CaO_8 and MgO_8 clustering in $Grs_{50}Prp_{50}$ garnet in diamond-bearing dolomite marble from the Kokchetav Massif

*Tomohiro Takebayashi[1], Takeaki Saito[2], Kunihiko Sakamaki[1], Hiroshi Suzuki[2,1], Yoshihide Ogasawara[2,1]

1. Department of Earth Sciences, Resources and Environmental Engineering, Graduate school of Creative Science and Engineering, Waseda University, 2. Department of Earth Sciences, Waseda University

Grossular-pyrope garnet (ca. $Grs_{50}Prp_{50}$) has long been attracted about crystal chemistry, mixing properties, and P-T stabilities. Many experimental and thermodynamic studies on grossular-pyrope garnet have been conducted (e.g., Ganguly et al., 1996; Geiger, 2013; Du et al., 2016). Garnet having near the $Grs_{50}Prp_{50}$ composition is extremely rare in nature. Only two occurrences have been reported, so far; (1) xenocrysts in the kimberlite from Garnet Ridge, Arizona (Wang et al., 2000) and (2) diamond-bearing dolomite marble from the Kokchetav UHP Massif, Kazakhstan (e.g., Ogasawara et al., 2000; Sobolev et al., 2001). This strange garnet from the Kokchetav Massif is a main constituent silicate mineral of dolomite marble (P > 6 GPa, T = ca. 1000 ˚C) and is a main host mineral of abundant microdiamond (Ogasawara et al., 2000; 2005). This garnet is chemically homogeneous and has its composition range: Grs: 43-46, Prp: 39-42, and Alm: 10-16 mol%. The closest composition to $Grs_{50}Prp_{50}$ is $Grs_{44}Prp_{42}Alm_{10}$. No exsolution and no symplectite were observed.

We conducted laser Raman spectrometry on this $Grs_{50}Prp_{50}$ garnet in the Kokchetav UHP dolomite marble. Among the obtained Raman bands at 366, 556, and 903 cm^{-1}, we focused on the band at 366 cm^{-1} that was assigned to $R(SiO_4)^{4-}$. FWHM of this band was significantly large (24.5 cm^{-1}), compared to those of Prp (14.3 cm^{-1}at 365 cm^{-1}) and Grs (14.0 cm^{-1} at 372 cm^{-1}). Such a large FWHM of $Grs_{50}Prp_{50}$ garnet suggested that two kinds of $R(SiO_4)^{4-}$ bands corresponding to Grs and Prp were obtained as one overlapped broad band because the peak positions of both bands are very close. The synthesized band from Grs and Prp end-member was well fitted to the observed band.

In the crystal structure of garnet, a SiO_4 tetrahedron is surrounded by six dodecahedra XO_8 (Geiger, 2013). A SiO_4 tetrahedron of grossular surrounded by six CaO_8, and that of pyrope by six MgO_8. The observed overlapping of two $R(SiO_4)^{4-}$ bands corresponding to Grs and Prp indicates two modes for $R(SiO_4)^{4-}$ in a single $Grs_{50}Prp_{50}$ crystal; $R(SiO_4)^{4-}$ of SiO_4 surrounded by six CaO_8 (CaO_8 clustering around SiO_4) and that by six MgO_8 (MgO_8 clustering around SiO_4). Such clustering stabilized garnet of ca. $Grs_{50}Prp_{50}$, and could be controlled by two factors: (1) bulk chemistry near Ca:Mg = 1:1 and (2) UHP conditions. No exsolution lamella and no symplectite mean that $Grs_{50}Prp_{50}$ garnet was stable under low P and T once it formed at high P and T.

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