Earth and Planetary Science Letters 308 (2011) 391–400

Contents lists available at ScienceDirect

Earth and Planetary Science Letters

journal homepage: www.elsevier.com/locate/epsl

Volcanic outgassing of CO_2 and H_2O on Mars

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ARTICLE INFO

Article history:
Received 3 May 2011
Received in revised form 15 June 2011
Accepted 17 June 2011
Available online 13 July 2011

Editor: Y. Ricard

Keywords:
Mars
volcanism
outgassing
CO_2
water
geophysics

ABSTRACT

Volcanic outgassing is one of the main sources of volatiles for the martian atmosphere and degassing of the martian interior potentially influenced the early martian climate. Using a parameterized thermo-chemical evolution model and considering two end-member melting models, we self-consistently calculate the amount of CO_2 and H_2O outgassed during the martian evolution. Outgassing rates are found to depend primarily on a factor describing the outgassing efficiency, the bulk mantle water content, the mantle oxygen fugacity, and the local melt fraction in the magma source regions. We find that significant outgassing ceased around 3.5–2 Gyr ago, depending on the adopted melting model. A total of 0.9–1 bar CO_2 is outgassed during this time period if a mantle oxygen fugacity corresponding to one $\log_{10}$ unit above the iron–wustite buffer is assumed. Additionally, a total of 17–61 m of water is delivered to the surface. Outgassing is most efficient in the pre-Noachian (up to 4.1 Gyr), but still significant during the Noachian, and 5–15 m of water and ~250 mbar of CO_2 are outgassed between 4.1 and 3.7 Gyr. Although this amount is probably insufficient for an appreciable greenhouse effect, pressures are found to be sufficient to stabilize transient liquid water on the surface well into the Hesperian period. Therefore, our results support the hypothesis that rather than being warm-and-wet, the martian climate was probably cold-and-wet. Outgassing is found to strongly decline during the Hesperian, and is insignificant during the Amazonian period. A simple parameterization for the outgassing of CO_2 and H_2O as a function of time is presented.

1. Introduction

1.1. Martian atmospheric evolution

The question of if and when the martian atmosphere was dense enough to allow liquid water to be stable on the planetary surface has attracted considerable attention and atmospheric conditions sensitively influence the habitability of the planet. Following accretion and core formation, Mars was likely covered by a global magma ocean, and an appreciable H_2O-CO_2 atmosphere probably built up during this time period. Estimates of the density of the primordial atmosphere range from 1 to 100 bar (Elkins-Tanton, 2008; Hirschmann and Withers, 2008), and the atmosphere was probably thick enough to significantly reduce magma ocean cooling (Elkins-Tanton, 2008).

During the early history of the solar system the extreme ultraviolet (EUV) flux from the young sun is believed to have been much larger than it is today and, as a consequence, atmospheric temperatures are assumed to have been significantly increased. This would have resulted in an expansion of the atmosphere, leading to efficient atmospheric loss through thermal escape of heavy, neutral particles. Models indicate that an early CO_2-dominated atmosphere could not have been maintained (Tian et al., 2009), and atmospheric loss rates could have been as large as 0.1–1 bar per Myr before 4.1 Gyr. In addition to thermal escape, atmosphere could have been lost through impact erosion (Melosh and Vickery, 1989; Pham et al., 2009), such that the primordial atmosphere was likely entirely eroded.

During the Noachian period between 4.1 and 3.7 Gyr b.p., atmospheric pressure was determined by the interplay between volcanic outgassing, impact erosion/delivery, CO_2 adsorption to the regolith, CO_2 storage in the polar caps, and CO_2 sequestration in carbonate rocks (e.g., Jakosky and Phillips, 2001; Manning et al., 2006). Furthermore, loss processes like sputtering, dissociative recombination, and ion escape became efficient, and although the timing of the dynamo shutdown is still controversial, it is generally assumed to have occurred at around the same time, and could have potentially resulted in enhanced atmospheric loss. Atmospheric pressures and temperatures during the Noachian have been extensively modeled and it was found that atmospheric conditions allowing for liquid water to be stable on the surface are difficult to achieve. For a CO_2-dominated atmosphere, climate models require surface pressures of several bar CO_2 to obtain surface temperatures above freezing (Kasting, 1991), although this value can be reduced to 0.5–1 bar if scattering of infrared radiation from CO_2 ice clouds is taken into account (Forget and Pierrehumbert, 1997).

Alternative models to account for warmer surface temperatures include additional greenhouse gasses like CH_4, SO_2 and H_2S, which could have been released by volcanism. While the release of CH_4 is probably not sufficient to account for appreciable greenhouse warming (Kasting, 1997), sulfur is highly soluble in martian basalts (Johnson et al., 2008),

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doi:10.1016/j.epsl.2011.06.014

and sulfur volatiles could therefore add significantly to an early martian greenhouse. Due to their short lifetimes, greenhouse warming caused by SO_2 and H_2S would only be efficient as long as these species are continuously supplied to the atmosphere, but they could cause warming by up to 25 K (Johnson et al., 2008). Furthermore, aqueous solutions with lower melting points have been extensively studied (see, e.g., Fairén (2010) and references therein) and instead of being warm-and-wet (Jakosky and Phillips, 2001), Mars might have been cold-and-wet in the sense that average surface temperatures were around 245 K (Fairén, 2010; Gaidos and Marion, 2003).

When outgassing and impact delivery of volatiles waned around the beginning of the Hesperian, loss processes prevailed and the D/H ratio in the martian atmosphere indicates that 60–90% of the martian water inventory has been lost to space (Jakosky and Phillips, 2001). The amount of atmospheric CO_2 lost in the last 3.5 Gyr is still under debate, but most estimates are of the order of tens to a few hundred millibars (Johnson et al., 2000; Lammer et al., 2008; Luhmann et al., 1992) rather than a substantial fraction of a bar, giving further support to the cold-and-wet Mars hypothesis. Note, however, that carbonates have been detected on the surface of Mars (Ehlmann et al., 2008; Michalski and Niles, 2010), and it has been suggested that carbonate minerals equivalent to 1 bar of CO_2 could have been deposited (Griffith and Shock, 1995). This would correspond to a global carbonate layer of 20 m thickness (Warren, 1987), but the total amount of CO_2 sequestered in crustal rocks remains unknown.

1.2. Surface geological record

Several lines of evidence suggest that liquid water was once a geological agent at and near the surface of Mars (Baker, 2001), but the exact timing and duration of water-related events are a matter of ongoing debate. Nevertheless, there is a consensus that liquid water was planet-wide available in the early history of Mars, although in unknown quantities. Later, the surface became more and more dry, until the environment approached the hyperarid conditions that prevail today.

Widespread fluvial valley networks in ancient cratered terrain were carved by surface runoff, but it is not entirely clear if the water was supplied by precipitation (rain or snow) (Craddock and Howard, 2002) or by groundwater seepage (Goldspiel and Squyres, 2000).Seepage alone as valley-forming process is considered unlikely, however, because some valleys have their origins at the crest of hills, which would not be expected if they were formed by seepage induced by hydrothermal activity (e.g., Mangold et al., 2004). Moreover, terrestrial experience shows that flash floods are required to remove the debris generated by seepage weathering (Irwin et al., 2008; Lamb et al., 2008). In any case the Noachian was characterized by an active hydrological cycle, because sapping also requires precipitation to recharge the groundwater system. Overall, however, the fluvial morphology of the Noachian landscape is poorly developed and suggests an arid climate (Barnhart et al., 2009; Irwin et al., 2011; Stepinski and Coradetti, 2004; Stepinski and Stepinski, 2005). Valley network formation occurred over an extended period of time, but in varying intensity and of perhaps ephemeral nature, and might have ended with an intense period of fluvial dissection (Howard et al., 2005; Irwin et al., 2005) between the end of the Noachian and the beginning of the Hesperian at ~3.8 to 3.5 Ga (Fassett and Head, 2008a).

The Noachian would also have been the most likely time during which an ocean in the northern lowlands acted as a natural global sink for water (Clifford and Parker, 2001), though unambiguous morphologic or compositional evidence for such a global ocean is still lacking (review by Carr and Head, 2003). Nevertheless, deltaic intra-crater sediments (e.g., Hauber et al., 2009) and craters with fluvial inlets and outlets (Fassett and Head, 2008b) indicate smaller-than-ocean-sized (though still substantial) standing bodies of water in the Noachian, but there is no consensus on their longevity. Most of the sedimentary bodies might have formed at very short timescales (e.g., Kleinhans et al., 2010) and may not require an exceptionally warm and wet climate. Unambiguous evidence for liquid water comes from the orbital discovery of widespread phyllosilicates (Mustard et al., 2008; Poulet et al., 2005) in ancient cratered terrain, products of the aqueous alteration of basaltic parent materials under neutral pH conditions.

The transition from the Noachian to the Hesperian is marked by a sharp decline in erosion rates (Craddock and Maxwell, 1993; Golombek et al., 2006). Fluvial processes were still active (Mangold et al., 2004), but the number of newly formed valley networks decreases and their morphology suggests that sapping became the predominant agent of erosion (Harrison and Grimm, 2005). The transition to a groundwater-dominated hydrology is also indicated by the characteristics of stratified sediments in Meridiani Planum, which is best explained by episodic wetting through upwelling surface water (Grotzinger et al., 2005) controlled by a fluctuating water table (Andrews-Hanna et al., 2010). While some lakes and associated deltaic deposits are dated as Hesperian (Di Achille et al., 2007; Malin and Edgett, 2003), local factors might have contributed to their formation and it is questionable if their existence reflects climatic conditions that were significantly different from today.

Other geological observations are also consistent with a thin Hesperian atmosphere, and olivine outcrops, which would weather rapidly in the presence of water (Hoefen et al., 2003) lend additional support for a generally dry Hesperian climate. A perhaps even more important mineralogical indication of a changing environment is the distribution of hydrated minerals, with more abundant outcrops found in Noachian terrains and less evidence for hydration observed in younger regions (e.g., Bibring et al., 2006; Murchie et al., 2009). While some of the observed phyllosilicates and carbonates in Noachian terrains might have formed in aqueous environments with neutral or alkaline pH (e.g., Murchie et al., 2009), sulfate-bearing Hesperian units might have experienced much drier and acidic conditions (e.g., Altheide et al., 2009; Berger et al., 2009). The abrupt beginnings of Hesperian-aged outflow channels clearly indicate that they were not fed by precipitation, but by some mechanism that released water from the subsurface, perhaps by melting or cracking the thickening cryosphere (Clifford, 1993). Although the amount of surface water implied by the huge channel dimensions is large, such processes do not require a thick atmosphere.

The Amazonian is characterized by very cold and hyperarid conditions and evidence for liquid water is even sparser than in the Hesperian. Late Hesperian to Early Amazonian mid-latitude valleys (Dickson et al., 2009) were probably formed by meltwater from snow and/or ice deposits, and fluvial and debris flow processes carved gullies (Malin and Edgett, 2000), which are very young (~10^5 to 10^6 years; Reiss et al., 2004). Their origin involved liquid water and might be related to recent changes in the orbital configuration of the planet.

In summary, the geological record displays a gradual decrease in the amount of liquid water at or near the surface and the poor development of fluvial features indicates that most of the Noachian probably never experienced a warm and wet climate similar to that of the current Earth. Towards the Hesperian, the global hydrology became groundwater-dominated (Andrews-Hanna and Lewis, 2011), surface water became episodic and short-lived, the groundwater table sank with time (Reiss et al., 2006), and Mars turned into the cold desert planet that it is today. Major uncertainties exist with respect to the total amount of water present at the surface during the different epochs, and the related evolution of atmospheric density. Nevertheless, it appears likely that water in the Hesperian and Amazonian was transient and related to local and regional factors, and consequently no dense atmosphere would be required.

1.3. Volcanic outgassing

Together with impact delivery (Pham et al., 2009) and the reactivation of subsurface reservoirs, volcanic outgassing is one of the main sources of volatiles for the martian atmosphere (Jakosky and