A NEW SOURCE FOR TITAN'S N_2 ATMOSPHERE: OUTGASSING FROM ACCRETED ORGANIC-RICH DUST IN TITAN'S INTERIOR.

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Introduction: The isotopic signature of N_2 in Titan's atmosphere is significantly heavier than the solar composition [1], but is similar to that of cometary NH_2, which is hypothesized to be a daughter product of NH_3 [2]. One hypothesis for the origin of nitrogen in Titan's atmosphere is conversion of comet-like NH_3 ices to N_2 [3, 4]. Models of Titan's atmospheric evolution are consistent with a ^{15}N-enriched source such as cometary NH_3 [5, 6].

While this scenario is the leading paradigm, it neglects an abundant cometary constituent that would have certainly been incorporated into Titan during these processes: comet-like dust. Recent data from Rosetta suggest that Comet 67P/Churyumov-Gerasimenko (hereafter, 67P) has a dust-to-ice mass ratio between 0.6 and 11 [7], with a preferred value of 4 [8]. This ratio is consistent with predictions from pebble accretion models [9]. Theoretical studies [10] and data from Comet 1P/Halley [11] suggest that cometary dust is organic-rich. This is corroborated by data from 81P/Wild 2 [12].

Here, we explore if heating of this cometary dust could significantly contribute to the volatile budget of outer Solar System bodies such as Titan. Comets are widely hypothesized to preserve the most faithful records of the outer Solar System during planet formation. They may also represent the building blocks from which larger planetary bodies formed [13]. As such, we consider how the development of a rocky core could result in heating of comet-like material in Titan's interior. We focus on the possible contribution of outgassed volatiles to Titan's atmosphere [14].

Description of the Model: To estimate the bulk cometary composition, we adopt a dust-to-ice mass ratio of 1. This ratio was chosen to reproduce the bulk density of Titan (1.9 g/cm^3) assuming a bulk dust density of 2.6 g/cm^3 [7], a bulk ice density of 1.2 g/cm^3, and no porosity. Ice chemistry is estimated using data from [15]. Dust is assumed to be 50% carbonaceous material by mass, as proposed by [10]. This carbonaceous material is likely most similar to C-bearing fractions from anhydrous interplanetary dust particles (IDPs) [16, 17]. As a first approximation, we utilize insoluble organic matter (IOM) from carbonaceous chondrites as an analogue for refractory cometary organics because this material is much more thoroughly characterized than organics from IDPs. Data suggest that IOM shares some similarities with refractory cometary organics and may provide a useful first approximation for bulk composition and the C/N ratio [17, 18].

For Titan's internal heating, we refer to [19]. They produce two models for differentiation that are consistent with the moment of inertia factor for Titan (I~0.342; [20]). These models suggest peak internal temperatures between ~600 and 1000 °C at depths of ~950 km and 2370 km respectively.

Estimates for the thermal degradation of Murchison IOM are based on [21]. These data are for instantaneous anhydrous pyrolysis of extracted IOM at 1 atm, and we caution that these conditions are significantly different from extended heating in Titan's core. However, in the absence of data that are more directly applicable, we use them here as a first-order estimate.

Bulk Abundances: There is a total mass of 9×10^{18} kg N in Titan's atmosphere. Scaling the volatile composition for 67P reported by [15] to the total mass of Titan (1.3×10^{23} kg), we calculate a total mass of 9×10^{19} to 2×10^{20} kg N accreted as ices using estimates from the winter and summer hemispheres respectively. For a dust-to-ice mass ratio of 1 and a carbonaceous fraction of 50% for dust, we calculate a total mass of 1×10^{21} kg N accreted as refractory organics. These calculations suggest that either reservoir – icy or dusty – is abundant enough to account for the mass of N in Titan's atmosphere.

Thermal Degradation of Organics: Using temperature-depth relationships ~4450 Myr after the end of accretion presented in models for Titan's interior [19], we calculated the mass of rocky material at 50 °C temperature intervals. We assume that this rocky material is 50% organic, consistent with our earlier calculations. Based on data from [19], we calculate the mass percent of organics lost as volatile N at each temperature step. Where interpolation is necessary, we use the lower value for N release, corresponding to an underestimate of N release. Based on these assumptions, we calculate a range $(1.3\text{-}1.5)\times10^{20}$ kg, or $(0.9\text{-}1)\times10^{22}$ moles, of organic N volatilized by Titan's internal heating. Based on outgassing of ^{36}Ar, the outgassing efficiency for N_2 is approximately 0.8-5% [22]. If we assume that all N is transformed to N_2 in the core, then this yields a mass of organic-derived N_2 equal to $(1.0\text{-}7.3)\times10^{18}$ kg outgassed from the core to the atmosphere.

Isotopic Considerations: N isotope data from various Solar System bodies suggest the presence of two or more distinct isotopic reservoirs in the solar nebula [23]. Here, we consider mixing of three different isotopic sources: primordial N_2, NH_3, and organic N. For N_2, we use the solar $^{14}N/^{15}N$ ratio of 441 [23]. For NH_3, we use the spectroscopically determined ratio for NH_2 in comets, $^{14}N/^{15}N = 127$ [2]. For organics, we note that bulk measurements from IDPs [24], Stardust samples [25], and primitive IOM from CR chondrites [26] typically range from ~200 to 250, and select a mid-range value of 225 for the present study. By combining these three components, we estimate for the first time the bulk $^{14}N/^{15}N$ isotope ratio for a comet: ~220. For the $^{14}N/^{15}N$ ratio of Titan's atmosphere, we use a value of 168 [1]. Results are shown in Fig. 1.

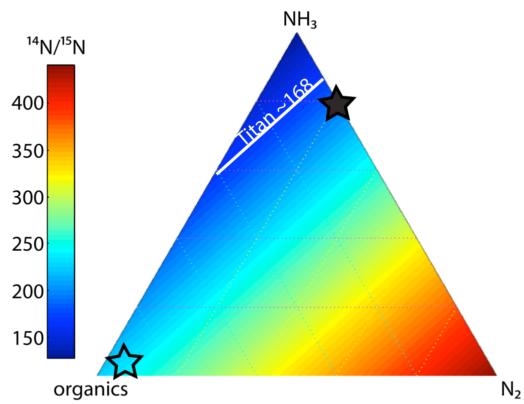

Fig. 1. Nitrogen isotopes from a three-member mixing model. The top of the triangle represents 100% NH_3, the left point represents 100% organics, and the right point represents 100% N_2. The white line shows Titan's isotopic composition. The open star shows the approximate location on the plot of comet 67P, while the filled star shows the approximate location of a hypothetical dust-free 67P.

These values allow for a maximum contribution of 13% of N from N_2, assuming no organic N is released. However, on the basis of noble gases, we can exclude a significant N_2 contribution to Titan's atmosphere. The $^{36}Ar/N$ ratio at Titan is $\sim 1\times10^{-7}$ [1]. If we assume that the $^{36}Ar/N$ ratio of 67P (5×10^{-3}; [27]) is representative of primordial N_2 ices, then it is clear that N_2 ices were not a significant source of Titan's atmosphere. In a mixing model for NH_3 and organic N, nitrogen isotopes suggest a mixture of ~40% organic N and 60% NH_3. This is equivalent to 3.6×10^{18} kg of N from organics, which is in the middle of the range suggested by outgassing estimates above.

Noble Gases: Since Phase Q is a major carrier of noble gases in primitive materials and is associated with carbonaceous phases [28], we expect that the release of N from these phases may be accompanied by release of noble gases. We utilize data from the stepped pyrolysis of Orgueil HF/HCl residue [29]. Using the thermal models of [19], we calculate that a total of $\sim 5\times10^{15}$ moles ^{36}Ar may be released in Titan's interior. Using the moles of volatilized organic N in the mantle reported above, we find a released $^{36}Ar/N$ ratio in the mantle of $(5\text{-}6)\times10^{-7}$. If we assume that ^{36}Ar and N_2 may outgas with similar efficiencies and take into account the 40% contribution constraint derived above from isotopic considerations, we calculate a corrected $^{36}Ar/N$ ratio of $\sim 2\times10^{-7}$. This is remarkably close to the measured $^{36}Ar/N$ ratio in Titan's atmosphere (1×10^{-7}; [1]).

Conclusions: We conclude that cometary dust was an important primordial constituent of icy satellites, and may have contributed significantly to their volatile budgets. Using internal temperature profiles that are consistent with Titan's moment of inertia, we find that heating refractory organics can liberate significant abundances of N and ^{36}Ar. Nitrogen isotope and $^{36}Ar/N$ constraints on the organic contribution to Titan's atmosphere are self-consistent.

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