AN ASSESSMENT OF THE METEORITIC CONTRIBUTION TO THE METHANE COMPONENT OF THE MARTIAN ATMOSPHERE. K. Nazarava[1], M.A. Sephton[1] and P.A. Bland[1], [1]Impacts and Astromaterials Research Centre (IARC), Department of Earth Science and Engineering, Imperial College London, South Kensington Campus, SW7 2AZ, London, UK, e-mail: katsiaryna.nazarava@imperial.ac.uk.

Introduction: Methane has been detected in the Martian atmosphere at an average concentration of 10±5 ppbv according to recent PFS observations [1]. Total photochemical loss of CH_4 in the Martian atmosphere is equal to 2.2x10^5 cm^{-1} s^{-1}, and methane should be uniformly mixed in the atmosphere. There are no processes of CH_4 formation in the atmosphere, so the photochemical loss must therefore be balanced by abiogenic and biogenic sources. By analogy to Earth, it is suggested that the three most productive methane sources on Mars include: active volcanism and hot springs; comet and meteoroid impact; extant microbial metabolism. From these three sources, we looked at the production of methane from meteoritic material entering Mars' atmosphere. Recent studies have concentrated on constraining the amount of methane released during impact at the surface [2,3]. In the current work, we estimate the amount of methane obtained due to ablation of meteoroids in Mars' atmosphere. In order to estimate methane production from this source we need to know the proportion of ablated mass from meteoroids passing through Mars' atmosphere; the efficiency with which organic material in meteorites can be converted to methane; and the flux of meteoroids entering the atmosphere.

Methane prone organic matter in meteorites. Most of the extraterrestrial material arriving at Mars' surface is in the form of stony meteorites and cosmic dust. The average carbon content of interplanetary dust particles (10^{-14} to 10^{-11} kg) collected from the stratosphere of the Earth has been measured at 10 to 12% [4]. The carbon content of the larger micrometeorites (> 10^{-10} kg) is not well established since most of these particles melt or vaporize on Earth atmospheric entry. Carbon content in stony meteorites varies from 3.2wt% (CI1) to ~0.1wt% (ordinary chondrite) [5]. Given that small particles contribute a significant portion of the overall mass flux, we consider 2wt% a conservative lower limit on the proportion of carbon in extraterrestrial material at the top of the atmosphere.

When considering contributions to atmospheres from extraterrestrial objects traditional interpretations use a simple addition approach where a gas concentration of the object is multiplied by the mass delivered [3]. The organic content of Murchison is the most comprehensively studied of any carbonaceous chondrite. Murchison has an average organic content of around 2% but only 0.14 ppm free methane [6]. Yet the majority of organic matter present is in the form of a macromolecular material [7], ignored in the addition approach, but after ablation, a potential major contributor to the overall methane budget.

Cody et al. [8] used elemental analysis to obtain the following weight percentages for the Murchison macromolecular material: 51.2 wt% C, 2.25 wt% H, and 1.74 wt% N. These data correspond to an empirical formula of $C_{100}H_{52.7}N_{2.9}$. From NMR measurement, it was established that the average CH_x (where x = 1, 2, or 3 for methane, methylene, and methyl carbon) ranges from 2.0 (Orgueil), 1.8 – 2.1 (Murchinson), to 1.7 (Tagish Lake) [8].

Meteoritic flux at Mars. The meteoritic flux measured at Earth provides a starting point to estimate the flux at Mars for this size fraction of the meteoroid complex. For meteoroids in the mass range from 10^{-13} to 10^{10} kg, the size-frequency distribution at the Earth's upper atmosphere can be approximated by using a series of power-law branches [10]. To extrapolate the mass influx at Earth to the corresponding value at Mars requires an estimate of the ratio of the Mars flux to the Earth flux. This ratio depends on the type of orbital evolution experienced by the particles. The two main mechanisms for perturbing particles from the Asteroid Belt into Mars-intersecting orbits are Poynting-Robertson drag (P-R drag), and planetary gravitational perturbations. The orbits of large meteorites are perturbed principally by gravitational interactions with the planet; for small particles, P-R drag causes significant orbital changes on timescales comparable to, or shorter than, the gravitational perturbation timescale [11]. For large, crater-producing objects Shoemaker [12] estimated the flux of objects at Mars producing craters > 10 km in diameter to be ~2.6 times the terrestrial value. When this cratering rate ratio is adjusted for the difference in planetary areas, the total meteoritic flux on Mars for large objects will be around 0.75 times the Earths flux. For particles up to 10^{-5} kg the ratio of the mass influx at Mars to that at Earth would be 0.17 [11].

Numerical model: By applying a "pancake" model [e.g. 10,13] to model the flight of impactors through Mars' atmosphere, we arrived at an estimate for the total mass of ablated meteoritic material ar Mars.

When meteorites pass through a planet's upper atmosphere, their surfaces are heated to above 900 K. Chemical equilibrium in the fireball is maintained until the reactions are quenched, at which point the temperature drops so low that the chemical reaction timescale exceeds the cooling time. Reactions on catalytically active dust grains can proceed down to about 500 K, providing kinetically viable pathways to form CH_4 and CO_2.

In the atmospheric flight simulations, individual meteoroids (assumed spherical) are started at an altitude of eight martian atmospheric scale heights (~87 km), where the atmospheric pressure is 0.03% of its surface value. "Pancake" model equations [13] were applied to impactors over a range of masses from 10^{-13} to 10^5 kg. The mean velocity for material at the top of Mars atmosphere was taken as 10.2 km/s [12]. For stony bodies the density value was 3500 kg/m^3. The strength value for a 1 kg sample of a stony meteoroid was taken as 4.4×10^6 N/m^2.

Results: Knowing the meteoroid flux for the Earth, N_i, for a range of initial masses, m_i, entering Mars' atmosphere, and how much of these initial masses was ablated, m_i^l, then scaling the results with scaling factor, f_i, according to different initial mass ranges, we can calculate the total ablated mass of meteoroids in Mars' atmosphere:

$$M_{ab} = \sum_i f_i \, m_i^l \, N_i \; .$$

We received the total mass loss of meteoroids due to ablation in Mars' atmosphere as $1.9 \bullet 10^{10}$ g.

The concentration of methane that could be obtained from the above amount of ablated meteoroid mass is as follows:

$$[CH_4]_{Ma} = \frac{M_{ab} \, f_{organic} \, f_{methyl}}{M_{Ma}}$$

where $f_{organic}$ is the fraction of organic matter (~2%), f_{methyl} is the fraction of organic matter which is methane prone (16% [9]), and M_{Ma} is the mass of the atmosphere of Mars ($2.5 \bullet 10^{19}$ g). Then, the concentration of methane is $2.4 \bullet 10^{-12}$ g g^{-1}.

Methane has a lifetime of around 340 (Earth) years in Mars' atmosphere, so the steady-state concentration can be calculated by multiplying the methane concentration by the average calculated residence time, t_r, of methane on Mars:

$$[CH_4]_{SS} = [CH_4]_{Ma} t_r \; .$$

The steady state concentration, then, is equal to $0.8 \bullet 10^{-9}$ g g^{-1} or 0.8•ppb. To convert ppb to ppbv (parts per billion by volume) we used the methane volume mixing ratio in Mars' atmosphere (equal to 2.7); the methane concentration will then be equal to 2.16 ppbv.

Influence of atmospheric density variations. Atmospheric density variations effect the proportion of material ablated from a meteoroid, and therefore the amount of methane produced. Several observations showed seasonal variations in atmospheric density [14] and some researchers have found that radical changes in Mars' obliquity may cause its surface pressure to vary between essentially zero and 30-40 mbar [15]. Other recent work suggests that Mars may presently be emerging from an "ice age", which, on Mars, is a period of high obliquity [16]. But variation in atmospheric density on more recent timescales (e.g. over the 340 year residence time for methane in Mars' atmosphere) is not well constrained, and not included as a variable in our analysis.

Conclusions: We estimated the methane production in Mars' atmosphere due to meteoroid ablation. The calculated value of methane production by this mechanism is of a similar order (approximately 20%) to the measured value for methane in Mars' atmosphere. It should be noted that for meteoroid flight simulations we used a standard "pancake" model [13]. Compared to a more sophisticated separate fragments model [e.g. 10,17], where ablation is calculated for individual separated fragments, the "pancake" model 'sees' a smaller ablated surface area, producing a lower estimate for the overall amount of ablated material.

References: [1] Formisano V. et al (2004) *Science, 306,* 1758–1761. [2] Krasnopolsky V.A. et al. (2004) *Icarus, 172,* 537-547. [3] Kress M.E., McKay Ch.P. *Icarus, 168*, 475-483. [4] Thomas K.L. et al. (1993) *Geochimica et Cosmochimica Acts, 57,* 1551-1566. [5] Wasson J.T. and Kallemeyn G.W. (1988) *Phil. Trans. R. Soc. Lond. A, 325,* 535-544. [6] Butterworth A.L. et al. (2004) *Monthly Notices of the Royal Astronomical Society, 347*, 807-812. [7] Sephton M.A. (2002) *Natural Product Reports, 19*, 292-311. [8] Cody G.D. et al. (2002) *Meteoritics & Planetary Science, 37,* A36. [9] Sephton M.A. and Gilmour I. (2000) *The Astrophysical Journal*, *540,* 588-591. [10] Bland P.A. and Artemieva N.A. (2005) *Meteoritics, 41,* 607-631. [11] Flynn G.J. and McKay D.S. (1996) *Journal of Geophysical Research, 95,* 14497-14509. [12] Shoemaker (1977) *Impact and explosion cratering: Proceedings of the Symposium on Planetary Cratering Mechanics,* 617-628. [13] Chyba C.F. et al. (1993) *Nature, 361,* 40-44. [14] Petropoulos B. and Macris C. (1989) *Earth, Moon, and Planets, 46,* 1-30. [15] James P.B. et al. (1992) *In Lunar and Planetary Inst., Workshop on the Martian Surface and Atmosphere Through Time*, 76-77. [16] Head J.W. et al. (2003) *Nature, 426,* 797-802. [17] Artemieva N. A. and Shuvalov V. V. (2001) *J. Geophys. Research, 106,* 3297-3309.