Hydrated clinopyroxene in the ultrahigh-pressure metamorphic rocks

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We analyzed hydroxyl content in the clinopyroxene of diamond-grade eclogite from the Kokchetav massif, using FTIR spectroscopy. Two hydroxyl absorptions occur in the 3430-3450 cm-1 and 3570-3610 cm-1 regions, respectively. The infrared spectra yielded 2060 ppm hydroxyl in the clinopyroxene, using the Lambert-Beers law. Since the clinopyroxene represents about 40-50 volume% of the eclogite, the bulk eclogite can contain approximately 1000 ppm hydroxyl, even in the absence of nominally hydrous minerals. Thus, clinopyroxene in deeply subducted crusts can carry a significant amount of water into the mantle, and have an important bearing on physico-chemical properties of the slab at great depth.

Input of water into the earths interior is restricted to subduction zones. However, the subducted oceanic crusts transform to dry eclogite containing no hydrous minerals at T>700C and P>30kbar. It is therefore believed that subducted crusts cannot carry water into deeper mantle. Recently, several researchers reported clinopyroxenes containing significant amount of water, up to 1840 ppm OH (Smyth et al. 1991). This hydroxyl is associated with cation vacancy in the pyroxene. In this study, we found omphacite containing cation vacancy from eclogite of the Kokchetav ultrahigh-pressure (UHP) metamorphic terrane, which had subducted to more than 150 km depth. Infrared (IR) spectra were measured on this sample to quantify hydroxyl contents in the clinopyroxenes of the UHP eclogite.

In the Kokchetav massif, eclogites occur as lenticular masses surrounding diamond-bearing gneisses, and have attained P-T conditions of P>60kbar and T>1000C (Okamoto et al. 2000). The eclogites consist of garnet + omphacite + rutile + quartz with minor amounts of apatite and zircon. Most omphacite grains contain crystallographically oriented quartz rods, which are a few um in diameter and about 100 um in length. Furthermore, coesite, omphacite, garnet, rutile, quartz and albite occur as inclusions in zircon. The omphacite inclusions are approximately 5-20 um in size, and characterized by the absence of quartz exsolution.

Doubly polished thin section of the eclogite with a thickness of 120 um was used for IR microspectroscopic study. IR spectra of the sample were measured using JASCO MFT-2000 micro-FTIR spectrometer with an IR light source, KBr beam-splitter and a MCT detector. One hundred scans were accumulated for each spectrum with 4 cm-1 resolution. Apertures of 100*100 um were used for selecting sample areas for measurement. The samples were also analyzed by a JEOL JXA 8800 electron microprobe with a 15 kV accelerating voltage and 12 nA beam current.

The matrix clinopyroxenes from the eclogite are almost homogeneous, and showed omphacite composition (XJd:0.38-0.40). On the other hand, the zircon-hosted clinopyroxenes from the same sample contain significant amount of CaEskola component (Ca0.5AlSi2O6), up to 9.6 mol%, in contrast to low contents (1.3 mol%, on average) of the matrix clinopyroxenes. Since the matrix clinopyroxene contains quartz exsolution lamellae, the original composition should be recalculated based on its quartz content. The resulted original pyroxene contains 6.8 mol% CaEskola component, which is consistent with the inclusions in zircon. Therefore, the primary clinopyroxene at the peak UHP metamorphism is considered to contain a high CaEskola component and so that a high M2 site vacancy, which can incorporate water in the clinopyroxene.

Two hydroxyl absorptions occur in the 3430-3450 cm-1 and 3570-3610 cm-1 regions, respectively, of all matrix clinopyroxenes. The absorbances of the hydroxyl bands are variable, because the pyroxenes show random orientations. The peak heights of two OH bands were therefore determined for 15 grains and the average values were added to obtain the total hydroxyl absorbance (2.05 for a normalized thickness of 1mm). The orientation factor of 1/3 is generally applied to this kind of unpolarized spectra (Paterson 1982). Using a molar absorptivity of 150 (L/molcm) (Skogby et al. 1990) and the density of the clinopyroxene (3.37 g/cm3), the hydroxyl content in the clinopyroxene can be calculated by the Lambert-Beers law. The resulted OH content is 2060 ppm for the clinopyroxene. Since the clinopyroxene represents about 40-50 volume% of the eclogite, the bulk eclogite can contain approximately 1000 ppm hydroxyl, even in the absence of nominally hydrous minerals. Thus, vacancy-containing clinopyroxene in deeply subducted crusts can carry a significant amount of water into the mantle, and have an important bearing on physico-chemical properties of the slab at great depth.