

Formation of methane on Mars by fluid-rock interaction in the crust

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[1] Recent spectroscopic detections of CH₄ in the atmosphere of Mars are the first definitive observations of an organic compound on that planet. The relatively short photochemical lifetime of CH₄ (~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 CH₄ flux of 1×10^7 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 $\sim 1 \times 1 \times 10$ km intruded during the past 10⁴ 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. **Citation:** Lyons, J. R., C. Manning, and F. Nimmo (2005), Formation of methane on Mars by fluid-rock interaction in the crust, *Geophys. Res. Lett.*, 32, L13201, doi:10.1029/2004GL022161.

1. Introduction

[2] 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 [Klein *et al.*, 1992; Maguire, 1977] 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 CH₄ [Mumma *et al.*, 2003; Krasnopolsky *et al.*, 2004; Formisano *et al.*, 2004] challenges this view. Because CH₄ has a short photochemical lifetime, ~300 yr [Summers *et al.*, 2002], it must be supplied by an active process. While it is tempting to propose a biogenic origin [Krasnopolsky *et al.*, 2004], CH₄ is in fact an expected product of low-temperature fluid-rock interaction, and its detection in the atmosphere could point to active magmatism and metamorphism on the planet.

[3] Hydrothermal processes at terrestrial mid-ocean ridges are a significant source of abiogenic methane on Earth [Welhan and Craig, 1979; Kelley, 1996; Charlou *et al.*, 2002]. Methane is produced from magmatic and seawater carbon during metamorphic reactions in the upper crust and mantle. This efficiently generates CH₄ on Earth because conditions necessary to drive the relevant reactions are met: a heat source and crustal permeability sufficient to

permit hydrothermal fluid flow, appropriate oxygen fugacity, and ample sources of reactants. These conditions also likely obtain in the upper crust of Mars.

[4] As on Earth, the dominant component of Martian hydrothermal fluid is expected to be H₂O. Evidence for near-surface water ice is widespread [Boynton *et al.*, 2002; Feldman *et al.*, 2002] and theoretical expectations suggest liquid water will exist at depths of a few km below the Martian surface [Clifford, 1993]. In the model we describe below, a subsurface magmatic intrusion either partly melts the basal ice layer or heats existing liquid H₂O, 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.

[5] Crater counts of lava flows and deposits at Cerberus Fossae suggest that both volcanic and hydrothermal activity have occurred within the last ~2–10 Myr [Hartmann, 2001; Manga, 2004; Neukum *et al.*, 2004]. The high abundance of volatile and mobile elements in Martian soils is consistent with a hydrothermal origin [Newsom *et al.*, 1999]. Observations of He in the Martian atmosphere, with a residence time of ~10⁵ years [Krasnopolsky and Gladstone, 1996], are also strongly suggestive of recent outgassing. The duration and scale of hydrothermal activity driven by individual intrusive events will depend primarily on the lengthscale of the magma body [Harrison and Grimm, 2002]. Martian magma chambers may be >100 km³ in volume, with cooling timescales of a few Myrs [McKenzie and Nimmo, 1999; Wilson *et al.*, 2001]. These timescales are much longer than the CH₄ residence timescale in the Martian atmosphere, implying steady-state production of CH₄ to balance that lost through photochemical oxidation.

2. Hydrothermal Fluid Model

[6] Forward progress of hydrothermal reactions requires transport of fluids. The ~50 km thick Martian crust [Zuber *et al.*, 2000] is probably fractured due to impacts and tectonic activity, though this permeability is likely to decay with depth [Clifford, 1993]. Although no permeability measurements are available, values of 10⁻⁹ m², similar to young terrestrial basalt aquifers, are sufficient to account for inferred surface discharge rates [Manga, 2004]. Lower bounds based on inferred hydrothermal alteration of SNC meteorites and soil chemistry are 10⁻¹⁶–10⁻¹⁵ m² [Harrison and Grimm, 2002], and typical terrestrial values are 10⁻¹³ to 10⁻¹⁴ m² [Manning and Ingebritsen, 1999].

[7] We adopt a very simple model of a 2D hydrothermal circulation driven by a constant line source of heat in a uniform permeable medium [Turcotte and Schubert, 2002].

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By a conservative choice of model parameters, particularly permeability and the size of the intrusion, we are able to demonstrate the plausibility of hydrothermally derived methane. Figure 1 shows the temperature structure generated by a line source emitting 8 kW/m of heat in a medium of permeability $3 \times 10^{-15} \text{ m}^2$. This heat flux is comparable to that across the top of a cooling dike $\sim 1 \text{ km}$ wide and 10 km high immediately after solidification [McKenzie and Nimmo, 1999]; the heat flux decays over a timescale of $\sim 10^4$ yrs. The heat source is assumed to be shallow (10 km depth) and generates a narrow ($\sim 2 \text{ km}$ half-width) upwelling plume of fluid. The methane production rate depends in part on the quantity of rising fluid per unit dike length. For regions in the range 250°C to 600°C, the total volume of rising fluid per meter of dike length was $\sim 50 \text{ m}^3 \text{ yr}^{-1}$.

3. Hydrothermal Fluid Composition in Equilibrium with Martian Crust

[8] Given a fluid flux and temperature profile, it remains to show that CH_4 is expected in a hydrothermal fluid containing a given carbon concentration. Equilibrium fluid composition depends on oxygen fugacity (f_{O_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

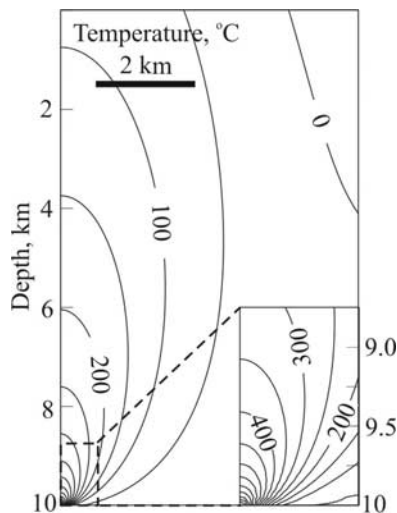


Figure 1. Contours of temperature (°C) resulting from fluid flow driven by a line source of heat [Turcotte and Schubert, 2002]. Assumed model values: heat source $8 \times 10^3 \text{ W m}^{-1}$, permeability $3 \times 10^{-15} \text{ m}^2$, fluid viscosity, density, thermal expansivity and heat capacity $1.33 \times 10^{-4} \text{ Pa s}$, 1000 kg m^{-3} , $2 \times 10^{-4} \text{ K}^{-1}$ and $4200 \text{ J kg}^{-1} \text{ K}^{-1}$, respectively; rock thermal conductivity $3 \text{ W m}^{-1} \text{ K}^{-1}$, acceleration 3.7 ms^{-2} . A background geothermal gradient of 10 K/km, appropriate to Mars, has been added to the temperature field. We have estimated that a factor of 10 increase in permeability with decreasing depth (not accounted for in the temperature contours shown) will reduce the temperature to $\sim 0^\circ\text{C}$ in the top 2–3 km of the Martian crust. Thus, we do not expect a significant hot spot from the small intrusion considered here.

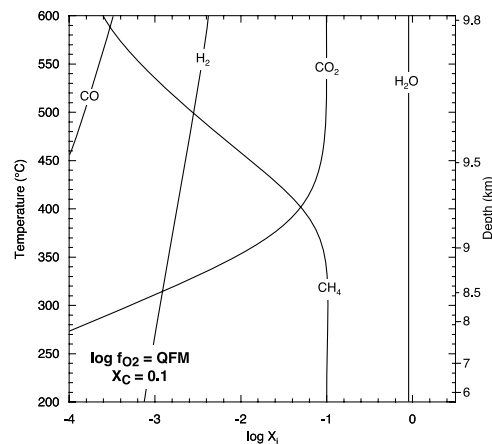


Figure 2. Logarithms of equilibrium mole fractions of species in C-O-H fluid as a function of temperature in Martian crust for the axial region above a 10-km-deep magmatic heat source. Distribution of species at total carbon mole fraction $X_C = 0.1$ assuming $f_{\text{O}_2} = \text{QFM}$. Calculations employed thermodynamic data of Holland and Powell [1998], fugacity coefficients of Belonoshko *et al.* [1992], and ideal mixing of nonideal gases. The latter assumption breaks down at $T < 400^\circ\text{C}$ where unmixing occurs (Figure 3), but bulk species abundances are similar because CH_4 predominates. Lithostatic pressure is about 100 bars (10 MPa) per km of depth.

has substantially lower f_{O_2} of QFM to QFM - 4.5 based on studies of shergottite meteorites (auxiliary materials¹). Because CH_4 is a reduced C species, a conservative estimate of abiogenic CH_4 production can be made by assuming that f_{O_2} is the highest value permissible (QFM). We demonstrate that CH_4 is the dominant C species in the fluid phase along the upflow path from a depth of $\sim 9.5 \text{ km}$ (430°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 (Figure 2). The same calculation in the presence of graphite or a CO_2 -buffering mineral assemblage such as wollastonite-calcite-quartz yields similar relative species abundances, although carbon concentration varies with depth. Lower f_{O_2} leads to CH_4 predominance at greater depth. Figure 2 shows that at equilibrium all fluids at low temperature are essentially binary H_2O - CH_4 mixtures for $f_{\text{O}_2} \leq \text{QFM}$.

[9] An important feature of the H_2O - CH_4 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 3, along with model paths of cooling fluids. A graphite-saturated fluid contains the maximum bulk C concentration at a given f_{O_2} (Figure 3). However, graphite has not been observed in SNC meteorites, and assuming its presence during fluid-rock interaction probably overestimates the C content of fluids. More realistic estimates can be derived by considering likely C sources: C already residing in the crust as carbonate, as in ALH84001 [McSween, 1994], and in dust at

¹Auxiliary material is available at <ftp://ftp.agu.org/apend/gl/2004GL022161>.

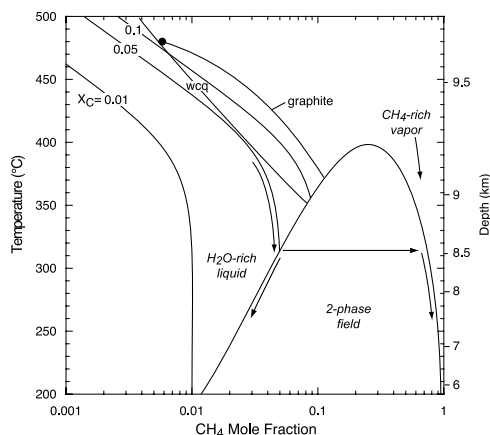


Figure 3. Variation in equilibrium mole fraction of CH_4 along the fluid flow path for different scenarios, including graphite saturation, f_{CO_2} buffered by wollastonite-calcite-quartz (wcq), and $X_{\text{C}} = 0.01, 0.05,$ and 0.1 . Oxygen fugacity is QFM. The filled circle denotes the maximum temperature of graphite stability. Upward flowing and cooling $\text{H}_2\text{O}-\text{CH}_4$ fluid will encounter the two-phase region [Churakov and Gottschalk, 2003] at different depths depending on X_{CH_4} . When this occurs, it unmixes into an H_2O -rich liquid and a CH_4 -rich vapor, as illustrated schematically with arrows for the $X_{\text{C}} = 0.05$ path.

the surface [Bandfield et al., 2003]; or C from a magmatic vapor phase. A carbonate-buffered crust can be modeled by assuming calcite-wollastonite-quartz equilibrium. At QFM, this yields phase separation at 9.1 km depth (Figure 3) and C mole fraction ~ 0.12 . Varying the CO_2 fugacity to carbonate-bearing assemblages more typical of hydrothermally altered basalt, such as epidote + calcite + quartz or actinolite + calcite + quartz, does not change the depth of phase separation significantly and yields similar or higher C contents of the fluid. 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 (Figure 3).

[10] Phase equilibrium considerations illustrate two features that strongly favor abiogenic hydrothermal methane production on Mars. First, for expected f_{O_2} , C is present in a Martian crustal fluid almost exclusively as CH_4 at $T < 430^\circ\text{C}$, and such fluids are essentially binary $\text{H}_2\text{O}-\text{CH}_4$ mixtures. Second, $\text{H}_2\text{O}-\text{CH}_4$ phase separation (Figure 3) will cause segregation of a CH_4 -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.

4. Methane Flux to the Martian Atmosphere

[11] The CH_4 flux to the atmosphere can be estimated using thermal and phase equilibrium constraints, along with estimates of C available for CH_4 production. A conservative estimate can be obtained by assuming that all C derives from the magma, with no crustal input. However, constraints on C in undegassed Martian magma are poor

(auxiliary materials), so we considered a range of carbon concentrations from 50 ppm (lowest value in SNC meteorites) to 6500 ppm (Hawaiian basalt) to assess the plausibility of CH_4 production by magmatic carbon. The flux of carbon from a degassing and cooling dike, q_d (kg yr^{-1} per m of dike length), can be computed from $q_d = c\rho v f_i$, where c is the concentration of carbon in the magma, ρ is magma density (3000 kg/m^3), v is magma volume per meter of dike length (here assumed to be $10 \text{ km} \times 1 \text{ km} = 10^7 \text{ m}^3 \text{ m}^{-1}$), and f_i is degassing rate (yr^{-1}). Theoretical considerations suggest that the rate of degassing is controlled by the rate of magma crystallization [Tait et al., 1989]. For a conductively cooling body 1 km wide, the crystallization timescale is of order 10^4 years, giving $f_i \sim 10^{-4} \text{ yr}^{-1}$. The fluid transport timescale to the zone of phase separation is ~ 7000 years, comparable to f_i^{-1} , which shows that fluid transport is not the limiting process in getting CH_4 to the surface. (Although crustal permeability may be larger than we have assumed here, we expect that transport timescales will exceed chemical equilibration timescales, justifying our assumption of equilibrium.) For a magma carbon concentration of 50 ppm, $q_d = 150 \text{ kg yr}^{-1} \text{ m}^{-1}$. Because nearly all C is converted to methane, the C flux to the Martian surface, q_s , per meter of dike length is $q_s = q_d f_c$, where f_c describes the fraction of available CH_4 that actually is delivered to the surface. The factor f_c accounts for retention of CH_4 by the liquid, loss to fluid inclusions or other crustal reservoirs, or kinetic barriers.

[12] The starting C content of the magma and the factor f_c are poorly constrained. Figure 4 shows that by assuming that 100% of available methane can reach the surface ($f_c = 1$), a single dike 10 km deep by 1 km wide with length of ~ 1 km is sufficient to produce the observed atmospheric methane under the assumption that magmatic C is 50 ppm. If Martian magmatic C is closer in concentration to MORB or Hawaiian basalt, a very small dike length (~ 10 – 100 meters) would be implied. Alternatively,

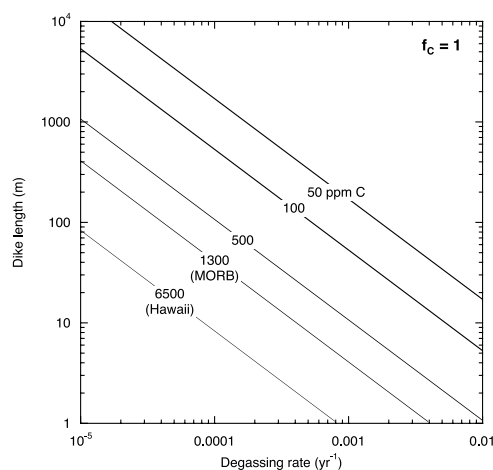


Figure 4. Variation in length of a dike 1 km wide and 10 km deep with C degassing rate required to generate observed CH_4 in the Martian atmosphere, assuming all C is magmatic and that 100% of available CH_4 leaves the crust. Different magmatic C contents are shown; terrestrial MORB average [Javoy and Pineau, 1991] and Hawaiian basalt are given for reference.

f_c may be $\ll 1$, or current observations may underestimate the flux of CH_4 to the Martian atmosphere.

[13] Measurement of the carbon isotopes in Martian methane will provide a necessary test of our hypothesis. Stepped-heating experiments on Zagami [Grady *et al.*, 1997] suggest $\delta^{13}\text{C}_{\text{PDB}}(\text{CO}_2) \sim -24\%$ for Martian magmatic CO_2 , significantly lighter than MORB carbon (~ -9 to -4%). For fluids that follow the carbon fraction $X_C = 0.1$ path on the $\text{H}_2\text{O}-\text{CH}_4$ phase diagram (Figure 3), CH_4 and water undergo phase separation at 9 km. Complete conversion of magmatic CO_2 to CH_4 will yield $\delta^{13}\text{C}_{\text{PDB}}(\text{CH}_4) \sim -24\%$, assuming that the Grady *et al.* [1997] values are truly representative of Martian magmatic carbon. Serpentinization (auxiliary materials) of crustal olivine and subsequent reduction of fluid bicarbonate derived from the crust can also yield CH_4 with a similar range of $\delta^{13}\text{C}$, but only if the reactions occur at $<200^\circ\text{C}$. The wide range of $\delta^{13}\text{C}$ values measured in SNC carbonates means that discriminating between a crustal and magmatic C source may not be easy. However, isotopically very light CH_4 ($\ll -30\%$ vs. PDB) would likely be evidence for a biogenic source.

[14] Early Mars probably generated volcanic intrusions substantially larger than the volume postulated here [McKenzie and Nimmo, 1999; Wilson *et al.*, 2001]. For example, dikes ~ 10 km in width and ~ 1000 km long have been proposed [McKenzie and Nimmo, 1999], but, if comprised of magma with 50 ppm C, would have generated a CH_4 flux only ~ 10 times that of the much smaller dike inferred here for present-day Mars. Each 1000 km long dike would have yielded ~ 0.1 ppm CH_4 in the atmosphere over the 1 Myr cooling timescale of the dike for the present Martian atmospheric pressure. This is 10^{-5} to 10^{-4} times the amount of CH_4 required to maintain clement surface conditions 3.8 Gyr ago with a thick CO_2 atmosphere [Kasting, 1997], and suggests that if fluid-rock interaction in the crust ever produced enough CH_4 to contribute significantly to a Mars greenhouse, the source of C was probably crustal rather than magmatic. However, it is clear that magma driven fluid interactions with a basaltic crust at QFM or lower could have generated moderately large fluxes of CH_4 over the cooling times of the magmas, and can easily explain the present-day flux of CH_4 to the atmosphere.

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References

- Bandfield, J. L., T. D. Glotch, and P. R. Christensen (2003), Spectroscopic identification of carbonate minerals in the Martian dust, *Science*, *301*, 1084–1087.
- Belonoshko, A. B., P. Shi, and S. K. Saxena (1992), SUPERFLUID: A FORTRAN77 program for calculation of Gibbs free energy and volume of C-H-O-N-S-Ar mixtures, *Comput. Geosci.*, *18*, 1267–1269.
- Boynnton, W. V., et al. (2002), Distribution of hydrogen in the near surface of Mars: Evidence for subsurface ice deposits, *Science*, *297*, 81–85.
- Charlou, J. L., J. P. Donval, Y. Fouquet, P. Jean-Baptiste, and N. Holm (2002), Geochemistry of high H_2 and CH_4 vent fluids issuing from ultramafic rocks at the Rainbow hydrothermal field ($36^\circ 14' \text{N}$, MAR), *Chem. Geol.*, *191*, 345–359.
- Churakov, S. V., and M. Gottschalk (2003), Perturbation theory based equation of state for polar molecular fluids: II. Fluid mixtures, *Geochim. Cosmochim. Acta*, *67*, 2415–2425.
- Clifford, S. M. (1993), A model for the hydrologic and climatic behavior of water on Mars, *J. Geophys. Res.*, *98*, 10,973–11,016.
- Feldman, W. C., et al. (2002), Global distribution of neutrons from Mars: Results from Mars Odyssey, *Science*, *297*, 75–78.
- Formisano, V., et al. (2004), Detection of methane in the atmosphere of Mars, *Science*, *306*, 1758–1761.
- Grady, M. M., I. P. Wright, and C. T. Pillinger (1997), A carbon and nitrogen isotope study of Zagami, *J. Geophys. Res.*, *102*, 9165–9173.
- Harrison, K. P., and R. E. Grimm (2002), Controls on Martian hydrothermal systems: Application to valley network and magnetic anomaly formation, *J. Geophys. Res.*, *107*(E5), 5025, doi:10.1029/2001JE001616.
- Hartmann, W. K. (2001), Martian seeps and their relation to youthful geothermal activity, *Space Sci. Rev.*, *96*, 405–410.
- Holland, T. J. B., and R. Powell (1998), An internally consistent data set for phases of petrologic interest, *J. Metamorph. Geol.*, *16*, 309–343.
- Javoy, M., and F. Pineau (1991), The volatiles record of a popping rock from the Mid-Atlantic Ridge at 14°N : Chemical and isotopic composition of gas trapped in vesicles, *Earth Planet. Sci. Lett.*, *107*, 598–611.
- Kasting, J. F. (1997), Warming early Earth and Mars, *Science*, *276*, 1213–1215.
- Kelley, D. S. (1996), Methane-rich fluids in the oceanic crust, *J. Geophys. Res.*, *101*, 2943–2962.
- Klein, H. P., N. H. Horowitz, and K. Biemann (1992), The search for extant life on Mars, in *Mars*, edited by H. H. Kieffer et al., Univ. Arizona Press, Tucson.
- Krasnopolsky, V. A., and G. R. Gladstone (1996), Helium on Mars: EUVE and PHOBOS data and implications for Mars' evolution, *J. Geophys. Res.*, *101*, 15,765–15,772.
- Krasnopolsky, V. A., J. P. Maillard, and T. C. Owen (2004), Detection of methane in the Martian atmosphere: Evidence for life?, *Icarus*, *172*, 537–547.
- Maguire, W. C. (1977), Martian isotopic ratios and upper limits for possible minor constituents as derived from Mariner 9 infrared spectrometer data, *Icarus*, *32*, 85–97.
- Manga, M. (2004), Martian floods at Cerberus Fossae can be produced by groundwater discharge, *Geophys. Res. Lett.*, *31*, L02702, doi:10.1029/2003GL018958.
- Manning, C. E., and S. E. Ingebritsen (1999), Permeability of the continental crust: Implication of geothermal data and metamorphic systems, *Rev. Geophys.*, *37*, 127–150.
- McKenzie, D., and F. Nimmo (1999), The generation of Martian floods by the melting of ground ice above dykes, *Nature*, *397*, 231–233.
- McSween, H. Y. (1994), What we have learned about Mars from the SNC meteorites, *Meteoritics*, *29*, 757–779.
- Mumma, M. J., R. E. Novak, M. A. DiSanti, and B. P. Bonev (2003), A sensitive search for methane on Mars, *Bull. Am. Astron. Soc.*, *35*, 937.
- Neukum, G., et al. (2004), Recent and episodic volcanic and glacial activity on Mars revealed by the High Resolution Stereo Camera, *Nature*, *432*, 971–979.
- Newsom, H. E., J. J. Hagerty, and F. Goff (1999), Mixed hydrothermal fluids and the origin of the martian soil, *J. Geophys. Res.*, *104*, 8717–8728.
- Summers, M. E., B. J. Lieb, E. Chapman, and Y. L. Yung (2002), Atmospheric biomarkers of subsurface life on Mars, *Geophys. Res. Lett.*, *29*(24), 2171, doi:10.1029/2002GL015377.
- Tait, S., C. Jaupart, and S. Vergnolle (1989), Pressure, gas content and eruption periodicity of a shallow, crystallizing magma chamber, *Earth Planet. Sci. Lett.*, *92*, 107–123.
- Turcotte, D., and G. Schubert (2002), *Geodynamics*, 2nd ed., Cambridge Univ. Press, New York.
- Welhan, J. A., and H. Craig (1979), Methane and hydrogen in East Pacific Rise hydrothermal fluids, *Geophys. Res. Lett.*, *6*, 829–831.
- Wilson, L., E. D. Scott, and J. W. Head (2001), Evidence for episodicity in the magma supply to the large Tharsis volcanoes, *J. Geophys. Res.*, *106*, 1423–1433.
- Zuber, M. T., et al. (2000), Internal structure and early thermal evolution of Mars from Mars Global Surveyor topography and gravity, *Science*, *287*, 1788–1793.

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