

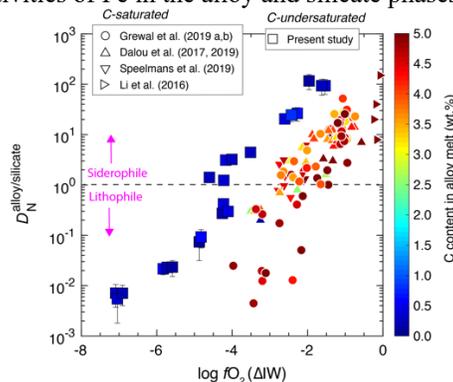
**PROTOPLANETARY DIFFERENTIATION IS THE PRIMARY CAUSE OF NITROGEN DEPLETION IN BULK SILICATE RESERVOIRS OF ROCKY BODIES** D. S. Grewal<sup>1</sup> ([dsg10@rice.edu](mailto:dsg10@rice.edu)), T. Hough<sup>1</sup>, R. Dasgupta<sup>1</sup>, S. Aithala<sup>1</sup>. <sup>1</sup>Department of Earth, Environmental, and Planetary Sciences, Rice University, 6100 Main Street, MS 126, Houston, TX 77005, USA.

**Introduction:** Bulk silicate reservoirs (mantle+crust+exosphere) of rocky bodies in the inner Solar System are extremely depleted in major volatiles like nitrogen (N), carbon (C), and water (H<sub>2</sub>O) [1,2]. Growth of these rocky bodies in the inner protoplanetary disk is assumed to have been proceeded by the accretion of almost volatile-free material due to the lack of condensation of volatiles in their growth zone, therefore, their volatile inventory is of a purported outer Solar System origin with addition of carbonaceous chondrite-like material to almost volatile-free bodies [1,2]. Although a nominally water-free nature of the inner protoplanetary disk is principally valid, “volatile-depleted” enstatite chondrites that source the inner Solar System reservoir contain several hundreds of ppm of N and C (which in itself might be a lower bound because they are thermally altered) in refractory phases [3]. Early differentiation processes such as core-mantle separation and atmospheric loss have been shown to play an important role in explaining N- and C-depletion in the bulk silicate Earth (BSE) [4]–[7]. However, the consequences of a differentiated character of the earliest forming protoplanets, which are the building blocks of larger rocky bodies, on the dynamics of N- and C- retention and loss during planetary growth, are not known.

N is an ideal proxy to explore the fate of volatiles during protoplanetary differentiation because its vapor pressure-imposed solubility in silicate melts is controlled by  $fO_2$  and  $PN_2$ , and  $D_N^{\text{alloy/silicate}}$  by  $fO_2$ , with minimal effect of other thermodynamic parameters.  $D_N^{\text{alloy/silicate}}$  combined with vapor pressure induced N solubility in silicate melts can be used to constrain coupled N partitioning between all three reservoirs accounting for the variation in the composition of accreting material as well as the sizes of the protoplanets. However, variation of  $D_N^{\text{alloy/silicate}}$  as a function of  $fO_2$  has only been determined under graphite-saturated conditions which yield C-saturated alloys containing 3.5–5.5 wt.% C [4]–[7]. As typical core-forming alloys were likely not C-saturated, previous experimental studies might have severely underestimated  $D_N^{\text{alloy/silicate}}$  values if negative interactions between N and C persist for high  $P$ - $T$  conditions relevant for protoplanetary core-mantle differentiation.

**Methods:** To accurately predict the effect of protoplanetary differentiation on N distribution between different reservoirs, we determined  $D_N^{\text{alloy/silicate}}$  from high pressure ( $P=3$  GPa)-temperature ( $T=1600$ – $1800$  °C) experiments in C-undersaturated conditions at a wide range of oxygen fugacity ( $\log fO_2$   $\Delta IW$   $-7.1$  to  $-1.5$ ) to cover the compositional range for protoplanets accreted at disparate heliocentric distances. We performed piston cylinder experiments using Fe-Ni-N $\pm$ Si alloys and mafic to ultramafic silicate mixtures in MgO capsules. The abundances of major element and minor elements as well as N contents of the quenched experimental alloy and silicate melts were determined using a JEOL JXA8530F Hyperprobe EPMA at Rice University.

**Results:** Quenched experimental products were composed of metal blobs embedded either in silicate glass or in a matrix of silicate glassy pools and quenched dendritic olivine crystals. In experiments where there was a co-existence of glass and quenched crystals, N measured only in the glassy pools was used for determining  $D_N^{\text{alloy/silicate}}$ .  $fO_2$  was calculated relative to the  $fO_2$  of the iron-wüstite buffer (IW) based on the activities of Fe in the alloy and silicate phases.



**Fig. 1:**  $D_N^{\text{alloy/silicate}}$  as a function  $\log fO_2$  and C-content in the alloy.

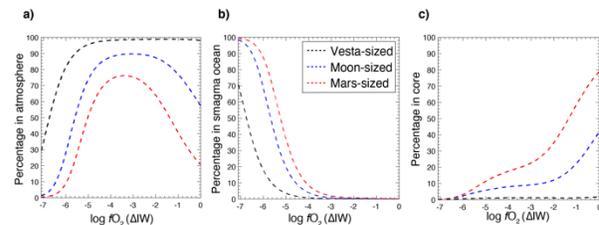
C contents in alloy melts of this study lie in the range of 0.1–0.8 wt.%, which is significantly lower than C contents of graphite-saturated alloys (3.5–5.5 wt.%) of previous studies [4]–[7]. In agreement with previous experiments, N content in the alloy decreases with decrease in  $fO_2$  followed by a sharp drop at  $\sim \Delta IW$   $-4$  where incorporation of Si causes significant depletion of N in the alloy melt. However, at a given

$fO_2$ , N contents are higher in graphite-undersaturated alloys by factor of 1-5 relative to graphite-saturated alloys for similar N contents in the starting mixtures. Consequently, at any given  $fO_2$ ,  $D_N^{\text{alloy/silicate}}$  in graphite-undersaturated systems is almost an order of magnitude higher than in graphite-saturated systems (Fig. 1). Therefore, N acts as a siderophile element over a wider  $fO_2$  range ( $> \sim \Delta IW-4$ ) in graphite-undersaturated systems compared to graphite-saturated conditions ( $> \sim \Delta IW-2$ ).

**Discussion:** The fate of N during protoplanetary differentiation depends upon the initial architecture of the Solar System (within  $\sim 1-2$  Myr), i.e., growth rate and size distribution of rocky bodies as well as their compositional range (primarily  $fO_2$  of the accreting material). To account for the effect of variation in sizes of protoplanetary bodies, we assume three end-members – Vesta ( $R \sim 250$  km), Moon ( $R \sim 1740$  km), and Mars ( $R \sim 2440$  km). Once a rocky body grows to its representative size, all of the accreted N is assumed to be initially degassed into the atmosphere assuming global melting. Vapor pressure induced solubility sets the N budget in the MO, which is available for exchange into core forming alloy melts. Alloy-silicate equilibration sets the  $fO_2$  of the MO. The effect of compositional gradient of the accreting material, i.e.,  $fO_2$ , is accounted by assuming alloy-silicate equilibration scenarios for each rocky body between  $\Delta IW-7$  and IW. Alloy melts are assumed to equilibrate with the entire MO because alloy-silicate equilibration is assumed to be extremely efficient in planetesimal- and planetary embryo-sized bodies. N abundances in the atmosphere, MO, and alloy melts are calculated simultaneously using parametrized N solubility equation from [8] and  $D_N^{\text{alloy/silicate}}$  parameterization from this study.

For a fixed alloy/silicate mass ratio ( $r = 0.5$ ; Earth's alloy/silicate ratio) and bulk N content (500 ppm; average N content of enstatite chondrites), distribution of N between the atmosphere, MO, and core reservoirs as a function of  $fO_2$  for end-member protoplanets is shown in Fig. 2. At any given  $fO_2$ , percentage of N in the atmosphere reservoir decreases with increase in the size of the rocky body. Therefore, a Vesta-sized protoplanets have most of their N in the atmospheric reservoir across the entire  $fO_2$  range (30-98% between  $\Delta IW-7$  to  $\Delta IW-5$  and  $> 98\%$  at  $> \Delta IW-5$ ), while larger protoplanets have proportionally lesser N in the atmospheric reservoir. As all the rocky bodies are assumed to have a similar density,  $PN_2$  scales as function of radius ( $R$ ) and gravitational constant such that larger bodies have a higher  $PN_2$  at a given  $fO_2$ . Therefore, for larger bodies, more amount of N dissolves into the MO

at a fixed  $fO_2$ , which means greater amount of N is available for fractionation between MO and alloy melts such that the percentage of N segregating into the core is higher for larger bodies at a fixed  $fO_2$ .



**Fig. 2:** Modelled N concentration in the a) atmosphere, b) magma ocean, and c) core as a function of  $\log fO_2$  for three end-member protoplanetary bodies.

For all rocky bodies, N in the atmosphere reservoir increases significantly from  $\Delta IW-7$  to  $\Delta IW-4$  because N solubility in the MO drops with increase in  $fO_2$  and the core reservoir cannot incorporate significant amount of N as it shows lithophile character under such conditions. Above  $\Delta IW-4$ , N in the atmosphere reservoir does not increase for Moon- and Mars-sized bodies even though solubility of N in MO decreases because N shows increasingly siderophile character with increase in  $fO_2$ . Therefore, with increase in protoplanetary size the cores become an increasingly important reservoir for N storage by subsequently bringing down N incorporation into the atmosphere because N shows increasingly siderophile character with increase in  $fO_2$ . This becomes especially important at  $> \Delta IW-2$  for Moon- and Mars-sized planetary embryos where despite low solubility of N in MO, the segregated cores contain 10-40% and 30-80%, respectively, of the accreted N budget. Consequently, MOs relevant only for Mercury and parent aubrite body ( $< \Delta IW-4$ ) can retain significant amounts of N in their MO reservoirs ( $\sim 10-100$  ppm for the smallest body and  $\sim 100-800$  ppm for the largest body). Above  $\Delta IW-4$ , MOs of protoplanetary bodies are extremely N depleted ( $< 1\%$  of the initial accreted N; between  $\sim 0.03-1$  ppm) irrespective of their sizes, either due to degassing of N into the atmosphere or via segregation into their cores.

**References:** [1] Marty B. (2012) *EPSL*, 313, 56–66. [2] Sarafian A.R. (2014) *Science*, 346, 623-626. [3] Grady M. and Wight I. (2003) *Spa. Sci. Rev. Adv.*, 5 [4] Dalou C. et al. (2017) *EPSL*, 458, 141-151. [5] Grewal D. S. et al. (2019) *GCA*, 251, 87-115. [6] Speilmanns I. et al. (2019) *EPSL*, 510, 186-197. [7] Grewal D. S. et al. (2019) *Sci. Adv.*, 5 [8] Libourel G. et al. (2003) *GCA*, 67, 4123-4135.