F430) that contains 2.8 mol% on average (Table 2). Thus, vacancies in the clinopyroxenes exist under ultrahigh-high pressure natural conditions in accordance with several high-pressure experiments (Mao 1971; Gasparik 1986).

HYDROXYL SPECTRA OF CLINOPYROXENES

In order to measure hydroxyl contents in the clinopyroxenes of these eclogites, we prepared doubly polished thin sections with a thickness of 100–140 μm for IR micro-spectroscopy. The polished sections were kept and cleaned in acetone to take

TABLE 1. Mineral parageneses of eclogites and FTIR results

Sample	Rock type	Mineral assemblage	Pressure	Temperature	OH Absorbance				
					3440-60 cm ⁻¹	3500-30cm ⁻¹	3600-25cm ⁻¹	Total	OH (ppm)
A21	Dia-Ec*	Coe + Omp + Grt + Qtz + Rt	60–80 kbar	940–1020 °C	1.045	0.9	1.035	2.98	3020
F430	Coe-Ec	Coe + Omp + Grt + Qtz + Rt	28–38 kbar	770–800 °C	0.948	0.854	0.590	2.392	2430
F446	Coe-Ec	Coe + Omp + Grt + Qtz + Phn + Rt	34–39 kbar	770–790 °C	0.773	0.632	0.268	1.673	1690
A530	Qtz-Ec	Omp + Grt + Amp + Qtz + Rt	20–27 kbar	610–660 °C	0.554	0.343	0.208	1.106	1110
C230	Qtz-Ec	Omp + Grt + Qtz + Phn + Rt	24–26 kbar	690–730 °C	0.468	0.396	0.184	1.047	1060
F349	Qtz-Ec	Omp + Grt + Amp + Qtz + Rt	20–27 kbar	660–680 °C	0.501	0.399	0.125	1.025	1030

Note: Mineral abbreviations; Coe = coesite, Omp = omphacite, Grt = garnet, Amp = amphibole, Qtz = quartz, Rt = rutile, Phn = phengite. OH absorbances are normalized to 1 mm thickness and averaged for 30 analyses.

* Diamond is absent in the eclogite, but occurs in surrounding pelitic gneisses. Pressure and temperature conditions were estimated using polymorph mineral relations (Bundy 1980; Bohlen and Boettcher 1982) and geothermobarometers (Ellis and Green 1979; Carswell et al. 1997).

TABLE 2. Representative compositions of clinopyroxenes

Rock type	Dia-Ec		Coe-Ec		Qtz-Ec	
Sample	A21-30	A21-30r*F430-12	F446-9	A530-8	C230-1	F349-8
wt% oxides						
SiO ₂	55.35	56.28	55.16	54.77	55.23	55.44
TiO ₂	0.18	0.17	0.17	0.09	0.09	0.09
Al ₂ O ₃	9.93	9.73	9.02	8.08	9.09	8.64
Cr ₂ O ₃	0.03	0.03	0.00	0.00	0.00	0.00
FeO†	5.59	5.48	4.62	5.88	7.39	5.41
MnO	0.04	0.04	0.08	0.00	0.02	0.03
MgO	9.00	8.81	9.54	9.61	7.71	9.03
CaO	15.20	14.88	16.69	16.41	13.41	14.44
Na ₂ O	5.19	5.08	4.61	4.77	6.47	6.01
K ₂ O	0.03	0.03	0.02	0.00	0.00	0.00
Total	100.53	100.52	99.90	99.61	99.40	99.89
Cations per 6 oxygen atoms						
Si	1.976	2.002	1.982	1.987	2.009	2.000
Ti	0.005	0.005	0.005	0.002	0.002	0.001
Al	0.418	0.408	0.382	0.346	0.390	0.368
Cr	0.001	0.001	0.000	0.000	0.000	0.001
Fe	0.167	0.163	0.139	0.178	0.225	0.164
Mn	0.001	0.001	0.002	0.000	0.001	0.001
Mg	0.479	0.467	0.511	0.520	0.418	0.487
Ca	0.582	0.567	0.642	0.638	0.522	0.560
Na	0.359	0.350	0.321	0.335	0.456	0.421
K	0.001	0.001	0.001	0.000	0.000	0.000

* A21-30r represents calculated original clinopyroxene including 2.1 wt% quartz lamellae.

† Total Fe calculated as FeO.

off glass substrate, and were stored in a desiccator. IR spectra of the samples were obtained using a JASCO MFT-2000 microscopic Fourier transform IR spectrometer with an IR light source, KBr beam-splitter, and an MCT detector. One hundred scans were accumulated for each spectrum with 4 cm⁻¹ resolutions. Apertures of 30 × 30 to 100 × 100 μm were used for selecting sample areas for measurement.

Infrared spectra of the clinopyroxenes in all eclogites show three hydroxyl absorption bands in the regions 3440–3460 cm⁻¹, 3500–3530 cm⁻¹ and 3600–3625 cm⁻¹ (Fig. 2). The absorbances of the hydroxyl bands are variable in the same sample because the pyroxenes show random orientations. It has been reported that the γ-polarized absorption peak is stronger than the α- and β-polarized spectra in clinopyroxenes from mantle eclogites (Smyth et al. 1991). Therefore, average values (30 grains) of the OH bands in unpolarized spectra were used to estimate the total hydroxyl absorbance in our unoriented samples. The band around 3450 cm⁻¹ is usually the strongest in the spectra, and the 3600 cm⁻¹ spectrum is the weakest. The latter peak and the ratio with the former band generally increased with the hydroxyl absorbance in the samples. This feature may have resulted from differences in the chemical environment around

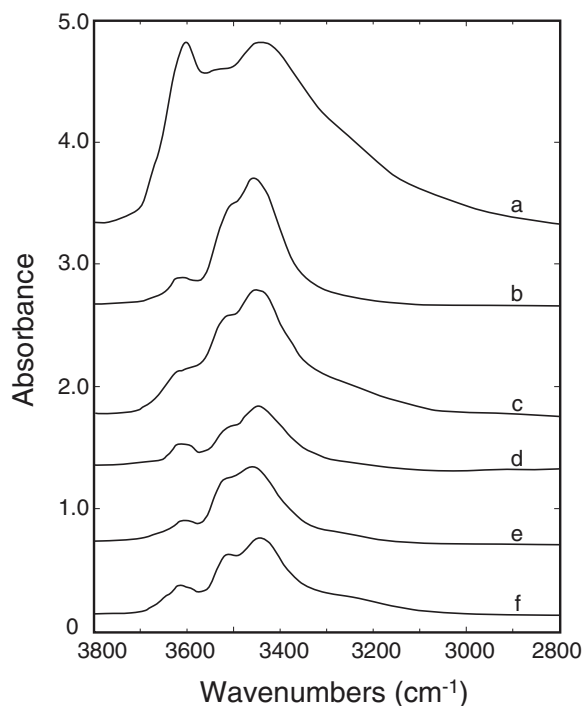


FIGURE 2. Representative unpolarized infrared spectra of clinopyroxenes. All clinopyroxenes have three hydroxyl bands in the regions 3440–3460 cm⁻¹, 3500–3530 cm⁻¹, and 3600–3625 cm⁻¹. The spectra are normalized to 1 mm thickness. Spectra (a): diamond-grade eclogite (A21); (b, c): coesite-eclogites (F430, F446); (d, e, f): quartz-eclogites (A530, C230, F349), respectively.

OH bonds. Total absorbances, which are the sums of the three hydroxyl bands, are related to recrystallization pressures of the host rocks and also to the abundance of the Ca-Eskola component in the clinopyroxenes, both increasing from quartz-eclogites, through coesite-eclogites, to diamond-grade eclogite (Fig. 3).

The OH concentrations in the clinopyroxenes were calculated from the height of the hydroxyl band according to Lambert-Beer's law as follows:

$$\text{Abs} = \epsilon \times d \times \zeta \times \text{OH concentration}$$

where Abs is the total sum of absorbances of the three OH bands (3450 cm⁻¹, 3500 cm⁻¹, and 3600 cm⁻¹) and averaged for 30

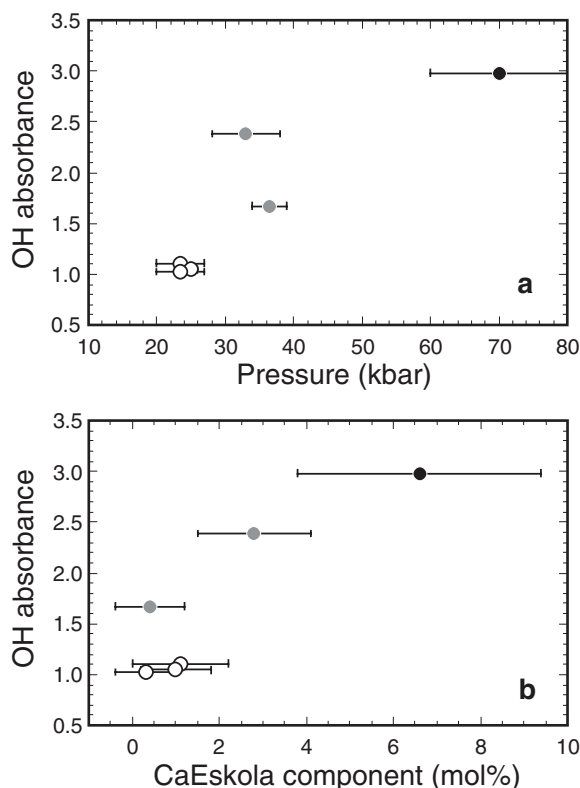


FIGURE 3. Hydroxyl absorbances in the studied clinopyroxenes from the different eclogites: diamond-grade eclogite (black circles), coesite-eclogite (gray circles) and quartz-eclogite (white circles). (a) Hydroxyl absorbances versus pressure of recrystallization of the host rocks. (b) Hydroxyl absorbances versus abundance of the Ca-Eskola component ($\text{Ca}_{0.5}\square_{0.5}\text{AlSi}_2\text{O}_6$) in the clinopyroxenes.

clinopyroxenes, ϵ is the molar absorption coefficient, d is the thickness of the samples, and ζ is the orientation factor derived from the empirical calibration of Paterson (1982). A molar absorptivity of $150 \text{ (l} \cdot \text{OH/mol} \cdot \text{cm)}$, which is calibrated from the hydrogen content using the nuclear profiling method of Skogby et al. (1990), was used for the pyroxenes. The orientation factor of $1/3$ is generally applied to these kinds of unpolarized spectra (Paterson 1982). The effect of using unpolarized radiation was the main uncertainty in the hydroxyl contents reported in this study, probably in the range of 30–50%. The resulting OH contents in the clinopyroxenes are 3020 ppm for the diamond-grade eclogite, 2430–1690 ppm for the coesite-eclogites, and 1110–1030 ppm for the quartz-eclogites (Table 1). An alternative approach for estimating the hydroxyl contents was also performed by using integrated absorbances of the OH bands with an integral molar absorption coefficient ($38300 \text{ l} \cdot \text{H}_2\text{O/mol} \cdot \text{cm}^2$) of Bell et al. (1995); this method yielded almost the same values, with differences of less than 5%.

DISCUSSION

Figure 3a shows the correlation between hydroxyl absorbance of the clinopyroxenes and recrystallization pressures for

the analyzed eclogites. The hydroxyl concentrations increase with pressure, from quartz-eclogite through coesite-eclogite to diamond-grade eclogite. It is known that water solubility is controlled by water fugacity. Bai and Kohlstedt (1992) reported that hydrogen solubility in synthesized olivine depends on H_2O fugacity. The same correlation was also reported in other nominally anhydrous minerals in high-pressure experiments, such as garnet and coesite (Lu and Keppler 1997; Mosenfelder 2000). However, the incorporation mechanism of hydroxyl into clinopyroxenes is still discussed because of its compositional complexities. Smyth et al. (1991) found a positive correlation between hydroxyl content and cation vacancy concentration in the pyroxene from mantle-derived eclogite in the Roberts Victor kimberlite pipes. In this study, diamond-grade clinopyroxenes contain significant amounts of the Ca-Eskola component, which forms a vacancy in the structure. The Ca-Eskola content of the diamond-grade pyroxene is higher than that in quartz- and coesite-eclogites. High-pressure experimental studies have shown that the content of the Ca-Eskola component is pressure dependent (Mao 1971; Gasparik 1986). Hydroxyl absorbances in the Kokchetav pyroxenes are plotted versus abundance of the Ca-Eskola component in Figure 3b. The hydroxyl contents appear to correlate with an increase of the Ca-Eskola component. Therefore, the M_2 site vacancy is the most likely mechanism for incorporating hydroxyl in the Kokchetav UHP clinopyroxenes. However, even in the quartz-eclogites, which have a low content of the Ca-Eskola component (Table 2), clinopyroxenes contain approximately 1000 ppm OH. Igneous pyroxenes are also reported to incorporate small amounts of hydroxyl, up to 270 ppm OH (Skogby et al. 1990). These low-grade pyroxenes contain considerable Fe^{3+} . Thus, the hydroxyl in relatively low-pressure pyroxenes may be correlated with the presence of trivalent cations. The substitution of trivalent ions for Si in the tetrahedral position is considered to be essential for OH incorporation in synthesized pyroxene (Skogby 1994). The observations suggest that the incorporation mechanism of hydroxyl in clinopyroxenes might be responsible for the recrystallization conditions.

Considering the modal proportion of clinopyroxene (44 vol% for the diamond-grade eclogite and 54 vol% for the coesite-eclogite), 1320 ppm and 1310 ppm hydroxyl exist in the bulk eclogites, respectively, even in the absence of hydrous minerals (Fig. 4). On the other hand, quartz eclogites contain much more hydroxyl (6850 ppm OH for A530 sample) because of the presence of hydrous minerals (amphiboles). Thus, H_2O content in the eclogites largely decreases from quartz-eclogite to coesite-eclogite. Aqueous fluids produced from the breakdown of amphiboles are considered to trigger island arc magma generation (e.g., Tatsumi 1989). However, approximately 1300 ppm OH included in clinopyroxene survives in eclogites under conditions where no hydrous minerals are stable (Fig. 4). Although the proportion of clinopyroxene decreases from the coesite-eclogite to the diamond-grade eclogite, increasing hydroxyl content in the pyroxenes can account for the H_2O transport deeper than 150 km into the mantle. Consequently, water released from pyroxenes at much higher pressures may migrate into the overlying peridotite, can be incorporated into other minerals such as wadsleyite (which can incorporate up to 3

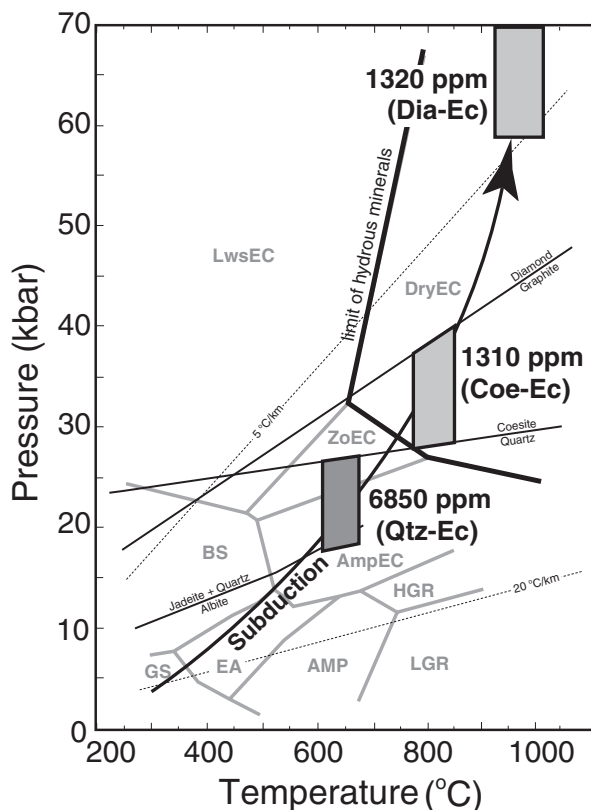


FIGURE 4. Hydroxyl content in Kokchetav eclogites from each P - T environment (Dia-Ec, Coe-Ec, and Qtz-Ec) with geotherms of $5\text{ }^{\circ}\text{C}/\text{km}$ and $20\text{ }^{\circ}\text{C}/\text{km}$. Thick lines are the limits of hydrous minerals in mid-ocean ridge basalt (MORB) composition (Okamoto and Maruyama 1999). H_2O content in eclogite decreases mostly from quartz-eclogite to coesite-eclogite because of the breakdown of hydrous minerals. However, approximately 1300 ppm OH included in clinopyroxene still exists above the hydrous limit. Abbreviations: GS = greenschist facies, EA = epidote-amphibolite facies, Am = amphibolite facies, GR = granulite facies, HGR = high-pressure granulite facies, BS = blueschist facies, AmpEC = amphibole eclogite facies, ZoEC = zoisite eclogite facies, LwsEC = lawsonite eclogite facies, DryEC = dry eclogite facies. Petrogenic grids, subdivision of eclogite facies are from Oh and Liou (1998) and Okamoto and Maruyama (1999), and reaction curves of diamond-graphite, coesite-quartz, and jadeite-quartz-albite from Blundy (1980), Bohlen and Boettcher (1982) and Holland (1980), respectively.

wt% H_2O , e.g., Inoue et al. 1995; Kohlstedt et al. 1996), and dense hydrous magnesium silicates (DHMS) or can be transferred into majoritic garnet in the descending slab. Garnets from UHP rocks were reported to contain trace hydroxyl, up to a few hundred ppm OH (Rossman et al. 1989; Langer et al. 1993). The water drastically changes the viscosity, the electrical conductivity, and the melting temperature of materials in the Earth's interior. Thus, hydrated clinopyroxene can be an important carrier of water into the mantle, and may have a great influence on the physico-chemical properties of the mantle dynamics.

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