METHANE FORMATION AND RETENTION ON TITAN AND TERRESTRIAL PLANETS. A. E. Gilliam[1] and A. Lerman[1], [1]Department of Earth and Planetary Sciences, Technological Institute F-379, 2145 Sheridan Road, Northwestern University, Evanston IL 60208-3130, ashley@earth.northwestern.edu

Introduction: Much research has been done on the behavior of CH_4 in Titan's atmosphere, including its photolytic decomposition to other hydrocarbons and escape from the atmosphere (e.g., [1][2][3][4][5]), but its possible origin is poorly understood on the planets and satellites other than Earth.

We examine the possibility of methane formation in a number of gas-gas and solid-gas reactions, based on chemical thermodynamic equilibria under the conditions approximating the reported atmospheric composition of Titan and the Terrestrial planets – Mercury, Venus, Earth, and Mars. The paths to chemical equilibrium provide insight into the retention of methane in the atmosphere of different planets vs. the possibility of its escape. This study does not imply that the equilibrium reactions *in fact occur*, but they *may occur* on thermodynamic grounds.

Methane Forming Reactions: The five reactions below may be responsible for the formation of methane on the Terrestrial planets and Titan. Equilibria in the system C-H-O, where oxygen fugacities are buffered by the coexisting phases in the system Fe-FeO-Fe_3O_4-Fe_2O_3 have been extensively studied by many authors with reference to the magmatic interior of primordial Earth (e.g., [6][7]). In this study, the possible production of methane is limited to the planetary atmospheres in contact with mineral solids.

Three reactions of CH_4 production:

R1 $C_{(s)} + 2H_{2(g)} \longrightarrow CH_{4(g)}$

R2 $2C_{(s)} + 2H_2O_{(g\ or\ l)} = CH_{4(g)} + CO_{2(g)}$

R3 $CO_{2(g)} + 4H_{2(g)} = CH_{4(g)} + 2H_2O_{(g)}$

Two reactions of serpentinization of iron-olivine fayalite that produce CH_4 from H_2O and C in graphite or CO_2:

R4 $3Fe_2SiO_4 + 2H_2O_{(g)} + C = 2Fe_3O_4 + 3SiO_2 + CH_{4(g)}$

R5 $6Fe_2SiO_4+2H_2O_{(g)}+CO_{2(g)} = 4Fe_3O_4+6SiO_2+CH_{4(g)}$

Equilibrium Reactions Producing CH_4: For reactions R1-R5, the equilibrium constants as a function of temperature can be calculated from:

$$\log K = -\Delta G^{\circ}_{r,T}/(2.3RT)$$

where K is the equilibrium constant, R is the gas constant (kJ mol^{-1} K^{-1}), T is temperature (K), and $\Delta G_r°$ is the Gibbs standard free energy change of the reaction (kJ mol^{-1}) at temperature T, computed from the data in [8]. The value of log K as a function of T for reactions R1-R5 are plotted as curves in Fig. 1. The equilibrium partial pressures of CH_4 in reactions R1-R5 are computed from log K, the activities of the pure solid components ($a_{mineral}$), and reported partial pressures of other reactant gases (p, in bar), taken as ideal gases, and are shown in Fig. 2. For primordial Earth [11] at 700 K and 342 bar atm. pressure, a small correction to log K is

$$\log K_{P>1} = \log K_{P=1} - \Delta\bar{V}_r(P-1)/(2.3RT)$$

where $\bar{V}_r$ is the reaction volume change (cm^3/mol).

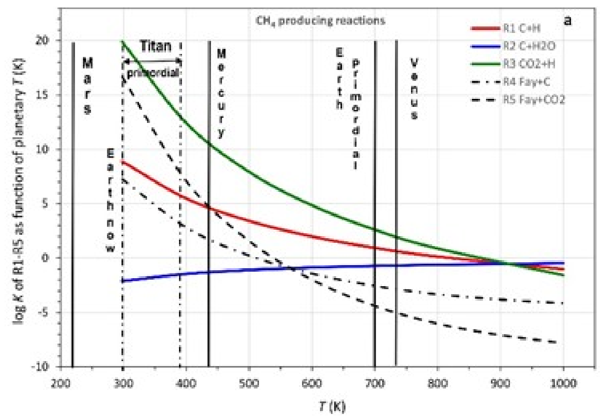

Fig. 1. Equilibrium constants log K for reactions R1-R5 as a function of temperature. Vertical lines show planetary temperatures.

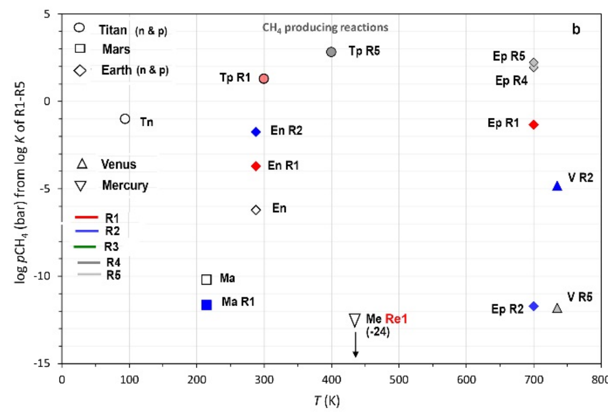

Fig. 2. Calculated CH_4 partial pressures from planertary atmosphere data.

Discussion of Methane-Producing Reactions: For the aforementioned five gas-gas and solid-gas reactions, R1-R5, we estimate the amount of methane that might have been produced on Titan and the Terrestrial planets.

(T, Titan) The assumed composition oc the primordial atmosphere of Titan, shortly after its accretion about 4.5 Ga, was about 80% CH_4 or 19.4 bar, and 20% NH_3 or 6 bar, at the accretion temperature of 300 to 355 K [9]. At present, it is 0.1 bar CH_4 and 1.4 bar N_2. The abundance of solid carbon as graphite in meteorites [4] and of H_2 in the Universe suggests that reaction R1 might have been a likely mechanism of formation of primordial CH_4. On Titan, reaction R1 between graphite and hydrogen gas can give partial pressures of CH_4 close to the model-computed value of 19.5 bar, if $pH_2 \geq 10^{-4}$ bar. Serpentinization reaction R4 that might have occurred on Titan [2] gives a higher partial pressure of CH_4, about 700 bar. This would account for an internal reservoir of CH_4 in Titan's interior that is needed to replenish the photolytic conversion of CH_4 to other hydrocarbons.

(Ma, Mars) Mean surface temperature of Mars is 210 to 215 K, below the freezing point of water. However, the temperature range (diurnal and seasonal) is from 133 to 303 K, and this lends to the possibility that reaction R2, CO_2 and atmospheric H_2O [10] makes a likely source of CH_4.

(E, Earth) Earth's rich atmospheric chemistry unlocks the use of multiple CH_4 producing reactions. On present-day Earth, the production of CH_4 is primarily biogenic near the surface and inorganic at depth. If reactions R1 and R2 were active on Earth in the recent, they would have produced reasonable values of log pCH_4 = -3.71 and -1.74, respectively, compared to observed log pCH_4 of -6.22 to -5.74.

(V, Venus) The Venusian atmosphere is hot and dense, and is presently devoid of CH_4. However, as a geologically likely situation, we apply reaction R2 between CO_2 and H_2O to the present-day composition of Venus. The result is a low partial pressure of methane, log pCH_4 = -4.83 or 1.5×10^{-5} bar, owing to the low partial pressure of H_2O. In reaction R2, CH_4 competes with CO_2 that is present at a high partial pressure in the Venusian atmosphere. However, in reaction R5, where fayalite, H_2O, and CO_2 drive the reaction towards CH_4, the equilibrium value of log pCH_4 is much lower, -11.8 because of the low abundance of H_2O vapor in Venus' atmosphere.

(Me, Mercury) Measurements of the Mercurian atmosphere at about 440 K also show that it is completely bereft of CH_4, but contains H_2. In an approximation to the geologically likely occurance of graphite in Mercury's crust, we apply reaction R1 to the known present-day composition, and calculate a possible log pCH_4 of -23.8 bar, indicating that practically no CH_4 should form in its atmosphere.

Potential Retention or Escape of CH_4 from Planets: If CH_4 were formed from the aforementioned reactions, would it have escaped or been retained in the atmospheres of the individual planets? The escape of a gas from an atmosphere depends on the fraction of the population of the gas molecules whose velocities are greater than the escape velocity of the planet. Gas escape rate parameter k (yr^{-1}) is defined as [9, with references]:

$$k = \frac{\mathcal{F}(v \geq v_e) \cdot \bar{v}_{>v_e} \cdot S_{\text{atm}}}{2V_{\text{atm}}}$$

where $\mathcal{F}(v \geq v_e)$ is a fraction of the Maxwell-Boltzmann frequency distribution of the gas molecules' velocities greater than Titan's escape velocity, $\bar{v}_{>v_e}$ (m/s) is the mean velocity in the interval $v \geq v_e$, and the quotient V_{atm}/S_{atm} (m) of the atmosphere volume to its outer surface area is effectively the scale thickness of the atmosphere. The calculated values of k for CH_4 are shown as a function of planetary T in Fig. 3. If CH_4 were produced on Mercury, the planet's high temperature would have made the escape of CH_4 as possible as on Titan. On Mars, Venus, and on primordial Earth, retention of CH_4 would have been more likely because of the much smaller values of k and larger escape velocities on the latter three planets.

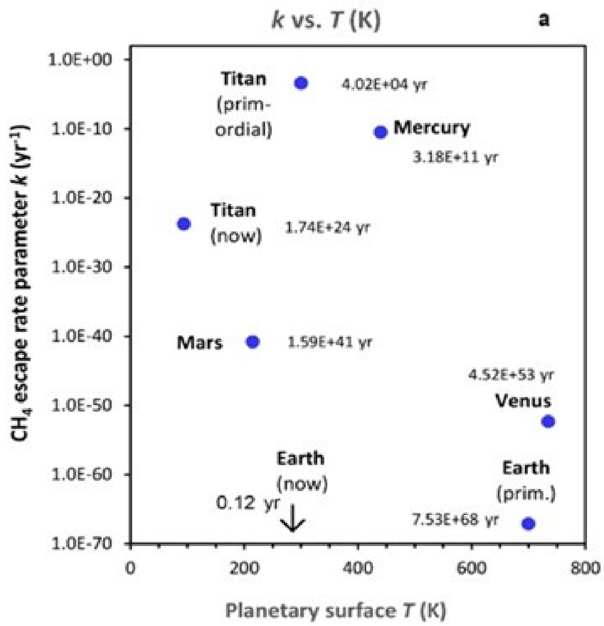

Fig. 3. CH_4 escape rate parameter k (yr^{-1}) vs. planetary temperature. Numbers in yr next to the planets' names are CH_4 residence times ($1/k$).

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