

## Effect of Al content on water partitioning between orthopyroxene and olivine: Implication for upper mantle dynamics

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Most minerals in the Earth's upper mantle contain small amounts of hydrogen (i.e. "water"), structurally bound as hydroxyl. Water has an important influence on the behavior of rock system. Water significantly affects physical property of minerals (e.g. ionic diffusion rates; (e.g., Goldsmith, 1987), electric conductivity; (e.g., Zhang et al., 2012), viscosity; (e.g., Karato and Jung, 2003)). Because small amount of water plays a key role in mantle rheology, precise knowledge on partitioning of water among mantle minerals is very important to understand the Earth's dynamics. For example, Mierdel et al. (2007) indicated that a high water solubility in aluminous orthopyroxene among mantle geotherm in the Earth's upper mantle would effectively contribute to a stiffening of the lithosphere. Water content of minerals is changed by chemical composition. For example, Al<sub>2</sub>O<sub>3</sub> solubility of orthopyroxene (Opx) in the Earth's upper mantle decreases significantly with increasing pressure. In addition, Rauch and Keppler (2002) investigated effect of Al<sub>2</sub>O<sub>3</sub> content on water solubility in orthopyroxene. The water solubility in orthopyroxene increases proportionally with increasing Al<sub>2</sub>O<sub>3</sub> content. Thus water partitioning coefficient between orthopyroxene and olivine (Ol) may change significantly in the Earth's upper mantle. Therefore it is necessary to investigate the influence of Al<sub>2</sub>O<sub>3</sub> in Opx on the partitioning coefficient of water between Opx and Ol under low OH concentration by high pressure temperature experiments.

In order to investigate the partitioning coefficient of water between Opx and Ol ( $D_{(Opx/Ol)}$ ) under low OH concentration (4~400 ppm), we performed high-temperature and high-pressure experiments using Kawai-type multi-anvil apparatus (SPI-1000) and piston-cylinder apparatus at the Magma Factory, Tokyo Institute of Technology, using starting materials of natural Ol (Ol; KLB-1) and synthetic orthopyroxene with various Al content (Opx; (Mg,Fe)<sub>2-x</sub>Al<sub>2x</sub>Si<sub>2-x</sub>O<sub>6</sub> (x=0, 0.0125, 0.025, 0.05)). Powdered minerals were enclosed in Mo foil capsule to form monomineralic layers with more than 300 micron meters in thickness each and put it in a Au<sub>75</sub>Pd<sub>25</sub> capsule at pressures of 1, 3, 4.5 and 6 GPa and temperature of 1300°C. Oxygen fugacity was controlled by Mo-MoO<sub>2</sub> buffers. Water contents were obtained with a vacuum type Fourier transform infrared spectrometer (FT-IR6100, IRT5000). Water content of minerals was calculated based on Paterson's (1982) calibration. Run products were polished down to doubly polished slab. After polishing and prior to FT-IR analysis, samples were stored in a vacuum oven at ~120°C overnight. Detection limit in the IR spectra at 3200-4000 cm<sup>-1</sup> is typically less than 1 ppm due to very low background of vacuum type FT-IR.

Water partitioning coefficient between Ol and Al-free Opx are  $D_{(Al-free\ Opx/Ol)} = 0.5\sim 1.8$ . On the other hand, that between Al-bearing Opx and Ol are  $D_{(Al-bearing\ Opx/Ol)} > 7.0$ . Thus  $D_{(Opx/Ol)}$  increases dramatically by incorporating Al<sub>2</sub>O<sub>3</sub> in Opx at given temperature.  $D_{(Opx/Ol)}$  also increases with increasing pressure at given Al<sub>2</sub>O<sub>3</sub> content in Opx. In other words, the slope of the curve exponential approximation increases with pressure. Under low water fugacity conditions,  $D_{(Opx/Ol)}$  stays nearly constant or increases with increasing pressure within the spinel-peridotite stability field. In the garnet peridotite field, however,  $D_{(Opx/Ol)}$  decreases dramatically with increasing pressure from about 3 GPa to 6 GPa. Especially, from 4.5 GPa to 6 GPa, this value becomes dramatically smaller (~ 2 order) with increasing pressure. Then,  $D_{(Opx/Ol)}$  becomes much smaller than unity in at pressures from 4.5 GPa to 6 GPa. A maximum value in  $D_{(Opx/Ol)}$  at 3 GPa. This results indicate that viscosity of the upper mantle might become softer at deeper than 150 km.

Keywords: water partitioning, orthopyroxene, olivine, upper mantle, Al content