

## Water behavior in diamond-bearing and diamond-free garnet-clinopyroxene rocks from the Kokchetav Massif

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Garnet and clinopyroxene are important nominally anhydrous minerals (NAMs) in the ultrahigh-pressure (UHP) rocks because they contain significant amounts of water as OH in their structures. Diamond-free and diamond-bearing garnet-clinopyroxene rocks from the Kokchetav Massif are mainly composed of garnet and clinopyroxene. In the rocks, UHP evidences are recognized; supersilicic titanite in diamond-free rock and diamond with three morphologies: cubic form (up to 200  $\mu\text{m}$ ), ball-shaped form (covered with graphite) (up to 150  $\mu\text{m}$ ), and fine-grain (ca. 10  $\mu\text{m}$ ) which was discovered recently (Takabe et al., 2014). The mineral assemblages are similar to skarn and suggest a metasomatic product in the subducted slab at UHP conditions.

Water contents of garnet and clinopyroxene by micro-FTIR proved water-rich environment of the formation of garnet-clinopyroxene rocks and support the metasomatic origin at UHP condition (Sakamaki et al. 2014). Garnet contains significant amounts of structural OH and nonstructural molecular  $\text{H}_2\text{O}$ ; 1727 ppm (wt.  $\text{H}_2\text{O}$ ) of OH and 1592 ppm of  $\text{H}_2\text{O}$  at maximum in garnet of diamond-bearing, and 1655 ppm of OH and 1203 ppm of  $\text{H}_2\text{O}$  at maximum in garnet of diamond-free rock. In clinopyroxene, structural OH in exsolved phases and clinopyroxene host and nonstructural molecular  $\text{H}_2\text{O}$  were identified. Total water (OH+ $\text{H}_2\text{O}$ ) contents in clinopyroxene are up to 8215 ppm in diamond-free rock and 4384 ppm in diamond-bearing rock, respectively.

Bulk water contents in garnet-clinopyroxene rocks reach into 3000 ppm which is much higher than that of diamond-facies eclogite from the Kokchetav Massif (e.g., 460 ppm by Katayama et al., 2006). Our analytical results suggest that formation of garnet-clinopyroxene rocks by metasomatism during deep continental subductions can be a trapping process of  $\text{H}_2\text{O}$ -rich metasomatic fluids and carrying into deep mantle. Such NAMs in UHP skarn means the birth of new water reservoirs and carriers into the mantle, as swapped for hydrous minerals in gneisses. This idea was based on "Intraslab UHP metasomatism" model and its improvement.

In gneisses, which play as a main water reservoir at relatively early stage during the slab subduction, water is transported as OH in phengite to the mantle up to the stability limit of phengite. Phengite is gradually dehydrated and releases  $\text{H}_2\text{O}$  fluids during subduction. The dehydrated  $\text{H}_2\text{O}$  fluids from gneisses infiltrate into subducted materials themselves, such as carbonate and calc-silicate rocks, to occur decarbonations. As a result, the calc-silicate protoliths (silicate and carbonate mixtures) are transformed to skarn-like rocks, e.g., garnet-clinopyroxene rocks. Since garnet and clinopyroxene were formed by  $\text{H}_2\text{O}$ -mediated metasomatic processes at UHP condition, significant amounts of water were dissolved into NAMs, garnet and clinopyroxene. Such water-rich environments and UHP condition during "Intraslab UHP metasomatism" are indispensable for water dissolution to NAMs.

Deep continental subduction has an aspect of the input of silicate rocks (e.g., gneisses) as "wet" materials, and carbonate and calc-silicate rocks as "dry" materials into the mantle. Dehydrations in gneisses are the extracting process of  $\text{H}_2\text{O}$  from "wet" materials while decarbonations, which are the extracting process of  $\text{CO}_2$  from "dry" materials, were triggered off by water supply from dehydrations of gneisses. Water infiltration into carbonate and calc-silicate rocks has three aspects: 1) water transportation from wet materials to dry materials ("dry" materials are getting a little "wet", and "wet" materials are getting "dry"), 2) formation of UHP skarn by metasomatism, and 3) hydration of NAMs by metasomatic fluid (the birth of new water carrier). These processes in "Intraslab UHP metasomatism" model are regarded as water transportation from "wet" materials to "dry" materials and expand the water input process into the mantle much deeper such as the mantle transition zone.

Keywords: the Kokchetav Massif, UHP metamorphism, diamond, supersilicic titanite, nominally anhydrous minerals, micro-FTIR spectroscopy