Nitrogen solubility in mantle minerals

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The Earth’s atmosphere is generally thought to have formed by degassing of the Earth’s interior. If one assumes a chondritic composition of the bulk Earth, mantle and core may still be major nitrogen reservoirs. However, little is known about how much nitrogen could be retained in mantle minerals during the cooling of the magma ocean in the Earth’s early history or in residual mantle minerals after partial melting. Consequently, it is not known how efficiently nitrogen could have degassed into the Earth’s early atmosphere and the nitrogen abundance in the bulk silicate Earth is poorly constrained. Therefore, we conducted a systematic study of nitrogen solubility in mantle minerals including olivine, clinopyroxene, orthopyroxene, and garnet. The experiments were done in a piston cylinder apparatus. The temperatures and pressures ranged from 1000 to 1300 °C and from 15 to 35 kbar, to simulate conditions typical of the upper mantle. The minerals were synthesized from well-mixed high purity oxides and hydroxides. About 5 wt% $^{15}$N-labeled $^{15}$NH$_4^+$NO$_3$ was added to the starting mixture as nitrogen source. A modified double capsule technique was used to buffer oxygen fugacity by three different buffers (Fe-FeO, Co-CoO, Ni-NiO). The recovered samples were measured by secondary ion mass spectrometer (SIMS; Cameca, ims 6f).

The results show that pressure and temperature do not have a major effect on the nitrogen solubility in mantle minerals but oxygen fugacity plays a significant role. At oxidizing conditions, all the mantle minerals contain very little nitrogen, generally below the 5 µg/g detection limit of SIMS. At reducing conditions, however, diopside, enstatite, and garnet contain considerable amount of nitrogen, up to 100 µg/g. The differences in solubility are likely related to nitrogen speciation. NH$_4^+$, produced at reducing conditions and similar in radius to K$^+$, may occupy cation sites in diopside, enstatite, and garnet, whereas N$_2$, which is stable at oxidizing conditions, can not. The present experimental results demonstrate that the reduced Earth’s mantle after core formation must have retained a large amount of nitrogen, and if the upper mantle became oxidized on a short time scale, the Earth’s early atmosphere must have been charged by violent nitrogen pulses from the Earth’s interior. Furthermore, the reduced lower mantle today may be an important nitrogen reservoir, which may balance the nitrogen abundance in the Earth’s atmosphere, crust, and oxidized mantle. This study also implies that the nitrogen abundance in the whole silicate Earth is much higher than the values previously estimated based on nitrogen in magmas derived from the oxidized upper mantle.