WATER IN EARTH'S MANTLE: HYDROGEN ANALYSIS OF MANTLE
OLIVINE, PYROXENES AND GARNET USING THE SIMS. Masanori
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Introduction: Hydrogen (or water) in the Earth's interior plays a key role in the evolution and
dynamics of the planet [1]. However, the abundance and the existence form of the hydrogen have
scarcey been clear in practice. Hydrogen in the mantle was incorporated in the interior during the
formation of the Earth [1]. The incorporated hydrogen was hardly possible to concentrate locally
inside the Earth considering its high mobility and high reactivity. The hydrogen, preferably, could
be distributed homogeneously over the mantle and the core by the subsequent physical and
chemical processes. Therefore, hydrogen in the mantle could be present in the form of trace
hydrogen in nominally anhydrous mantle minerals [2]. In this study, we have determined the
hydrogen and the other trace elements in mantle olivines, orthopyroxenes, clinopyroxenes and
garnets using secondary ion mass spectrometry (SIMS) for elucidating (1) the exact hydrogen
contents, (2) the correlation between the hydrogen and the other trace elements and (3) the
dependence of the hydrogen contents on the depth, (4) the dependence of the whole rock water
contents on the depth.

Analytical: We have analyzed hydrogen and the other trace elements in the minerals using the
SIMS ( Cameca IMS-3F) at the University of Tsukuba. A 100 nA, 14.5 keV 16O+ primary beam
was focused to a ~100 μm diameter spot. Secondary ions (1H+, 7Li+, 28Si2+, 23Na+, 27Al+, 30Si+, 39K+, 40Ca+, 47Ti+, 52Cr+, 56Fe+, 59Co+ and 60Ni+) were collected from the central region (60 μm
diameter) of the sputtered area using a mechanical aperture. For quantitative hydrogen analysis,
H+-implanted olivines, orthopyroxenes, clinopyroxenes and garnets were prepared as standard
materials by an ion-implantation technique with an acceleration energy of 50 keV [3]. For
determinations of the other trace elements, fused glass beads of the JB-1a rock powder which is a
standard rock reference issued by the Geological Survey of Japan was used as standard material
[4]. The elements of Si, Ti, Al, Cr, Fe, Mn, Ni, Mg, Ca, Na and K in the samples were analyzed
using EPMA. In addition, the infrared spectra for single crystal part of the samples were measured
in the range from 4000 to 2000 cm⁻¹ in wavenumbers, in order to check the presence of secondary
hydrous minerals. The olivine, orthopyroxene, clinopyroxene and garnet samples were selected
from spinel and garnet peridotites (hartzbergite and lherzolite) occurred in island arc, the continental
rifts and the craton, and were also selected from mineral inclusions in diamonds.

Results and Discussion: The hydrogen concentrations range from 10 to 60 ppm wt. H₂O in
olivines; 90 to 350 ppm in orthopyroxenes; 90 to 350 ppm in clinopyroxenes; 10 to 70 ppm in
garnets and the results are consistent with the previous studies [5]. SIMS and infrared
spectroscopic studies showed that most of the hydrogen contents are not derived from the weathering, secondary alterations and hydrogen reequilibrium with a host magma during the transportation from the mantle to the surface. Olivine, orthopyroxene and pyrope inclusions in diamonds show similar hydrogen contents to peridotitic olivines, orthopyroxenes and garnets, so that hydrogen contents in xenolith's minerals can be little affected by the contamination during the transportation.

The hydrogen contents in the minerals showed good positive correlations with Al, Cr, Fe$^{3+}$, and showed no relationship with cation deficiencies. This suggests that hydrogen in the mantle minerals is incorporated by substitutional mechanisms. In addition, the hydrogen contents in orthopyroxenes and clinopyroxenes increased in proportion to temperature and pressure of the parent peridotite rocks. However, hydrogen contents in olivines decreased with increasing temperature and increased linearly with pressure, and those in garnets reduced with increasing temperature and pressure. These trends are able to explain by the hydrogen partitioning among the minerals and the hydrogen solubilities.

Whole rock water content of peridotites, which was calculated from mineral proportions and hydrogen contents in minerals, ranged from 50 to 140 ppm wt. H$_2$O. The concentration raised basically as temperature and pressure increased. Pyroxenes contain most abundant hydrogen among peridotite minerals, so that they contribute largely to the total water contents in peridotites. The increase of whole rock water contents with the depth suggests that ascending mantle rocks are capable of providing water which the amount corresponds to difference in the whole rock water contents between the ascending rock and mantle rock of shallower region. The suggestion is important for magma genesis and mantle fluid generation and supports the importance of hydrogen in anhydrous minerals as a water reservoir in the mantle.