Supplementary Information for

Nitrogen isotope evidence for Earth's heterogeneous accretion of volatiles

Lanlan Shi^{1,2,3#}, Wenhua Lu^{1,2,3#}, Takanori Kagoshima⁴, Yuji Sano^{4,5}, Zenghao Gao^{1,2,3}, Zhixue Du^{1,2}, Yun Liu⁶, Yingwei Fei⁷, Yuan Li^{1,2*}

¹State Key Laboratory of Isotope Geochemistry, Guangzhou Institute of

Geochemistry, Chinese Academy of Sciences, Guangzhou 510640, China

²CAS Center for Excellence in Deep Earth Science, Guangzhou 510640, China

³College of Earth and Planetary Sciences, University of Chinese Academy of Sciences, Beijing 100049, China

⁴Division of Ocean-Earth System Science, Atmosphere and Ocean Research Institute, University of Tokyo, Kashiwa, Chiba 277-8564, Japan

⁵Center for Advanced Marine Core Research, Kochi University, Nanokoku, Kochi 783-8502, Japan.

⁶International Center for Planetary Science, College of Earth Sciences, Chengdu University of Technology, Chengdu 610059, China ⁷Earth and Planets Laboratory, Carnegie Institution for Science, Washington DC 20015, USA

These authors contributed equally. *Corresponding author. E-mail address: Yuan.Li@gig.ac.cn

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1. Supplementary Figs. 1–14:

Supplementary Figure 1. Reflected-light photomicrographs of typical run products synthesized in graphite-lined Pt₉₅Rh₀₅ or graphite capsules. a Coexisting metallic melt and silicate melt synthesized at 1.5 GPa and 1700 °C using silicate MORB (run N-1) in a graphite-lined Pt95Rh05 capsule. The silicate melt was quenched into glass. b Close-up view of the quenched metallic melt in (a). c , d The separated metallic melt and silicate melt from run PY-2 synthesized at 8 GPa and 2000 °C using silicate pyrolite in a graphite capsule. The pyrolite melt had a typic dendritic quench texture.

Supplementary Figure 2. Typical Raman spectral of silicate glasses from this study showing regions associated with N-C-H-O volatile species. Note that the water peak intensity increases with increasing the amount of $Mg(OH)$ ₂ added in the starting silicate. The experiments (N-1, N-6, and N-7; Supplementary Data 2) were synthesized at 1.5 GPa and 1700 °C, and fO_2 of ~IW-0.5. These observed N-C-H-O species are consistent with those observed in previous studies¹⁻⁴, including the one that determined the metal/silicate N-isotopic fractionations⁵.

Supplementary Figure 3. a Comparison of the experimentally determined $D_N^{metal/silicate}$ with the calculated $D_N^{metal/silicate}$ using Eq. (1) in the main text. **b** The plot of activity coefficient of N in the metallic melt as a function of oxygen fugacity (ΔIW). Note the nonideal interaction of C and N.

Supplementary Figure 4. Weak correlations occur between sample fQ_2 , the light element and Ni content in metallic melt, and the metallic melt $\delta^{15}N$. a The Ni + Si + S content in the metallic melt is in a weak negative correlation with fQ_2 . **b** The Ni + Si + S content in the metallic melt is in a weak positive correlation with $\delta^{15}N$ of the metallic melt.

The fraction of N losing during the experiment

Supplementary Figure 5. The negative correlation between $\Delta^{15}N^{metal-silicate}$ and the fraction of N losing during the experiment. The data were taken from Dalou et al.⁵. The large $\Delta^{15}N^{metal-silicat}$ values are likely caused by kinetic processes, rather than representing equilibrium N-isotopic fractionations. See main text for more detailed explanations.

Supplementary Figure 6. The metal/silicate N-isotopic fractionation $(\Delta^{15}N^{metal-silicate})$ as a function of experimental duration. The independence of $\Delta^{15}N^{metal-silicate}$ on the experimental duration indicates that 60 mins was sufficient for approaching equilibrium at 1700 °C.

Supplementary Figure 7. Modeling N-isotopic composition of Earth's core and mantle assuming that Earth accreted its 100% mass through the collisions of differentiated impactors that have a $\delta^{15}N$ value of −30‰. The results show that core-formation alone cannot lead to a $\delta^{15}N$ value of −5‰ of Earth's present-day mantle from a starting $\delta^{15}N$ value of −30‰.

Supplementary Figure 8. The N-content and $\delta^{15}N$ of the proto-Earth's atmosphere and mantle as a function of mass accreted based on a combined model of Earth's accretion and differentiation^{6,7}. a, b The N-content of the proto-Earth's atmosphere and mantle. The N-content of the atmosphere is relative (normalized) to the mass of the silicate Earth. c, d The $\delta^{15}N$ of the proto-Earth's atmosphere and mantle. This figure shows the effect of varying the mass percentage $(\Phi = 20 - 60\%)$ of the silicate magma ocean that is in equilibrium with the overlying atmosphere on the N-content and -isotopic composition of the proto-Earth's atmosphere and mantle. The degree of impact-induced atmosphere loss was fixed at 45% throughout all accretion stages.

Supplementary Figure 9. The N-content and $\delta^{15}N$ of the proto-Earth's atmosphere and silicate mantle as a function of mass accreted. a, b The N-content of the proto-Earth's atmosphere and mantle. The N-content of the atmosphere is relative (normalized) to the mass of the silicate Earth. c, d The $\delta^{15}N$ of the proto-Earth's atmosphere and mantle. This figure shows that constant impact-induced atmosphere loss (varying from 40% to 60%) in each impact only affects the N-content and -isotopic composition of the atmosphere, without affecting those of the mantle. Φ was fixed at 20% throughout all accretion stages. Note that the case of varying the degree of atmosphere loss (deep brown curves), as presented in Fig. 4 in the main text, was also plotted for comparison.

Supplementary Figure 10. Modeling results of the case with 60% impact-induced atmosphere loss (bule curve in Supplementary Fig. 9) after changing Φ from 20% to 30% and the mass of last added CI chondritic materials from 0.04% to 0.025%. a, b This figure shows that the low atmosphere N content and high atmosphere $\delta^{15}N$, caused by a high degree of impact-induced atmosphere loss as modeled in Supplementary Fig. 9 using Φ of 20%, can be increased and decreased, respectively, by changing the other parameters used in the model. The N-content of the atmosphere is relative (normalized) to the mass of the silicate Earth.

Supplementary Figure 11. The N-content and $\delta^{15}N$ of the proto-Earth's atmosphere, mantle, and core as a function of mass accreted. a, b This figure provides supplementary information to Fig. 4 in the main text, and shows that varying the timing of the delivery of CI chondrite-like materials would not change significantly the N-content and -isotopic composition of the proto-Earth's core, silicate mantle, and atmosphere. The N-content of the atmosphere is relative (normalized) to the mass of the silicate Earth.

Supplementary Figure 12. The N-content and $\delta^{15}N$ of the proto-Earth's atmosphere (Atm.), silicate mantle (Man.), and core as a function of mass accreted. a, b This figure provides supplementary information to Fig. 4 in the main text, and shows that varying the C-content, from 0.5 to 2 wt.%, in Earth's core would not change significantly the N-content and -isotopic composition of the proto-Earth's atmosphere, silicate mantle, and core. The N-content of the atmosphere is relative (normalized) to the mass of the silicate Earth.

Supplementary Figure 13. Effect of varying the $\delta^{15}N$ of the Moon-forming giant impactor on the $\delta^{15}N$ of the proto-Earth's atmosphere, mantle, and core at the end of accretion. This figure shows a limited effect of the Moon-forming giant impactor on the proto-Earth $\delta^{15}N$.

Supplementary Figure 14. The N-content and $\delta^{15}N$ of the proto-Earth's atmosphere (Atm.), silicate mantle (Man.), and core as a function of mass accreted. a, b This figure shows that the N-content in the impactors varying from 20 to 100 ppm or from 80 to 200 ppm could also explain the N-content and $\delta^{15}N$ of the proto-Earth's atmosphere and silicate mantle by slightly modifying the mass of CI-chondritic materials delivered, but the N-content in Earth's core increases clearly with increasing the impactor N content. The N-content of the atmosphere is relative (normalized) to the mass of the silicate Earth.

2. Supplementary Note 1. The references cited for the $\delta^{15}N$ data plotted in Fig. 1.

In Fig. 1, we used ref. 8 for Earth's mantle, refs. $9-11$ for mantle peridotite diamonds, ref. 12 for solar wind (SW), ref. 13 for comets, refs. $^{14-19}$ for OIB, refs. 8,20 for average δ^{15} N values of modern and Archean sediments and Earth's crust, refs. 21,22 for enstatite chondrites (EC), and refs. $^{23-33}$ for the $\delta^{15}N$ values of OC, CI, CM, CR, CV, and CO chondrites.

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