ARTICLE IN PRESS
EPSL:14044

Earth and Planetary Science Letters ••• (••••) •••–•••

Contents lists available at ScienceDirect

Earth and Planetary Science Letters

www.elsevier.com/locate/epsl

Climate cycling on early Mars caused by the carbonate–silicate cycle

Natasha E. Batalha[a,b,c,*], Ravi Kumar Kopparapu[c,d,e,f], Jacob Haqq-Misra[c,d], James F. Kasting[b,c,g]

[a] Department of Astronomy & Astrophysics, Penn State University, University Park, PA 16802, USA
[b] Center for Exoplanets and Habitable Worlds, Pennsylvania State University, University Park, PA 16802, USA
[c] NASA Astrobiology Institute's Virtual Planetary Laboratory, P.O. Box 351580, Seattle, WA 98195, USA
[d] Blue Marble Space Institute of Science, 1001 4th Ave Suite 3201, Seattle, WA 98154, USA
[e] NASA Goddard Space Flight Center, 8800 Greenbelt Road, Mail Stop 699.0 Building 34, Greenbelt, MD 20771, USA
[f] Department of Astronomy, University of Maryland, College Park, MD 20771, USA
[g] Department of Geosciences, Penn State University, University Park, PA 16802, USA

ARTICLE INFO

Article history:
Received 26 January 2016
Received in revised form 23 August 2016
Accepted 31 August 2016
Available online xxxx
Editor: C. Sotin

Keywords:
Mars
martian climate
valley formation

ABSTRACT

For decades, scientists have tried to explain the evidence for fluvial activity on early Mars, but a consensus has yet to emerge regarding the mechanism for producing it. One hypothesis suggests early Mars was warmed by a thick greenhouse atmosphere. Another suggests that early Mars was generally cold but was warmed occasionally by impacts or by episodes of enhanced volcanism. These latter hypotheses struggle to produce the amounts of rainfall needed to form the martian valleys, but are consistent with inferred low rates of weathering compared to Earth. Here, we provide a geophysical mechanism that could have induced cycles of glaciation and deglaciation on early Mars. Our model produces dramatic climate cycles with extended periods of glaciation punctuated by warm periods lasting up to 10 Myr—much longer than those generated in other episodic warming models. The cycles occur because stellar insolation was low, and because CO_2 outgassing is not able to keep pace with CO_2 consumption by silicate weathering followed by deposition of carbonates. While CO_2 by itself is not able to deglaciate early Mars in our model, we assume that the greenhouse effect is enhanced by substantial amounts of H_2 outgassed from Mars' reduced crust and mantle. Our hypothesis can be tested by future Mars exploration that better establishes the time scale for valley formation.

1. Introduction

Observational evidence for large-scale fluvial features on the martian surface dates back to NASA's Mariner 9 and Viking Missions (Masursky et al., 1977). Most of these features formed in the Late Noachian and Early Hesperian, ∼3.8 Gyr ago, based on ages determined from crater counting (Fassett and Head, 2008). The geomorphological evidence includes the presence of valley networks (Cabrol and Grin, 2001), tributaries (Irwin et al., 2008), meandering channels (Hynek et al., 2010), open and closed-basin lakes (Goldspiel and Squyres, 1991), and the presence of phyllosilicates (Poulet et al., 2005). New findings from Mars Science Laboratory (MSL) indicate that Gale Crater was also once filled with liquid water for 10,000 to 10 million years (Grotzinger et al., 2015), implying that surface liquid water persisted for prolonged periods of time. Recent ground-based observations of deuterium-to-hydrogen (D/H) ratios in martian ground ice imply that at least 137 m of exchangeable water was originally available (Villanueva et al., 2015). The implied initial water inventory could be significantly larger if much of the H escaped hydrodynamically, carrying D with it (Batalha et al., 2015).

Despite the abundant evidence for sustained liquid water, climate modelers have had difficulty explaining how early Mars could have maintained a temperate environment. The Sun was ∼25 percent less bright at the time when most of the valleys formed, making it difficult or impossible to warm the surface using only the greenhouse gases CO_2 and H_2O (Kasting, 1991). Even 3-D climate models that include seasonal cycles and obliquity variations are unable to produce warm conditions (Forget et al., 2013). Adding SO_2 or CH_4 to the mix of greenhouse gases does not generate significant warming: the SO_2 either rains out (Batalha et al., 2015; Halevy and Head III, 2014) or photolyzes to form sulfate aerosols (Kerber et al., 2015; Tian et al., 2010), whereas CH_4 absorbs incoming solar near-infrared radiation in the stratosphere, creating anti-

* Corresponding author.
E-mail address: neb149@psu.edu (N.E. Batalha).

http://dx.doi.org/10.1016/j.epsl.2016.08.044

greenhouse cooling that offsets its greenhouse warming (Ramirez et al., 2014).

One supplementary greenhouse gas, H_2, can produce a warm climate, provided that it is supplied in sufficient quantities (Ramirez et al., 2014). H_2 absorbs effectively across the thermal-infrared spectrum as a consequence of collision-induced excitation of its rotational energy levels (Wordsworth and Pierrehumbert, 2013). 1-D climate modeling suggests that CO_2 partial pressures of >1.5 bar, combined with H_2 mixing ratios of 5 percent or more, could have kept early Mars' mean surface temperature above the freezing point of water (Ramirez et al., 2014). Outgassing of H_2 could result from a highly reduced mantle (Batalha et al., 2015; Ramirez et al., 2014) or from serpentinization of ultramafic crust (Batalha et al., 2015; Chassefière et al., 2014). Greenhouse warming by H_2 plays a critical role in the episodic warming mechanism described below.

In addition to H_2, the Ramirez et al. (2014) greenhouse warming mechanism also requires substantial amounts (1.5–3 bar) of CO_2. From the standpoint of initial planetary inventories, this amount of CO_2 is not unreasonable. Earth has the equivalent of ~60 bar of CO_2 tied up in carbonate rocks in its crust (Walker, 1985). If Mars was endowed with the same amount of carbon per unit mass, its initial inventory should have been on the order of 10 bars, accounting for its 9 × smaller mass, 4 × smaller surface area, and 3 × smaller gravity. Questions remain as to how fast this carbon would have been outgassed and whether CO_2, or any atmospheric gas, could have been retained, given the intense solar EUV flux early in solar system history (Lammer et al., 2013). But if much of the carbon was sequestered in carbonates early on, then perhaps it could have been protected from loss during this time. Continued recycling of volatiles between the crust and the mantle would be required to revolatilize CO_2 later on and sustain significant volcanic outgassing rates, as discussed further below.

The scarcity of visible carbonate outcrops near Mars' surface has been used to argue that such a dense CO_2 atmosphere never existed (Hu et al., 2015). But carbonate has been observed in martian dust (Bandfield et al., 2003), in SNC meteorites (Bridges et al., 2001), and in the bottoms of fresh craters (Michalski and Niles, 2010), so it is definitely present within the crust. The lack of surface outcrops could be caused by the high acidity of rainwater under a dense CO_2 atmosphere, which may have dissolved carbonate minerals near the surface and reprecipitated them at depth (Kasting, 2010, Ch. 8).

Despite the evidence for fluvial activity, the difficulties in producing warm climates discussed above have spawned the idea that the early martian surface was generally frozen. Outflow channels on Mars have been interpreted as large flooding events, perhaps caused by magmatic heating of subsurface ice followed by breaching of groundwater through an icy surface (Baker, 1962; Cassanelli et al., 2015). Valley networks have been interpreted as snow migration, perhaps caused by obliquity variations and seasonal melting (Wordsworth et al., 2015). In short, the evidence for the state of the early martian climate is mixed, which is consistent with the hypothesis outlined below.

Even if early Mars was generally cold, there are several proposed mechanisms by which the climate could have been warmed transiently, perhaps long enough to form the valleys. (We refer to these as 'cold early Mars' hypotheses.) One theory suggests that impacts during the Late Heavy Bombardment created thick steam atmospheres that then rained out to form the valleys (Segura et al., 2012). But the thousands of years of warm climates and the ~600 m of planet-wide rainfall that impacts would have produced are probably several orders of magnitude too short or too low to carve the valleys (Hoke et al., 2011). Extending these warm periods with cirrus clouds (Urata and Toon, 2013) requires 100 percent cloud cover within each cloudy grid cell, combined with a low

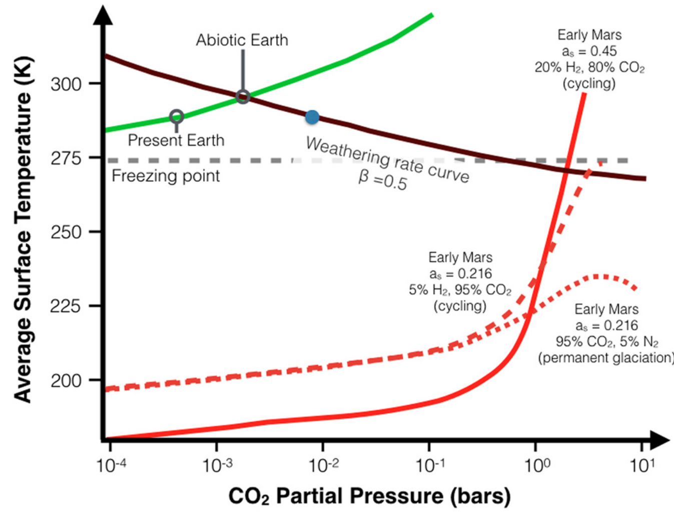

Fig. 1. Diagram showing where climate cycles should and should not occur. The green and red curves represent surface temperatures calculated using a 1D climate model (Kopparapu et al., 2013) for present Earth (green) and early Mars (red) with three different atmospheric compositions and two different surface albedos (0.216 for dry land and ocean, 0.45 for a fully glaciated planet). The solar flux for early Mars is 0.3225 times the flux for present Earth. The brown curve shows the temperature at which the weathering rate balances the present terrestrial CO_2 outgassing rate, assuming a $pCO_2^{0.5}$ dependence (solutions for Eqn. (3) when $W/W_\oplus = 1$). The blue circle shows the location of the present soil pCO_2 level. These curves define three regions of climate stability: 1) *Warm stability*: The surface temperature and weathering rate curves intersect above the freezing point (abiotic Earth) and planets remain permanently de-glaciated. 2) *Cold Stability*: The surface temperature fails to ever rise above the freezing point of water (red dotted early Mars case). Such planets remain permanently glaciated. 3) *Limit Cycling*: The surface temperature and weathering rate curves intersect below the freezing point, but temperatures above freezing are possible as CO_2 and H_2 build up (solid/dashed red early Mars case with H_2). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

conversion efficiency of cloud particles to precipitation (their autoconversion parameter, B), both of which seem unlikely. Other GCM studies of CO_2-rich early martian atmospheres do not produce warm climates unless additional (unspecified) radiative absorbers are added (Wordsworth et al., 2013, 2015). Alternatively, sporadic volcanic outgassing of SO_2 has been suggested as a warming mechanism (Halevy and Head III, 2014), but these authors ignored rainout, as noted earlier.

All of these theories of martian valley formation have overlooked a phenomenon that has been suggested to be important for early Earth, as well as for planets orbiting near the outer edge of their star's habitable zone. Planets on which the CO_2 outgassing rate is small (Tajika, 2003), or for which stellar insolation is low (Menou, 2015), are predicted to undergo repeated cycles of global glaciation/deglaciation as a consequence of the dependence of the CO_2 removal rate on temperature and CO_2 partial pressure, pCO_2. These 'limit cycles' occur because when the planet is in a glaciated state, CO_2 consumption by silicate weathering cannot keep pace with CO_2 outgassing from volcanoes. Atmospheric CO_2 builds up and increases the planet's surface temperature until it is able to deglaciate. But once the planet is ice-free, CO_2 outgassing cannot keep pace with consumption by weathering, so the planet falls back into global glaciation, and the cycle repeats. Such limit cycling does not occur on modern Earth because the solar flux is sufficiently high that weathering can balance outgassing at relatively low atmospheric pCO_2 (Fig. 1). Furthermore, on an inhabited planet like Earth, soil pCO_2 is decoupled from atmospheric pCO_2 by the activities of vascular plants (Berner, 1992). Here we show that on a poorly illuminated early Mars, the high pCO_2 values required for climatic warmth could have induced rapid weathering, perhaps triggering limit cycles.