# **Climate Transition on Mars: A Simple Solution U23E-0091**





## The evidence for climate transition on Mars

## resent climate

Surface temperature ranges from -140 C to 20 C, average -65 C

- Surface atmospheric pressure is 1-9mm (7mm average), mostly due to  $CO_2$  (95%) Water vapor in atmosphere is about 0.03%, less than  $O_2$  or CO.
- Significant polar caps of water (with CO<sub>2</sub> veneer) (Plaut et al., 2007)
- No liquid water at surface due to combination of low temperature (most latitudes) and low surface water vapor pressure (low latitudes where T occasionally exceeds normal freezing point)
- In summary, present-day Mars is very cold and very dry

- Highly integrated, high stream order drainage networks heading at/near crater rims indicate extensive and widespread surface water flow (Hynek and Phillips, 2003)
- Deltaic channels and meandering stream patterns
- Geomorphic evidence for extensive denudation of highlands and sedimentary deposition in adjacent lowlands suggests prolonged surface water flow, perhaps for hundreds of millions of years in the mid-late Noachian (Hynek
- and Phillips. 2001) Valles Marineris is an enormous canyon, probably partly tectonic, but the floor shows features likely due to surface water flow

In summary, Mars had a warm, wet climate during the first billion years

## We thus have two problems

1) How could a warm, wet climate be produced on the early Mars By what mechanism did the climate change to the present cold, dry climate?

Problem 1) is actually much more difficult because of the Faint Young Sun problem, the astrophysical observation/calculation that the early Sun had a luminosity about 25% less than at present (Schwarzschild, 1958; Sagan and Mullen, 1972; Newman and Rood, 1977; Gough, 1981)

# The Problem with Carbon Dioxide

Climate/atmosphere calculations with higher atmospheric  $CO_2$  indicated that 2 atm (present-day solar luminosity) to 5 atm (for early faint Sun) is required to give mean surface temperature sufficient for liquid water (at obviously much higher surface pressure) (Pollack et al., 1987).

BUT, revised calculations incorporating the effect of formation of CO<sub>2</sub> clouds indicate even higher atmospheric  $CO_2$  would be necessary, indeed that  $CO_2$  could not produce the necessary warming (Kasting, 1991). On the other hand, scattering of infrared by CO<sub>2</sub> clouds might make the CO<sub>2</sub> model tenable (Forget and Pierrehumbert, 1997).

More problematical for the  $CO_2$  greenhouse on Mars is the lack of a reservoir for e CO<sub>2</sub> at present (Bandfield et al., 2003; Bibring et al., 2007) nor is there an atmospheric loss mechanism sufficient to remove the  $CO_2$  (Barabash et al., 2007). In fact, the problem is much more severe than most investigators have indicated. If 5 atm of CO<sub>2</sub> (say) is necessary for a warm, wet Martian climate at 3.5 billion years ago, with the increasing luminosity of the Sun it is necessary to remove that  $CO_2$  from the atmosphere efficiently and effectively to prevent the climate from staying warm and wet. This is true even if we can explain the (necessary) drop in production of CO<sub>2</sub> (presumably from volcanic sources) as a consequence of decreasing internal heat output (volcanism) on Mars through time. The reason is simple: the major part of the climate transition occurred about 3.5 GABP, while the Sun was still relatively faint and when nearly 5 atm of CO<sub>2</sub> would have been required. If Mars' atmosphere contained several atmospheres equivalent of CO<sub>2</sub> just before the shift to cold and dry, the earliest freezing of the planet surface, including any seas present (of which we may be reasonably certain there was at least one), would leave that CO<sub>2</sub> "trapped" in the atmosphere. The shutting down of weathering processes would virtually eliminate CO<sub>2</sub> absorption by surface processes, or by dissolution in the ocean. Ultimately, lacking an atmospheric loss mechanism sufficiently potent (Barabash et al., 2007), that CO<sub>2</sub> should quickly, and by a fairly obvious negative feedback process, end up frozen in/on the polar caps. The present inventory of polar cap CO<sub>2</sub> is about two orders of magnitude too small. Considerations of the enormous amount of  $CO_2$  that must have been already dissolved in Martian water at the time of the climate transition only makes the problem still worse.

## **Proposed solutions to the Mars climate conundrum**

- 1) An early more massive, more luminous sun (Sackman and Boothroyd, 2003) very unlikely (Wood et al., 2005)
- 2) Changes in orbital parameters
- a) Distance from Sun (Leubner, 2007) unlikely, especially given probable attending effects on Earth's climate, etc.
- b) Obliquity (Jakosky et al., 2005) can produce some climate variability, perhaps enough to get periodic (?) warmer, wetter climates
- at the current solar luminosity, but probably insufficient for early Mars with a fainter Sun Enhanced greenhouse effect
- a) Carbon dioxide
- b) Water vapor not sufficient as it is a condensable gas under any
- reasonable circumstances c) Methane
- d) Ammonia





NE Holden Crater Delta

The Problem with Methane and Ammonia

Both of these potent greenhouse gases have been suggested as possible solutions to the early climate problem on Mars (and Earth) (Sagan and Mullen, 1972, Sagan and Chyba, 1997). Both gases have generally been rejected because of their short lifetimes in atmospheres subject to solar radiation (Kuhn and Atreya, 1979; Kasting and Ono, 2006): it seems too difficult to maintain high enough concentrations for prolonged periods of time, especially in the absence of biological processes that might regenerate them.

Sagan and Chyba (1997) tried to overcome this difficulty by invoking a protective shield of upper atmosphere organic solids to increase the lifetime of ammonia in particular. This suggestion was negated by the discovery that the organic haze would also reflect incoming radiation, producing an "antigreenhouse effect" (Pavlov et al., 2001), who also showed that the organics were not a particularly effective shield for the ammonia-destroying UV radiation.

Lacking a sufficient mechanism to either produce or maintain high enough levels of either methane or ammonia on early Mars, these gases appear to be incapable of solving the climate transition problem, to say nothing of producing a warm, wet early Mars. However, "reduced gases probably were present in significant concentrations on both early Earth and Mars, and they played an important role in climate evolution on both planets. Sagan himself had been fond of this idea for many years. It seems likely that his excellent scientific intuition will once again be found correct" (Kasting, 1997).

Hot (?) Springs on Mars, after Allen and Oehler, 2008





## The Missing Piece of the Puzzle and the Simple Solution

roduction of methane (and ammonia) by biological processes has been suggested as a source of either or both of these gases for the early Earth (e.g. Sagan and Chyba, 1977: Kasting, 1997), but not until the necessary biological systems had originated and blved to a suitable state. For Mars such sources are highly problematical until such ime as we have evidence for Martian biology. Non-biological sources, in particular submarine volcanism, have also been suggested (for both planets), but appear to require assuming a rather reduced state for the mantles of both planets, usually considered unlikely after core formation (which probably occurred early, perhaps during accretion) (Kasting, 1997; Nisbet and Sleep, 2001; Righter, 2007). Most investigators clearly do not (in fact flatly reject) the possibility of significant reduced gases coming from the mantle, strongly favoring degassing of CO<sub>2</sub>.

BUT, there is an obvious and proven means of generating significant amounts of both methane and ammonia from abiotic sources, requiring only low temperature hydrothermal conditions and a source of reduced carbon and nitrogen compounds Observations of terrestrial submarine hydrothermal systems (Seewald et al., 1994; Cruse and Seewald, 2006), theoretical calculations (Seewald et al., 1990, 1994) and laboratory experiments (Seewald et al., 1990, 1994, 2006; Seewald, 2001) all support this idea, and demonstrate the potential to produce very large amounts of both methane and ammonia. Calculation of possible production rates for early Earth (Shaw, 2008) suggest that such a source on early Mars could have maintained (regenerated) methane and ammonia concentrations sufficient to provide for a warm, wet climate, for as long as the heat source for hydrothermal processing continued at a high enough level. Rover missions certainly indicate hydrothermal activity has been substantial on Mars in the past. But this source of reduced gases also depends on a large reservoir of reduced carbon and nitrogen compounds.

Vent	Sample	CH4	C2H4	C2H6	C3H6	C3H8	i-C4H10	n-C4H10	Benzene	Toluen
		mmol/kg	nanomol/kg	µmol/kg	nanomol/kg	µmol/kg	µmol/kg	µmol/kg	µmol/kg	
Dead Dog Field			Ū					. ŭ		
H'ken Hollow	BGT-3597-1	0.45		4.74	1.6	1.21	0.12	0.1	0.5	30.0
	BGT-3597-2	17.7	3.9	186		47.7	4.9	5.3	22	4.3
	Endmember	22.6	4	236	41	60.7	6.2	6.8	28	
Chowder Hill	BGT-3596-3	19.2	6	219	4.7	53.2	5.8	6	24	4.6
	BGT-3596-4	20.3	2.9	231	2.4	56.8	6.1	6.2	22	
	Endmember	20.3	4.6	232	3.7	56.6	6.2	6.2	23	4.9
Insp. Mounds	BGT-3597-3	7.58	48	219	47	53.2	21	6	24	4
	BGT-3597-4	4.88	4.0	213	24	56.8	1.4	62	27	
	Endmember	21.6	14	232	16	57.5	5.9	6.1	24	4.
Puppy Dog	BGT-3599-3	16.4	3.4	175		44.3	4.4	5.2	19	3.3
	BGT-3599-4	2.88		31.6		7.77	0.75	0.83	3.1	0.5
	Endmember	18.5	3.8	198		50.1	5	5.9	22	4.
ODP Mound Field										
1035F	BGT-3598-3	0.56	5.6	2.07	2.2	0.48	_	_	0.19	0.0
	Endmember	2.99	30	11.1	12	2.58	_	_	0.99	0.0
Shipor Book	BOT 2505 4	6.02	0.4		4	4 47	0.25	0.09	26	0.4
Shiner Bock	BG1-3595-1	6.92	0.4	23.2	4	4.47	0.35	0.90	2.0	0.13
	Endmember	7.07	8.4	23.1	3.7	4.50	0.35	0.90	2.5	0.
Spire	BGT-3595-3	6.52	19	23.4	5.7	4.26	0.31	0.8	2.2	0.1:
	BGT-3595-4	3.84	13	14.3	3.9	2.74	0.23	0.59	1.5	0.1:
	Endmember	6.71	20	24.3	6.1	4.48	0.34	0.87	2.3	0.1
1035H	BGT-3599-1	3.98	94	15.6	35	3,09	0.24	0.71	15	01
	BGT-3599-2	3.54	_	14.3		2,72	0.2	0,65	1.3	_
	Endmember	5.85	14	23.2	5.2	4.52	0.34	1.1	2.1	0.1
BS₩⊾	0	0	0	0	0	0	0	0	0	

## References

Bandfield, J.L., Glotch, T.D., Christensen, P.R., 2003, Spectroscopic identification of carbonate minerals in the Martian dust, Science 301, 1084-1087. Barabash, S., Fedorov, A., Lundin, R., Sauvaud, J.-A., 2007. Martian atmosphere erosion rates. Science 315, 501-503.

Bibring, J.-P., Langevin, Y., Mustard, J.F., Poulet, F., Arvidson, R., Gendrin, A., Gondet, B., Mangold, N., Pinet, P., Forget, F., and the OMEGA team, 2006. Global mineralogical and aqueous Mars history derived from OMEGA/Mars Express data. Science 312, 400-404.

Cruse, A.M., Seewald, J.S., 2006. Geochemistry of low-molecular weight hydrocarbons in hydrothermal fluids from Middle Valley, northern Juan de Fuca Ridge. Geochim. Cosmochim. Acta 70, 2073–2092. Forget, F., Pierrehumbert, R.T., 1997. Warming early Mars with carbon dioxide clouds

that scatter infrared radiation. Science 278, 1273-1275. Gough, D. O., 1981. Solar interior structure and luminosity variations. Solar Physics 74, 21-34.

Hynek, B.M., Phillips, R.J., 2003, New data reveal mature, integrated drainage systems onMars indicative of past precipitation, Geology, 31, 757-760. Hynek, B.M., Phillips, R.J., 2001, Evidence for extensive denudation of the Martian highlands, Geology, 29, 407-410.

Jakosky, B.M., Haberle, R.M., Arvidson, R.E., 2005, The Changing Picture of Volatiles and Climate on Mars, Science 310, 1439-1440. Kasting, J., 1991. CO<sub>2</sub> condensation and the climate of early Mars. Icarus 94, 1-13.

Kasting, J.F., 1997. Warming early Earth and Mars. Science 276, 1213-1215. Kasting, J.F., Ono, S., 2006. Paleoclimates: the first two billion years. Phil. Trans. R. Soc. B 361, 917-929.

Assembly Supplement. Malin, M.C., Edgett, K.S., Posiolova, L.V., McColley, S.M., Dobrea, E.Z.N., 2006. Science 314, 1573-1577.

Plaut, J.J., Picardi, G., Safaeinili, A., Ivanov, A.B., Milkovich, S.M., Cicchetti, A.,

Deposits of Mars, Science 316, 92-95.

583, 1024-1039. labile greenhouse gases. Science 276, 1217-1221.

Kuhn, W.R., Atreya, S.K., 1979. Ammonia photolysis and the greenhouse effect in the primordial atmosphere of the Earth. Icarus 37, 207-213. bner, I.H., 2007, Quantifying the Planetary-Solar interaction, EOS, 88(23), Joint

Present-day impact cratering rate and contemporary gully activity on Mars. Newman, M.J., Rood, R.T., 1977. Implications of solar evolution for the Earth's early atmosphere. Science 198, 1035-1037.

Nisbet, E.G., Sleep, N.H., 2001. The habitat and nature of early life. Nature 409, 1083-Pavlov, A.A., Brown, L.L., Kasting, J.F., 2001. UV shielding of NH<sub>3</sub> and O<sub>2</sub> by organic hazes in the Archean atmosphere. J. Geophys. Res. 106, 23267-23287.

Kofman, W., Mouginot, J., Farrell, W.M., Phillips, R.J., Clifford, S.M., Frigeri, A., Orosei, R., Federico, C., Williams, I.P., Gurnett, D.A., Nielsen, E., Hagfors, T., Heggy, E., Stofan, E.R., Plettemeier, D., Watters, T.R., Leuschen, C.J., Edenhofer, P., 2007, Subsurface Radar Sounding of the South Polar Layered

Pollack, J.B., Kasting, J.F., Richardson, S.M., Poliakoff, K., 1987. The case for a warm, wet climate on early Mars. Icarus 71, 203-224. Righter, K., 2007. Not so rare Earth? New developments in understanding the origin of the Earth and Moon. Chemie der Erde 67, 179-200.

Sackman, I-J., Boothroyd, A.I., 2003. Our Sun. V. A bright young sun consistent with helioseismology and warm temperatures on ancient Earth and Mars. Astrophys. J. Sagan, C., Chyba, C., 1997. The early faint Sun paradox: organic shielding of ultraviolet-

laboratory experiments. Geochim. Cosmochim. Acta 65, 1641–1664. Seewald, J.S., Seyfried, Jr., W.E., Shanks III, W.C., 1994. Variations in the chemical and stable isotope composition of carbon and sulfur species during organic-rich sediment alteration: an experimental and theoretical study of hydrothermal activity at Guaymas Basin, Gulf of California. Geochim. Cosmochim. Acta 58, 5065-5082

543 0.8 0 2.3

temperatures. Science 177, 52-56

186, 462-483.

Princeton, NJ, 1958

Seewald, J.S., Seyfried Jr., W.E., Thornton, E.C., 1990. Organic-rich sediment alteration: an experimental and theoretical study at elevated temperatures and pressures, Appl. Geochem. 5, 193-209.

Seewald, J.S., Zolotov, M.Y., McCollom, T., 2006. Experimental investigation of single carbon compounds under hydrothermal conditions. Geochim. Cosmochim. Acta 70, 446–460.

Sagan, C., Mullen, G., 1972. Earth and Mars: evolution of atmospheres and surface

Schaefer, L., Fegley, Jr., B., 2007. Outgassing of ordinary chondritic material and some

Schwarzschild, M., 1958, Structure and Evolution of the Stars, Princeton Univ. Press,

Seewald, J.S., 2001. Aqueous geochemistry of low molecular weight hydrocarbons at

elevated temperatures and pressures: constraints from mineral buffered

of its implications for the chemistry of asteroids, planets and satellites. Icarus

Shaw, G.H., 2008, Earth's atmosphere – Hadean to early Proterozoic, Chemie der Erde, 235-264.

Wood, B.E., Mueller, H.-R., Zank, G.P., Linsky, J.L., Redfield, S., 2005. New mass loss measurements from astrospheric Ly- $\alpha$  absorption. Astrophys. J. Lett. 628, L143-L146.

Would this model produce effects observable at present? This map of Mars shows recent impact sites. Below it are images from some of them. images from: http://www.msss.com/crater2006catalog map from: MOLA/NASA JPL 400-942A 04/01 After the Transition When the climate transition occurs under the methane/ammonia greenhouse cenario the surface conditions are much different than they would be under a  $CO_2$ scenario. In the latter there should be very large carbonate mineral reservoirs at the surface, the result of a billion years of intense weathering under the high density, warm wet and acidic conditions of a high pressure CO<sub>2</sub> atmosphere. These should be preserved as a consequence of the rapid freezing. There is NO EVIDENCE for any such carbonate (or sufficiently large frozen  $CO_2$ ) reservoirs. In the methane/ammonia case, the atmosphere consists mostly of a much smaller inventory of the much more potent reduced greenhouse gases, but a large reservoir of

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The secular decrease in volcanic activity that has been invoked to explain the upposed drop in CO<sub>2</sub> content of Mars' atmosphere, leading to the climate shift about 3.5 GABP, is a logical result of loss of radiogenic heat sources through time, and the more effective loss of primordial (accretional) heat on Mars compared to the much larger Earth. But the same argument also applies to hydrothermal heat, which ultimately has the same source. It should be obvious that magmatic temperatures, which favor the production of CO<sub>2</sub> when carbon compounds equilibrate with iron metal poor silicate melts, are much more localized than hydrothermal temperatures that, while often ssociated with volcanic centers, are typically much more widespread and last longer than the magma itself. In other words, even in volcanic systems, there is a much larger

Mars' Climate Transition

volume of rock (and/or seawater) exposed to a hydrothermal regime for a much longer eriod of time than the silicates (and associated carbon) exposed to magmatic conditions. Hydrothermal regimes capable of producing significant amounts of methane and ammonia may be present without producing striking (at least in a topographic sense) surface features, although interesting deposits that may be associated with (former?) springs have been seen on Mars imagery. Ultimately the decay of volcanic sources will also lead to a drop in hydrothermal

ctivity and the loss of sufficient methane and ammonia production to maintain the necessary greenhouse effect, even with increasing luminosity of the Sun, and the climate transition occurs. During the transition it is possible (probable?) that climate will be unstable and may include both warm and cold periods.

-----methane ir atmosphere

This schematic graph illustrates the variables for Mars. As the methane wanes, neither the increase in CO2 nor solar luminosity can keep up, and Mars shifts from a warm, wet state o a cold, dry state. The precise time of the transition is not indicated. Feedbacks — carbon dioxide in atmospheric chemistry and physics in atmosphere would affect the precise timing of the transition. The transition could cover an extended period, with "ice ages" and warm periods interspersed.

arbon dioxide is the primary component of Mars atmosphere at resent. It is conventional wisdom that CO2 was the dominant atmospheric gas from the time of earliest degassing of the Martian interior. The dominant degassed volatile on/near the Martian surfac was (and probably is) water. The evidence for very large volumes of for any significant length of time. Considering the increase in luminosity of the sun over the last 4.5 BY, the presence of liquic water on Mars surface in the distant past would require even high concentrations of greenhouse gases at that time. To get from such an early warm, wet climate with a faint sun and high atmospheric C levels to the present cold climate seems to require loss of huge quantities of CO2 and perhaps water (hydrogen). Recent results suggest that atmospheric loss mechanisms are not sufficient to the produced by a water and CO2-rich surface environment. Clearly w have a problem.

The solution is simple. The primary carbon species degassed fro Mars interior was methane, probably accompanied by ammonia, and ertainly by a much larger amount of water. Methane is a much mo emical destruction, at sufficient levels for greenhous ethane to temporarily restore mild conditions. With secular cooli the water of the Martian ocean froze, along with its residual dissolve reservoir of carbonaceous compounds. The oxidized surface we see nay be a thin veneer produced and maintained by hydrogen loss oxygen production) from the small amount of water released into he atmosphere over time.

# The Topography of Mars



reduced carbon and nitrogen compounds, most of which are likely to be found in the ocean. The freezing of the Martian surface leaves the reduced gases trapped in the atmosphere, where they are rapidly destroyed by photolysis. Any continued production of the gases by residual hydrothermal activity leads also to destruction of the added gases. The products of photolysis (accompanied by hydrogen escape from the Martian atmosphere) are  $N_2$ , CO and CO<sub>2</sub>, all of which are present in Mars' atmosphere and surface environment at reasonable levels. Any reduced compounds condensed on the land surface would be rapidly oxidized by formation of photolytic OH and O, while the (probably) much larger reduced carbon reservoir in the oceans would be trapped by freezing. At present, the largest carbon reservoir on Mars is probably to be found in the frozen (and now dust/debris covered) oceans and lakes (if there be any), perhaps with some unknown amount of carbonaceous material buried (perhaps at relatively shallow depths) below the dust-covered land areas. Recent impacts of small meteoroids may expose these organics to the surface, followed rapidly by oxidation (Malin et al., 2007)