Ammonium-bearing clinopyroxene: A potential nitrogen reservoir in the Earth's mantle

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K-bearing high-pressure phases generated at subducting slab and upper mantle conditions may incorporate significant amounts of NH_4 [1]. High-pressure clinopyroxene (cpx) from peridotites and eclogites may contain up to 2 wt% K_2O [2] depending on pressure and bulk composition. Cpx is thus another potential candidate for nitrogen transport into the deep Earth.

We experimentally investigated the incorporation of $NH_4CrSi_2O_6$ and $NH_4AlSi_2O_6$ components into diopside in the pseudobinary system $CaMgSi_2O_6$-$NH_4(Cr,Al)Si_2O_6$. NH_4-incorporation follows the coupled substitution $Ca^{2+} + Mg^{2+} \leftrightarrow NH_4^+ + (Cr, Al)^{3+}$.

Experiments were performed in a rotating multi-anvil press using oxide mixtures with varying $CaMgSi_2O_6$/ □$(Cr, Al)Si_2O_6$-ratios plus excess NH_4OH solution at 12 GPa, 750°C, and 13.5 GPa, 725°C. Run products were characterized by SEM, powder XRD with Rietveld refinement, and temperature-dependent IR spectroscopy. Major element chemistry of cpx was determined by EMP.

Runs produced cpx as major phase, along with additional Cr- or Al-bearing phases. NH_4 incorporation into cpx is shown by IR spectroscopy, where at room temperature the NH_4 ν_4-vibration mode appears at 1414 cm^{-1}. Between -180 and 200°C this band shifts by about 30 cm^{-1}, whereas the lattice vibration modes shift only to very minor extents. NH_4 contents derived from IR spectra amount to several hundred with a maximum of about 1500 wt ppm NH_4. This holds for incorporation of the NH_4Cr-component; uptake of the NH_4Al-component is significantly lower. NH_4 concentrations estimated by EMP determination of Cr and Al and assuming charge balance broadly agree with these values. Incorporation of small NH_4 and (Cr, Al) amounts into diopside has very minor effects on its lattice parameters; only a slight increase in the *c* lattice parameter is observable.

It is demonstrated that a small but significant ammonium solubility in cpx is possible at high-pressure. Considering the proportion of cpx in the upper mantle (~10 Vol%), cpx possibly represents an important reservoir for nitrogen in the deep Earth.

[1] Watenphul *et al.* (2009), *Am Mineral*. **94**, 283-292.
[2] Bindi *et al.* (2002) *Eur. J. Mineral.* **14**, 929-934.

XAS study on Cr^{3+} local environment in ruby samples

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X-ray absorption spectroscopy (XAS), a non-destructive technique for material characterisation, can also be applied to study mineral and gem samples. The facility has been provided at Synchrotron Light Research Institute, Nakornratchasima, northeastern Thailand.

Experiment

The ruby samples were cut into parallel pieces perpendicular to c-axis. Cr content as well as other trace elements have been analysed by LA-ICP-MS prior to the XAS experiment. A piece of each sample were doped with beryllium compound by heating at 1700 °C for 15 hrs. X-ray absorption near edge spectra of the samples were measured.

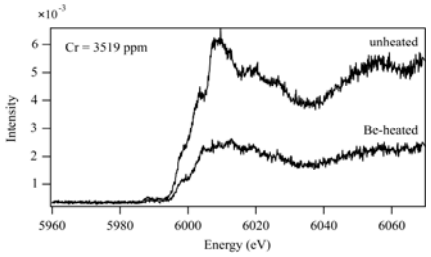

Figure 1: Difference in XANES spectra of a ruby sample, untreated and doped with Be.

Discussion of the Results

Cr-O-Cr environment has been suggested (Fig. 1, untreated sample); this has also been confirmed by the photoluminescence spectroscopy for the presence of n-lines [1]. The XANES spectra of the same samples doped with Be showed significant deviation from the untreated ones. Therefore, the dopant, i.e., Be^{2+} influents the Cr^{3+} environment. Applications to ruby geographic origins and treatments have been expected.

[1] Wongkokua *et al*. (2009) submitted to *J. Phys.: Conf. Ser.*