EXPLORING A POTENTIALLY SIGNIFICANT NEW(?) MECHANISM FOR METHANE GENERATION ON MARS. M. Fries[1], [1]NASA Astromaterials Acquisition and Curation Office, Johnson Space Center, Houston, Texas 77058. marc.d.fries@nasa.gov

Introduction: An unexplored mechanism for methane production on Mars is presented here. Meteor showers have been hypothesized [1] as an explanation for episodic martian methane events [2-7], as the timing of meteor showers consistently correlates with the episodic methane events. The hypothesis [1] relied on production of methane via UV photolysis of extraterrestrial carbonaceous material [8,9] following dissemination of material into the martian atmosphere and onto the surface. Recently, new insights have emerged about an overlooked mechanism for methane production – *plasma methanation* [10,11] of martian atmospheric CO_2 in meteor plasma. This mechanism can generate methane in addition to that produced by the previously explored methods of direct thermal evolution and UV photolysis, adding to the total methane budget produced through meteor infall. It also delivers methane in a rapid manner consistent with past observations of episodic methane “plumes” on Mars, and at altitudes where methane is rapidly removed afterwards. Methane produced by plasma methanation occurs at high altitude, which matches observations made on Mars where measurements collected through the full thickness of the martian atmosphere are of consistently higher methane concentrations (>10 ppbv [2-6]) than those recorded on the surface by the Mars Science Laboratory (MSL) rover (<10 ppbv [7]). High-altitude methane should be detected by the ESA Trace Gas Orbiter (TGO) which has not noted any methane to date. This result is puzzling regardless of the source of methane, but may be explained by the random nature of meteor shower outbursts – a significant infall may simply not have occurred (yet) during the ~3-Earth-year period of TGO observations.

Plasma Methanation: Methane is generated from CO_2 plasma by addition of hydrogen, or *methanation* [10,11]. This method, also called the *Sabatier reaction*, is an efficient producer of methane that has been proposed for manufacturing methane for fuel from the martian atmosphere [many refs, e.g. 12]. It has also been proposed as a contributor of methane to the early Earth’s atmosphere [13]. It is technically not a new discovery, but its place as a source of episodic martian methane has not been explored. Methanation reactions pertinent to martian meteor plasma chemistry are chemically simple and exothermic, to include [14]:

1) $CO + 3 H_2 \rightarrow CH_4 + H_2O$ $\Delta H_{298} = -206.1$ kJ.mol
2) $CO_2 + 4 H_2 \rightarrow CH_4 + 2 H_2O$ $\Delta H_{298} = -165.0$ kJ/mol
3) $2 CO + 2 H_2 \rightarrow CH_4 + CO_2$ $\Delta H_{298} = -247.3$ kJ/mol

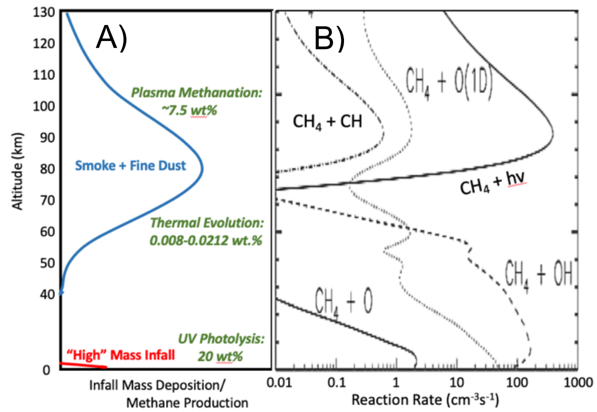

Figure 1:A) Diagram showing meteorite fall behavior on Mars, with most mass deposited as smoke and fine dust in the upper atmosphere with a maximum around 80 km altitude. Three methods of methane production appear with CH_4 wt.% yield (green text): plasma methanation [this abstract], direct thermal evolution [15], and UV photolysis of carbon solids [8,9]. *B)* Comparison of methane destruction mechanisms [from 16] showing how methane produced above ~75 km is rapidly removed by UV photolysis (CH_4+h*v*), possibly explaining rapid loss of methane from Mars. Note the logarithmic X axis scale.

To perform these reactions on Mars, the only requirements are an energetic plasma and hydrogen – the CO_2 is provided by Mars’ atmosphere. Meteors are energetic plasmas, and cometary-origin meteor shower infall is rich in hydrogen which evaporates readily. These reactions are not seen in meteors on Earth because our atmosphere is CO_2-poor, but abundant hydrogen release from meteors has been observed [17]. Reaction times in meteor plasma will be short, but ion temperatures readily exceed 4,400 K [14] and dissociation is complete for small objects in particular, driving methanation. Jenniskens and Stenbaek-Nielsen [13] found that, in a CO_2 atmosphere, all CO_2 would dissociate to CO and O at 4,300 K, driving Sabatier reactions and, “making meteors a relatively efficient source of reduced molecules in an oxidizing atmosphere” [18]. Faster meteors do not produce appreciably higher plasma temperatures, but do generate larger reactor volume and hence a greater reaction yield [*ibid*].

Meteors and Hydrogen: Meteors are visibly luminous plasmas generated by the infall of cosmic dust and meteoroids. These bodies arise from either the randomly distributed material of the sporadic cosmic dust background, or in debris streams shed by comets which closely follow their parent comet's orbit. These debris streams generate meteor showers when a planet's course intersects them. While sporadic meteors originate from both comets and asteroids are assumed to consist of approximately 32wt.% refractory organic materials [19] overall, meteor shower meteors originate directly from comets and feature a greater abundance of carbon. The COSIMA instrument on board the Rosetta mission to comet 67P/Churyumov-Gerasimenko directly measured cometary material to contain ≥45wt.% carbon with a H/C ratio of ~1 [20]. Therefore meteor shower infall carries a greater abundance of both carbon and hydrogen. A 1:1 ratio of hydrogen to carbon and ≥45wt.% carbon which translates to ≥0.083 mol C per gram of infall and therefore 0.083 mol H/g, 0.0046 mol H overall (assuming Eqn. 2 from the previous list dominates), and therefore ≥0.075g CH_4 per gram of infall mass. This yield rate of 7.5wt.% methane yield assumes complete transfer of hydrogen from the original meteoroid, which is reasonable for the 29% of infall mass Flynn [21] calculated to vaporize on infall, and close to this value for the larger 71% reduced to a refractory carbon-bearing residuum by meteor plasma ion temperatures in excess of 4,000 K [17]. A portion of the surviving infall mass range will still be subject to methane production via UV photolysis [8,9], as will meteoritic smoke [1], allowing a portion of the infall mass to produce methane by direct evolution, plasma methanation, UV photolysis, or a combination thereof. Experiments are needed to refine the total methane yield in this complex system.

Most infall mass is deposited in the upper atmosphere (Figure 1) as fine dust and smoke, leading to the possibility that methane is produced at high altitude both in plasma methanation and UV pyrolysis of freshly dissociated, suspended infall. The extent of each is unknown, but the result should be rapid and nearly complete degradation of the original carbon into methane. For small meteors, all mass is dissociated [21], and even large falls deposit most of their mass into the upper atmosphere. A good example of this behavior is the Almatta Sitta (AS) meteorite fall, which produced a fireball similar to cometary-origin infall [22]. Popova (2011) [23] found that ~70% of AS evaporated in its fireball, producing ~25,000 kg of suspended dust while only 39±6 kg of meteorites reached the ground [22]. If both plasma methanation and UV pyrolysis contribute methane from infall events, the amount of methane produced may have been underestimated to date.

Summary: A previously unexplored hypothesis for methane formation on modern Mars – methanation of atmospheric CO_2 via meteor plasma – has been presented for consideration. This mechanism appears to feature a high methane yield, and operates in addition to other potential sources of methane to include UV photolysis, serpentization, decomposition of clathrates, biology, etc. Regardless of whether all or none of martian methane is biological in origin, a critical step in assessing potential biogenicity of martian methane is a full understanding and accounting of all abiogenic sources. This hypothesis is an important part of that process.

It is worth noting that this process should function on other planets with a CO_2-majority atmosphere, to include exoplanets and Venus. To date, Venus has not been examined for episodic methane similar to that noted on Mars. Perhaps we should do that.

Experiments are needed to test this hypothesis, but should be reasonable to produce. A suitable experiment would measure production of methane, water, and other potential products from a suitable cometary analogue in a short-lived CO_2 plasma exceeding 4,000 K. Examination of the refractory residuum is also necessary, to assess the potential for methane production from UV photolysis of residual carbon.

References: [1] Fries, M., et al , 2016. *Geochem. Perspect. Lett.,* 2, pp.10-23. [2] Krasnopolsky, V.A., et al., 1997. *JGR: Planets,* 102(E3), pp.6525-6534. [3] Krasnopolsky, V.A., et al 2004. *Icarus*, 172(2), pp.537-547. [4] Mumma et al. (2009) *Science* 323:1041-1045. [5] Krasnopolsky, V.A., 2012. *Icarus*, 217(1), pp.144-152.[6] Formisano, V., et al 2004. *Science*, 306(5702), pp.1758-1761. [7] Webster, et al 2015. *Science*, 347(6220), pp.415-417. [8] Keppler, F., et al 2012. *Nature*, 486(7401), p.93. [9] Schuerger, et al 2012. *JGR: Planets*, 117(E8). [10] Rönsch, S., et al 2016. Fuel, 166, pp.276-296. [11] Wei, W. and Jinlong, G., 2011. *Front. Chem. Sci. and Eng*., 5(1), pp.2-10. [12] Sullivan, T.A et al 1995. *J. of Prop. and Power*, 11(5), pp.1056-1062. [13] Jenniskens, P. and Stenbaek-Nielsen, H.C., 2004. *Astrobiology*, 4(1), pp.95-108. [14] Gao, J., et 2012. *Rsc. Advances*, 2(6), pp.2358-2368. [15] Court, R.W. and Sephton, M.A., 2009. *EPSL*, 288(3-4), pp.382-385. [16] Wong, A.S., et al 2003. *JGR: Planets*, 108(E4). [17] Jenniskens, P. and Mandell, A.M., 2004. *Astrobiology*, 4(1), pp.123-134. [18] Jenniskens, P., et al 2004. *Astrobiology*, 4(1), pp.81-94. [19] Greenberg, J.M. and Li, A., 1999. *Space Sci. Rev*., 90(1-2), pp.149-161. [20] Isnard, R., et al, 2019. *Astron. & Astrophys.,* 630, p.A27. [21] Flynn, G.J., 1996. In Worlds in Interaction: Small Bodies and Planets of the Solar System (pp. 469-474). Springer, Dordrecht. [22] Shaddad, M.H., et al, 2010. *MAPS* 45(10-11), pp.1557-1589. [23] Popova, O., 2011. In Meteoroids: The Smallest Solar System Bodies; p. 232-242