A PROPOSED UV/CH4 LINKED MODEL FOR THE GLOBAL METHANE BUDGET ON MARS. A. C. Schuerger[1], J. E. Moores[2], C. Clausen[3], N. G. Barlow[4],and D. Britt[3]. [1]University of Florida, Bldg. M6-1025, Space Life Sciences Lab, Kennedy Space Center, FL 32899; email: schuerg@ufl.edu; [2]Physics and Astronomy Dept., University of Western Ontario, London, Ontario, Canada, N6A 3K7; john.e.moores@gmail.com [3]Dept. of Chemistry, University of Central Florida, Orlando, FL 32816; email: clausen@mail.ucf.edu; [4]Dept. of Physics and Astronomy, Northern Arizona University, Flagstaff, AZ 86011; nadine.barlow@nau.edu [5]Dept. of Physics, University of Central Florida, Orlando, FL 32816; email: britt@physics.ucf.edu.

Introduction: Methane (CH_4) has been detected in the martian atmosphere at a global mixing ratio of 10-15 ppbv with spatial and temporal variations ranging between 0 and 45 ppbv [1,2,3,4]. Furthermore, spatially constrained methane plumes up to 45 ppbv have been observed but appear to only persist for a few months [1,5]. However, the lifetime of CH_4 in the Martian atmosphere appears to be ~ 340 years [6] due to photocatalytic processes in the upper atmosphere. Thus, if the CH_4 detected on Mars is to be maintained, an active and contemporary source of CH_4 evolution must persist near the surface on in the atmosphere. Because most CH_4 on Earth is derived primarily from biological processes [7], there has been great interest in the detection of CH_4 on Mars. Furthermore, the dissipation of CH_4 plumes over a period of a few months argues strongly against a subsurface process, and suggests that an impact-related mechanism may be involved in the production of CH_4 plumes on Mars.

Reviews of recent literature [8,9] suggest that at least eight possible mechanisms may be involved in the production of CH_4 on Mars including (not in priority): (1) outgassing from comet and asteroid impacts, (2) outgassing from interplanetary dust particles (IDPs), (3) subsurface clathrates, (4) subsurface serpentinization of olivine, (5) UV photolysis of H_2O in the presence of CO yielding intermediates that can quickly recombine to form methane, (6) geothermal outgassing, (7) presumptive biological processes, and (8) UV photolysis of organics. Of these mechanisms, the UV photolytic process for the formation of methane on Mars (henceforth, the UV/CH_4 model) has been confirmed recently for organic carbon, but not inorganic carbon, under simulated martian conditions [8] and will be the mechanism studied here.

Materials and Methods: A Mars Simulation Chamber (MSC; Fig. 1) was used to create conditions similar to equatorial Mars (details described in [10]). The MSC system can accurately simulate five key components of the surface environment of Mars including: (a) pressures down to 0.1 mb; (b) UVC, UVB, and UVA irradiation from 190 to 400 nm; (c) dust loading in the atmosphere from optical depths of 0.1 to 3.5; (d) temperatures from –100 to +30 C; and (e) an atmospheric mixture of CO_2 (95.53%), N_2 (2.7%), Ar (1.6%), O_2 (0.13%), and H_2O (0.03%). Two Organic

Reaction Vessels (ORV; Fig. 1, right) were placed on the upper surface of a liquid nitrogen thermal control plate, and fitted with gas sampling lines.
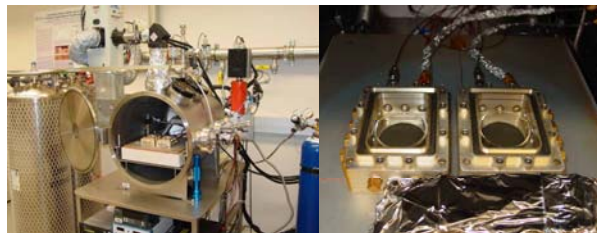

Fig. 1. Mars Simulation Chamber (MSC) (left); and Organic Reaction Vessels (ORV's) loaded with 1-g each of crushed Murchison (right).

Experimental procedures. Organic (C) compounds (i.e., reagent grade organics and crushed carbonaceous chondrites) were loaded into the ORV units (Fig. 1, right), the ORV's were closed, the Mars chamber sealed, and all components equilibrated at the martian conditions required for each test. Ultraviolet irradiation was then applied to the top surfaces of the organic compounds at a rate of 4.1 W/m^2 (3.6 kJ/m^2/hr) for UVC (200-280 nm). The atmospheric pressure was maintained at 6.9 mb with a Mars gas mixture (see above). The temperature was maintained between -80 to 20 ^{o}C. The organic compounds were exposed either 8 hrs (reagent-grade organics) or 24 h (carbonaceous chondritic samples), and then gas samples collected from the head space over each material in each ORV. The sampling procedure was tested and calibrated extensively with a series of controlled lab standards. Results from the calibration assays indicated that the accuracy of quantitative CH_4 measurements in the MSC/ORV system was in the range of +/- 0.5 ppm.

Methane evolution rates from crushed and sieved Murchison samples ($\leq$ 212 µm particles) exposed to martian conditions at 20 ^{o}C were combined with a Mars UV model [11] to model the global methane budget from accreted IDP organics [12]. Impact models [13] were used to estimate the size, impact angles, and masses of bolides that might deliver large quantities of organics to the martian atmosphere or surface with the goal of determining if a carbonaceous bolide of sufficient size could deliver adequate organics to explain the observed CH_4 plumes on Mars [1,5].

Results: All organic compounds evaluated in the experiments yielded CH_4 when exposed to UV irradiation under martian conditions. Schuerger et al. [8] presented results of the reagent-grade organics, and demonstrated that CH_4 was evolved from all organic (#15 materials), but not inorganic (#2), compounds, and suggested that the hydrogen (H) was derived directly from the parent organics and did not involve UV photochemistry in the bulk atmosphere present in the headspace of the ORV units. Furthermore, kapton tape was identified as a potential source for CH_4 contamination during the upcoming MSL mission.

In new experiments with crushed carbonaceous chondritic materials (#4 chondrites tested), CH_4 was again evolved from all samples with quantifiable organics. Methane evolution rates from carbonaceous chondrites were found to be positively correlated to temperature (-80 to 20 ^{o}C) and the concentration of organic carbon in the chondrites, and decreased over time with Murchison samples (1.69 wt% C) exposed for 20 days to martian conditions at 6.9 mbar (simulating 120 sols on equatorial Mars). Using a Mars UV model [11], the quantum efficiency (QE) was estimated at 5.2 x 10^{-13} mol J^{-1} for Murchison tested at 20 ^{o}C under martian conditions.

Most carbon (90%) accreting to Mars is in the form of organics on IDP particles containing on average 10 wt% carbon [12]. The QE from the Mars chamber experiments using Murchison organics was used to model the global methane budget based on a 10 wt% C content of accreted IDP and small-mass carbonaceous chondrites. Results suggested that if 100% of IDP organics were converted to CH_4, the global average of CH_4 would approach 11 ppbv over geological time, and might explain at least a portion of the global average of 10-15 ppbv observed on Mars [1,2,3,4]. However, because the accretion of IDP organics is isotropic, the UV/CH_4 model from IDP organics alone cannot explain latitudinal, seasonal, or plume heterogeneity of CH_4 detected on Mars [1,3,5]. Even though UV fluence rates and temperature vary in space and time on the surface, the effects of both factors on the evolution of CH_4 from organics do not yield the dynamic range of the reported fluctuations in the martian atmosphere.

Using impact models for low-density unconsolidated bolides (e.g., a rubble-pile comet) [13], and with a set of assumptions for a high-angle (80° off-nadir) airburst beginning at 150 km, it was estimated that a 150-m bolide with 11 wt% C could break-up in a series of dispersing airbursts that would distribute adequate mass (1.8 x 10^9 kg) over a wide enough area (9 x 10^6 km^2) to plausibly explain the 45 ppbv CH_4 plumes reported by Mumma et al. [5]. Although the airburst

delivery of adequate C for the UV/CH_4 process to produce 45 ppbv plumes would be rare, if such events occurred once on average every 10-20 years, the injection of CH_4 into the martian atmosphere would be adequate to periodically create high-concentration CH_4 plumes without requiring ultra-short CH_4 lifetimes, as is currently implicated by the dispersion of plumes over short time scales [1,5].

Discussion: The UV/CH_4 model suggests that methane derived from UV irradiation of IDP organics may be a significant source of CH_4 on Mars, and may explain a portion of the global average of ~ 10 ppbv [1,2,3,4]. If infrequent airbursts of low-density rubble-pile like bolides (≥11 wt% C) occur on Mars, the delivered surge in organics could be acted upon by the UV/CH_4 process to yield transient plumes of up to 45 ppbv and lasting for up to 120 sols. Although the airburst scenario requires unusual impact dynamics of a rare low-density bolide, the UV/CH_4 model predicts (1) a global average of no more than 11 ppbv from accreting IDP particles, (2) infrequent CH_4 plumes up to 45 ppbv that can dissipate quickly over time, and (3) does not require an ultra-fast CH_4 destruction mechanism in the martian atmosphere. Future research is required to further constrain the assumptions of the UV/CH_4 model, but the advantage of the model is that it is based on two widely accepted processes on Mars: (1) accretion of IDP organics [12], and (2) UV photons down to 190 nm reaching the surface [11]. UV photons between 200 and 400 nm have been shown to degrade organics yielding CH_4 under various martian conditions [8,9,14]. If we accept the two assumptions given above, then the current work, might plausibly explain a portion of the global CH_4 budget on Mars.

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