METHANE-RICH IMPACT-INDUCED ATMOSPHERES ON MARS AND POST-ACCRETION EARTH.

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Introduction: The composition of impact-induced atmospheres controls planetary climatic conditions during and immediately after accretion. In particular, the chemical composition of the early Mars and Earth atmosphere is extremely important because it may have played an important role in maintaining a warm and wet climate during the young faint young sun period. When an accreting planet grows to Mars size, impact velocity exceeds 5 km/s. In such hypervelocity impacts, the increase in internal energy during the shock compression phase is large enough to induce melting and degassing of impactors. Consequently, young terrestrial planets acquire dense steam atmospheres during the accretion phase [e.g., 1]. Previous studies on impact-generated atmospheres have discussed equilibrium compositions as a function of temperature under constant pressures [2, 3, 4].

In reality, however, impact-induced vapor adiabatically expands. Such behaviors, nevertheless, have not been considered explicitly in the previous studies. Entropy gain during the shock-compression phase controls the temperature-pressure pathway of the decompression phase. In other words, initial conditions of impact strongly influence the chemical compositions of impact-induced vapor. Because the impact-induced entropy gain may be very different between low-impact-velocity cases, such as Mars and post-accretion Earth, and high-impact-velocity cases, such as Earth during the late heavy bombardment (LHB). Thus, the goal of this study is to model chemistry within adiabatically expanding impact-induced vapor, and investigate how sensitively impact-generated atmospheres depend on impact velocity.

Equilibrium calculations: Thermodynamically stable chemical compositions depend on temperature, pressure, and elemental compositions. Thus, constraints on these values are required for modeling chemical compositions of impact-generated terrestrial atmospheres. In this study, we assume CI chondrites as the impactor that mainly contributes volatiles to terrestrial planets during the heavy bombardment [e.g., 5].

To determine the temperature-pressure paths of adiabatically expanding impact-induced vapor, we estimate the entropy gain during the shock-compression phase of chondrites using the Hugoniot equation of state for silica [6]. The impact velocity depends both the impactor population and the gravity of the planet. Because the impactor population would change with time, it is difficult to estimate the mean impact velocity

for a planet. However, in general, the main impactor would have been located near planets during post-accretion phase. Thus, it is likely that impact velocities during post-accretion phase were relatively low. In contrast, later impactors, such as during LHB, would be much faster, because they come directly from the main asteroid belt to Mars and Earth. Based on these assumptions, we estimated the range of the entropy achieved by the most frequent oblique impacts (45°) to be ~4 kJ/K/kg, for low-impact-velocity cases (≤12km/s), such as Mars and post-accretion Earth, and 5-6 kJ/K/kg for high-impact-velocity cases (17-25km/s), such as Earth during LHB.

We calculate the major compositions of a gas and condensed phase in equilibrium with CI chondrites along isentropic lines (4.0-5.5 kJ/K/kg) within a range of pressures (0.01-10000 bars) and temperatures (500-2500 K). The model calculations are performed using a Gibbs free energy minimization code [7]. Elements included in our calculations are H, C, O, N, S (volatiles) and Mg, Al, Si, Fe (major rock-forming elements). Because other minor elements are not considered in our calculations, the compositions of the gas and condensed phase in our calculations may be slightly oxidized than previous studies. Elemental abundances used in our calculations are taken from [8].

Calculation results: The major compositions in the gas phase are shown in Fig. 1. as a function of temperature. The gas composition in equilibrium with CI chondrites is dominated by CO, CO_2, H_2, H_2O, H_2S, and SO_2. In particular, CO_2 and H_2O are constantly more abundant than other gas species. This result is qualitatively consistent with previous studies [2, 3]. However, the abundance of minor reduced species, such as CH_4, is slightly less than that of previous studies under the same temperature-pressure condition. This is probably due to the difference in the elemental compositions used in calculations.

On isentropic curves, the CO/CO_2 ratios decrease as temperature decreases, whereas H_2/H_2O ratio is approximately constant. Sulfur-bearing gases become less abundant as temperature decreases, because sulfur is incorporated into iron at low temperatures. N_2 is always the dominant nitrogen specie under a wide range of temperature-pressure conditions. NH_3 is thermodynamically stable at the pressure only above 10^3.

The entropy state of adiabatically expanding vapor also affects the chemical equilibrium compositions. At low entropy states below around 4.0 kJ/K/kg, CH_4 be-

come thermodynamically stable at high quenching temperatures even above 1000K. This is because the adiabatic curve for low entropy states undergoes higher pressures at a given temperature. High pressure is favorable for the formation of polyatomic molecules, such as CH_4 and NH_3; i.e., Le Chatelier's principle.

The major compositions in the condensed phase are also shown in Fig. 1. In our calculations, $MgSiO_3$ is always the dominant condensed specie. Other less abundant magnesium silicate and oxide are Mg_2SiO_4 and $MgAl_2O_4$. The abundance of these magnesium oxides is approximately constant regardless of temperature-pressure conditions used in our calculations. Iron-bearing species condense out as $Fe_{0.947}O$, FeS, and Fe_3O_4. At low temperatures below around 1600 K, $Fe_{0.947}O$ becomes more thermodynamically unstable than FeS and Fe_3O_4, and the temperature at which $Fe_{0.947}O$ transforms into FeS or Fe_3O_4 becomes higher at low entropy states.

Oxygen partition between gas and solid phases: As entropy decreases, the CO/CO_2 ratios and H_2/H_2O ratios decrease, whereas H_2S/SO_2 ratios increase. This interconversion of oxygen occurs not only in the gas phase but also in the condensed phase. As mentioned above, iron sulfides become more stable than iron oxides at low temperatures. Consequently, oxygen combined with iron or sulfur is released into the gas phase as temperature decreases. In the range of temperatures and pressures used in our calculations, oxygen abundances in magnesium oxides and silicates are approximately constant, whereas that in other major oxygen-bearing species are variable. Given this variation in oxygen phase partitioning, the net reaction which interconverts oxygen between a gas and condensed phase is as follows:

$$2CO(g) + H_2(g) + H_2S(g) + SO_2(g) + 2FeO$$
$$\leftrightarrows 2CO_2(g) + 2H_2O(g) + 2FeS \quad (1)$$
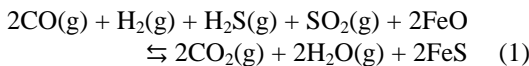
Reaction (1) tends to shift to right side at lower entropy states, because the temperature range thermodynamically favorable for the formation of iron sulfide becomes wider.

High-temperature formation of CH_4: For the vapor of CI chondrites, at low entropy states below around 4.0 kJ/K/kg, CH_4 becomes thermodynamically stable regardless of temperature. Previous studies have shown that CH_4 is thermodynamically stable at low temperatures only below around 1000K under constant pressures (1~100bar) [2, 3, 4]. Thus, it has been widely believed that the catalytic reaction, such as the Fischer-Tropsch reaction, is required for the formation of CH_4 because the conversion of $CO \rightarrow CH_4$ is thought to be kinetically inhibited at low temperatures [2]. However, we found that the P-T curve at which CO transforms into CH_4 is roughly along isentropic curves as shown

in Fig. 2. This suggests that the entropy of adiabatically expanding vapor may determine the formation of CH_4. Consequetly, the atmospheres of Mars and post-accretion Earth generated by low-velocity impacts ($\leq$12km/s) may have been rich in CH_4, whereas that of Earth during the LHB with higher average impact velocities ($\geq$17km/s) may have been poor in CH_4.

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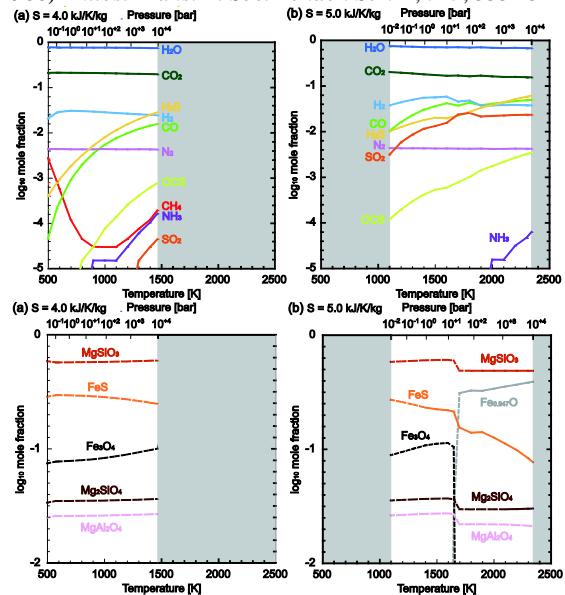
Fig. 1. Major gas phase and condensed compositions of adiabatically expanding vapor of CI chondrites. The entropy used in each calculation is (a) 4.0 kJ/K/kg, (b) 5.0 kJ/K/kg. Grey area represents out of range in our calculations.
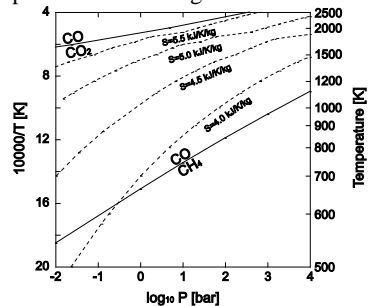
Fig. 2. Equimolar curves of CO/CO_2 and CO/CH_4 in the composition of CI chondrites vapor. Solid curves are the equimolar ratios of CO/CO_2 and CO/CH_4. Dashed curves are isentropic P-T curves. The entropy achieved by the most frequent oblique impacts to be ~4 kJ/K/kg for Mars and post-accretion Earth, and 5-6 kJ/K/kg for Earth during LHB.