OXIDIZING PROTO-TITAN: CONSTRAINT FROM THE IMPACT ORIGIN OF ITS N_2 ATMOSPHERE.

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Introduction: One of important issues concerning planetary atmospheres is why Saturn's largest satellite Titan possesses a huge amount of N_2 in the atmosphere. Answering this question would provide an insight for understanding the origin of N_2 in planetary atmospheres as well as the formation of satellite system around gas planets in the solar system [1-5]. Titan and other regular satellites around gas giants were formed in circumplanetary disks at the early stage of the Solar System [1-3]. Its proto-atmosphere would have been formed during accretion due to melting and vaporization of its outer layer [6, 7]. Thus, the early evolution of Titan's atmosphere would have been determined by the chemical composition of its building blocks and geological alteration processes in the proto-atmosphere.

The composition of Titan's satellitesimals was strongly influenced by the chemistry of circum-Saturnian subnebula. Previous studies have proposed two models for satellite formation: early models invoke satellite formation in a dense and hot disk at the early stage of gas giant formation [1,2] whilst more recent models suggest that satellites formed in a thin and cold disk at later epochs of its evolution, in which icy planetesimals were actively supplied into the disk from the feeding zone of the gas giant in the solar nebula [3] (so-called a gas-starved disk model). In the case of former model [1, 2], the chemical composition of its proto-atmosphere would have been highly reducing and composed of large amounts of CH_4 and NH_3 produced in the circum-Saturnian disk [1, 2] via active gas-phase and heterogeneous reactions [2]. In the case of more recent models, the chemical composition of its proto-atmosphere would derive from that of icy planetesimals produced in the solar nebula and, thereby, might be oxidizing containing more CO_2 than CH_4 and NH_3 [3].

Previous studies have proposed that NH_3 in the proto-atmosphere would have been converted to N_2 via impact shock heating during accretion [4, 5]. However, the validity of this mechanism strongly depends on both the composition of the proto-atmosphere and the kinetics of shock chemistry.

Here we compare the efficiency of impact shock production of N_2 for various chemical compositions of Titan's proto-atmosphere to determine which one allows the formation of the present N_2-rich atmosphere. Bow shock wave, which forms in front of a projectile entering into an atmosphere, heats entrained atmospheric gas species to high temperatures. Subsequent cooling by expansion quenches the chemical composition of shocked gas. Based on the results of shock chemistry in the terrestrial atmosphere [8], previous studies [4, 5] of shock heating in Titan's proto-atmosphere assumed that shock temperatures in Titan's reducing proto-atmosphere become high (> 2000 K) sufficient to achieve thermodynamic equilibrium. Then, the gas species are left with characteristics of thermodynamic equilibrium at quenching temperature of ~2000 K. However, given that each molecule owns a different heat capacity, shock temperatures in planetary atmospheres should vary depending on their chemical composition, resulting in different efficiencies of shock production of chemical species. To examine shock chemistry in its proto-atmosphere more precisely, we have constructed a one-dimensional shock chemistry model to calculate kinetics of chemical reactions accompanying a bow shock induced by the entry of an impactor into the atmosphere.

Methods: To calculate chemical reactions along a streamline in flow behind bow shock, we follow the previous approximation [9, 10] that considers the reactions along a streamline behind bow shock as that behind a steady-state plane shock. In this approximation, the enthalpy of postshock gas for the plane shock is given by that of the streamline behind the bow shock. The enthalpy of postshock gas in the bow shock flow varies with the shock angle between free stream and shock wave front. In this paper, we assume a shock angle of 90 degree. Chemical reactions in the flow are calculated numerically using the rate equations of chemical reactions and one-dimensional hydrodynamic equations combined with Rankine-Hugoniot equation and the ideal equation of state. We also assume the vibrational equilibrium in shocked gas species in the flow. The rate equations of chemical reactions are constructed by combining schemes of pyrolysis of CH_4 and of NH_3 with GRI Mech [10-13]. Chemical reactions in a flow behind bow shock are quenched through cooling due to a rapid adiabatic expansion to the rear of the projectile. In our model, we thereby consider that chemical reactions are quenched after the flow reaches the distance corresponding to projectile radius [10].

Result and Discussion: We calculated shock production yields of N_2 for different impact velocities and atmospheric CH_4 concentrations in the reducing atmospheres composed of NH_3 and CH_4 (see Figure 1a). According to our results, higher impact velocities tend to produce more N_2 because higher velocity impacts result in higher shock temperatures. On the other hand, higher CH_4 concentrations produce less N_2. This is because CH_4 acts as an effective coolant gas in the shock heating owing to its large heat capacity (9 vibrational modes). Such a large heat capacity of CH_4 results in much lower shock temperatures to inhibit the N_2 production contrary to the previous studies [4, 5]. Considering the formation of the last half of Titan's mass by successive impacts of 1 km-sized satellitesimals, a N_2 yield of ~10^{17} molecules/J is required to account for both the present atmospheric N_2 amount and loss of N_2 over Titan's history [14]. When we assume the atmospheric composition ((CH_4/(CH_4+NH_3) ~0.8) inferred from a thick and hot circum-Saturnian disk [1, 2], we found that an impact velocity of ~3.8 km/s is at least needed to achieve the required N_2 yield (10^{17} moles/J) (see Figure 1a). If we consider an oblique shock wave front in actual impact conditions, the impact velocity sufficient for the present amount would become greater. This velocity is higher than the impact velocity of satellitesimals during Titan's accretion (~2.5–4 km/s [5]). So, our results suggest that the shock N_2 production in the reducing proto-atmosphere cannot account for the present N_2 amount.

Next, we calculated N_2 shock yields for different impact velocities and atmospheric CO_2 concentrations in the oxidizing proto-atmospheres composed of NH_3 and CO_2 (Figure 1b). In contrast to the reducing proto-atmosphere, the required N_2 yield (10^{17} moles/J) is achieved under most of the calculated conditions. Because the heat capacity of CO_2 (4 vibrational modes) is small relative to CH_4, the shock temperature becomes much higher in the oxidizing proto-atmosphere than in the reducing one. With the atmospheric composition (CO_2/(CO_2+NH_3) ~0.7-0.9) based on the gas-starved disk model [3], the N_2 yield reaches ~10^{17} molecules/J or higher at a reasonable velocity range for the satellitesimal impacts on the growing Titan (2.5–4 km/s [5]). We thus conclude that a CO_2-rich oxidizing proto-atmosphere is required for the N_2 production to explain the current N_2 inventory.

Our conclusion supports the hypothesis of accretion of CO_2-rich satellitesimals predicted by the gas-starved disk model [3]. In this scenario, regular satellites are formed at the final stage of gas planet formation using materials condensed in the solar nebula. This implies that the chemical composition of satellitesimals is likely to have been less altered by the subnebula and to reflect the thermal history of the solar nebula at the stage of gas planet formation. Furthermore, because the chemical composition of satellitesimals accreted by Titan and Enceladus should be similar, our conclusion supports the hypothesis that the main chemical species observed in Enceladus jets [15], such as CO_2 and NH_3, are also primordial [16].

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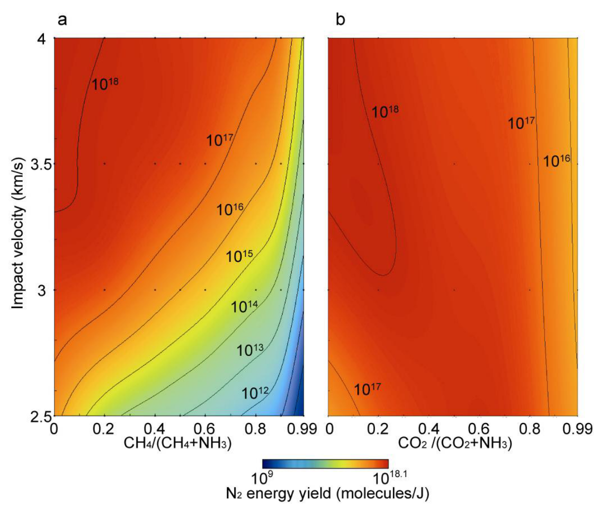

Figure 1: Shock production yields of N_2 calculated for various impact velocities and atmospheric compositions. (a), the case of an impact into CH_4-NH_3 atmosphere (CH_4 mixing ratio from 0 % to 99 %). (b), the case of an impact into CO_2-NH_3 atmosphere (CO_2 mixing ratio from 0 % to 99 %). The impactor size is set to 1 km. The results for the streamline of shock angle θ = 90° in bow shock flow are shown as a representative result. Black solid lines indicate the contour line of N_2 energy yield that is the amount of the N_2 molecules divided by the shock energy added to the shocked gas. The initial atmospheric pressure is set to 1 bar.