

IMPACT GENERATION OF METHANE-RICH ATMOSPHERES ON EARLY TERRESTRIAL PLANETS.

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Summary: Recent geochemical measurements and theoretical studies on the origin of terrestrial planetary atmospheres suggest that terrestrial planetary atmospheres may be greatly contributed by impact delivered gases [e.g., 1]. One of the most important properties of impact-generated atmospheres is their reducing nature; previous studies have revealed that chondritic compositions of impactors would produce reducing gases containing H₂, CO, and/or CH₄ [2, 3]. However, the molecular compositions of such atmospheres are not well constrained because the thermodynamic cooling path of the impact-induced vapor, which controls the thermodynamic stability of chemical composition, has been not investigated. Here we theoretically assess the molecular composition within impact-induced vapor that cools adiabatically, and found that CH₄ of 100's ppm to a few percent may have been formed by meteoritic impacts on early Mars and Earth. Such high concentration of atmospheric CH₄ would have a great impact on prebiotic chemistry and climates of early terrestrial planets.

Background: The molecular composition of primordial planetary atmospheres directly affects the radiative forcing of the atmosphere and products of chemical reactions induced by lightning and ultraviolet light [e.g., 4, 5]. In particular, CH₄ abundance may have played an important role in early climates and prebiotic chemistry of terrestrial planets. More specifically, extreme ultraviolet light-induced reaction of N₂ with CH₄ yields a reduced form of nitrogen HCN [6], which could have been an important nutrient for early life especially before life had not acquired the ability to assimilate nitrite-nitrate reduction. For ancient climates on Mars, the strong absorption of CH₄ in the near-Infrared region raises the temperature of middle-upper atmosphere, inhibiting formation of CO₂ clouds at high altitudes [4]. Such effect of CH₄ may be important for considering planetary albedo. Thus, molecular composition, particularly CH₄ abundance, of the atmosphere is extremely important for understanding the formation and evolution of a habitable planet. However, the molecular composition of earliest atmospheres of terrestrial planets has been still an open issue.

The composition of primordial atmospheres is determined mainly by two factors: origins of volatiles and pressure-temperature (*P-T*) pathway during degassing processes. Thus, constraints on these factors are needed to estimate the composition of the earliest atmosphere of terrestrial planets.

Geochemical aspects of the origin of the atmosphere: Because terrestrial planets are depleted in volatiles compared to the solar composition, the origin of the atmosphere of terrestrial planets is widely considered as either magmatic degassing from planetary interior or impact degassing from primitive meteorites, such as chondrites [7]. Because differentiated magma is likely to be chemically different from chondrites, to identify the source of the major fraction of the atmosphere provides clues for elucidating molecular composition of the earliest atmosphere.

The fact that the stable isotope composition of Kr and Xe in Earth's mantle is heavier than that of the present atmosphere [8] suggests that mantle degassing cannot be major source of terrestrial atmosphere. Although magma degassing may have contributed to the primordial atmospheres [e.g., 9], such atmospheres may have been lost during the giant impacts stage [10]. The high H₂O/Xe ratios of terrestrial planets relative to that of any types of chondrites and comets may be a consequence of preferential loss of primordial atmospheres [11]. If the present atmosphere of terrestrial planets is not a residue of the magma degassing, the impact delivery of volatiles from extraterrestrial materials is the most likely atmospheric origin.

The excess of highly siderophile elements in mantles of terrestrial planets indicates the late accretion of chondritic materials after core formation [12, 13]. Moreover, the similarity in the isotopic compositions of H, C, and N between the Earth and carbonaceous chondrites [e.g., 14] also supports addition of volatiles from carbonaceous chondrites. Thus, impact degassing processes from carbonaceous chondrites and subsequent chemical reaction are extremely important for understanding the molecular composition of the earliest atmosphere of terrestrial planets.

Impact degassing of volatiles from carbonaceous chondrites: Typical impact velocity of meteorites is high enough to induce partial vaporization of silicates [15, 16]. Thus, the vapor containing both volatile and rock-forming elements is generated by high-velocity impacts of meteorites.

Because the timescale for pressure heterogeneities within an impact plume to equilibrate is typically much shorter than that for temperature heterogeneities [e.g., 17], the process of impact degassing of volatiles can be assumed adiabatically. If this is the case, the entropy-gain during shock compression would strongly regulate the *P-T* path of the impact-generated vapor. This sug-

gests that the molecular composition of the impact-generated vapor may vary with impact velocity even if the composition of impactors is similar. Consequently, terrestrial planets may have had different types of impact-generated atmospheres during the heavy bombardment. Nevertheless, such an aspect of impact degassing processes is poorly understood yet.

The entropy gain during shock compression is controlled mainly by two factors: impact velocity and the presence/absence of the global ocean. With respect to the presence of the global ocean, ancient ocean on Mars would not have been large enough to cover the surface globally [e.g., 18], whereas early Earth is likely to have been globally covered with the ocean. When we take into account this difference of the target property, the entropy gain of impactors during shock compression may be similar though the mean impact velocities on Mars and Earth are different.

Based on the estimate of the entropy gain of the impactor, then we calculate the equilibrium composition of the adiabatically expanding vapor of chondrites using the Gibbs energy minimization code [19]. The composition of the main impactor is assumed to be CI-like based on the inference from elemental ratios of volatile chalcogens in Earth's mantle [20]. The detail calculation method is described in [21].

Calculation results and discussion: The major gas compositions are shown in Figure 1. In general, the molecular composition of the vapor from carbonaceous chondrites is dominated by CO_2 and H_2O ; this result is consistent with previous studies [2, 3]. Our calculation result shows that the P - T paths of the impact-induced vapor of CI-like composition may be favorable for the formation of CH_4 and CO_2 in the case of impacts onto Mars and Earth as shown in Figure 2. Specifically, CH_4 of 100's ppm to a few percent could be efficiently formed in a wide range of temperatures including typical quenching temperatures of carbon-bearing gases [e.g., 22]. Because the vapor at low entropy states undergoes higher pressure at a given temperature, the vapor generated by low-velocity impacts tend to be rich in CH_4 (i.e., Le Chatelier's principle) compared to that generated by high-velocity impacts.

Previous studies, which assume radiative cooling of impact vapor, have claimed that Fischer-Tropsch reaction is needed for the formation of CH_4 , because CH_4 is thermodynamically stable and the conversion of CO to CH_4 is kinetically inhibited at low temperatures (i.e., < 1000K at 100 bars) [e.g., 23]. However, the formation efficiency of a highly active catalyst may be difficult, because volatile-rich carbonaceous chondrites are abundant in sulfur, which is known as catalyst poison. Thus, entropy of the vapor may be a better controlling factor

for estimating the molecular composition of an expanding vapor.

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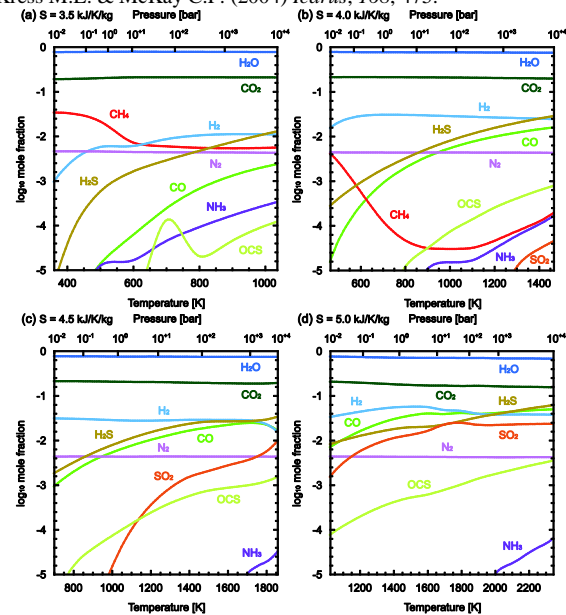


Figure 1 Major gas phase compositions of adiabatically expanding vapor of CI chondrites.

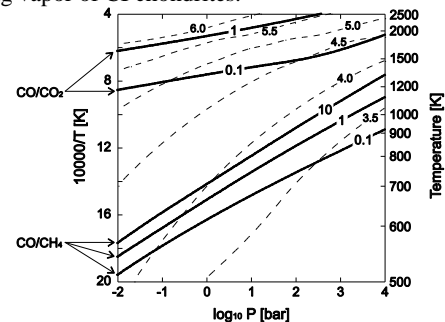


Figure 2 The CO/CO_2 and CO/CH_4 ratios in the equilibrium composition of CI-chondrites vapor. Solid curves are the labeled ratios of CO/CO_2 and CO/CH_4 . Dashed curves are isentropic cooling curves. The labeling numbers are the entropy in $\text{kJ}/\text{K}/\text{kg}$. The entropy achieved by the most frequent oblique impacts to be 3.5-4.5 $\text{kJ}/\text{K}/\text{kg}$ for Mars and Earth.