Minimum estimates of the amount and timing of gases released into the martian atmosphere from volcanic eruptions

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A B S T R A C T

Volcanism has been a major process during most of the geologic history of Mars. Based on data collected from terrestrial basaltic eruptions, we assume that the volatile content of martian lavas was typically $\sim$0.5 wt.% water, $\sim$0.7 wt.% carbon dioxide, $\sim$0.14 wt.% sulfur dioxide, and contained several other important volatile constituents. From the geologic record of volcanism on Mars we find that during the late Noachian and through the Amazonian volcanic degassing contributed $\sim$0.8 bar to the martian atmosphere. Because most of the outgassing consisted of greenhouse gases (i.e., CO_2 and SO_2) warmer surface temperatures resulting from volcanic eruptions may have been possible. Our estimates suggest that $\sim$1.1 $\times$ 10^{21} g ($\sim$8 $\pm$ 1 m m^{-2}) of juvenile water were released by volcanism; slightly more than half the amount contained in the north polar cap and atmosphere. Estimates for released CO_2 (1.6 $\times$ 10^{21} g) suggests that a large reservoir of carbon dioxide is adsorbed in the martian regolith or alternatively $\sim$300 cm cm^{-2} of carbonates may have formed, although these materials would not occur readily in the presence of excess SO_2. Up to $\sim$120 cm cm^{-2} (2.2 $\times$ 10^{20} g) of acid rain (H_2SO_4) may have precipitated onto the martian surface as the result of SO_2 degassing. The hydrogen flux resulting from volcanic outgassing may help explain the martian atmospheric D/H ratio. The amount of outgassed nitrogen ($\sim$1.3 mbar) may also be capable of explaining the martian atmospheric $^{15}N/^{14}N$ ratio. Minor gas constituents (HF, HCl, and H_2S) could have formed hydroxyl salts on the surface resulting in the physical weathering of geologic materials. The amount of hydrogen fluoride emitted (1.82 $\times$ 10^{18} g) could be capable of dissolving a global layer of quartz sand $\sim$5 mm thick, possibly explaining why this mineral has not been positively identified in spectral observations. The estimates of volcanic outgassing presented here will be useful in understanding how the martian atmosphere evolved over time.

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1. Introduction

There is substantial evidence to suggest that liquid water was present on the martian surface in the geologic past. Outflow channels (Baker and Milton, 1974; Baker, 1979; Carr, 1979), valley networks (Pieri, 1976, 1980; Masursky et al., 1977; Carr and Clow, 1981), and degraded impact craters (Jones, 1974; Chapman and Jones, 1977; Craddock and Maxwell, 1990, 1993a; Craddock et al., 1997; Craddock and Howard, 2002) indicate that liquid water was once eroding the martian surface at rates comparable to many climates on present-day Earth. However, the current atmospheric pressures and temperatures do not support liquid water at the surface, so somehow conditions must have been different in the past. Determining the nature of the ancient climate of Mars is compli-

cated by a number of unknown factors, including variations in the luminosity of the sun over time (Gough, 1981), obliquity variations (Touma and Wisdom, 1993), volatile contributions from impact cratering, and changes in the composition and thickness of the atmosphere over time. In many climate models the ancient atmospheric pressure on Mars varies widely from a few tens or hundreds of millibars (e.g., Cess et al., 1980) to tens of bars (e.g., Pollack et al., 1987). Typically, however, such estimates are proposed simply to satisfy some parameter in a particular climate model without any consideration being given to the possible constraints that might be imposed by the geologic record. There are several potential sources for creating and maintaining the ancient atmosphere including impact degassing (e.g., Ahrens et al., 1989) cometary impacts (e.g., Chyba, 1990), volcanic outgassing, and volatile recycling from putative tectonism (Sleep, 1994) or simple burial (Pollack et al., 1987). In this paper we begin an examination of the geologic record in an effort to place some constraints on the atmospheric contributions that may have resulted from volcanic outgassing over time.

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Volcanism was a major geologic process on Mars throughout most of the planet's history spanning the time from heavy bombardment (~4.0 billion years ago) to some of the youngest geologic units on the surface. Today volcanic materials cover roughly half of the surface (Tanaka et al., 1988; Greeley and Schneid, 1991). It is probable that gases released during volcanic eruptions not only played a role in creating and maintaining an early warm and wet atmosphere, but controlled many of the other geologic processes that were active during martian history. Our approach is unique in that we use volatile abundances based on well-established measurements of terrestrial basaltic lava flows that are similar in composition to most martian volcanic flows. We also examine all of the possible gas constituents, including the primary gases such as water (H_2O), sulfur dioxide (SO_2), and carbon dioxide (CO_2), but also the minor constituents as well. The estimates presented here are subject to a certain amount of error, as we discuss; however, they represent the most accurate estimates possible given our current understanding of Mars. We have also attempted to make the most conservative estimates possible. In addition to providing some constraints in understanding the evolution of the martian atmosphere, the estimates presented here will also help us to better understand the history of water on the surface as well as the types of weathering and alteration of surface materials that may have occurred through time.

2. Background

2.1. Previous work

There have been a number of previous studies that have attempted to estimate the volatile contribution from volcanic outgassing on Mars, particularly water. In one of the earliest attempts, Mutch et al. (1976a, p. 279) assumed that 30% of the martian surface was covered in volcanic material 2 km deep and that water released during crystallization of these materials was 3% by volume. Their estimate suggested that volcanism had released enough water to cover the entire surface of the planet in a layer 20 m deep. The related amount of outgassed carbon dioxide from their calculation is 0.5 precipitable meters, which is roughly the amount observed today. Using geologic maps based on Viking Orbiter data, Greeley (1987) calculated the approximate amount of volcanic material erupted through time on Mars. Assuming 1 weight percent (wt.%) water for erupted martian lavas, he estimated that a layer of water equal to 46 m deep was outgassed through time. Plescia and Crisp (1992) suggested that the CO_2 content for Elysium volcanics was also 1 wt.%, yielding a combined gas content of over 2 wt.% during eruption. Numerical modeling of the eruption and emplacement of possible pyroclastic flows on the flanks of Tyrrhena and Hadriaca Paterae suggest an exsolved water content of 1.5–3.0% for the associated magmas (Crown and Greeley, 1993).

More recently Phillips et al. (2001) estimated the total volume of volcanic material in the Tharsis-rise using topography from the Mars Orbiter Laser Altimeter (MOLA) and gravity from the Mars Global Survey to compensate for deformational response of the lithosphere due to loading by the volcanoes. Assuming a magmatic content of 2 wt.% water (H_2O) and 0.65 wt.% carbon dioxide (CO_2), they estimate that Tharsis volcanism released an integrated equivalent of 1.5 bar of CO_2 along with a 120-m thick global layer of water. These studies emphasize the potential importance of volcanic outgassing, particularly the contribution to the total water inventory on Mars as well as to the atmosphere. However, our understanding of volcanic outgassing is far from complete, and as to date little attention has been paid to the minor gas constituents that are also commonly associated with volcanism.

2.2. Volcanism through time

The basis for our estimates of volcanic outgassing is predicated on our understanding of the geology of the martian surface as well as the estimated ages of basaltic surface units. Previously Greeley and Schneid (1991) published volume estimates and ages of martian volcanic materials (Table 1). Obviously since their estimates were originally published a number of recent spacecraft have provided data to significantly improve the available image resolution and quality. If anything these data reaffirm the importance of volcanism as a geologic process on Mars. As an example, the Spirit rover found evidence that Gusev crater had been flooded by volcanic material (Greeley et al., 2005), which was contrary to many assessments made prior to landing (e.g., Squyres et al., 2004). However, after examining the new imagery and topographic data it is clear that the results from Greeley and Schneid (1991) continue to provide valid minimum estimates for the volume of volcanic material erupted through time on Mars. For example, their estimates for lava flow thicknesses were determined from partially buried craters, and our understanding of these features has not changed. Also, while there have been advancements in our understanding of small crater populations on Mars (e.g., Hartmann, 2005), the techniques for relative age-dating surfaces from larger diameter craters has not changed significantly from Tanaka's (1986) discussion. Simply stated, our ability to map and age-date basaltic material on Mars has not changed significantly, and the only study to challenge the challenge the Greeley and Schneid (1991) estimates was presented by Phillips et al. (2001).

In their study, Phillips et al. (2001) suggest that loading of the martian lithosphere by the emplacement of the Tharsis-rise would have induced an antipodal topographic high. They present an analysis of long valley network segments showing that many valley networks follow the slope that may have been created by their modeled uplift. Because the valley networks in the highlands are generally Noahian in age (e.g., Fassett and Head, 2008), Phillips et al. (2001) argue that a bulk of the Tharsis-rise must have been emplaced prior to the Noachian and valley network formation. There are many problems with this interpretation, however. First, it is not clear which valley networks were included in their slope analysis, and mapping valley networks from imagery data alone has proven to be a subjective exercise (Luo and Stepinski, 2006; Molloy and Stepinski, 2007; Hynek et al., 2008). Ejecta from the Hellas impact basis has also been proposed to explain the topographic highs in this area (e.g., Korteniemi et al., 2005), and in the Phillips et al. (2001) model the slope of pre-existing topography north of Hellas would have only been accentuated. The most obvious argument against this interpretation, however, comes from the geology of the Tharsis-rise itself. If the Tharsis-rise was emplaced during the Noachian, then the impact crater population in this area should reflect this age, and Tharsis should contain

Table 1
Extrusive volumes (10^6 km^3) of martian volcanic material with time[a].

Epoch	Volume of plains	Volume of edifices	Extruded volume	Mass[b] (10^{22} g)
Late Amazonian	0.33	1.78	2.11	0.7
Middle Amazonian	1.42	7.07	8.49	2.8
Early Amazonian	3.61	12.15	15.76	5.2
Late Hesperian	4.54	11.09	15.63	5.16
Early Hesperian	10.83	6.82	17.65	5.82
Late Noachian	4.31	3.46	7.77	2.56
Middle Noachian	1.39	0	1.39	0.46
Early Noachian	?	?	?	?
Total	26.43	42.37	68.8	22.7

[a] Data from Greeley and Schneid (1991).
[b] Assumes a density of 3.3 g/cm^3.

many large impact craters and basins tens to hundreds of kilometers in size. Potentially even the volcanic edifices would have been partially destroyed by impact cratering. In order to bury a Noachian cratered surface with an average relief of 8–10 km a minimum of 10 km of volcanic material must have been emplaced on the Tharsis-rise during the Amazonian. These problems are not addressed in the Phillips et al. (2001) model, and thus it is difficult to accept their interpretation that the Tharsis volcanics are Noachian in age.

Another caveat to consider is the effect the ambient atmospheric pressure may have had on the style of volcanic eruption that occurred on Mars. Wilson and Head (1983) suggest that under current atmospheric pressures magmas containing volatiles >0.01 wt.% would have erupted explosively. Because the highland patera are some of the oldest central vent volcanoes on the martian surface (~3.7–3.9 Gy) and younger materials do not appear to have been erupted explosively (Williams et al., in press), it has been proposed that the volatile content of the martian mantle may have changed with time (Francis and Wood, 1982; Schubert et al., 1989). Local, young deposits of pyroclastic materials have been identified on Mars, however (Mouginis-Mark et al., 1988, 1992), and it has been suggested that there was some heterogeneity in the volatile content of the mantle or that near-surface waters were assimilated into the shallow magma reservoirs (Schubert et al., 1989). A majority of the volcanic materials included in our analyses, however, were erupted effusively, and we assume that the volatile content was the same over time.

2.3. The influence of volcanism on surface temperatures

On Earth large volcanic eruptions are well known for their ability to create short-term climatic variations (Gow and Williamson, 1971; Lamb, 1971; Bray, 1974). For example, the 10^9 tons of gas and dust placed into the stratosphere by the 1991 eruption of Mount Pinatubo is estimated to have decreased the average global temperature of the Earth by 0.3–0.5 °C for a 2- to 4-year period following the eruption (Robock et al., 1991). Because most people are familiar with such dramatic decreases in temperatures from terrestrial volcanic eruptions, it is not immediately obvious how martian volcanism could have the opposite effect. In actuality either decreases or increases in surface temperatures are possible, but it depends on the style of eruption.

Typically most terrestrial eruptions are contained within the Earth's troposphere (Fig. 1), which contains >80% of the mass of the entire Earth's atmosphere. Most of the solar radiation at wavelengths >0.35 μm (i.e., visible wavelengths) is capable of penetrating the Earth's atmosphere and falling incident on the surface. This radiation is subsequently re-emitted by the surface in the infrared where it is trapped by gases in the troposphere. The efficiency of the troposphere to insulate the surface is generally dependent upon the abundance, composition and phase of gases it contains. A gas that is inefficient at absorbing solar radiation passed through the atmosphere in the visible wavelengths, but which is efficient at absorbing the infrared radiation re-emitted by the surface is referred to as a "greenhouse" gas, which includes many of the gases released from volcanic eruptions. However, the amount of greenhouse gases released into the troposphere by a typical volcanic eruption is small when compared to the amounts released by anthropomorphic mechanisms (e.g., CO_2; Gerlach, 1991) and even smaller when compared to the total amount of gas already contained within the troposphere. The potential increase in surface temperature from most terrestrial volcanic eruptions is thus very small.

Occasionally a large explosive eruption will occur on Earth. Such eruptions, like Mt Pinatubo, are capable of reaching into the Earth's stratosphere ~10 km above the surface. The stratosphere

Fig. 1. Recent outgassing from Kilauea is composed primarily of water vapor with elevated amounts of sulfur dioxide. Released into Earth's troposphere these gases would help retain solar radiation that is re-radiate from the surface in infrared wavelengths, but their abundances are small relative to the ambient atmosphere, thus the resulting increase in temperature is negligible. On Mars, however, effusive eruptions could have potentially released more gas into the lower atmosphere than is present currently. This would result in an increase in the atmosphere's capacity for retaining re-radiated solar radiation, thus increasing surface temperatures.

is characterized by very little vertical mixing of materials, unlike the troposphere, and volcanic gases and dust particles placed into this portion of the atmosphere behave very differently as a result. Sulfur dioxide gas quickly combines with water vapor to form droplets of sulfuric acid, which are spread laterally throughout the stratosphere. The haze created by these droplets reduces the amount of solar radiation capable of passing to the Earth's surface. This decrease in solar radiation thus in turn decreases surface temperatures.

On Earth, temperature decreases associated with explosive eruptions into the stratosphere are much more dramatic than the small increases that could occur in association with volcanic outgassing within the troposphere. On Mars, however, the mass of the atmosphere is much less, and volcanic outgassing within the troposphere may have been capable of increasing the surface temperature significantly (e.g., Postawko and Fanale, 1993). Decreases in temperatures may have also been possible, if a martian volcano erupted explosively or, alternatively, if some of the larger volcanoes grew into the martian stratosphere over time.

2.4. Composition of martian volcanics

There are many lines of evidence indicating that martian volcanic materials are predominately basaltic in composition, including in situ analyses conducted by lander spacecraft, geomorphic assessments of landforms, and remotely sensed data. For example, Viking (Mutch et al., 1976b; Binder et al., 1977; Garvin et al., 1981; Greeley and Spudis, 1981; Sharp and Malin, 1984; Arvidson et al., 1989), Mars Pathfinder (Golombek et al., 1997; Smith et al., 1997), and the Spirit Rover (Squyres et al., 2004; Bell et al., 2004) have imaged many rocks containing vesicles and vugs. Measurements made by the Viking landers' X-ray fluorescence spectrometer indicate that the composition of the martian regolith is consistent with altered mafic igneous rocks (i.e., palagonite) (Toulmin et al., 1977; Allen et al., 1981). Soils with similar compositions as identified by alpha proton X-ray spectrometers (APXS) were also found at the Mars Pathfinder landing site (Rieder et al., 1997) and in Gusev Crater (Gellart et al., 2004). The ubiquitous nature of these soils is due to global mixing of fine particles driven by dust storms (Bell et al., 2004). At Meridiani Planum the surface was seen to be relatively dust-free, but the soils there were found to be composed

predominately of fine-grained basaltic sand (Soderblom et al., 2004), which again attests to the importance of basaltic material on Mars.

While lander measurements are limited to specific areas on Mars, there are many other observations indicating that basaltic materials are in fact widespread, including: (1) the morphology of the volcanoes and associated flows is consistent with basaltic volcanism (Carr et al., 1977; Greeley and Spudis, 1981; Mouginis-Mark et al., 1992). For example, Olympus Mons, the Tharsis Montes, Apollinaris Patera, and the Elysium and Syrtis Major volcanoes resemble terrestrial shield volcanoes (Carr, 1973; Carr et al., 1977; Arvidson et al., 1980; Greeley and Spudis, 1981; Schaber, 1982; Plescia, 1990; Mouginis-Mark et al., 1992; Robinson et al., 1993). Leveed, channelized flows with lobate fronts also resemble basaltic lava flows. Models relating the morphometry of these flows to rheologic properties suggest that they are basaltic to basaltic andesite in composition (Hulme, 1976; Schaber et al., 1978; Moore et al., 1978; Zimbelman, 1985). (2) Comparison of global Thermal Emission Spectrometer (TES) data with terrestrial rock samples indicates that most of the martian surface is basaltic in composition (Bandfield et al., 2000). (3) The SNC meteorites are basaltic in composition (Wood and Ashwal, 1981; Shih et al., 1982; McSween, 1985). Earth-based spectral reflectance measurements of the martian surface show a strong Fe^{2+} absorption, which suggests a mafic composition (Singer et al., 1979; Guinness et al., 1987; Pinet and Chevrel, 1990). (4) Finally, based on Lewis' (1972) cosmochemistry model, a partial melting of the martian mantle would produce lavas with basaltic compositions (McGetchin and Smyth, 1978). These observations suggest that the few in situ measurements made by lander are applicable to most of the martian surface.

However, it is important to mention the evidence suggesting that some volcanic materials on Mars may be more silica-rich. During the Viking era there was evidence suggesting that perhaps some martian volcanic materials are siliceous in composition. For example, Scott and Tanaka (1982) proposed that possible ignimbrites in the Amazonis Planitia region were erupted from magmas silicic to intermediate in composition. More recently, the Spirit rover found opaline silica deposits in association with volcanic materials in Gusev crater (Squyres et al., 2008). Also, rocks analyzed by the APXS at the Mars Pathfinder landing site are considered to be andesite (Rieder et al., 1997). Although there was some speculation at the time that the APXS used on Mars Pathfinder may not be properly calibrated, analyses of Thermal Emission Spectrometer (TES) data suggests that the surface of Mars is composed of both basalt (Surface Type 1) and, to a lesser extent, andesite (Surface Type 2) (Bandfield et al., 2000), the latter of which is primarily confined to the northern lowlands. This interpretation is somewhat controversial, however, and other alternatives include weathered basalt (Wyatt and McSween, 2002), oxidized basalts (Minitti et al., 2002), silica-coated basalt (Kraft et al., 2003), or a mobile sand unit (Ruff and Christensen, 2007). If the TES result is valid, then it is possible that andesites resulted from a late-stage partial melting of the martian mantle (Xiao et al., 2008). Regardless, the volatile content of andesite is generally higher than theolitic basalt that is more commonly found on Mars. The water (H_2O) content of magmas from Arenal Volcano in Costa Rica, for example, was found to be 1–4 wt.% (Wade et al., 2006), whereas the water content of magmas at Kilauea is fairly typically ~0.5 wt.% (Moore, 1970). It is possible that a late-stage, volatile-rich pulse of andesitic volcanism may have created the climatic conditions necessary to produce some of the anomalously young valley networks observed in isolated areas on Mars (e.g., Mangold et al., 2004); however, our primary objective is to provide a conservative, baseline estimate of the total volatile inventory outgassed through time, so we assume that basaltic volcanism dominated Mars' history.

While it is probable that most volcanic edifices on Mars are basaltic in composition, the nature of plains material is less clear. For the most part a basaltic composition for these materials is inferred solely on the presence of wrinkle ridges (Lucchitta and Klockenbrink, 1981; Plescia and Golombek, 1986; Watters, 1988, 1991). Although such features are common on lunar mare materials, which are known directly to be basaltic in composition (e.g., Hubbard and Gast, 1971), such an argument for the martian materials is weak. Wrinkle ridges can also form in sedimentary deposits (Watters, 1988), which may be contained in local basins in the martian highlands (Goldspiel and Squyres, 1991; Craddock and Maxwell, 1993a; Maxwell and Craddock, 1995). Occasionally, however, lobate flow fronts and even proposed fissures have been identified in plains units, thus strengthening the argument for a volcanic origin (e.g., Craddock and Maxwell, 1991). Over $84 \times 10^6 \ km^2$ or roughly 58% of the surface of Mars is covered by material interpreted as volcanic (Tanaka et al., 1988). A more conservative estimate by Greeley and Schneid (1991) places this number at $66.2 \times 10^6 \ km^2$ (46% of the surface). We estimate that approximately one-sixth of this value comes from plains material interpreted as volcanic material based solely on the presence of wrinkle ridges. Most of these deposits were emplaced during the Hesperian (Tanaka et al., 1988).

2.5. Terrestrial volcanic gas measurements and constituents

Obviously attempting to measure the gases released during a volcanic eruption is both difficult and dangerous. Some of the earliest efforts to measure volcanic gases occurred at the turn of the century when Gautier (1906) and Chamberlain (1908) attempted to extract gases from cooled lavas. Until modern analytical techniques became available, however, the prevailing view was that such measurements had been contaminated by the atmosphere and did not reflect the true composition of the magma (Williams and McBirney, 1979, p. 324). Today gases are typically collected in evacuated flasks while the eruption is occurring (Symonds et al., 1994). The most commonly used technique was originally developed by Giggenbach (1975): a long titanium or silica tube is attached to a dewared tube to prevent condensation, and the entire device is inserted into the volcanic vent. An evacuated, pre-weighed sampling bottle partially filled with a solution of NaOH with a normality of ~4 N is attached to the other end of the tube. Water vapor condenses in the sampling bottle, the acidic gases (e.g., carbon dioxide) are absorbed by the NaOH solution, and the noncondensable gases (e.g., nitrogen) are collected in the headspace of the bottle. The amount of each gaseous species collected in the headspace is determined typically by gas chromatography. The solutions resulting from the reaction of NaOH to the acidic gas species are analyzed by a variety of techniques, such as ion chromatography. The amount of water condensed in the sampling bottle is determined by the difference in the weight gained by the bottle minus the weight determined for the non-water gas species. To prevent contamination from non-magmatic sources samples are typically collected from eruptions with temperatures of >500 °C. Often the samples are analyzed for stable isotope abundances to determine whether the gas constituents come from the magma, meteoric fluids, seawater, sedimentary rocks, or some other source (Allard, 1983; Taylor, 1986; Symonds et al., 1994). Symonds et al. (1994) present an excellent review of the possible sources of contamination of volcanic gases collected by this technique and the corrections that are typically applied.

Because of the inherit danger of sampling volcanic gases in situ, a number of analytical methods have been developed for measuring volatiles from glasses which form within phenocrysts as the magma crystallizes. Methods such as bulk vacuum extraction, energetic particle bombardment (e.g., Secondary Ion Mass

Spectroscopy or SIMS), and phase equilibrium studies are useful for determining the total volatile content of a sample, but they do not offer much information on the abundances of individual gaseous species (Ihinger et al., 1994). SIMS is useful for determining the volatile element content of glasses and crystals down to the parts per million level, and this technique has also been applied successfully to measuring the D/H ratio in SNC meteorites (Watson et al., 1994). Spectroscopic techniques (e.g., Fourier transform infrared absorption or FTIR) are useful for determining the concentrations of individual species, but these data rely on the calibration standards determined from bulk techniques.

More recent efforts to measure volcanic gas emissions include airborne and ground-based sensors and a variety of instruments onboard orbiting satellites. However, because of the distances involved only gaseous species that are significantly higher or compositionally different from gases contained in the atmosphere can be measured. As a result, sulfur dioxide (SO_2) is easiest and most reliable measurement to be made from remote sensors. An important result from data collected by the Total Ozone Mapping Spectrometer (TOMS) during the June 15, 1991, Mt. Pinatubo eruption indicates that measurements made by energetic particle bombardment techniques tend to underestimate the amount of SO_2 contained within the magma (Westrich and Gerlach, 1992). Closer analysis of primary vapor bubbles in the glass inclusions and unaltered anhydrite phenocrysts in samples of pumice suggested that sulfur was present in water-rich gas phase prior to the eruption (Westrich and Gerlach, 1992). As discussed below, this indicates that both CO_2 and SO_2 are exsolved from most magmas prior to an eruption, and this must be taken into account when modeling the amount of gases released from martian volcanism.

Regardless of magma composition, the principal gas constituents released from terrestrial volcanoes include water (H_2O), carbon dioxide (CO_2), and sulfur dioxide (SO_2) (e.g., Heald et al., 1963). Water is by far the most abundant volatile outgassed and measured during an eruption (Greenland et al., 1985; Gerlach and Graeber, 1985; Gerlach, 1986; Greenland, 1987a,b; Symonds et al., 1994; Jambon, 1994). Frequently lesser amounts of carbon monoxide (CO), hydrogen (H_2), hydrogen chloride (HCl), hydrogen fluoride (HF), chlorine (Cl_2), fluorine (F_2), sulfur (S_2), hydrogen sulfide (H_2S), sulfur trioxide (SO_3), oxygen (O_2), nitrogen (N_2), and argon (Ar) are also emitted (White and Waring, 1963), but because of the abundance of nitrogen in Earth's atmosphere as a possible source of contamination the amounts of nitrogen outgassed during an eruption are not commonly reported.

Recent detection of methane (CH_4) in the martian atmosphere from Earth-based telescopic observations (Mumma et al., 2009) and the Planetary Fourier Spectrometer onboard Mars Express (Formisano et al., 2004) has generated some controversy. Most of the methane in the Earth's atmosphere is generated from biogenic processes; however, several nonbiogenic sources such as volcanism, hydrothermal, and cometary impacts have been suggested. Although volcanism as a source for methane is questionable (Basharina, 1960), Holland (1978, p. 48) suggests that volcanic gases may added "significant quantities" of methane providing they originated from a carbon-rich part of the mantle. Krauskopf (1957) reports that under strong reducing conditions methane could be outgassed during an eruption. Because early conditions on the Earth were reducing (Kasting, 1993), it is not improbable that reducing conditions also existed on early Mars (Fanale, 1971). It is possible that methane could be released if volcanism (i.e., magmatic or geothermal activity) is presently occurring in reducing conditions on Mars (Lyons et al., 2005; Oze and Sharma, 2005), or if organic material is interacting with this activity. Unfortunately, the amount of methane released during typical basaltic eruptions has not been recorded, so we are unable to provide estimates for this gas constituent.

2.6. Martian volatile content

Realistically there was probably some variability in the volatile content of martian magma, and it is possible that the volatile content changed over time as well. However, there are limits as to what the volatile content could be without affecting the composition of a basaltic magma. An obvious assumption to make is that martian volcanic material had a similar volatile content as ordinary terrestrial basalt. To make our estimates we looked at data obtained from in situ measurements of gases exsolved during eruptions at Mauna Loa and Kilauea eruptions described previously. These data are useful because there are over 80 years of reliable data taken from a number of different eruptions (e.g., Shepard, 1921; Greenland, 1987a,b; Gerlach et al., 2002), so temporal and (albeit limited) spatial variations in the volatile content can be assessed. These data are also some of the very few that assess the abundances of all the individual gas constituents that are emitted during a basaltic eruption (Symonds et al., 1994), thus allowing us to model each constituent as it relates to the others (Table 2). It is also important to consider the fact that magmas come from depth, so they are subjected to much higher pressures and temperatures as they are forming than they experience at or near the surface. As a result, volatiles are exsolved as the magma ascends to the surface and gases are emitted even before the actual eruption begins. In fact, the rate at which exsolution takes place coupled to the rate of magma ascent can greatly influence the style of volcanic eruption (Roggensack et al., 1997; Giordano and Dingwell, 2003). Basically, it is the pre-eruptive volatile content that is important.

There is actually a great deal of variability in the volatile content of an "ordinary terrestrial basalt." The water abundance found in basalt samples that were quenched rapidly during submarine eruptions at Kilauea contain fairly constant concentrations of ∼0.5 wt.% (Moore, 1970; Dixon et al., 1991; Coombs et al., 2006) with the average reported value of 0.45 wt.% (Jambon, 1994). A lower limit for water abundances comes from measurements of subaerially erupted Hawaiian magmas using the evacuated flask technique, which indicated that the pre-eruptive water content was ∼0.32 wt.% (Greenland et al., 1985; Gerlach and Graeber, 1985; Gerlach, 1986). This number also compares well to the average reported water abundance in mid-ocean ridge basalts (0.33 wt.%, Jambon, 1994), which may not be directly comparable to martian basalts in terms of their eruptive source but represent the most abundant basalts on Earth. An upper limit of the pre-eruptive water content of Hawaiian magma comes from numerical

Table 2
Average amounts of principal volcanic gas constituents in basaltic magmas.

Constituents	Volume percent[a]	Weight percent
H_2O	72.548 ± 15.512[b]	0.5000 (±0.1700)
SO_2	19.507 ± 7.948	0.14
CO_2	6.448 ± 8.569	0.7
H_2S	1.139 ± 0.837[b]	0.0069
H_2	0.933 ± 0.420[b]	0.0065
N_2	0.316 ± 0.316[c]	0.0022
HCl	0.131 ± 0.068	0.0008
HF	0.126 ± 0.063	0.0008
CO	0.169 ± 0.295	0.0006
Total	101.317	1.2678

[a] Data includes 21 samples collected from active vents during the 1983 Kilauea eruption (Gerlach and Graeber, 1985, Tables 1 and 2, Greenland, 1987a, Table 28.4), and 22 samples collected from active vents during the 1984 Mauna Loa eruption (Greenland, 1987b, Table 30.1).
[b] Data for water was corrected for estimated equilibrium temperatures, thus removing contamination introduced by oxidizing hydrogen (H_2) and hydrogen sulfide (H_2S). Includes 21 samples from the 1983 Kilauea eruption (Greenland, 1987a, Table 28.4) and 13 samples from the 1984 Mauna Loa eruption (Greenland, 1987b, Table 30.5).
[c] Estimated from Symonds et al. (1994, Fig. 3) using data from Erta' Ale.

modeling of the 1959 Kilauea eruption (Wilson and Head, 1981). After correcting for possible post-disruption exsolved H_2O, Jambon (1994) estimated the pre-eruption water content of this magma to be 0.67 wt.%. This value however does not include the effects of CO_2 or SO_2 on the eruption dynamics, and Jambon (1994) suggested that this value should be taken as an extreme upper limit for the Hawaiian basalts. However, more recent analyses of basaltic glasses collected from Loihi Seamount suggest that water abundances of 0.4–0.8 wt.% are not uncharacteristic pre-eruptive values of Hawaiian basalts and even abundances as high as 1.01 wt.% are possible (Dixon and Clague, 2001).

There are several analyses of basaltic magmas from other parts of the world that provide evidence for even higher pre-eruptive volatile contents. Examination of melt inclusions found in samples from eruptions at Cerro Negro volcano in Nicaragua, for example, indicates that the pre-eruptive abundance of water (H_2O) was 1.18 to as high as 6.08 wt.% (Roggensack et al., 1997). Geochemical modeling indicates that when Plinian eruptions occur at Mount Etna in Italy the magmas may have water abundances of 0.5–2.3 wt.% depending on the subsurface temperature (Giordano and Dingwell, 2003). However, these results likely describe the extreme upper limits of water abundances that are possible in basaltic volcanism because in each setting the volcanoes occur in subduction zones, which would have enriched the volatile content of the magma (e.g., Sisson and Layne, 1997). Although Sleep (1994) suggested that the northern plains of Mars resulted from plate tectonics, the geologic evidence does not support this hypothesis (Pruis and Tanaka, 1995), and the implication is that most martian volcanoes are more likely analogous to terrestrial hot-spot volcanism whose location is favored by the thinner crust in the northern plains (Wise et al., 1979; Carr, 1981, p. 112, Mouginis-Mark et al., 1992). Thus the water abundances from Hawaii volcanism would seem to be the most applicable to Mars.

Several analyses the Shergotty meteorites provide us with a more direct idea as to what the water abundances may have been in martian magmas, but such studies are limited. Hydrous amphibole found in the melt inclusions of pyroxene cores led to speculation that the Shergotty magma contained 1–2 wt.% water (McSween and Harvey, 1993). While these results were somewhat controversial (e.g., Watson et al., 1994), further analyses of the distribution of trace elements within pyroxenes of the Shergotty meteorite as well as hydrous and anhydrous crystallization experiments indicated that the pre-eruptive water content of martian magmas may have been as high as 1.8 wt.% water (McSween et al., 2001). Additional analyses of lithium (Li), beryllium (Be), and boron (B) show that the abundances of these soluble elements changes from the pyroxene cores to the rims indicating that as the pyroxene crystal grew there was a loss of hot, aqueous fluid from the magma as it ascended towards the surface (Lentz et al., 2000), supporting the conclusions of McSween et al. (2001) that volatiles exsolved from the magma as it ascended. The problem with these analyses is that the represent only one Shergotty meteorite, and not all Shergottites show evidence for hydrous minerals. Repeated studies of ALH 77005, for example, have found no hydrous mineral at all (e.g., Calvin and Rutherford, 2008). Again, as with terrestrial basalts, it is likely there were spatial and temporal variations in the volatile content of martian magmas. While the McSween et al. (2001) analyses provide an estimate to the maximum water abundance that may be found on Mars a more conservative estimate would be 0.5 wt.% water as found in most pre-eruptive Hawaiian basalts (Dixon and Clague, 2001).

Until recently it was believed that water was the main gas phase in Kilauea magmas, but much of this thinking was based on gas measurements taken during the eruption without taking into account the exsolution during magma ascent and storage in near surface reservoirs. This thinking changed as monitoring programs began to accurately record background emission rates of CO_2 and SO_2. Gerlach et al. (2002) report that prior to the current phreatic eruption, Kilauea emitted an average of 8500 metric tons of CO_2 per day from magmas contained in the summit reservoir. Essentially an order of magnitude more carbon dioxide is released as magma resides in a near surface reservoir than is measured during the actual eruption (Gerlach, 1980, 1982; Greenland et al., 1985; Gerlach and Graeber, 1985; Greenland, 1987a; Allard et al., 1991). Based on their CO_2 emission rates and magma supply rates, Gerlach et al. (2002) determined that the bulk CO_2 of Kilauea primary magmas is $\sim$0.70 wt.%. Although CO_2 is now known to be the most abundant gas in Hawaiian magmas, presently there is no evidence for CO_2 in the parent magmas of the SNC meteorites (Longhi et al., 1992). However, this does not preclude the possibility that the volatile content of the martian magma has changed with time. Wänke et al. (1992) have also asserted that the water content of the SNC meteorites suggests that CO_2 or SO_2 may have been more abundant in martian magmas.

SO_2 degassing during periods of quiescence is also typical, but Gerlach (1986) determined that exsolution of sulfur (S) as sulfur dioxide only occurs after the magma has ascended to pressures <30 bars ($\sim$150 m). Prior to the April 2008 phreatic eruption episode at Kilauea the average the SO_2 emission rates were $\sim$230 metric tons per day (t d^{-1}) (Gerlach et al., 2002). Stoiber and Jepsen (1973) measured over seven times more SO_2 from the Pacaya Volcano in Guatemala than could be accounted for by simple degassing of erupted lavas. Commonly both CO_2 and SO_2 emission rates will increase prior to an eruption (Noguchi and Kamiya, 1963; Malinconico, 1979; Casadevall et al., 1983; Casadevall, 1987) or seismic event (Gerlach et al., 2002). The amounts of SO_2 emitted by Kilauea are roughly in balance with the amount of expected dissolved sulfur content in the magma (Andres et al., 1989), and the amount of sulfur that can be dissolved in a magma is dependent on the iron content. Estimates of the typical amounts of SO_2 for Hawaiian magmas range from 0.02 to 0.15 wt.%, so for the purposes of our study we used an average value of $\sim$0.14 wt.% SO_2 derived from reported measurements (Gerlach and Graeber, 1985; Greenland, 1987a,b; Andres et al., 1989).

Based on the data available for Hawaiian volcanism, the best estimates for the gas constituents that may have been present in martian magmas are presented in Table 2. The principal gases, including water, carbon dioxide, and sulfur dioxide, have been adjusted for their pre-eruption concentrations. Concentration of minor gas constituents were determined from published data on gases sampled during actual eruptions and do not include exsolution losses that may have occurred as the magma ascended to the surface or resided in subsurface reservoirs. As a result, these values should be considered minimums. It should also be noted that concentrations of nitrogen were estimated from measurements taken at Erta' Ale, which like the Hawaiian volcanoes is also tholeiitic in composition. Because of the high amounts of nitrogen (and argon) in the Earth's atmosphere, determining the amount of nitrogen typically outgassed during an eruption is especially problematic. Most analyses using the post-1975 Giggenbach method show that samples containing >1% nitrogen have N_2/Ar ratios close to that of air (83.6, Symonds et al., 1994). These values are useful in determining the amount of air contaminating the sample and suggest that only small amounts of juvenile nitrogen are outgassed. Abundances of $\sim$0.3 mol% nitrogen are reported when a N_2/Ar ratio of >100–400 are measured (Symonds et al., 1994).

3. Amount and timing of martian volcanic gases

The calculated masses of the individual gas constituents released through time are listed in Table 3. From these estimates

Table 3
Mass (10^{18} g) of martian volcanic gases released through time.

Epoch	Constituents								
	H_2O	SO_2	CO_2	H_2S	H_2	N_2	HCl	HF	CO
Late Amazonian	35	9.8	49	0.48	0.46	0.15	0.06	0.06	0.04
Middle Amazonian	140	39.2	196	1.93	1.82	0.62	0.22	0.22	0.17
Early Amazonian	260	72.8	364	3.59	3.38	1.14	0.42	0.42	0.31
Late Hesperian	258	72.2	361	3.56	3.35	1.14	0.41	0.41	0.31
Early Hesperian	291	81.5	407	4.02	3.78	1.28	0.47	0.47	0.35
Late Noachian	128	35.8	179	1.77	1.66	0.56	0.2	0.2	0.15
Middle Noachian	23	6.44	32.2	0.32	0.3	0.01	0.04	0.04	0.03
Early Noachian	?	?	?	?	?	?	?	?	?
Total	1135	318	1589	15.7	14.8	5	1.82	1.82	1.36

we calculated the resulting partial pressures (Table 4 and Fig. 2). The cumulative atmospheric pressure from all the volcanic gas constituents would amount to ~800 mbar. It is possible that the atmosphere on Mars periodically reached pressures of up to ~200 mbars from volcanic degassing, but these pressures, as discussed below, may have been short-lived.

3.1. Carbon dioxide

Based on the volatile abundances from Hawaiian magmas, the most abundant gas that may have been release from volcanic outgassing on Mars would be carbon dioxide. We estimate that a total of 1.6×10^{21} g (~400 mbar) of carbon dioxide was released into the martian atmosphere from volcanic eruptions. The amount of carbon dioxide in the present atmosphere (2.5×10^{19} g) is fairly insignificant in comparison. Assuming that the south polar layered deposit is composed water ice instead of carbon dioxide (Zuber et al., 2007), then potentially the outgassed CO_2 has been adsorbed into the regolith, deposited as carbonates, removed during silica weathering, or has been injected into space through impact cratering (Brain and Jakosky, 1998).

The adsorptive capability of the martian regolith is dependent on mineralogy, grain size, and the adsorbate material (Kieffer and Zent, 1992, and it possible the martian regolith has a wide range of adsorptive capabilities. Clay minerals have been detected by the Observatoire pour la Mineralogie, l'Eau, les Glaces et l'Activité (OMEGA) instrument on board the Mars Express spacecraft. Specifically three different phyllosilicate minerals have been identified, including nontronite, chamosite, and montmorillonite (Poulet et al., 2005). While deposits of these minerals are typically restricted to dark deposits and isolated outcrops, the presence of smectites in some SNC meteorites (Bridges et al., 2001) suggests that they may be present at depth. Clay minerals (Toulmin et al., 1977; Banin et al., 1988; Poulet et al., 2005) have specific surface areas of a few thousand $m^2 g^{-1}$, and palagonite, which was detected at the Viking landing sites (Toulmin et al., 1977), has a specific surface area of only a few tens of $m^2 g^{-1}$. Models of a uniform,

fine-grained particulate blanket predict the amount of exchangeable CO_2 contained in the martian soil based on the different proposed mineralogies. The exchangeable CO_2 we estimate that is available from volcanic eruptions is ~2400 kg m^{-2}. If the martian regolith is mostly nontronite or basalt, then a minimum regolith depth of ~120 m or ~960 m, respectively, is predicted by the Fanale et al. (1982) model. Assuming a palagonite composition, the Zent et al. (1987) model predicts a minimum regolith depth of ~240 m. As proposed by Kieffer and Zent (1992), the amount of CO_2 we calculate as having been released by volcanic eruptions suggests that the martian atmosphere could be buffered by an ocean of adsorbed CO_2.

Alternatively, the remaining CO_2 might be sequestered as carbonate rocks. Massive, kilometers thick carbonate deposits have been proposed on Mars to explain the formation of Valles Marineris (Spencer and Fanale, 1990), thumbprint terrain in the northern hemisphere (Schaefer, 1990), and the disappearance of several bars of primordial atmosphere (e.g., Pollack et al., 1987). In the presence of a CO_2-rich atmosphere and liquid water, carbonates might form easily (Fanale et al., 1982; Kahn, 1985). In fact, it is even possible to form carbonates under present martian climatic conditions (Booth and Kieffer, 1978). However, with the exception of global TES data suggesting that concentrations of ~2–5 wt.% of carbonates may be present in surficial dust (Bandfield et al., 2003), carbonate deposits have not been detected (e.g., Bibring, 2006), and these missing deposits have been called one of the "major conundrums" of Martian science (Carr, 1998). There are, however, several reasons why carbonate formation may have been inhibited or why carbonate deposits may elude detection by multispectral data (Craddock and Howard, 2002). For example, terrestrial juvenile water has a very low pH (<1–3) (Ivanov, 1967), and carbonates precipitate only in very neutral conditions. Free cations (e.g., Ca^{2+}) must be released from weathered rock first to neutralize the water before carbonate formation could begin. If liquid water was indeed present on early Mars or if conditions were such that precipitation occurred, then it is possible that oxidizing conditions existed in small "oases" such as impact craters, intercrater basins, and zones near volcanoes or

Table 4
Resulting partial pressures (10^{-3} bar) of martian volcanic gases with time.

Epoch	Constituents								
	H_2O	SO_2	CO_2	H_2S	H_2	N_2	HCl	HF	CO
Late Amazonian	8.85	2.48	12.4	0.12	0.12	0.04	0.01	0.01	0.01
Middle Amazonian	35.4	9.91	49.6	0.49	0.46	0.16	0.06	0.06	0.04
Early Amazonian	65.7	18.4	92	0.91	0.85	0.29	0.11	0.11	0.08
Late Hesperian	65.2	18.3	91.3	0.9	0.85	0.29	0.1	0.1	0.08
Early Hesperian	73.6	20.6	103	1.02	0.96	0.32	0.12	0.12	0.09
Late Noachian	32.3	9.06	45.3	0.45	0.42	0.14	0.05	0.05	0.04
Middle Noachian	5.82	1.63	8.14	0.08	0.08	0.03	0.01	0.01	0.07
Early Noachian	?	?	?	?	?	?	?	?	?
Total	287	83.4	402	3.96	3.73	1.26	0.46	0.46	0.34
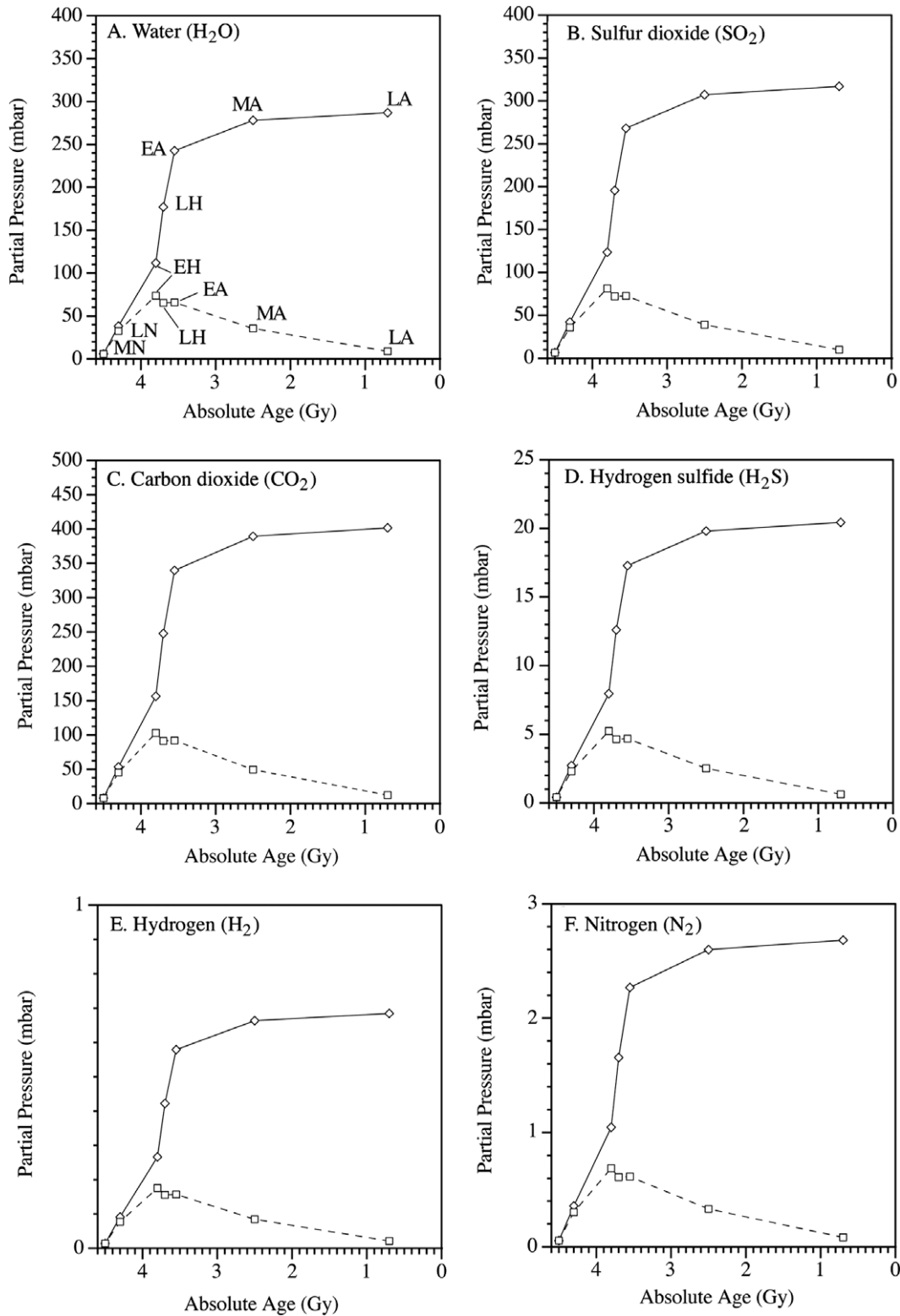
Fig. 2. Plots of partial pressures from volcanic gases released on Mars. Squares represent incremental amounts and diamonds represent cumulative amounts. The gas constituents include: (A) water, (B) sulfur dioxide, (C) carbon dioxide, (D) hydrogen sulfide, (E) hydrogen, (F) nitrogen, (G) hydrogen chloride, (H) hydrogen fluoride, (I) carbon monoxide, and (J) the total amount of gas released during each epoch. Abbreviations: MN, Middle Noachian; LN, Late Noachian; EH, Early Hesperian; LH, Late Hesperian; EA, Early Amazonian; MA, Middle Amazonian; and LA, Late Amazonian. The "absolute" age scale is from Tanaka (1986) and Tanaka et al. (1992) derived from the Neukum and Wise (1976) model.

plutons (Craddock and Maxwell, 1993b). The presence of sulfur dioxide would also inhibit formation of carbonate deposits, which in our model is in excess of CO_2 (Fairén et al., 2004; Halevy et al.,

2007). Sulfur dioxide would be transformed quickly into SO_3 and dominant the reactions occurring with free cations. However, if one assumes that the remaining carbon dioxide went into
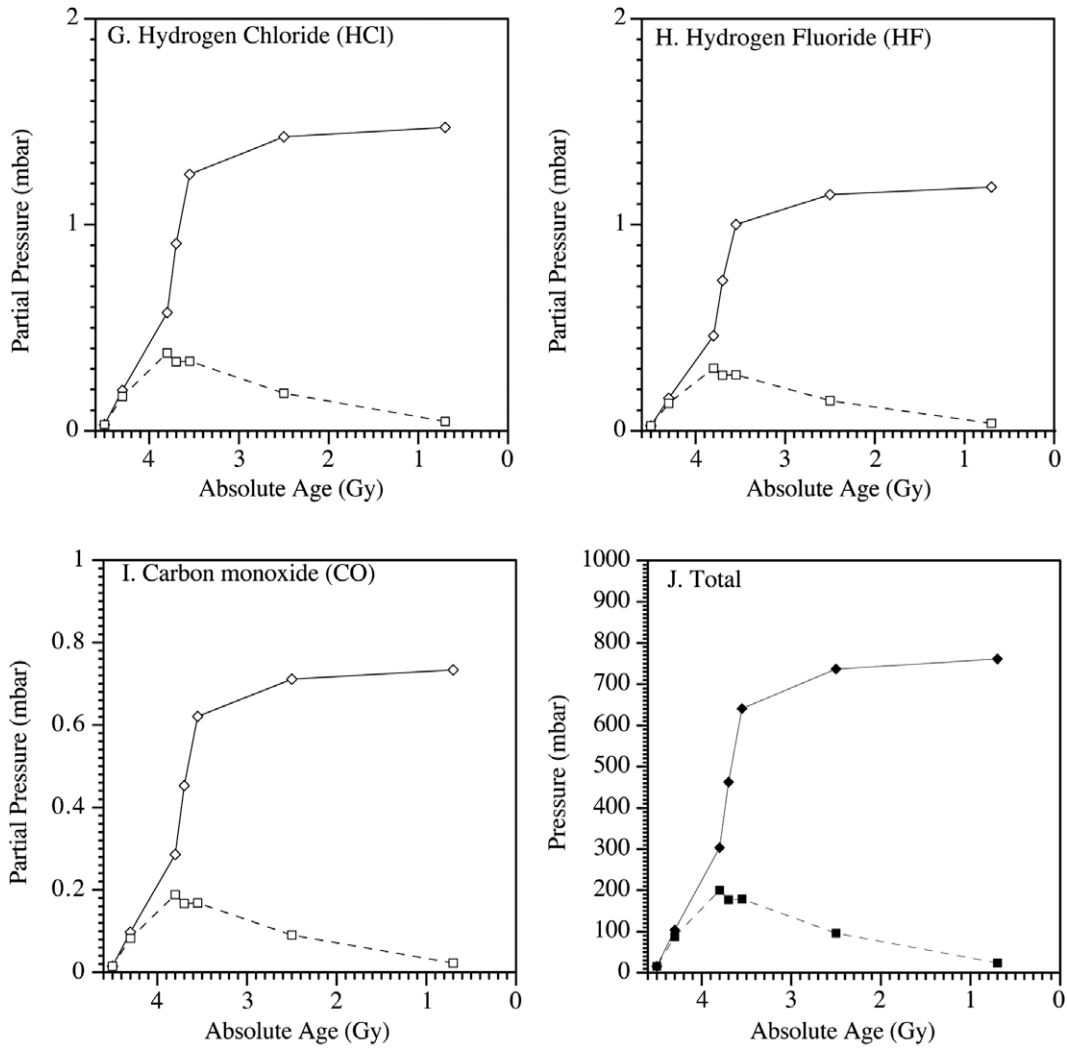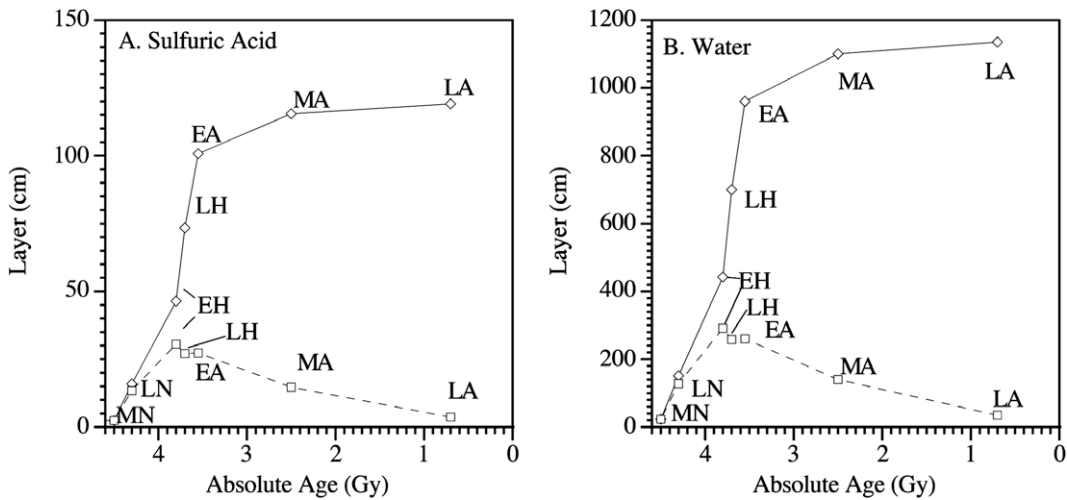
Fig. 2 (*continued*)

Fig. 3. Plots of sulfuric acid (A) formed and water (B) released on Mars as the result of volcanic degassing. Squares represent incremental amounts and diamonds represent cumulative amounts. Abbreviations: MN, Middle Noachian; LN, Late Noachian; EH, Early Hesperian; LH, Late Hesperian; EA, Early Amazonian; MA, Middle Amazonian; and LA, Late Amazonian. The "absolute" age scale is from Tanaka (1986) and Tanaka et al. (1992) derived from the Neukum and Wise (1976) model.

carbonate formation, then a global layer of limestone ~300 cm thick is necessary to sequester the amount released from volcanic outgassing.

Although carbonate formation is often treated as a panacea for removing CO_2 from the martian atmosphere on Earth carbonate and silica weathering represent important processes for controlling the amount of carbon dioxide in our atmosphere and oceans over time (e.g., Brady and Carrol, 1994). Carbonate weathering is represented by the reaction

$$CO_2 + H_2O + CaCO_3 \rightarrow Ca^{++} + 2HCO_3^-$$
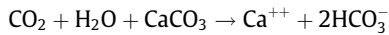
On Earth only about half of the carbon dioxide used in this reaction is of atmospheric origin, and the remaining amount comes from the breakdown of plant biomass. In silica weathering, however, all of the carbon dioxide comes from atmospheric origin (Subramanian et al., 2006). This process can be represented by the reaction

$$2CO_2 + 3H_2O + CaSiO_3 \rightarrow Ca^{++} + 2HCO_3^- + H_4SiO_4$$
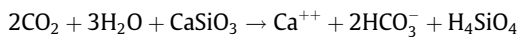
where calcium (Ca) could also be substituted by magnesium (Mg). These reactions are dependent upon temperature and precipitation (Brady and Carrol, 1994; White and Blum, 1995) as well as the supply of weatherable products (Subramanian et al., 2006). Undoubtingly such parameters varied both spatially and temporally on Mars, so assessing the efficiency of carbonate and silica weathering at removing carbon dioxide released through volcanism is difficult; however, it is likely such processes affected the residence time of any released CO_2.

3.2. Water, hydrogen, and the martian D to H ratio

We estimate that an amount equivalent to 8 ± 1 m m^{-2} of juvenile water was released onto the surface of Mars from volcanism (Fig. 3B). This is equivalent to a volume of 1.1×10^6 km^3, which is approximately the same amount estimated to be contained in the north polar cap (1.2×10^6 km^3 to 1.7×10^6 km^3, Zuber et al., 1998). The volume of frozen material in the south polar cap has also be calculated to be ~1.2×10^6 km^3 (Smith et al., 2001). Although it was previously thought the south polar cap contained frozen carbon dioxide (CO_2) (Paige and Keegan, 1994) the shape of the cap is inconsistent with the rheology of solid CO_2 (Nye et al., 2000), and calculations of the density of the deposit are indicative of water ice (Zuber et al., 2007). The total amount of water vapor in the martian atmosphere varies seasonally between ~1 and 2 km^3 (Jakosky and Haberle, 1992), which is negligible compared to the estimated amount to be contained in the polar caps. Our estimate for outgassed water does not account for other potential sources such as release from intrusive volcanic materials, implantation from comets, and outgassing that may have occurred in the early Noachian. However, volcanism was a major contributor to the total water inventory on Mars through time.

A critical clue for understanding the history water on Mars comes from the atmospheric deuterium-to-hydrogen ratio, which is 5.2 ± 0.2 based on airborne telescopic observations (Bjoraker et al., 1989). As Yung and Kass (1998) explain by knowing the processes that created this fractionation as well the current water reservoirs and their associated isotopic values it is possible to reconstruct the past climate and the history of water on Mars. The three current reservoirs include the atmosphere, the polar caps, and subsurface ground ice that is stable at higher latitudes (Mellon and Jakosky, 1995; Boynton et al., 2002). Presently on Mars the rate of photodissociation of water in the atmosphere is low: oxygen is lost at ~6×10^7 atoms cm^{-2} s^{-1} and hydrogen is escaping at a rate of ~1.2×10^8 atoms cm^{-2} s^{-1} (McElroy et al., 1977). Because of the low gravity, the amount of energy necessary

to free an oxygen atom from the martian atmosphere (1.99 eV) is much less than the amount produced from dissociative recombination (3.5–5.3 eV depending on excitation state). Basically, when oxygen atoms are photodissociated in the martian atmosphere their recombination reactions cause oxygen atoms to be lost to space (McElroy and Donahue, 1972). The amount of H_2 in the upper atmosphere is controlled by the concentration of atmospheric O_2 (McElroy and Donahue, 1972). Hydrogen is lost through thermal evaporation, or Jeans escape, in a ratio 2 to 1 over oxygen. The result is that under current atmospheric conditions Mars losses a water molecule at a rate of 6×10^7 molecules cm^{-2} s^{-1}.

If the present rate of hydrogen loss from Mars has remained constant with time, McElroy et al. (1977) calculated that only a 2.5 m layer of water would have been destroyed by photodissociation. To explain the martian D/H ratio this water would have had to have come from an initial inventory of 3.0 m (Owen et al., 1988). Kass and Yung (1995) showed that this amount is a lower limit because the water inventory on early Mars was probably much larger and the early sun may have driven a more active photochemical system. They suggest that ~80 m of water has escaped. A higher initial volatile inventory, such as the 1 km global layer suggested by Carr (1987), would require some other mechanism for increasing the rate of hydrogen escape. Owen et al. (1988) proposed several, including a high flux of ultraviolet light from the early sun that would have increased the rate of hydrogen escape from Mars by 4–8 times (Hunten et al., 1989). However, this must be increased by another 25–50 times to explain the D/H fractionation from such a large initial inventory, and Owen et al. (1988) suggested a large flux of free hydrogen to the exobase released by the oxidation of basaltic rock. Using the oxidation rate of rocks on Venus, copious amounts of water (10's of meters) and basalt (kilometers) are required to obtain the necessary hydrogen flux from oxidation, which even in a warm and wet early Mars does not seem practical. Owen et al. (1988) concluded that warmer temperatures were necessary. Temperature increases in the lower atmosphere would have the affect of increasing the carrying capacity of water vapor in this region. Because most of the water-destroying photochemistry occurs below the tropopause, this increase in water vapor would in turn increase the rate at which it was destroyed. Two mechanisms then have the greatest potential for explaining the martian D/H ratio: an early hydrogen flux or "pulse" and higher atmospheric temperatures.

Analyses of hydrous minerals in the SNC meteorites show that the D/H ratio ranges from not only the present D/H ratio but downward to only 1.5 times greater than Standard Mean Ocean Water (SMOW), suggesting that deuterated ground water and magmatic water intermixed during crystallization of the magma. The other important observation Watson et al. (1994) made was that the high martian D/H ratio was set prior to the crystallization age of these rocks, which is between 180 million to a maximum of 1.3 billion years ago (Watson et al., 1994). Using this information, Donahue (1995) determined the range of possible water abundances both initially and currently residing in the martian crust. If the D/H ratio has changed only 4% since the SNC crystallized 180 millions ago, then the initial crustal inventory was 42 m and is currently only 3.4 m. If the ratio was set within the first billion years of martian history, then the initial inventory may have been has large as 2200 m, with 190 m currently in the crust. However, the rate at which hydrogen escapes to create the martian D/H ratio is controlled by its availability. The focus has been on freeing hydrogen from water so it can escape into space, but the problem is getting rid of the freed oxygen too. Warmer temperatures and the oxidation of rock are important considerations, but the pulse of free hydrogen from volcanism may be important as well.

Cumulatively, ~15×10^{18} g of hydrogen would have been released into the martian atmosphere from volcanism with time

(Table 3). Based on the temporal distribution of volcanic mass (Table 1), a large fraction ($\sim 9.1 \times 10^{18}$ g) would have been released during the early history of Mars (middle Noachian to the early Amazonian). Higher values released through volcanism are possible; hydrogen may constitute up to ~ 2.8 vol.% of the released gas (Greenland, 1987a, Table 28.6), and we have only considered a lower limit. Besides oxidizing rock to release hydrogen, an additional mechanism could be within the early martian mantle. The presence of metallic iron in the mantle would have changed the fugacity of oxygen and caused volcanic eruptions to have outgassed hydrogen at the expense of water as suggested for the early Earth (Holland, 1978, p. 89). As the mantle became depleted in metallic iron, most likely due to core formation, the oxygen fugacity could have changed to permit volcanic outgassing of water, but not enough to alter the then established high D/H ratio. The effectiveness of this mechanism is of course highly dependent upon the time of core formation.

There are two simple solutions to explain the D/H ratio that play off one another. The first, obviously, is an atmospheric mechanism for increasing the current loss rate of hydrogen. As Owen et al. (1988) concluded, warmer atmospheric temperatures are desirable in order to decouple the nonthermal escape of oxygen to the Jeans escape of hydrogen. Perhaps accompanying temperature increases from volcanically released SO_2 and total atmospheric pressure increases to ~ 0.3 bar would be enough to permit this to happen, but such modeling is beyond the scope of this paper. The second, albeit unpopular solution, is a "dry" Mars that reduces the amount of light hydrogen that has to be removed. The cumulative 8 m water inventory from volcanism must have been depleted to 1.3 m to explain the D/H ratio. Alternatively Mars could have lost all of its outgassed hydrogen and still retained ~ 2.5 m of the volcanic water. Because of the potential increase in temperatures and the potential of aiding or creating an early hydrogen pulse, the change in atmospheric conditions as the result of volcanic outgassing must be considered when explaining the martian D/H ratio.

3.3. Sulfur dioxide

The amount of outgassed SO_2 on Mars would have had a cumulative partial pressure of ~ 0.06 bars. In the Earth's atmosphere, SO_2 has a short lifetime (only a few years), so it is likely the influence on total atmospheric pressure from outgassed SO_2 would have also been short-lived. SO_2 becomes SO_3 in the presence of odd hydrogen species, an intermediate step to becoming a sulfate aerosol (Postawko and Fanale, 1992). The amount of odd hydrogen species is directly proportional to the amount of water in the atmosphere, which would be released simultaneously with the SO_2 during the eruption. Settle (1979) calculated that in the present martian atmosphere SO_2 would last only for ~ 3 martian years. Under terrestrial atmospheric conditions the lifetime of SO_2 is reduced to only a few months (Settle, 1979).

Using the original erupted magma volumes by Greeley (1987), Postawko et al. (1987) suggested that at 1 wt.% SO_2, volcanism may have been capable of episodically warming the martian atmosphere by as much as 10 K. Including the gas released during periods of quiescence, our effective weight percent SO_2 is also ~ 1.0. Combined effects from simultaneously released water, carbon dioxide, and other constituents should be considered in climate models.

Settle (1979) noted that sulfate aerosols (i.e., sulfuric acid vapor, H_2SO_4) would grow in size by vapor nucleation and coagulation. The final fate of the degassed SO_2 would be on the martian surface as a form of acid rain. Settle (1979) suggested that SO_2 released from volcanic eruptions could be dispersed globally and trigger leaching of surface materials upon deposition, thus explaining the high sulfur content of the soil and duricrust measured at all the landing sites (Toulmin et al., 1977; Rieder et al., 1997; Gellert et al., 2004; Squyres et al., 2004). Global acid rain evolved from volcanic degassing would have deposited ~ 120 cm of H_2SO_4 (Fig. 3A). The influence of this process may have been more pronounced locally if the eruption was contained within the troposphere. It is interesting to note that the largest pulse in volcanic activity occurs during the early Hesperian (Fig. 2), which roughly corresponds to the ages of most valley networks (e.g., Fassett and Head, 2008). It is possible that volcanic outgassing created the conditions necessary to initiate valley network incision.

3.4. Nitrogen

The Viking entry mass spectrometers measured a $^{15}N/^{14}N$ ratio that is a factor of 1.6 ± 0.2 over the telluric value (Nier et al., 1976; McElroy et al., 1977). Assuming a constant nitrogen escape rate, McElroy et al. (1977) calculated that this enhanced ratio started from a partial pressure of 1.3 mbar. If chemical fixation of nitrogen in the soil is considered, then they calculated a partial pressure as high as 30 mbar was present initially. The partial pressure derived from our calculations, ~ 1.3 mbar, matches their lower value and suggests that chemical fixation of nitrogen did not occur. McElroy et al. (1977) also used the measured ^{15}N enrichment to place a limit on the rate at which the martian atmosphere gained nitrogen. Assuming that the past escape rate of nitrogen was never higher than the present rate, and that this rate was dependent upon the instantaneous abundance of nitrogen, they found that most of the N_2 would have been outgassed early in martian history (~ 3 billion years ago). Not unexpectedly, the early outgassing of nitrogen also correlates with the timing of martian volcanism (Fig. 3). However, it should be noted that recently Tian et al. (2009) showed that heavy gases, including N, C, and O, should have escaped thermally at high rates early in Mars' history if there was strong EUV heating from the young Sun. Under such conditions, the assumption of a constant nitrogen escape rate proposed by McElroy et al. (1977) is almost certainly incorrect, and their calculated initial nitrogen partial pressure is probably low by several orders of magnitude.

3.5. Minor constituents

The hydrogen sulfide released would act as a good reducing agent. If heated in the presence of SO_2 during the eruption it would yield additional water vapor by the reaction:

$$2H_2S + SO_2 \rightarrow 2H_2O + 3S$$
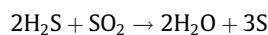
adding several 10's of centimeters of water into the martian environment. Hydrogen sulfide is also a weak acid and will react with most metals. Mixed with water it becomes hydrosulfuric acid, which could react with certain hydroxides on the martian surface to form salts (i.e., an ionic hydrogen compound). The other acidic gas constituents, hydrogen chloride and hydrogen fluoride, have also been suggested as forming salts on the martian surface (Malin, 1974). Through the exchange of atmospheric water vapor with the regolith and surface material it may be possible to recrystallize these compounds in rock pores and crevices repeatedly, thus creating an effective physical weathering agent even in the current martian environment (Malin, 1974). Malin (1974) also speculates that the reddish color of Mars may be due to oxidized iron accompanying such salt weathering.

A unique property of hydrogen fluoride is its ability to react with quartz through the reaction:

$$SiO_2 + 4HF \rightarrow SiF_4(g) + 2H_2O$$
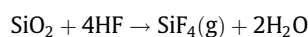
Through the release of volcanic hydrogen fluoride 1.82×10^{18} g of quartz sand, or ~ 5 mm distributed globally, may have been removed from the martian environment. Multispectral measurements

made by TES suggest that quartz is not a dominant mineral on martian (Bandfield et al., 2000). Basalt in particular could withstand the acids released by volcanic eruptions; however, it would weather quickly from any potential salt crystallization.

The total amount of carbon monoxide released through volcanic degassing (1.36×10^{18} g) is significantly more than what is present currently ($\sim 7 \times 10^{15}$ g), suggesting that some of this gas went into reducing metal oxides and produced carbon dioxide or, more likely, has combined with atmospheric oxygen to form carbon dioxide. In the presence of atmospheric odd hydrogen (H, OH, and HO_2), which would be provided by the disassociation of water vapor, carbon monoxide readily combines with free oxygen to form CO_2. This process works so efficiently in the martian atmosphere that the mixing ratios of carbon monoxide and oxygen are kept at levels of only approximately one part per thousand (Barth et al., 1992). This suggests that another 0.5 cm cm^{-2} of carbon dioxide was produced by degassing, which is relatively insignificant when compared to the amount of CO_2 produced directly from outgassing.

4. Conclusions

(1) During its early history (Noachian through the Hesperian) release of volcanic gases may have increased the atmospheric pressure up to ~ 0.3 bar for several martian years. It may be possible that the greenhouse effect of these gases, primarily SO_2 and CO_2, were enough to raise the surface temperature above freezing and permit liquid water or carbon dioxide to exist on the surface.

(2) Acid rain (H_2SO_4) was probably produced as the result of SO_2 degassing. As much as ~ 120 cm of this liquid may have precipitated onto the martian surface with time, contributing to the high sulfur content of the martian soil and perhaps creating runoff channels on the flanks of young volcanoes. Collectively with released water and CO_2, acid rain may have aided in the degradation of the martian highlands and formation of the valley networks.

(3) Revised estimates of juvenile water suggest that a global layer equivalent to ~ 8 mm^{-2} was produced by volcanic degassing. Assuming that volcanism was the only source of water on Mars, ~ 6.7 m would have been lost to space to explain the high martian D/H ratio. Estimates for released CO_2 suggest that most of it most be adsorbed in the martian regolith. Depending on the mineralogy, estimates for the amount of adsorbed CO_2 suggest that the martian regolith is a minimum of 50–400 m thick. Alternatively, ~ 130 cm cm^{-2} of carbonates may be present.

(4) Providing that the temperature increases accompanying early volcanic gas emissions were high enough to decouple the nonthermal escape of oxygen to the Jeans escape of hydrogen, the hydrogen flux from degassing may be able to explain the high martian atmospheric D/H ratio.

(5) The amount of nitrogen outgassed appears to be able to explain the current atmospheric ^{15}N/^{14}N ratio, implying that chemical fixation of nitrogen to the martian soil did not occur.

(6) Minor gas constituents (HF, HCl and H_2S) could have formed hydroxyl salts on surface materials. Under current martian conditions these salts would continually recrystallize, perhaps resulting in physical weathering of geologic material (Malin, 1974). The amount of hydrogen fluoride emitted would be capable of dissolving a layer of quartz sand ~ 5 mm thick distributed globally, perhaps explaining the absence of this material in spectral studies.

5. Implications

Based on the conservative estimates presented here, the entire present-day atmospheric and volatile inventory on Mars can be explained by volcanic degassing. This is further supported by the relative abundances of ^{40}Ar and ^{36}Ar in the martian atmosphere, which on Mars must have been transported to the atmosphere by volcanism. Assuming that only a small amount of ^{40}Ar has been lost from the atmosphere and that martian volcanic materials have a concentration of potassium similar to the Earth's (1.16%), Turcotte and Schubert (1988) calculated that the mass of the potassium reservoir on Mars is 2.5×10^{20} kg. Coincidentally, the mass of the erupted volcanic materials on Mars calculated by Greeley and Schneid (1991) is 2.3×10^{20} kg (Table 1). This suggests that the martian atmosphere has been static for a long period of time. This does not necessarily preclude the possibility that erosion of an earlier, primordial atmosphere occurred during heavy bombardment (Cameron, 1983). This atmosphere, however, would have had to have been completely removed before the middle Noachian (3.85 Gy) to explain the concentration of atmospheric argon.

Climatic modeling will have to determine whether liquid water could exist under the atmospheric conditions suggested in this paper and if the amount of volatiles released by volcanic degassing alone could explain the formation of the outflow channels, valley network formation, and the degradation of the martian highlands. Of course there are other potential sources of atmospheric volatiles, such as impact devolatilization (i.e., "impact degassing") that may have occurred during accretion in creating the primordial atmosphere (e.g., Ahrens et al., 1989) and subsequent cometary impacts (e.g., Carr, 1989) that should be considered, too. One consequence of periods of higher atmospheric pressure that is clear is a potential increase in eolian activity. The windspeeds required for entrainment of sand and dust are a function of atmospheric density, with lower winds being capable of moving material under higher atmospheric surface pressures (i.e., higher density) (Greeley et al., 1980). Moreover, if periods of higher atmospheric pressure did allow active surface water, then the generation of small particles through weathering and erosion is increased, providing even more material capable of wind entrainment. Another implication is the presence of relatively recent pyroclastic deposits on the martian surface that are stratigraphically older than more effusive flows (Mouginis-Mark et al., 1988), suggesting that the changes in atmospheric pressure accompanying initial eruptions prohibited explosive volcanism during later eruptions.

Acknowledgments

References

Ahrens, T.J., O'Keefe, J.D., Lange, M.A., 1989. Formation of atmospheres during accretion of the terrestrial planets. In: Atreya, S.K., Pollack, J.B., Matthews, M.S. (Eds.), Origin and Evolution of Planetary and Satellite Atmospheres. The University of Arizona Press, Tucson, pp. 328–385.

Allard, P., 1983. The origin of hydrogen, carbon, sulphur, nitrogen, and rare gases in volcanic exhalations: Evidence from isotope geochemistry. In: Tazieff, H., Sabroux, J.C. (Eds.), Forecasting Volcanic Events. Elsevier, Amsterdam. pp. 337–386.

Allard, P., and 10 colleagues, 1991. Eruptive and diffuse emissions of CO_2 from Mount Etna. Nature 351, 387–391.

Allen, C.C., Gooding, J.L, Jercinovic, M., Keil, K., 1981. Altered basaltic glass: A terrestrial analog to the soil of Mars. Icarus 45, 347–369.

Andres, R.J., Kyle, P.R., Stokes, J.b., Rose, W.I., 1989. Sulfur dioxide emissions from episode 48A, East Rift zone eruption of Kilauea volcano, Hawaii. Bull. Volcanol. 52, 113–117.

Arvidson, R.E., Gooding, J.L., Moore, H.J., 1989. The martian surface as imaged, sampled, and analyzed by the Viking landers. Rev. Geophys. 27, 39–60.

Arvidson, R.E., Koettel, K.A., Hohenberg, C.M., 1980. A post-Viking view of martian geologic evolution. Rev. Geophys. Space Phys. 18, 565–603.

Baker, V.R., 1979. Erosional processes in channelized water flows on Mars. J. Geophys. Res. 84, 7985–7993.

Baker, V.R., Milton, D.J., 1974. Erosion by catastrophic floods on Mars and Earth. Icarus 23, 27–41.

Bandfield, J.L., Hamilton, V.E., Christensen, P.R., 2000. A global view of martian surface compositions from MGS-TES. Science 287, 1626–1630.

Bandfield, J.L., Glotch, T.D., Christensen, P.R., 2003. Spectroscopic identification of carbonate minerals in the martian dust. Science 301, 1084–1087. doi:10.1126/science.1088054.

Banin, A., Carle, G.C., Cheng, S., Coyne, L.M., Orenberg, J.B., Scattergood, T.W., 1988. Laboratory investigations of Mars: Chemical and spectroscopic characteristics of a suite of clays as Mars soil analogs. Origins Life 18, 239–265.

Barth, C.A., Stewart, A.I.F., Bougher, S.W., Hunten, D.M., Bauer, S.J., Nagy, A.F., 1992. Aeronomy of the current martian atmosphere. In: Kieffer, H.H., Jakosky, B.M., Synder, C.W., Matthews, M.S. (Eds.), Mars. University of Arizona Press, Tucson, pp. 1054–1089.

Basharina, L.A., 1960. Fumarolic activity of the volcano Bezymyannyi in 1956–57: Akad. Nauk SSSR, Lab. Vulkanol. (in Russian), Vulkanol. Stantsii Biull. 29, 15–27.

Bell III, J.F., and 43 colleagues, 2004. Pancam multispectral imaging results from the Spirit Rover at Gusev Crater. Science 305, 800–806.

Bibring, J.-P., and 52 colleagues, 2006. Global mineralogical and aqueous Mars history derived from OMEGA/Mars Express data. Science 312, 400–404. doi:10.1126/science.1122659.

Binder, A.B., Arvidson, R.E., Guinness, E.A., Jones, K.L., Morris, E.C., Mutch, T.A., Pieri, D.C., Sagan, C., 1977. The geology of the Viking Lander 1 site. J. Geophys. Res. 82, 4439–4451.

Bjoraker, G.L., Mumnya, M.J., Larson, H.P., 1989. The value of D/H in the martian atmosphere. Bull. Am. Astron. Soc. 21, 990 (abstract).

Booth, M.C., Kieffer, H.H., 1978. Carbonate Formation in Mars like environments. J. Geophys. Res. 83 (B4), 1809–1815.

Boynton, W.V., Feldman, W.C., Squyres, S.W., Prettyman, T., Brückner, J., Evans, L.G., Reedy, R.C., Starr, R., Arnold, J.R., Drake, D.M., Englert, P.A.J., Metzger, A.E., Mitrofanov, I., Trombka, J.I., d'Uston, C., Wänke, H., Gasnault, O., Hamara, D.K., Janes, D.M., Marcialis, R.L., Maurice, S., Mikheeva, I., Taylor, G.J., Tokar, R., Shinohara, C., 2002. Distribution of hydrogen in the near-surface of Mars: Evidence for subsurface ice deposits. Science. doi:10.1126/science.1073722.

Brady, P.V., Carrol, S.A., 1994. Direct effects of CO_2 and temperature on silicate weathering: Possible implications for climate control. Geochim. Cosmochim. Acta 58, 1853–1856.

Brain, D.A., Jakosky, B.M., 1998. Atmospheric loss since the onset of the martian geologic record: Combined role of impact erosion and sputtering. J. Geophys. Res. 103, 22689–22694.

Bray, J.R., 1974. Volcanism and glaciation during the past 40 millennia. Nature 252, 679–680.

Bridges, J.C., Catling, D.C., Saxton, J.M., Swindle, T.D., Lyon, I.C., Grady, M.M., 2001. Alteration assemblages in martian meteorites: Implications for near-surface processes. Space Sci. Rev. 96, 365–392.

Calvin, C., Rutherford, M., 2008. The parental melt of lherzolitic shergottite ALH 77005: A study of rehomogenized melt inclusions. Am. Mineral. 93 (11–12), 1886–1898. doi:10.2138/am.2008.2659.

Cameron, A.G.W., 1983. Origin of the atmospheres of the terrestrial planets. Icarus 56, 195–201.

Carr, M.H., 1973. Volcanism on Mars. J. Geophys. Res. 78, 4049–4062.

Carr, M.H., 1979. Formation of martian flood features by release of water from confined aquifers. J. Geophys. Res. 84, 2995–3007.

Carr, M.H., 1981. In: The Surface of Mars. Yale University Press, New Haven. 232 pp..

Carr, M.H., 1987. Water on Mars. Nature 326, 30–35.

Carr, M.H., 1989. Recharge of the early atmosphere of Mars by impact-induced release of CO_2. Icarus 79, 311–327.

Carr, M.H., 1998. Masursky lecture. Mars: Aquifers, oceans, and the prospects of life. Lunar Planet. Sci. XXIX. Lunar Planet. Inst. Houston.

Carr, M.H., Clow, G.D., 1981. Martian channels and valleys: Their characteristics, distribution, and age. Icarus 48, 91–117.

Carr, M.H., Greeley, R., Blasius, K.R., Guest, J.E., Murray, J.B., 1977. Some martian volcanic features as viewed from the Viking orbiters. J. Geophys. Res. 82, 3985–4015.

Casadevall, T.J., Rose Jr., W.I., Gerlach, T.M., Greenland, L.P., Ewert, J., Wunderman, R., Symonds, R., 1983. Gas emissions and the eruptions of Mount St. Helens through 1982. Science 221, 1383–1385.

Casadevall, T.J., Stokes, J.B., Greenland, L.P., Malinconico, L.L., Casadevall, J.R., Furukawa, B.T., 1987. SO_2 and CO_2 emission rates at Kilauea volcano 1979–1984. In: Volcanism in Hawaii, vol. 1. U.S. Geol. Surv. Prof. Pap. 1350. U.S. Gov. Printing Office, Washington, pp. 771–780 (Chapter 29).

Cess, R.D., Ramanathan, V., Owen, T., 1980. The martian paleoclimate and enhanced carbon dioxide. Icarus 41, 159–165.

Chamberlain, R.T., 1908. The gases in rocks. Carnegie Inst. Wash. Pub. 106, 80.

Chapman, C.R., Jones, K.L., 1977. Cratering and obliteration history of Mars. Annu. Rev. Earth Planet. Sci. 5, 515–540.

Chyba, C.F., 1990. Impact delivery and erosion of planetary oceans in the early inner Solar System. Nature 343, 129–133.

Coombs, M.L., Sisson, T.W., Lippon, P.W., 2006. Growth history of Kilauea inferred from volatile concentrations in submarine-collected basalts. J. Volcan. Geotherm. Res. 151, 19–49. doi:10.1016/j.jvolgeores.2005.07.037.

Craddock, R.A., Howard, A.D., 2002. The case for rainfall on a warm, wet early Mars. J. Geophys. Res. 107, 5111. doi:10.1029/2001JE001505.

Craddock, R.A., Maxwell, T.A., 1990. Resurfacing of the martian highlands in the Amenthes and Tyrrhena region. J. Geophys. Res. 95, 14265–14278.

Craddock, R.A., Maxwell, T.A., 1991. Geologic and tectonic history of northern Lunar Planum, Mars. Lunar Planet. Sci. XXII, 247–248 (abstract).

Craddock, R.A., Maxwell, T.A., 1993a. Geomorphic evolution of the martian highlands through ancient fluvial processes. J. Geophys. Res. 98, 3453–3468.

Craddock, R.A., Maxwell, T.A., 1993b. The early martian environment: Clues from the cratered highlands and the Precambrian Earth. In: Workshop on Early Mars: How Warm and How Wet? LPI Tech. Report No. 93-03. Lunar and Planetary Institute, Houston, pp. 9–10 (abstract).

Craddock, R.A., Maxwell, T.A., Howard, A.D., 1997. Crater morphometry and modification in the Sinus Sabaeus and Margaritifer Sinus regions of Mars. J. Geophys. Res. 102, 13,321–13,340.

Crown, D.A., Greeley, R., 1993. Volcanic geology of Hadriaca Patera and the eastern Hellas region of Mars. J. Geophys. Res. 98, 3431–3451.

Dixon, J.E., Clague, D.A., 2001. Volatiles in basaltic glasses from Loihi Seamount, Hawaii: Evidence for a relatively dry plume component. J. Petrol. 42, 627–654.

Dixon, J.E., Clague, D.A., Stopler, E.M., 1991. Degassing history of water, sulfur, and carbon in submarine lavas from Kilauea volcano, Hawaii. J. Geol. 99, 371–394.

Donahue, T.M., 1995. Evolution of water reservoirs on Mars from D/H ratios in the atmosphere and crust. Nature 374, 432–434.

Fairén, A.G., Fernández-Remolar, D., Dohm, J.M., Baker, V.R., Amils, R., 2004. Inhibition of carbonate synthesis in acidic oceans on early Mars. Nature 431, 423–426. doi:10.1038/nature02911.

Fanale, F.P., 1971. History of martian volatiles: Implications for organic synthesis. Icarus 15, 279–303.

Fanale, F.P., Salvail, J.R., Banerdt, W.B., Saunders, R.S., 1982. Mars: The regolith-atmosphere-cap system and climate change. Icarus 50, 381–407.

Fassett, C.I., Head III, J.W., 2008. The timing of martian valley network activity: Constraints from buffered crater counting. Icarus 195, 61–89.

Formisano, V., Atreya, S., Encrenaz, T., Ignatiev, N., Giuranna, M., 2004. Detection of methane in the atmosphere of Mars. Science 306, 1758–1761.

Francis, P., Wood, C., 1982. Absence of silicic volcanism on Mars: Implications for crustal composition and volatile abundance. J. Geophys. Res. 87 (B12), 9881–9889.

Garvin, J.B., Mouginis-Mark, P.J., Head III, J.W., 1981. Characterization of rock populations on planetary surfaces: Techniques and a preliminary analysis of Mars and Venus. Moon and Planets 24, 355–387.

Gautier, A., 1906. La genèse des eaux thermales et ses rapports avec le volcanisme. Econ. Geol. 1, 688–697 (translated by Ransome, F.L.).

Gellert, R., and 14 colleagues, 2004. Chemistry of rocks and soils in Gusev Crater from the alpha proton x-ray spectrometer. Science 305(5685), 829–832. doi:10.1126/science.1099913.

Gerlach, T.M., 1980. Evaluation of volcanic gas analysis from Kilauea Volcano. J. Volcan. Geotherm. Res. 7, 295–317.

Gerlach, T.M., 1982. The interpretation of volcanic gas data from tholeiitic and alkaline mafic lavas. Bull. Volcan. 45 (3), 235–244.

Gerlach, T.M., 1986. Exsolution of H_2O, CO_2, and S during eruptive episodes at Kilauea Volcano, Hawaii. J. Geophys. Res. 91, 12177–12185.

Gerlach, T.M., 1991. Present-day CO_2 emissions from volcanoes. EOS Trans. Am. Geophys. Union 72, 249–255.

Gerlach, T.M., Graeber, E.J., 1985. Volatile budget of Kilauea Volcano. Nature 313, 273–277.

Gerlach, T.M., McGee, K.A., Elias, T., Sutton, A.J., Doukas, M.P., 2002. Carbon dioxide emission rate of Kilauea Volcano: Implications for primary magma and the summit reservoir. J. Geophys. Res. 107. doi:10.1029/2001JB000407.

Giggenbach, W.F., 1975. A simple method for the collection and analysis of volcanic gas samples. Bull. Volcanol. 39, 15–27.

Giordano, D., Dingwell, D.B., 2003. Viscosity of hydrous Etna basalt: Implications for Plinian-style basaltic eruptions. Bull. Volcanol. 65, 8–14. doi:10.1007/s00445-002-0233-2.

Goldspiel, J.M., Squyres, S.W., 1991. Ancient aqueous sedimentation on Mars. Icarus 89, 392–410.

Golombek, M.P., Cook, R.A., Economou, T., Folkner, W.M., Haldemann, A.F.C., Kallemeyn, P.H., Knudson, J.M., Manning, R.M., Moore, H.J., Parker, T.J., Rieder, R., Schofield, J.T., Smith, P.H., Vaughan, R.M., 1997. Overview of the Mars Pathfinder mission and assessment of landing site predictions. Science 278, 1743–1748.

Gough, D.O., 1981. Solar interior structure and luminosity variations. Solar Phys. 74, 21–34.

Gow, A.J., Williamson, T., 1971. Volcanic ash in the Antarctic ice sheet and its possible climatic implications. Earth Planet. Sci. Lett. 13, 210–218.

Greeley, R., 1987. Release of juvenile water on Mars: Estimated amounts and timing associated with volcanism. Science 236, 1653–1654.

Greeley, R., Leach, R., White, B., Iversen, J., Pollack, J., 1980. Threshold windspeeds for sand on Mars: Wind tunnel simulations. Geophys. Res. Lett. 7, 121–124.

Greeley, R., Schneid, B.D., 1991. Magma generation on Mars: Amounts, rates, and comparisons with Earth, Moon, and Venus. Science 254, 996–998.

Greeley, R., Spudis, P.D., 1981. Volcanism on Mars. Rev. Geophys. Space Phys. 19, 13–41.

Greeley, R., and 14 colleagues 2005. Martian variable features: New insight from the Mars Express Orbiter and the Mars Exploration Rover Spirit. J. Geophys. Res. 110, E06002. doi:10.1029/2005JE002403.

Greenland, L.P., 1987a. Composition of gases from the 1984 eruption of Mauna Loa volcano. In: Volcanism in Hawaii, vol. 1, U.S. Geol. Surv. Prof. Pap. 1350. U.S. Gov. Printing Office, Washington, pp. 781–790 (Chapter 30).

Greenland, L.P., 1987b. Hawaiian eruptive gases. In: Volcanism in Hawaii, vol. 1. U.S. Geol. Surv. Prof. Pap. 1350, U.S. Gov. Printing Office, Washington, pp. 759–770 (Chapter 29).

Greenland, L.P., Rose, W.I., Stokes, J.B., 1985. An estimate of gas emissions and magmatic gas content from Kilauea Volcano. Geochim. Cosmo. Acta 49, 125–129.

Guinness, E.A., Arvidson, R.E., Dale-Bannister, M.A., Singer, R.B., Bruckenthal, E.A., 1987. On the spectral reflectance properties of materials exposed at the Viking landing sites. Proc. Lunar Planet. Sci. Conf. Part 2. J. Geophys. Res. 92 (Suppl.), E575–E587.

Halevy, I., Zuber, M.T., Schrag, D.P., 2007. A sulfur dioxide climate feedback on early Mars. Science 318, 1903–1907. doi:10.1126/science.1147039.

Hartmann, W.K., 2005. Martian cratering 8: Isochron refinement and the chronology of Mars. Icarus 174, 294–320.

Heald, E.F., Naughton, J.J., Barnes, I.L., 1963. The chemistry of volcanic gases. Use of equilibrium calculations in the interpretation of volcanic gas samples. J. Geophys. Res. 68, 546–567.

Holland, H.D., 1978. In: The Chemistry of the Atmosphere and Oceans. John Wiley, New York. 351 pp.

Hubbard, N.J., Gast, P.W., 1971. Chemical composition and origin of nonmare lunar basalts. Proc. Lunar Sci. Conf., second ed., pp. 999–1020.

Hulme, G., 1976. The determination of the rheological properties and effusion rate of an Olympus Mons lava. Icarus 27, 207–213.

Hunten, D.M., Donahue, T.M., Walker, J.C.G., Kasting, J.F., 1989. Escape of atmospheres and loss of water. In: Atreya, S.K., Pollack, J.B., Matthews, M.S. (Eds.), Origin and Evolution of Planetary and Satellite Atmospheres. The University of Arizona Press, Tucson, pp. 386–422.

Hynek, B.M., Beach, M., Hoke, M.R.T., 2008. Updated global map of martian valley networks: Implications for hydrologic process. In: Craddock, R.A. (Ed.), Second Workshop on Mars Valley Networks. Smithsonian Institution, Washington, DC, pp. 39–42 (abstract).

Ihinger, P.D., Hervig, R.L., McMillan, P.F., 1994. Analytical methods for volatiles in glasses. In: Carroll, M.R., Holloway, J.R. (Eds.), Volatiles in magmas, Reviews of Mineralogy, vol. 30. Mineralogy Society of America, Washington, pp. 67–122.

Ivanov, V.V., 1967. Principal geochemical environments and processes of the formations of hydrothermal waters in recent volcanic activity. Chemistry of the Earth's Crust 2, 260 (Israel Program for Scientific Translations, Jerusalem).

Jakosky, B.M., Haberle, R.M., 1992. The seasonal behavior of water on Mars. In: Kieffer, H.H., Jakosky, B.M., Synder, C.W., Matthews, M.S. (Eds.), Mars. The University of Arizona Press, Tucson, pp. 969–1016.

Jambon, A., 1994. Earth degassing and large-scale geochemical cycling of volatile elements. In: Carroll, M.R., Holloway, J.R. (Eds.), Volatiles in Magmas. Reviews of Mineralogy, vol. 30. Mineralogy Society of America, Washington, pp. 479–517.

Jones, K.L., 1974. Evidence for and episode of crater obliteration intermediate in martian history. J. Geophys. Res. 79, 3917–3931.

Kahn, R., 1985. The evolution of CO_2 on Mars. Icarus 62, 175–190.

Kass, D.M., Yung, Y.L., 1995. Loss of atmosphere from Mars due to solar wind-inducted sputtering. Science 268, 697–699.

Kasting, J.F., 1993. Earth's early atmosphere. Science 259, 920–926.

Korteniemi, J., Kostama, V.-P., Törmänen, T., Aittola, M., Öhman, T., Lahtela, H., Raitala, J., Neukum, G., 2005. Complex geology of two large impact craters in Tyrrhena Terra, Mars: Detailed analysis using MEX HRSC camera data. J. Geophys. Res. 110, E12S18. doi:10.1029/2005JE002427.

Kieffer, H.H., Zent, A.P., 1992. Quasi-periodic climate change on Mars. In: Kieffer, H.H., Jakosky, B.M., Synder, C.W., Matthews, M.S. (Eds.), Mars. The University of Arizona Press, Tucson, pp. 1180–1220.

Kraft, M.D., Michalski, J.R., Sharp, T.G., 2003. Effects of pure silica coatings on thermal emission spectra of basaltic rocks: Considerations for martian surface mineralogy. Geophys. Res. Lett. 30, 2288. doi:10.1029/2003GL018848.

Krauskopf, K.B., 1957. The heavy metal content of magmatic vapor at 600 °C. Econ. Geol. 52, 786–807.

Lamb, H.H., 1971. Volcanic activity and climate. Palaeogeogr. Palaeo-climatol. Palaeo-ecol. 10, 203–230.

Lentz, R.C.F., Ryan, J.G., Riciputi, L.R., McSween Jr., H.Y., 2000. Water in the martian mantle: Clues from light lithophile elements in martian meteorites. Lunar Planet. Sci. XXXI, 1672 (abstract).

Lewis, J.S., 1972. Metal/silicate fractionation in the Solar System. Earth Planet. Sci. Lett. 15, 286–290.

Longhi, J., Knittle, E., Holloway, J.R., Wänke, H., 1992. The bulk composition, mineralogy and internal structure of Mars. In: Kieffer, H.H., Jakosky, B.M., Synder, C.W., Matthews, M.S. (Eds.), Mars. The University of Arizona Press, Tucson, pp. 184–208.

Lucchitta, B.K., Klockenbrink, J.L., 1981. Ridges and scarps in the equatorial belt of Mars. The Moon and Planets 24 (4), 415–429.

Luo, W., Stepinski, T.F., 2006. Topographically derived maps of valley networks and drainage density in the mare tyrrhenum quadrangle on Mars. Geophys. Res. Lett. 33, L18202. doi:10.1029/2006GL027346.

Lyons, J.R., Manning, C., Nimmo, F., 2005. Formation of methane on Mars by fluid–rock interaction in the crust. Geophys. Res. Lett. 32, L13201. doi:10.1029/2004GL022161.

Malin, M.C., 1974. Salt weathering on Mars. J. Geophys. Res. 79, 3888–3894.

Malinconico, L.L., 1979. Fluctuations in SO_2 emission during recent eruptions of Etna. Nature 278, 43–45.

Mangold, N., Quantin, C., Ansan, V., Delacourt, C., Allemand, P., 2004. Evidence for precipitation on Mars from dendritic valleys in the Valles Marineris area. Science 305, 78–81.

Masursky, H., Boyce, J.M., Dial, A.L., Schaber, G.G., Strobell, M.E., 1977. Classification and time formation of martian channels based on Viking data. J. Geophys. Res. 82, 4016–4038.

Maxwell, T.A., Craddock, R.A., 1995. Age relations of martian highland drainage basins. J. Geophys. Res. 100, 11765–11780.

McGetchin, T.R., Smyth, J.R., 1978. The mantle of Mars: Some possible geological implications of its high density. Icarus 34, 512–536.

McElroy, M.B., Donahue, T.M., 1972. Stability of the martian atmosphere. Science 177, 986–988.

McElroy, M.B., Kong, T.Y., Yung, Y.L., 1977. Photochemistry and evolution of Mars' atmosphere: A Viking perspective. J. Geophys. Res. 82, 4379–4388.

McSween Jr., H.Y., 1985. SNC meteorites: Clues to martian petrologic evolution? Rev. Geophys. 23, 391–416.

McSween Jr., H.Y., Harvey, R.P., 1993. Outgassed water on Mars: Constraints from melt inclusions n SNC meteorites. Science 259, 1890–1892.

McSween Jr., H.Y., Grove, T.L., Lentz, R.C.F., Dann, J.C., Holzheld, A.H., Riciputi, L.R., Ryan, J.G., 2001. Geochemical evidence for magmatic water with Mars from pyroxenes in the Shergotty meteorite. Nature 409, 487–490.

Mellon, M.T., Jakosky, B.M., 1995. The distribution and behavior of martian ground ice during past and present epochs. J. Geophys. Res. 100, 11781–11799.

Minitti, M.E., Mustard, J.F., Rutherford, M.J., 2002. Effects of glass content and oxidation on the spectra of SNC-like basalts: Application to Mars remote sensing. J. Geophys. Res., 107. doi:10.1029/2001JE001518.

Molloy, B.I., Stepinski, T.F., 2007. Automated Mapping of Valley Networks on Mars. Comput. Geosci. 33, 728–738.

Moore, H.J., Arthur, D.W.G., Schaber, G.G., 1978. Yield strengths of flows on Earth, Mars and Moon. Proc. Lunar Planet. Sci. Conf. 9, 3351–3378.

Moore, J.G., 1970. Water content of basalt erupted on the ocean floor. Contrib. Mineral Petrol. 41, 105–108.

Mouginis-Mark, P.J., Wilson, L., Zimbelman, J.R., 1988. Polygenitic eruptions on Alba Patera, Mars: Evidence of channel erosion on pyroclastic flows. Bulletin 50, 361–379.

Mouginis-Mark, P.J., Wilson, L., Zuber, M.T., 1992. The physical volcanology of Mars. In: Kieffer, H.H., Jakosky, B.M., Synder, C.W., Matthews, M.S. (Eds.), Mars. The University of Arizona Press, Tucson, pp. 424–452.

Mumma, M.J., Villanueva, G.L., Novak, R.E., Hewagama, T., Bonev, B.P., DiSanti, M.A., Mandell, A.M., Smith, M.D., 2009. Strong release of methane on Mars in northern summer 2003. Science 323, 1041–1045. doi:10.1126/science.1165243.

Mutch, T.A., Arvidson, R.E., Head III, J.W., Jones, K.L., Saunders, R.S., 1976a. In: The Geology of Mars. Princeton University Press, Princeton, p. 400.

Mutch, T.A., and 9 colleagues, 1976b. The surface of Mars: The view from the Viking 1 Lander. Science 193, 791–801.

Neukum, G., Wise, D.U., 1976. Mars: A standard crater curve and possible new time scale. Science 194, 1381–1387.

Nier, A.O., Hanson, W.B., Seiff, A., McElroy, M.B., Spencer, N.W., Duckett, R.J., Knight, T.C.D., Cook, W.S., 1976. The composition and structure of the martian atmosphere: Preliminary results from Viking 1. Science 193 (4255), 786–788. doi:10.1126/science.193.4255.786.

Noguchi, K., Kamiya, H., 1963. Prediction of volcanic eruption by measuring the chemical composition and amounts of gases. Bull. Volcan. 26, 367–378.

Nye, J.F., Durham, W.B., Schenk, P.M., Moore, J.M., 2000. The instability of a south polar cap on Mars composed of carbon dioxide. Icarus 144, 449–455.

Owen, T., Maillard, J.P., de Bergh, C., Lutz, B.L., 1988. Deuterium on Mars: The abundance of HDO and the value of D/H. Science 240, 1767–1770.

Oze, C., Sharma, M., 2005. Have olivine, will gas: Serpentinization and the abiogenic production of methane on Mars. Geophys. Res. Lett. 32, L10203. doi:10.1029/2005GL022691.

Paige, D.A., Keegan, K.D., 1994. Thermal and albedo mapping of the polar regions of Mars using Viking thermal mapper observations, 2, South polar region. J. Geophys. Res. 99, 25993–26013.

Phillips, R.J., Zuber, M.T., Solomon, S.C., Golombek, M.P., Jakosky, B.M., Banerdt, W.B., Smith, D.E., Williams, R.M.E., Hynek, B.M., Aharonson, O., Hauck II, S.A., 2001. Ancient geodynamics and global-scale hydrology of Mars. Science 291, 2587. doi:10.1126/science.1058701.

Pieri, D., 1976. Distribution of small channels on the martian surface. Icarus 27, 25–50.

Pieri, D., 1980. Martian valleys: Morphology, distribution, age, and origin. Science 210, 895–897.

Pinet, P., Chevrel, S., 1990. Spectral identification of geological units on the surface of Mars related to the presence of silicates from Earth-based near-infrared telescopic charge-coupled device imaging. J. Geophys. Res. 95, 14435–14446.

Plescia, J.B., 1990. Recent flood lavas in the Elysium region of Mars. Icarus 88, 465–490.

Plescia, J.B., Crisp, J.B., 1992. Recent Elysium volcanism – Effects on the martian atmosphere. In: Workshop on the martian Surface and Atmosphere Through Time. LPI Tech. Rept. No. 92-02. Lunar and Planetary Institute, Houston, pp. 115–116 (abstract).

Plescia, J.B., Golombek, M.P., 1986. Origin of planetary wrinkle ridges based on the study of terrestrial analogs. Geol. Soc. Am. Bull. 97, 1289–1299.

Pollack, J.B., Kasting, J.F., Richardson, S.M., Poliakoff, K., 1987. The case for a wet, warm climate on early Mars. Icarus 71, 203–224.

Postawko, S.E., Fanale, F.P., 1992. Regional climatic effects of atmospheric SO_2 on Mars. In: Workshop on the Martian Surface and Atmosphere Through Time. LPI Tech. Rept. No. 92-02. Lunar and Planetary Institute, Houston, pp. 24–25 (abstract).

Postawko, S.E., Fanale, F.P., 1993. Changes in erosional style on early Mars: External versus internal influences. J. Geophys. Res. 98, 11017–11024.

Postawko, S.E., Fanale, F.P., Zent, A.P., 1987. Episodic vs. epochal release of SO_2 on Mars (abstract). In: MEVTV Workshop on Nature and Composition of Surface Units on Mars. LPI Tech. Rept. No. 103-104. Lunar and Planet. Inst., Houston, pp. 115–116.

Poulet, F., Bibring, J.-P., Mustard, J.F., Gendrin, A., Mangold, N., Langevin, Y., Arvidson, R.E., Gondet, B., Gomez, C.The Omega Team, 2005. Phyllosilicates on Mars and implications for early martian climate. Nature 438, 623–627. doi:10.1038/nature04274.

Pruis, M.J., Tanaka, K.L., 1995. The martian northern plains did not result from plate tectonics. Lunar Planet Sci. XXVI, 1147–1148 (abstract).

Rieder, R., Economou, T., Wänke, H., Turkevich, A., Crisp, J., Bruckner, J., Driebus, G., McSween Jr., H.Y., 1997. The chemical composition of martian soil and rocks returned by the mobile alpha proton X-ray spectrometer: Preliminary results from the X-ray mode. Science 278, 1771–1774.

Robinson, M.S., Mouginis-Mark, P.J., Zimbelman, J.R., Wu, S.S.C., Ablin, K.K., Howington-Kraus, A.E., 1993. Chronology, eruption duration, and atmospheric contribution of the martian volcano Apollinaris Patera. Icarus 104, 301–323.

Robock, A., Yuhe, L., Jianping, M., 1991. Climatic effects of the Mt. Pinatubo eruption. EOS Trans. Am. Geophys. Union 72, 65 (abstract).

Roggensack, K., Hervig, R.L., McKnight, S.B., Williams, S.N., 1997. Explosive basaltic volcanism from Cerro Negro volcano: Influence of volatiles on eruptive style. Science 277, 1639–1642. doi:10.1126/science.277.5332.1639.

Ruff, S.W., Christensen, P.R., 2007. Basaltic andesite, altered basalt, and a TES-based search for smectite clay minerals on Mars. Geophys. Res. Lett. 34, L10204. doi:10.1029/2007GL029602.

Schaber, G.G., 1982. Syrtis major: A low-relief volcanic shield. J. Geophys. Res. 87, 9852–9866.

Schaber, G.G., Horstman, K.C., Dial Jr., A.L., 1978. Lava flow materials in the Tharsis regions of Mars. Proc. Lunar Planet. Sci. Conf. 9, 3433–3458.

Schaefer, M.W., 1990. Geochemical evolution of the northern plains of Mars: Early hydrosphere, carbonate development, and present morphology. J. Geophys. Res. 95, 14291–14300.

Schubert, G., Turcotte, D.L., Solomon, S.C., Sleep, N.H., 1989. Coupled evolution of the atmospheres and interiors of planets and satellites. In: Atreya, S.K., Pollack, J.B., Matthews, M.S. (Eds.), Origin and Evolution of Planetary and Satellite Atmosphere. The University of Arizona Press, Tucson, pp. 450–486.

Scott, D.H., Tanaka, K.L., 1982. Ignimbrites of Amazonis Planitia region of Mars. J. Geophys. Res. 87, 1179–1190.

Settle, M., 1979. Formation and deposition of volcanic sulfate aerosols on Mars. J. Geophys. Res. 84, 8343–8354.

Sharp, R.P., Malin, M.C., 1984. Surface geology from Viking landers on Mars: A second look. Geo. Soc. Am. Bull. 95, 1398–1412.

Shepard, E.S., 1921. Kilauea gases, 1919. Hawaiian Volcano Obs. Bull. 9, 83–88.

Shih, C.-Y., Nyquist, L.E., Bogard, D.D., McKay, G.A., Wooden, J.L., Bansal, B.M., Wiesmann, H., 1982. Chronology and petrogenesis of young achondrites, Shergotty, Zagami and ALHA 77005: Late magmatism on the geologically active planet. Geochim. Cosmochim. Acta 46, 2323–2344.

Singer, R.B., McCord, T.B., Clark, R.N., Adams, J.B., Huguenin, R.L., 1979. Mars surface composition from reflectance spectroscopy: A summary. J. Geophys. Res. 84, 8415–8426.

Sisson, T.W., Layne, G.D., 1997. H_2O in basalt and basaltic andesite glass inclusions from four subduction-related volcanoes. Earth Planet. Sci. Lett. 117 (93), 619–635. doi:10.1016/0012-821X(93)90107-K.

Sleep, N.H., 1994. Martian plate tectonics. J. Geophys. Res. 99, 2955–2968.

Smith, P.H., Bell III, J.F., Bridges, N.T., Britt, D.T., Gaddis, L., Greeley, R., Keller, H.U., Herkenhoff, K.E., Jaumann, R., Johnson, J.R., Kirk, R.L., Lemmon, M., Maki, J.N., Malin, M.C., Murchie, S.L., Oberst, J., Parker, T.J., Reid, R.J., Sablotny, R., Soderblom, L.A., Stoker, C., Sullivan, R., Thomas, N., Tomasko, M.G., Ward, W., Wegryn, E., 1997. Results from the Mars Pathfinder Camera. Science 278, 1758–1765.

Smith, D.E., Zuber, M.T., Neumann, G.A., 2001. Seasonal variations of snow depth on Mars. Science 294 (5549), 2141–2146. doi:10.1126/science.1066556.

Soderblom, L.A., and 43 colleagues, 2004. Soils of eagle crater and meridiani planum at the opportunity Rover landing site. Science 306, 1723–1726.

Spencer, J.R., Fanale, F.P., 1990. New models for the origin of Valles Marineris closed depressions. J. Geophys. Res. 95, 14301–14314.

Stoiber, R.E., Jepsen, A., 1973. Sulfur dioxide contributions to the atmosphere by volcanoes. Science 182, 577–578.

Subramanian, V., Ittekkot, V., Unger, D., Madhavan, N., 2006. Silicate weathering in South Asian Tropical River Basins. In: Ittekkot, V., Unger, D., Humborg, C., Tac An, N. (Eds.), Role of Silica in Land–Sea Interactions. SCOPE, Washington, pp. 3–13.

Squyres, S.W., and 49 colleagues, 2004. The Spirit Rover's Athena science investigation at Gusev Crater, Mars. Science 305, 794–799.

Squyres, S.W., Arvidson, R.E., Ruff, S., Gellert, R., Morris, R.V., Ming, D.W., Crumpler, L., Farmer, J.D., Des Marais, D.J., Yen, A., McLennan, S.M., Calvin, W., Bell III, J.F., Clark, B.C., Wang, A., McCoy, T.J., Schmidt, M.E., de Souza Jr., P.A., 2008. Detection of silica-rich deposits on Mars. Science 320, 1063–1067.

Symonds, R.B., Rose, W.I., Bluth, G.J.S., Gerlach, T.M., 1994. Volcanic-gas studies: Methods, results, and applications. In: Carroll, M.R., Holloway, J.R. (Eds.), Volatiles in Magmas, Reviews of Mineralogy, vol. 30. Mineralogy Society of America, Washington, pp. 1–66.

Tanaka, K.L., 1986. The stratigraphy of Mars. Proc. Lunar Planet. Sci. Conf. 17th, Part 1. J. Geophys. Res. 91 (Suppl.), E139–E158.

Tanaka, K.L., Isbell, N.K., Scott, D.H., Greeley, R., Guest, J.E., 1988. The resurfacing history of Mars: A synthesis of digitized, Viking-based geology. Proc. Lunar Planet. Sci. 18, 665–678.

Tanaka, K.L., Scott, D.H., Greeley, R., 1992. Global stratigraphy. In: Kieffer, H.H., Jakosky, B.M., Synder, C.W., Matthews, M.S. (Eds.), Mars. The University of Arizona Press, Tucson, pp. 345–382.

Taylor, B.E., 1986. Magmatic volatiles: Isotopic variations of C, H, and S. In: Valley, J.W., Taylor, H.P., O'Neil, J.R. (Eds.), Stable isotopes in high temperature geological processes, Reviews of Mineralogy, vol. 16. Mineralogy Society of America, Washington, pp. 185–225.

Tian, F., Kasting, J.F., Solomon, S.C., 2009. Thermal escape of carbon from the early martian atmosphere. Geophys. Res. Lett. 36, L02205. doi:10.1029/2008GL036513.

Toulmin, P., Baird, A.K., Clark, B.C., Keil, K., Rose, H.J., Christian, R.P., Evans, P.H., Kelliher, W.C., 1977. Geochemical and mineralogical interpretations of the Viking inorganic chemical results. J. Geophys. Res. 82, 4625–4634.

Touma, J., Wisdom, J., 1993. The chaotic obliquity of Mars. Science 259, 1294–1297.

Turcotte, D.L., Schubert, G., 1988. Tectonic implications of radiogenic noble gases in planetary atmospheres. Icarus 74, 36–46.

Yung, Y.L., Kass, D.M., 1998. Deuteronomy: A puzzle of deuterium and oxygen isotopes on Mars. Science 280, 1545.

Wade, J.A., Plank, T., Melson, W.G., Soto, G.J., Hauri, E.H., 2006. The volatile contest of magmas from Arenal Volcano, Costa Rica. J. Volcan. Geotherm. Res. 157, 94–120.

Wänke, H., Dreibus, G., Jagoutz, E., Mukhim, L.M., 1992. Volatiles on Mars: The role of SO_2. Lunar Planet Sci. XXIII, 1489–1490 (abstract).

Watson, L.L., Hutcheon, I.D., Epstein, S., Stolper, E.M., 1994. Water on Mars: Clues from deuterium/hydrogen and water contents of hydrous phases in SNC meteorites. Science 265, 86–90.

Watters, T.R., 1988. Wrinkle ridge assemblages on the terrestrial planets. J. Geophys. Res. 93, 10236–10254.

Watters, T.R., 1991. Origin of periodically spaced wrinkle ridges on the Tharsis plateau of Mars. J. Geophys. Res. 96, 15599–15616.

Westrich, H.R., Gerlach, T.M., 1992. Magmatic gas source for the stratospheric SO_2 cloud from the June 15 1991, eruption of Mount Pinatubo. Geology 20, 867–870.

White, A.F., Blum, A.E., 1995. Effects of climate on chemical weathering in watersheds. Geochim. Cosmochim. Acta 59, 1729–1747.

White, D.E., Waring, G.A., 1963. Data of Geochemistry, sixth ed., Volcanic Emanations, U.S. Geol. Surv. Prof. Pap. 440-K. U.S. Government Printing Office, Washington. 29 pp. (Chapter K).

Williams, D.A., Greeley, R., Fergason, R.L., Kuzmin, R., McCord, T.B., Combe, J.-P., Head III, J.W., Xiao, L., Manfredi, L., Poulet, F., Pinet, P., Baratoux, D., Plaut, J.J., Raitala, J., Neukem, G., in press. The HRSC Co-Investigator Team, in press. The circum-Hellas volcanic province, Mars: Overview. Planet. Space Sci. doi:10.1016/j.pss.2008.08.010.

Williams, H., McBirney, A.R., 1979. Volcanology. Freeman, Cooper, and Company, San Francisco. 397 pp.

Wilson, L., Head III, J.W., 1981. Ascent and eruption of basaltic magma on Earth and Moon. J. Geophys. Res. 86, 2971–3001.

Wyatt, M.B., McSween, H.Y., 2002. Spectral evidence for weathered basalt as an alternative to andesite in the northern lowlands of Mars. Nature 417, 263–266.

Wilson, L., Head III, J.W., 1983. A comparison of volcanic eruption processes on Earth, Moon, Mars, Io and Venus. Nature 302, 663–669.

Wise, D.U., Golombek, M.P., McGill, G.E., 1979. Tharsis Province of Mars: Geologic sequence, geometry, and a deformation mechanism. Icarus 38, 456–472.

Wood, C.A., Ashwal, L.D., 1981. SNC meteorites: Igneous rocks from Mars? Proc. Lunar Planet. Sci. Conf. 12th. Geochim. Cosmochim. Acta 16 (Suppl.), 1359–1375.

Xiao, L., Greeley, R., Williams, D., 2008. Volcanism on Mars: Integrated constraints and implications for martian thermal history. Lunar Planet. Sci. XXXIX, 1038 (abstract).

Zent, A.P., Fanale, F.P., Postawko, S.E., 1987. Carbon dioxide: Adsorption on palagonite and partitioning in the martian regolith. Icarus 71, 241–249.

Zimbelman, J.R., 1985. Estimates of rheological properties for flows on the martian volcano Ascraeus Mons. Proc. Lunar Planet. Sci. Conf. 16th, Part 1. J. Geophys. Res. 90 (Suppl.), D157–D162.

Zuber, M.T., and 20 colleagues, 1998. Observations of the north polar region of Mars from the Mars Orbiter Laser Altimeter. Science 282, 2053–2060.

Zuber, M.T., Phillips, R.J., Andrews-Hanna, J.C., Asmar, S.W., Konopliv, A.S., Lemoine, F.G., Plaut, J.J., Smith, D.E., Smrekar, Suzanne E., 2007. Density of Mars' south polar layered deposits. Science 317, 1718–1719.