Reaction between olivine and nitrogen at high pressure and high temperature

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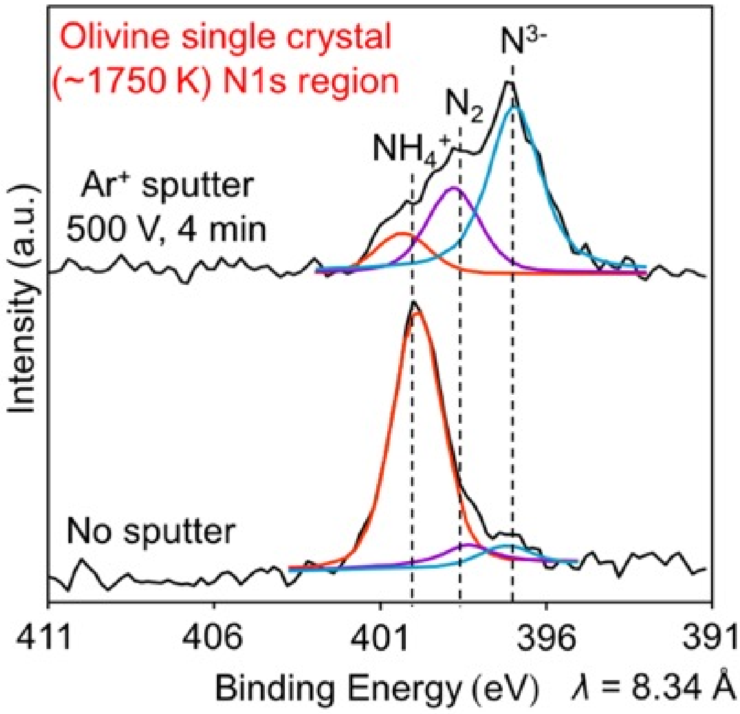
Volatiles represented by hydrogen greatly affect deep-earth dynamics. Behavior of volatiles will contribute to understandings of budget of light elements, evolution of the earth, geodynamics and so on. Among volatile components, behavior of nitrogen in the deep earth is still unclear. Nitrogen is a main constituent of atmosphere and also exists in the crust by substituting potassium ions in silicate minerals. Chondrite-normalized nitrogen concentration of the bulk earth is one order of magnitude lower than those other volatiles such as He, Ne, Ar, H_2O and so on. There could be a hidden nitrogen reservoir in the deep earth. We are going to test a possibility of a hidden nitrogen reservoir from high pressure and high temperature experiments.
San Carlos olivine or synthetic forsterite were loaded as a starting material in a diamond anvil cell with nitrogen in liquid state or compressed gas (180 MPa). After applying pressure at 5 GPa, a sample was heated using CO_2 laser or fiber laser. X-ray diffraction patterns, SEM-EDS images, XPS spectra were obtained on the recovered samples.
XRD measurements on the recovered samples revealed the formation of enstatite ($MgSiO_3$) suggesting the decomposition of Mg_2SiO_4 into $MgSiO_3$ and MgO. This reaction is contrastive to the reaction occurring in H_2 fluid (Shinozaki et al., 2013), Mg_2SiO_4 decomposed into SiO_2 and MgO. Moreover, EDS mapping observations revealed that there are some Mg-rich (Si-depleted) spots.
XPS spectra shown in Fig. 1 revealed that nitrogen was detected from an olivine sample recovered from 5 GPa and 1700 K. Before Ar-sputtering, species assignable to NH_4^+ is dominant. Presumably, the sample surface is covered with adsorbed molecules. After Ar-sputtering, a broad band attributable to intrinsic nitrogen reacted with the mineral was observed. The present results suggest the formation of nitride species (N^{3-}) in a mantle-derived silicate mineral. This study proposes nitride as a hidden nitrogen reservoir in the deep mantle.

Keywords: nitrogen, mantle, olivine


Olivine single crystal
(~1750 K) N1s region
N3-
N2
NH4+
Ar+ sputter
500 V, 4 min
No sputter
Intensity (a.u.)
411
406
401
396
391
Binding Energy (eV)
λ = 8.34 Å