A VERY EARLY ORIGIN OF ISOTOPICALLY DISTINCT NITROGEN IN INNER SOLAR SYSTEM PROTOPLANETS

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Introduction: The origin of life-essential volatiles in the rocky bodies of the inner Solar System is a subject of major debate. Owing to a broad similarity of $^{15}N/^{14}N$ and D/H ratios in the rocky bodies and carbonaceous chondrites, the major volatiles are generally believed to have been delivered primarily via volatile-rich carbonaceous chondrite-like material from the outer Solar System [1], [2]. The outer Solar System material was displaced inwards within the first few Myr of Solar System formation either due to the perturbations in the protoplanetary disk caused by the growth or migration of giant planets, or admixing of pristine outer Solar System material associated with mass accretion of the proto-Sun. However, affinity of $^{15}N/^{14}N$ and D/H ratios in Earth's primitive mantle with enstatite chondrites (isotopically similar to the primary building blocks of inner Solar System planets) suggests that some portion of volatiles in the inner Solar System planets may have been sourced from the inner Solar System reservoir [3]. Although enstatite chondrites contain N, C, and H in significant amounts, their rather late accretion (~2 Myr after the formation of CAIs) [4] precludes them from providing information on the presence of volatiles in the rocky planet forming material of the inner disk at the very beginning of the formation of the Solar System. However, the earliest volatile history can be investigated by looking at iron meteorites, which represent the cores of the earliest-formed protoplanets (possibly within ~0.3 Myr of the formation of CAIs).

Compared to H (not present in all classes of meteorites), and C, (having limited isotopic variation in meteorites; $\delta^{13}C$ <40‰), N is present in all classes of meteorites and displays one of the largest isotopic variations ($\delta^{15}N$ >500‰); in both undifferentiated and differentiated meteorites [5]. In contrast to chondrites and achondrites, which are disequilibrium aggregates of various phases formed by different processes over varying timescales and have their $^{15}N/^{14}N$ ratios affected by thermal and aqueous alteration, iron meteorites preserve primitive $^{15}N/^{14}N$ ratios better as N is hosted in chemically resistant Fe, Ni alloy phases (kamacite and taenite) [6], [7]. Therefore, iron meteorites more reliably track the formation of the earliest forming rocky body reservoirs. $\delta^{15}N$ of iron meteorites vary between –95‰ and +164‰. $\delta^{15}N$ of each iron meteorite group (thought to represent a distinct parent body) lie in small clusters, while N abundances vary from 0.12 to 131 ppm with each group showing variable distribution. N isotope composition of iron meteorites and its relation, or lack thereof, with the accretion zones of carbonaceous (CC) - non carbonaceous (NC) reservoirs [8], [9] provides the best candidate to explore the distribution of volatiles in the protoplanetary disk because of the large inter-group variations of their $^{15}N/^{14}N$ ratios.

Results: Because a three-isotope plot cannot be used to accurately determine the cosmochemical history of N, correlations of its isotopic variations with nuclides having well-determined cosmochemical pathways can be helpful in tracking the evolution of the earliest N reservoirs. Combining mass-independent isotopic signatures of non-volatile siderophile elements (Mo, Ni, W, and Ru) with N isotope ratios, we show that CC and NC iron meteorites plot in compositionally distinct clusters in $\delta^{15}N$-$\varepsilon^{64}Ni$ and $\delta^{15}N$-$\varepsilon^{94}Mo$ space (*Fig.1*; where ε represents parts per 10^4 deviation relative to the terrestrial standards). NC iron meteorites have $\delta^{15}N$ <0 ‰ and CC iron meteorites have $\delta^{15}N$ >0 ‰. This shows that the parent bodies of NC iron meteorites with a purported inner Solar System origin sourced their N from a ^{15}N-poor environment, while those of CC iron meteorites sourced their N from a ^{15}N-rich environment. This observation is in line with the heterogeneous distribution of the isotopes of non-volatile elements and provides the first evidence of CC and NC reservoirs containing isotopically distinct N during the growth of the earliest protoplanets.

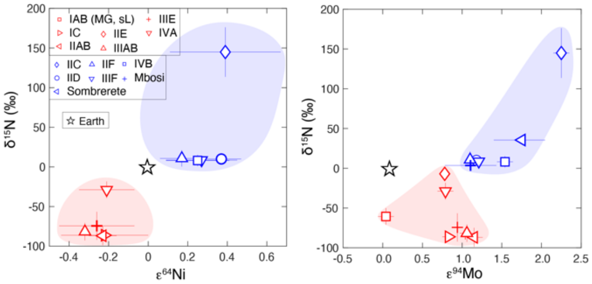

Fig. 1: CC-NC dichotomy of iron meteorites plotted in $\delta^{15}N$-$\varepsilon^{64}Ni$ and $\delta^{15}N$-$\varepsilon^{94}Mo$ space.

Discussion: Does the CC-NC dichotomy of N isotopes reflect the N isotopic heterogeneity in the nebular gas, or does it reflect N being hosted in N-bearing non-volatile phases akin to other non-volatile elements? N isotopic analyses of the modern solar wind ($\delta^{15}N$ = –407 ± 7 ‰), Jupiter's atmosphere ($\delta^{15}N$ = –375 ± 160 ‰), and CAI-hosted TiN (the first solid N-bearing phase to condense from the nebular gas; $\delta^{15}N$ = –364 ± 24 ‰) all point towards an extremely ^{15}N-poor nebular composition, the best estimate being $\delta^{15}N$ = –383 ± 8 ‰ (*Fig. 2*). Using thermodynamic models, we show that nebular ingassing can provide at most ~0.1 ppm N into the alloy, which is lower than the N content of the most N-poor iron meteorites. Therefore, an intermediate parent body process is required to explain N abundances in iron meteorites. N can partition into the metallic cores during core-mantle differentiation in rocky planetary bodies [10], [11]. For oxygen fugacities (fO_2s) relevant for core-mantle differentiation in the parent bodies of iron meteorites, we show that N abundances in iron meteorites can be explained by partitioning of N into the core forming Fe, Ni-alloy melts owing to higher P_N during core-mantle differentiation.

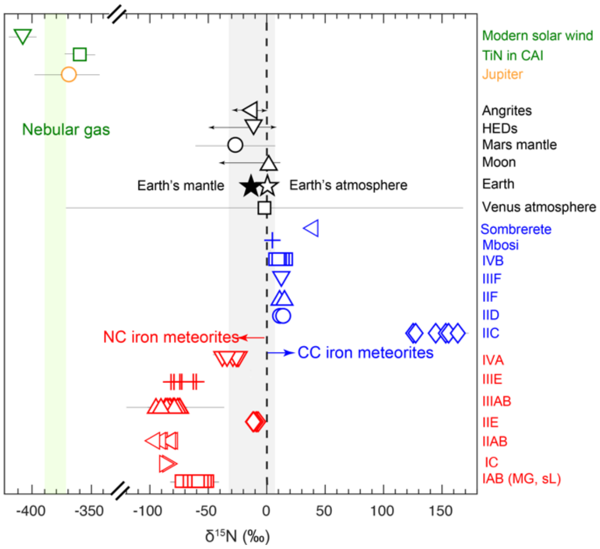

Fig. 2: Variations in $^{15}N/^{14}N$ ratios of various Solar System objects and reservoirs.

Because the accretion zones of NC iron meteorites lie within the thermally processed inner disk, non-volatile dust carriers or refractory organics, rather than ices or labile organics, should have been the primary source of N in their parent bodies. This is contrary to the conventional classification of N as a highly volatile element during protoplanetary disk processes. Enstatite chondrites attest for the presence of hundreds of ppm N in refractory phases like osbornite (TiN), nierite (Si_3N_4), sinoite (Si_2N_2O), and isostructural substitution for O in silicate lattice. This is in agreement with the presence of noble gases (even more volatile than N) in enstatite chondrites, likely to be hosted by refractory phases related to organic precursors. N-bearing refractory organics have also been identified in carbonaceous chondrites, comets, and interstellar medium. Production of N-bearing refractory organics via photon-gas interactions within the protoplanetary disk, and/or as a heritage of the molecular cloud, followed by widespread dispersal via turbulent diffusion could have efficiently distributed organic precursors in the midplane of the disk.

Irrespective of the cause of its origin, the CC-NC dichotomy for N isotopes in iron meteorites portrays a nuanced picture for the distribution of N in the early Solar System. A distinct N isotopic composition of the parent bodies of iron meteorites and CAIs growing concomitantly with ^{15}N-poor Sun and Jupiter shows that the N reservoirs from which the earliest protoplanets accreted their N were isotopically decoupled from the nebular reservoir (*Fig. 2*). Even though most of the N in the protoplanetary disk was hosted by nebular gas, rocky protoplanets forming on similar timescales in the inner and outer Solar System accreted their N from much smaller, non-volatile reservoirs. The enrichment of ^{15}N in non-volatile carriers relative to nebular gas and a ^{15}N gradient from the inner to the outer Solar System in these carriers either predated, or was synchronous, with the growth of the earliest formed protoplanets. This has important implications for the transport of N, and potentially other volatiles, in the planet forming region of the early Solar System, which needs to be further explored in future models on the dynamics of early Solar System. Distinct N isotopic signatures in CC and NC iron meteorites coupled with extremely short accretion timescales of their parent bodies (less than ~0.3 and ~0.9 Myr for NC and CC, respectively) provides the first conclusive evidence that the earliest formed protoplanets in the inner Solar System sourced their N from an isotopically distinct reservoir.

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