METHANE AND AMMONIA IN TITAN'S PRIMORDIAL AND COOLING ATMOSPHERE. A. E. Gilliam and A. Lerman, Department of Earth and Planetary Sciences, Northwestern University, Evanston IL, 60208-3130 (ashley@earth.northwestern.edu).

Introduction: To date, only the *Cassini-Huygens* spacecraft has been able to peer beneath Titan's thick clouds. Even less is known about early Titan, how it formed, and how it evolved from 4.55 Ga until today. We use available information about Titan's present-day atmosphere composition and internal structure and propose a new model for the chemical and physical composition of Titan and its atmosphere post-accretion. We show how the two main gases in Titan's primordial atmosphere, NH_3 and CH_4, could escape from the atmosphere with thermal escape as the only sink, the final result being the present-day gas masses in the atmosphere. For this, we estimate the structure of primordial Titan based on its present-day internal composition, calculate its accretion temperature, estimate its mean heat capacity, and develop its cooling model. We also model the composition of the primordial Titan atmosphere, with NH_3 and CH_4 as the only gases, and calculate the corresponding volume, height, density, and outer surface area of the atmosphere in each case. Finally, we calculate the escape rates of NH_3 and CH_4 as a function of time by mechanisms of gas thermal escape alone and by thermal escape accompanied by emissions from Titan's interior.

Chemical and Mineral Composition of Titan: The internal structure for Titan is thought to consist of an antigorite core overlain by a thin layer of brucite, a layer of ice VI, an aqueous ammonium sulfate ocean, and a crust made of methane clathrate, ice Ih, and solid ammonium sulfate [1]. We assume an internal structure based on the preceding, with the volatiles in the outer fluid shell: aqueous solution of NH_3, $(NH_4)_2SO_4$, and CH_4 gas. It has been suggested that Titan's differentiated structure evolved from a more homogeneous structure shortly after accretion [2]. A post-accretional homogeneous Titan would be much warmer than present-day Titan, averaging 300-355 K. At this temperature, the components will likely be in a different phase than they are in the present-day differentiated Titan.

Accretion Temperature and Cooling: Accretion temperature, T_{ac}, is based on a balance of the release of gravitational accretion energy and cooling by an ideal black body radiation emission, with no other internal heat sources or heat storage [3]. The overall cooling rate (Fig. 1) is based on our estimates of Titan's composition and heat capacity and it is unaffected by the different accretion temperatures: the two curves are essentially identical at $t > 1$ Myr after accretion. The initial cooling period of both curves between 0.5 and 0.6 Myr is relatively fast, where the Titan temperature decreases to 150 K. It takes about 5 Myr for the temperature to decrease to 90 K.

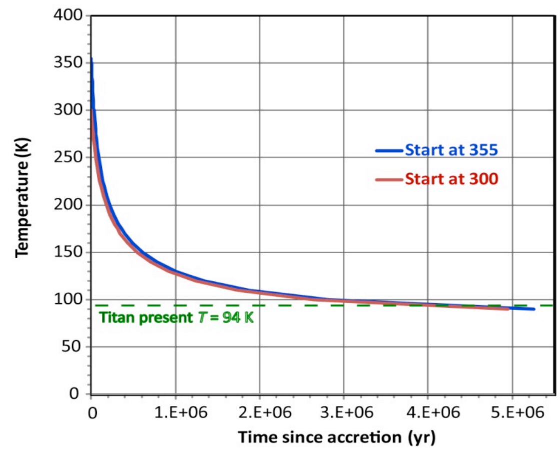

Fig. 1. Titan cooling after accretion for two different accretion temperatures, T_{ac} = 355 and T_{ac} = 300 K.

Present-Day and Primordial Atmosphere: We consider two cases for Titan's present-day atmosphere, with N_2 or NH_3 and CH_4 as the only gases, and three cases for the primordial atmosphere. It is generally accepted that Titan's primordial atmosphere was much more massive and denser than at present, and dominated by NH_3 and CH_4: two to ten times today's mass [4] or an atmosphere of a N_2 pressure 5-10 bar and a CH_4 pressure 30-80 bar [5]. From our results of the gas-escape calculation, primordial atmosphere scale thickness was five to six times greater than at present (109 to 128 km), a total pressure of 25 bar, in comparison to 1.5 bar at present, and densities of 14 to 16.6 kg/m^3, compared to 5.2 kg/m^3 at present.

Gas Escape: In a gas, the directions of the gas molecules are on average outward and inward [6], and the fraction of the gas moving away from the planet is ½ of the fraction of gas molecules that have velocities greater than the escape velocity of the planet. The gas mass remaining in the atmosphere $N_t = N_0 e^{-kt}$ (kg or %), where N_0 is the initial gas mass at time $t = 0$, is taken as a first-order flux that is controlled by the escape rate parameter, k. The value of k depends on temperature and molecular mass of the gas, the Titan escape velocity, and on the atmosphere thickness. Fig. 2 shows the CH_4 and NH_3 escape since accretion.

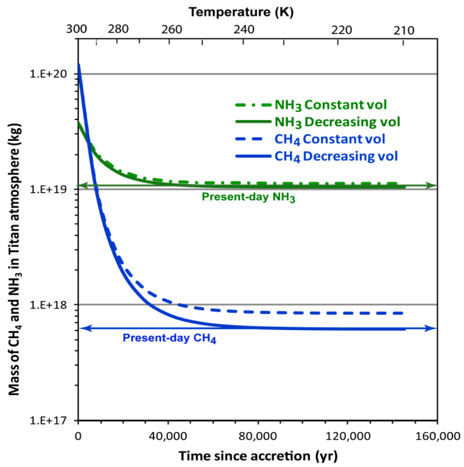

Fig. 2. The amount of NH_3 and CH_4 remaining in the atmosphere as a function of time since accretion assuming a T_{ac} = 300 K.

Possible Emissions from the Interior: Possible cryovolcanic features on Titan's surface have been identified by the *Cassini* spacecraft [7]. Cryovolcanism is considered by some the leading mechanism for the replenishment of CH_4 in Titan's atmosphere, where it may be irreversibly lost due to photochemical dissociation [8]. Among the many possible emission scenarios that may be thought of, the case we explore is gas thermal escape accompanied by emission from Titan's interior, a process that is a combination of a constant input rate to the atmosphere, F (% N_0/yr), with a first-order escape: $dN/dt = F - kN$, as shown in Fig. 3.

Discussion and Conclusions: Our work showcases a new model of the chemical and physical composition of primordial Titan and its atmosphere, and explains how the two main gases in Titan's primordial atmosphere, NH_3 and CH_4, could leave the atmosphere by thermal escape as the only sink, the final result being the present-day gas masses in the atmosphere. The calculated Titan T_{ac} = 355 to 300 K, and it takes about 5 Myr for the temperature to decrease to the present-day temperature.

At the initial 355 K, very little of the gas mass would be left in the atmosphere after a few hundred years, except under certain hypothetical conditions or if emissions from the interior supplied the two gases over certain periods of time. To avoid complete depletion of CH_4 and NH_3 in the internal reservoir, and to satisfy that stable gas concentrations do not exceed present-day levels, emissions would need to be discontinuous and stop at different times, depending on the emission rate. The emission of NH_3 ends 60,000 to 70,000 yr ($F = 1.45\times10^{-3}$ to 9.0×10^{-4} %/yr) after start, and the gas mass declines shortly to its present-day level. The different emission rates of CH_4 need to last 60,000 to 600,000 yr ($F = 1.0\times10^{-4}$ to 1.0×10^{-6} %/yr) to attain a steady-state value. However, a model of a lower accretion temperature of 300 K leads to a more straightforward process of gas loss by thermal escape down to their present-day masses.

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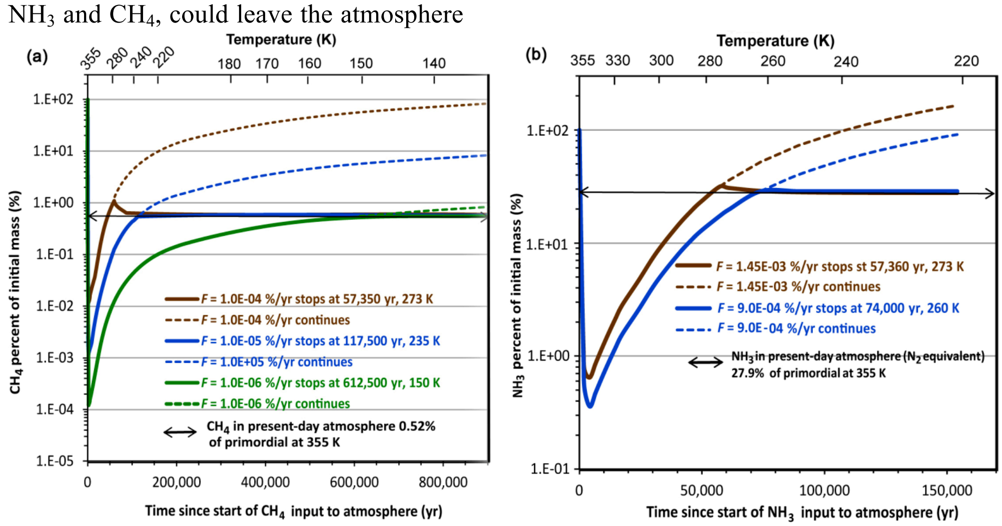

Fig. 3. Input of (a) CH_4 and (b) NH_3 from Titan's interior to the atmosphere, added to the escaping gases. Final masses are stabilized at their present-day values.