

Solubility of hydroxyl groups in pyroxenes: effect of oxygen fugacity at 0.2-3 GPa and 800-1200 °C

HANYONG LIU, XIAOZHI YANG*

State Key Laboratory for Mineral Deposits Research, School of Earth Sciences and Engineering, Nanjing University, Nanjing 210023, PR China. (*: xzyang@nju.edu.cn)

It is well accepted that a trace amount of water such as hydroxyl groups (OH) incorporated in the crystal structure of the host minerals affects strongly many of their physical and chemical properties. Clinopyroxene (cpx) and orthopyroxene (opx) are important constituents in the upper mantle, and determines greatly the water budget. Despite considerable efforts on water storage in pyroxenes, however, less attention has been paid to the effect of oxygen fugacity (fO_2), a key thermodynamic factor in the upper mantle.

In this study, we have systematically investigated the OH dissolution in cpx and opx at 0.2-3 GPa, 800-1200 °C and peridotite- and H₂O-saturated conditions, with gem-quality natural diopside and enstatite single crystals as the starting materials. fO_2 were buffered by the commonly used Fe-FeO, Ni-NiO, Re-ReO₂ and Fe₃O₄-Fe₂O₃ pairs. The OH contents of the recovered pyroxene crystals were determined by polarized FTIR analyses. The H-annealed pyroxenes show typical OH-related absorption bands and the measured H₂O contents are ~14-394 and 34-227 wt. ppm in cpx and opx, respectively. For each mineral under otherwise identical conditions, the OH content increases with increasing pressure or temperature but decreases with increasing fO_2 . The OH content is enhanced by ~40% and 60% in Fe-poor cpx and opx, respectively, at Fe-FeO buffered reducing than at Ni-NiO buffered oxidizing conditions, and the enhancement appears greater if the pyroxenes are more Fe-enriched. This differs strongly from the enhanced OH solubility at more oxidizing conditions observed for olivine. the partitioning of OH between pyroxenes and olivine and the inventory of OH in the upper mantle are influenced by fO_2 . The storage capacity of OH in the shallow mantle is probably greater in Mars than in the Earth, because of the relatively more reduced state and more Fe-enriched pyroxenes in the former. The enhanced OH solubility of pyroxenes under very reducing conditions could also be important for insights into the early differentiation of Earth's shallow mantle, in that hydrous melting may have been induced by redox-involved dehydration of pyroxenes when the shallow mantle evolved into its modern oxidizing state.