FORMATION OF METHANE ON MARS BY FLUID-ROCK INTERACTION IN THE CRUST. J. R. Lyons<sup>1</sup>, C. E. Manning<sup>2</sup>, F. Nimmo<sup>2</sup>, <sup>1</sup>Institute of Geophysics and Planetary Physics, UCLA, Los Angeles, CA 90095; jrl@ess.ucla.edu; <sup>2</sup>Department of Earth and Space Sciences, UCLA, Los Angeles, CA 90095; manning@ess.ucla.edu; nimmo@ess.ucla.edu.

**Abstract:** Recent spectroscopic detections of CH<sub>4</sub> in the atmosphere of Mars are the first definitive observations of an organic compound on that planet. The relatively short photochemical lifetime of CH<sub>4</sub> (~300 years) argues for a geologically young source. We demonstrate here that low-temperature alteration of basaltic crust by carbon-bearing hydrothermal fluid can produce the required CH<sub>4</sub> flux of 1 x 10<sup>7</sup> moles year-1, assuming conservative values for crustal permeability and oxygen fugacity as implied by martian basaltic meteorites. The crustal thermal disturbance due to a single dike ~ 10 x 1 x 10 km during the past 10<sup>4</sup> years is capable of driving the alteration, if all carbon is supplied by magmatic degassing from a dike with only 50 ppm C. Atmospheric methane strongly suggests ongoing magmatism and hydrothermal alteration on Mars.

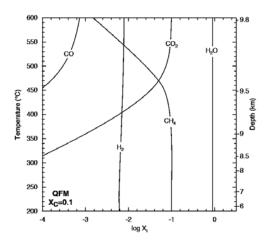
Introduction: The existence of organic compounds on Mars has been a subject of intense interest because it could imply extant or ancient life. Past non-detection of soil or atmospheric organics has been taken as evidence that Mars not only was devoid of life, but also lacked interior processes that could generate organics. However, the recent detection of atmospheric CH<sub>4</sub> [1-3] challenges this view. Because CH<sub>4</sub> has a short photochemical lifetime, ~300 yr [4], it must be supplied by an active process. While it is tempting to propose a biogenic origin [2], CH<sub>4</sub> is in fact an expected product of low-temperature fluid-rock interaction, and its detection in the atmosphere points to active magmatism and metamorphism on the planet.

Hydrothermal fluid model: In our model a subsurface magmatic intrusion either partly melts the basal ice layer or heats existing liquid H<sub>2</sub>O, causing downward fluid transport toward the heat source. After heating, the fluid buoyantly rises and cools. Reactions with the rock matrix along this path of decompression and cooling govern the geochemical byproducts of the process. The rate of generation of byproducts such as methane depends primarily on the heat source, crustal permeability and reactant concentrations. Crater counts from lava flows and deposits associated with several martian volcano systems suggest volcanic activity has occurred within the last ~ 2 Myr [5] and may occur on present-day Mars.

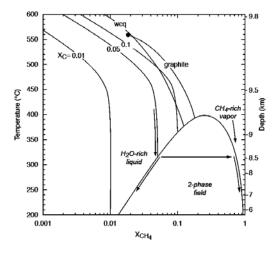
We adopt a very simple model of a 2D hydrothermal circulation driven by a constant line source of heat in a uniform permeable medium [6]. By a conservative

choice of model parameters, particularly permeability and the size of the intrusion, we are able to demonstrate the plausibility of geochemically derived methane. We assumed a line source emitting 8 kW/m of heat in a medium of permeability  $3 \times 10^{-15}$  m<sup>2</sup> [7]. This heat flux is comparable to that across the top of a cooling dike ~1 km wide and 10 km high immediately after solidification [8]; the heat flux decays over a timescale of ~  $10^4$  yrs. The heat source is assumed to be shallow (10 km depth) and generates a narrow (~2 km half-width) upwelling plume of fluid. The methane production rate depends in part on the quantity of rising fluid per unit dike length. We calculated values ~  $10^4$  yr<sup>-1</sup> per meter of dike length from  $10^4$  yr<sup>-1</sup> yr<sup>-1</sup> per meter of dike length from  $10^4$  yr<sup>-1</sup> yr<sup>-1</sup>

Hydrothermal fluid composition: Equilibrium fluid composition depends on oxygen fugacity ( $fO_2$ ), which at low fluid-rock ratios is controlled by the intrinsic value of the crust as in terrestrial fluid-rock interactions. Although weathered martian regolith is sufficiently oxidized as to contain hematite and sulfates, the sub-regolith basaltic crust has substantially lower fO<sub>2</sub> of QFM to QFM - 4.5 [9-16]. Because CH<sub>4</sub> is a reduced C species, a conservative estimate of abiogenic CH<sub>4</sub> production can be made by assuming that  $fO_2$  is the highest value permissible (QFM). We demonstrate that CH<sub>4</sub> is the dominant C species in the fluid phase along the upflow path from a depth of  $\sim 9.5$  km (470 °C) to the surface by calculating the equilibrium distribution of molecular C-O-H species at a fixed carbon mole fraction of  $X_C = 0.1$  and at QFM (Fig. 1).



An important feature of the H<sub>2</sub>O-CH<sub>4</sub> binary is phase separation, and the dependence of the depth of phase separation on the C concentration. The compositions of the liquid and vapor phase are mapped onto the upflow path directly above the magma source in Figure 2, along with model paths of cooling fluids. A graphite-saturated fluid contains the maximum bulk C concentration at a given fO2. A carbonate-buffered crust can be modeled by assuming calcite-wollastonitequartz equilibrium. At QFM, this yields phase separation at 9.1 km depth (Fig. 2) and C mole fraction ~ 0.12. If the source of carbon is a magmatic vapor phase, then the fluid is probably undersaturated with graphite or carbonate. In this case it will have lower total C and will intersect the two-phase field at lower temperatures.



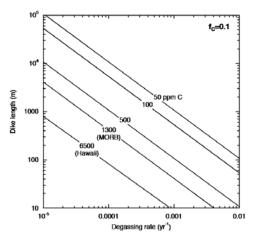
Phase equilibrium considerations illustrate two features that strongly favor abiogenic hydrothermal methane production on Mars. First, for expected  $fO_2$ , C is present in a martian crustal fluid almost exclusively as CH<sub>4</sub> at T<470°C, and such fluids are essentially binary H<sub>2</sub>O-CH<sub>4</sub> mixtures. Second, H<sub>2</sub>O-CH<sub>4</sub> phase separation (Fig. 2) will cause segregation of a CH<sub>4</sub>-rich vapor phase in the crust. Once formed, this low-density phase will rise rapidly through the crust and become more methane rich as it approaches the surface. Rapid rise through permeable crust will yield minimal capacity for reaction with host rock, minimizing C loss by precipitation of graphite.

**Methane flux to the atmosphere:** The CH<sub>4</sub> flux to the atmosphere can be estimated using thermal and phase equilibrium constraints, along with estimates of C available for CH<sub>4</sub> production. Graphite or carbonate saturation (as modeled by wollastonite-calcite-quartz) would produce abundant CH<sub>4</sub> with relatively small intrusion sizes. A more conservative estimate can be

obtained by assuming that all C derives from the magma, with no crustal input.

The starting C content of the magma and the fraction of CH<sub>4</sub> that reaches the surface,  $f_c$ , are poorly constrained. Figure 3 shows that by assuming conservatively that  $f_c = 0.1$ , a single dike 10 km deep by 1 km wide with length of ~10 km is sufficient to produce the observed atmospheric methane under the assumption that magmatic C is 50 ppm, a value well below that of terrestrial MORB or ocean-island basalt such as Hawaii.

We conclude that magma driven fluid interactions with a basaltic crust at QFM or lower can generated moderately large fluxes of CH<sub>4</sub> over the cooling times of the magmas, and can easily explain the present-day flux of CH<sub>4</sub> to the atmosphere.



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