A METHANE-RICH EARLY MARS: IMPLICATIONS FOR HABITABILITY AND THE EMERGENCE OF LIFE. M. L. Wong<sup>1</sup>, P. Gao<sup>2</sup>, A. J. Friedson<sup>3</sup>, Y. L. Yung<sup>1,3</sup>, M. J. Russell<sup>3</sup> <sup>1</sup>California Institute of Technology, Division of Geological and Planetary Sciences (mlwong@caltech.edu), <sup>2</sup>NASA Ames Research Center, <sup>3</sup>NASA Jet Propulsion Laboratory

We present radiative transfer and photochemical models for the atmosphere of a young Mars-like planet that outgasses carbon primarily in the form of CH<sub>4</sub> rather than CO2. While volcanic emissions on Earth have always been high in CO<sub>2</sub> and low in CH<sub>4</sub>, this may not be the case for smaller terrestrial planets. All rocky bodies in the Solar System formed from planetesimals that, based on meteoritic studies, are generally at or below the iron-wüstite buffer and contain reduced organic compounds [1]. In spite of this, Earth's mantle has existed in a high oxidation state throughout geologic history thanks to ferrous iron's tendency to disproportionate to ferric and native iron in the presence of silicate perovskite [2,3]. The spinel-toperovskite transition occurs at 24 GPa and 1900 K; on Earth, this creates the 660 km discontinuity [4]. Mantles of smaller terrestrial bodies may never reach the requisite pressure and temperature for this phase change. If a Mars-sized planet had a lower oxygen fugacity mantle, magmatic outgassing would have produced a CH<sub>4</sub>-rich atmosphere [5]. In addition, impact degassing would have contributed a sizeable amount of  $CH_4$  to the atmosphere [6]. These processes would be expected for any Mars-sized exoplanet.

A CH<sub>4</sub> atmosphere has profound implications for the emergence of life on a wet, rocky world. According to the alkaline hydrothermal vent theory, nascent life gained its carbon and energy by burning CO<sub>2</sub> with hydrothermal H<sub>2</sub> and perhaps CH<sub>4</sub> [7,8,9]. A terrestrial world whose atmosphere is laden with CH<sub>4</sub> would not drive the emergence of metabolism in such a manner; instead, it may exhibit prebiotic chemistry similar to that of Titan. However, the presence of H<sub>2</sub>O may oxidize the outgassed CH<sub>4</sub> to CO<sub>2</sub>; if this process is efficient enough, there will be CO<sub>2</sub> aplenty for life.

On the other hand, if  $CH_4$  is destroyed too efficiently, then a young Mars-sized planet may lose the greenhouse warming necessary to maintain liquid water at the surface. Atmospheric models have demonstrated that a purely CO<sub>2</sub> atmosphere, even one as massive as 7 bars, is incapable of heating Mars above an annualmean surface temperature of 273 K [10], although recent studies show that recurring wet states could have been induced in an H<sub>2</sub>-rich atmosphere [11,12]. While  $CH_4$  alone is probably insufficient to warm the planet above freezing, it would raise middle atmosphere temperatures and prolong the photochemical lifetime of  $SO_2$ , another potent greenhouse gas.

Using the non-gray 1-D radiative-convective equilibrium model "RC1D" and the Caltech/JPL 1-D chemistry transport model "KINETICS" [11], we investigate the chemistry of a C-H-N-O atmosphere blanketing a ~0.5 Gyr-old Mars-like world orbiting a Sun-like star at 1.52 AU. The atmosphere is sourced from CH<sub>4</sub>-N<sub>2</sub> outgassing, in vapor pressure equilibrium with an H<sub>2</sub>O ocean [14] or massive glaciation [15], losing hydrogen to space via hydrodynamic escape, and irradiated by the spectrum of the faint-young Sun. RC1D is be used to calculate the atmospheric thermal structure consistent with the radiative heating and cooling associated with the composition computed at each chemical model time step, the Sun's luminosity at that time, and global average insolation conditions. KINETICS will determine how effectively the CH<sub>4</sub> can be oxidized to CO<sub>2</sub> and evaluate the synthesis of organic molecules in the atmosphere. This study is a step towards a grander, more realistic model of Mars-like terrestrial planets that includes sulfur chemistry, atmospheric dust and haze, and aqueous chemistry.

References: [1] C.W. Dale, K.W. Burton, R.C. Greenwood, A. Gannoun, J. Wade, B.J. Wood, D.G. Pearson, Science 336 (2012) 72-75. [2] C. a. McCammon, Nature 387 (1997) 694–696. [3] B.J. Wood, M.J. Walter, J. Wade, Nature 441 (2006) 825-833. [4] L. Chudinovskikh, R. Boehler, Nature 411 (2001) 574-577. [5] M. Wadhwa, Science 291 (2001) 1527-1530. [6] L. Schaefer, B. Fegley, Icarus 186 (2007) 462-483. [7] W. Martin, J. Baross, D. Kelley, M.J. Russell, Nat. Rev. Microbiol. 6 (2008) 805-814. [8] M.J. Russell, A.J. Hall, W. Martin, Geobiology 8 (2010) 355-371. [9] M.J. Russell, L.M. Barge, R. Bhartia, D. Bocanegra, P.J. Bracher, E. Branscomb, R. Kidd, S. McGlynn, D.H. Meier, W. Nitschke, T. Shibuya, S. Vance, L. White, I. Kanik, Astrobiology 14 (2014) 308-343. [10] F. Forget, R. Wordsworth, E. Millour, J.B. Madeleine, L. Kerber, J. Leconte, E. Marcq, R.M. Haberle, Icarus 222 (2013) 81–99. [11] N. Batalha, S.D. Domagal-Goldman, R. Ramirez, J.F. Kasting, Icarus 258 (2015) 337-349. [12] N.E. Batalha, R.K. Kopparapu, J. Hagq-Misra, J.F. Kasting, Earth Planet. Sci. Lett. 455 (2016) 7-13. [13] H. Nair, M. Allen, A.D. Anbar, Y.L. Yung, R.T. Clancy, Icarus 111 (1994). [14] G.L. Villanueva, M.J. Mumma, R.E. Novak, H.U. Kaufl, P. Hartogh, T. Encrenaz, A. Tokunaga, A. Khayat, M.D. Smith, Science 348 (2015) 218-221. [15] J.L. Fastook, J.W. Head, Planet. Space Sci. 106 (2015) 82-98.