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LESC XXIV

N94 -

## EVOLUTION OF TRITON'S VOLATILE BUDGET; J.I. Lunine, University of Arizona, Tucson AZ 85721

Triton's volatile budget provides important links to planetary formation processes in the cold outer solar nebula. However, the budget has been modified by processes subsequent to the accretion of this body. It is of interest to assess whether certain formation environments can be ruled out for Triton on the basis of its current volatile abundances, and also to quantify some of the post-accretional processes by which the abundances have been modified.

*Current surface abundances:* A combination of Voyager UVS, IRIS and RSS data strongly point to the nitrogen atmosphere being in saturation equilibrium with surface frost on the sunlit hemisphere. Since Triton is approaching southern summer solstice, a minimum surface abundance can be computed based on the continued presence of nitrogen in the southern hemisphere. The energy-limited mass flux of nitrogen northward is  $\sim 10^{-7}$  g cm<sup>-2</sup> s<sup>-1</sup>; over 50 years a layer 2 meters thick can be sublimated. An upper limit to the nitrogen abundance is obtained by considering limits to the thickness of nitrogen frost deposits. The scale of topography on Triton is limited to of order kilometers in cliffs, ridges, etc. The edges of the polar frost deposits do not seem to exhibit such relief. More significant is that heat flow models of the nitrogen cap yield a thermal gradient of 15K per kilometer [3]; a 2-3 km-thick cap would reach the melting point of nitrogen at its base. Before then, viscous spreading of the cap would decrease its thickness [4], so that 1-2 km is a good upper limit to the cap thickness. Averaged over the surface, an upper limit of 0.5-1 km thickness is obtained for the amount of nitrogen ice; this is converted in the accompanying table to an equivalent mass.

Carbon monoxide has a saturation vapor pressure roughly an order of magnitude below that of nitrogen at 38K. Application of Raoult's law to the atmospheric upper limit of 1% mixing ratio CO/N<sub>2</sub> from UVS data [2] yields a ratio in the mixed ice of 15%. Alternatively, one could postulate that carbon monoxide ice is physically separate from the nitrogen ice, but the CO vapor is compelled to move northward in the general nitrogen vapor flow. Then the areal coverage of CO frost in the summer hemisphere can be computed to be <1% to produce an undersaturation of at least 10% in the atmosphere. Thus whether the CO is mixed with the nitrogen or separate, a reasonable upper limit to its abundance range is 1-10% of the surface nitrogen abundance. Recent work [14] suggests that the atmospheric mixing ratio limit might be 3 orders of magnitude smaller than given in [2], leading to a surface abundance commensurately smaller. Methane is present in Triton's atmosphere and is within a factor of 10 of saturation at 38 K. Because it is close to or at saturation the methane abundance is not constrained by the nitrogen abundance in surface frosts. An upper limit to the methane frost abundance can be obtained by similar arguments to those presented above for nitrogen, though the higher melting point of methane allows a thicker layer. A lower limit for methane is obtained by considering the amount of methane photolyzed over the age of the solar system, which is the equivalent of roughly a meter-thickness of products spread over the surface.

The photolysis rate implies that the volatile frosts are underlain by a meter or so of photolysis products. This raises the question as to how carbon dioxide frost has remained exposed to view; perhaps impact stirring has allowed some  $CO_2$  to be present at the optical surface, or perhaps recent internal activity has allowed fresh  $CO_2$  to be outgassed. More intriguing is the idea that the  $CO_2$  seen in the spectra is the product of photolysis of CO and subsequent addition of oxygen through infalling ice particles. Such a photochemistry is predicted for Titan, although the rate is computed to be only 0.1% of the methane photolysis rate [13]. If the same holds on Triton, the photochemically-produced  $CO_2$  could be highly diluted in the detritus of higher hydrocarbons.

Models for initial volatile inventory. The first two models use the computations presented in [12] to compute molecular abundances in the gas phase of a model solar nebula and proto-satellite nebula. The molecules are then assumed to either condense or become trapped in water ice as clathrate hydrate, with abundances determined from the computations of [6]. The gas phase molecular abundances in [12] are determined by equilibration reactions with finite rates which are allowed to proceed for a disk lifetime fixed at  $10^{13}$  seconds, for concreteness. Likewise for concreteness the proto-satellite disk model is that for Jupiter; a detailed temperature-pressure profile for a nebula around Neptune has not been published, but the circum-Jovian disk case illustrates sufficiently well the effect of a more reducing environment. For both nebular models we consider results for two different types of chemistry: A fully gas-phase chemistry with no catalysis by grains, and a much more rapid set of reaction rates appropriate for efficient grain catalysis.

Given the molecular abundances, we assume that ammonia and carbon dioxide condense out directly and mix with the water ice either at the molecular or grain level. This is appropriate for ammonia, but a small amount of the carbon dioxide may instead be incorporated in clathrate hydrate [6]. Nonetheless, even for the small mixing ratios in the proto-satellite nebula, the partial pressure of carbon dioxide is sufficient to allow condensation below 60-70K. At 30 AU from the sun, the environment of Triton was colder than this during planet formation. Methane, carbon monoxide and molecular nitrogen were assumed to be trapped in clathrate hydrate; we use the published results at 80 K [6], though the fractionation effects are likely more severe at lower temperatures.

These cosmochemical models are undoubtedly oversimplified. The gas phase molecular abundances at 30 AU, in the solar nebula, are almost certainly not determined by chemical quenching much closer to the center of the nebula, because radial mixing may be severely limited [15] (but see [11]). Instead, infalling material from the surrounding collapsing cloud core will be partially processed but still retain a strong signature of molecular cloud abundance [7]. Additionally, volatile trapping in water ice was equally complex, may have involved several stages, and probably did

## LPSC XXIV

## TRITON'S VOLATILE BUDGET: Lunine J.I.

not involve clathrate hydrate formation [1, 7]. Rather than put together a more complicated model here, we include an additional column in the table which assumes a volatile inventory for Triton based on comets [8]. While cometary and proto-Triton material might have undergone modestly different histories, the inventory is instructive in its differences from the first two columns. The methane abundance in Comet Halley could be zero [10]; however, the observation of interstellar methane [5] strongly argues for this molecule being introduced into outer solar system bodies, and we adopt a finite lower value here. Likewise, the amount of formaldehyde in comets is controversial; we use a non-zero lower value here based on [9].

Comparison of initial and present-day (surface) inventories: Sufficient amounts of nitrogen, carbon monoxide and methane exist in the solar nebula and cometary models to account for the surface abundances, but the proto-satellite inventory falls short on nitrogen. The nitrogen abundance is not fatal to the proto-satellite model since the present-day surface amounts could have been derived from ammonia. Because the surface CO abundance is only an upper limit, it is not inconsistent with the proto-satellite model.

What is striking about the solar nebula and cometary models is that the surface *ratio* of carbon monoxide to nitrogen, required by the data to be <0.1, is very poorly matched in either case. Carbon monoxide is much more abundant than nitrogen in either model volatile inventory. Selective outgassing could be invoked to achieve the surface ratio, but the chemical differences between CO and N<sub>2</sub> are not so large as to make this particularly appealing. The surface ratio of CO/CH<sub>4</sub> does not appear to cause problems for either model: One can choose an intermediate amount of grain catalysis in the solar nebula model to yield the right surface ratio, and one is free to choose for the surface ratio CH<sub>4</sub>/CO = 0.1 which is consistent with the cometary model.

Perhaps the most profound process modifying Triton's volatile inventory is early escape of gases from an atmosphere raised by tidal heating; [8] presents estimates for the total amount of escape during the lifetime of the atmosphere. If the atmosphere survives for a time of order a gigayear, which is plausible based on the models in [8] and the cratering record, then *most* of the initial volatile budget could be lost through escape. More detailed calculations are required to quantify the relative amounts of each gas which is lost through early, rapid atmospheric escape. *Acknowledgment*. This work was supported by NASA grant NAGW-1039.

Molecule	Solar Nebula <sup>2</sup>	Proto-satellite <sup>2</sup>	Cometary model <sup>3</sup>	Present Surface 4
$N_2$ $NH_3$ HCN $CH_4$ CO $CO_2$ $H_2CO$ $CH_4OH$	$10^{-3}, 10^{-8}$ $10^{-6}, 10^{-4}$ $10^{-7}, 10^{-1}$ $10^{-1}, 10^{-7}$ $10^{-3}, 10^{-6}$	$10^{-11}, 10^{-17}$ $10^{-1}$ $10^{-1}$ $10^{-12}, 10^{-16}$ $10^{-8}, 10^{-12}$	$10^{-4}$ $10^{-3} \cdot 10^{-2}$ $10^{-3}$ $10^{-3} \cdot 10^{-2}$ $10^{-2} \cdot 10^{-1}$ $10^{-1}$ $10^{-3} \cdot 10^{-1}$ $10^{-2} \cdot 10^{-1}$	10 <sup>-6</sup> -10 <sup>-3</sup> ? 10 <sup>-6</sup> -10 <sup>-3</sup> < 10 <sup>-7</sup> -10 <sup>-4</sup> * ?

## TRITONIC VOLATILE BUDGET

<sup>1</sup> Masses given, as order of magnitude only, in units of  $10^{25}$  g.

<sup>2</sup> Predictions of solar and proto-satellite nebula models. First number assumes gas phase reactions are not catalyzed by grains; second number assumes efficient grain catalysis. Where only one number is given, results for the two cases are the same. Symbol (--) indicates no prediction available from [12], or too uncertain.

<sup>3</sup> Volatile budget based on abundances in comets. Cometary data from review by [10].

<sup>4</sup> Estimated mass of surface frost deposits. The ranges for CO and N<sub>2</sub> are coupled, that is, CO/N<sub>2</sub> < 0.1 in any case. Symbols:? = not yet observed ; \* = observed but no abundance constraint available.</p>

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914