JOURNAL OF GEOPHYSICAL RESEARCH, VOL. 102, NO. E4, PAGES 9183–9189, APRIL 25, 1997

Impact of a paleomagnetic field on sputtering loss of Martian atmospheric argon and neon

Kevin S. Hutchins and Bruce M. Jakosky
Laboratory for Atmospheric and Space Physics and Department of Geological Sciences, University of Colorado, Boulder

Janet G. Luhmann
Space Sciences Laboratory, University of California, Berkeley

Abstract. We examine the implications of including a paleomagnetic field on sputtering loss of argon and neon from the Martian atmosphere. In a previous investigation [*Hutchins and Jakosky*, 1996], we found that collisional sputtering from the exobase by oxygen pickup ions dramatically modified the evolution of atmospheric argon and neon (removing greater than 85% of outgassed ^{36}Ar over time and the present atmospheric allotment of ^{20}Ne in < 100 Myr) and could easily reproduce the anomalous isotopic fractionation of $^{36}Ar/^{38}Ar$. However, the existence of an intrinsic magnetic field could limit sputtering loss by deflecting the solar wind around the upper atmosphere, reducing the number of oxygen pickup ions produced. Evaluation of argon and neon atmospheric evolution including a magnetic field results in lower sputtering loss rates if the magnetic field shut off between 2.5 and 3.6 Gyr. Nonetheless, the extent of sputtering loss requires atmospheric input from sources, in addition to outgassing by intrusive and extrusive volcanism, capable of providing 4 - 100 times more argon and 40 - 1800 times more neon (than provided by volcanic outgassing), dependent on the time that sputtering begins. The additional volatile source(s) must also preferentially outgas neon relative to argon by a factor of between 10 and 26.

Introduction

Geologic and atmospheric evidence both strongly indicate that the Martian climate has changed dramatically over geologic time. The present-day Martian atmosphere is very thin and cold, with an atmospheric pressure of only 6 mbars (> 150 times lower than Earth's atmospheric pressure) and average surface temperature of 210 K. Under these climatic conditions, liquid water is not stable at the surface of the planet. However, a much warmer, wetter early Mars is supported by evidence of extensive valley networks in the heavily-cratered terrain, eroded crater features, and proposed layered deposits which all point to substantial physical erosion by liquid water on the surface [*Carr*, 1986; *Pollack et al.*, 1987; *Lucchita et al.*, 1992; *Craddock and Maxwell*, 1993]. Based on the geomorphology, it has been postulated that the Martian atmosphere was much thicker (1-5 bars) in the past in order to supply the greenhouse warming necessary for liquid water and erosion [*Pollack et al.*, 1987; however, see *Kasting*, 1991]. Thus this implies that the present-day atmosphere must be a remnant of a thicker early atmosphere.

Loss of atmospheric species to space has played a distinctive role in the evolution of the Martian atmosphere. This is best evidenced by the anomalous $^{36}Ar/^{38}Ar$ ratio of 4.1 (measured from the trapped gas component within the SNC meteorites [*Pepin*, 1991], which is approximately 30% smaller than that measured in the atmospheres of the other terrestrial planets and 40% smaller than the assumed solar ratio [see *Pepin*, 1991, Figure 3]. Collisional sputtering at the exobase has recently been shown to be a powerful mechanism for removing species from the atmosphere [*Luhmann et al.*, 1992a], with the Io torus in Jupiter's magnetosphere as the most visible example [*Johnson and McGrath*, 1993]. Sputtering loss occurs when gas atoms at the top of the atmosphere are ionized, "picked up" by the solar wind magnetic field, and re-impacted into the atmosphere with kinetic energy substantial enough to remove heavy atoms or molecules such as CO_2 and Ar [*Luhmann and Kozyra*, 1991; *Luhmann et al.*, 1992a]. Calculations for Mars using early solar ionizing flux and solar wind models suggest that sputtering was more important in the past. For available models of solar EUV flux and solar wind evolution, the Martian atmosphere would have lost the oxygen in the equivalent of tens of meters of H_2O and the constituents of ~ 100 mbars of CO_2 by sputtering over the last 4.0 Gyr [*Luhmann et al.*, 1992a].

Above the homopause, lighter atomic species will exhibit a larger scale height and will be more abundant (relative to heavier atoms, molecules, or isotopes) at the exobase. Therefore these lighter species will be more efficiently removed by sputtering over time, strongly fractionating the remaining isotopic reservoir [*Jakosky et al.*, 1994]. Applying simple Rayleigh fractionation, *Jakosky et al.* [1994] estimated that greater than 50% of Martian argon must have been lost in order to reproduce the observed $^{36}Ar/^{38}Ar$ ratio.

Paper number 96JE03838.
0148-0227/97/96JE-03838$09.00

Recently, we developed an evolutionary model for argon and neon [*Hutchins and Jakosky*, 1996] (hereafter Paper 1) in which we considered a simple mass balance between the Martian mantle, the atmospheric reservoir, and loss to space. Fluxes of noble gases between reservoirs included outgassing of intrusive and extrusive volcanic material and loss from the atmosphere by collisional sputtering. Other evolutionary mechanisms were also considered, such as early catastrophic degassing and hydrodynamic escape, but these were restricted to the first 600 Myr of Martian history. (Gyr and Myr refer to time in billions of years and millions of years, respectively, from the time of planetary formation (taken as zero). Ga and Ma refer to ages in billions of years and millions of years, respectively, from the present day (i.e., conventional geochronology usage). Time from formation (Gyr) can be easily converted to age (Ga) by Age = 4.5 - Time from formation.) Outgassing was related to the history of magma production as determined by *Greeley and Schneid* [1991] and *Tanaka et al.* [1988]. Similarly, a volatile-depleted outgassing model, similar to that of *Pepin* [1994], was also evaluated.

As there is approximately an order of magnitude uncertainty in the sputtering rate calculated by *Luhmann et al.* [1992a], we applied the atmospheric $^{36}Ar/^{38}Ar$ as a key model constraint. We found that sputtering rates of 2-6 times the *Luhmann et al.* rate (sf = 2-6, where sf represents a multiplicative factor of the *Luhmann et al.* [1992a] sputtering rate) were capable of creating the observed argon isotopic fractionation. At these rates, Martian sputtering loss has been quite extensive, responsible for removing >70% of outgassed ^{40}Ar and >85% of ^{36}Ar in 4.0 Gyr, and the present atmospheric abundance of ^{20}Ne in ≤100 Myr. With respect to the global budget of CO_2 (potentially a major control of climate), sputtering loss likely removed between 250 and 750 mbar resulting in an initial atmosphere of ~1.5 bars at 4.0 Ga. In light of this loss, we concluded that supply of volatiles from intrusive and extrusive volcanic outgassing alone is unable to reproduce the present-day Martian atmospheric abundances of ^{36}Ar and ^{20}Ne. Thus we calculated volcanic release factors for argon (vf_{36}) and neon (vf_{20}) which represent the ratio of the measured atmospheric abundance to the abundance predicted by a model with volcanic outgassing as the only volatile source, and thus the contribution (relative to volcanic outgassing) of additional source(s) of atmospheric volatiles. We found vf_{36} values ranging from about 10-100 and vf_{20} values ranging from approximately 100 to 1800, requiring the presence of additional volatile sources to the atmosphere. Furthermore, comparison of vf values between argon and neon (vf_{20}/vf_{36}) argued that the additional source(s) must preferentially outgas neon relative to argon by a factor of 10-18. The ratio vf_{20}/vf_{36} is indicative of elemental fractionation implicit in the evolution of Martian argon and neon, which were not included in the model. Therefore the vf_{20}/vf_{36} ratio provides an additional, important constraint by which to evaluate alternative volatile sources.

The possibility of a planetary magnetic field during the Martian past has dramatic implications for solar-wind-induced sputtering and the extent of atmospheric loss. Early spacecraft flybys of Mars have indicated that the planet's magnetic field is quite weak (see review by *Luhmann et al.* [1992b]. An upper limit estimate of the inferred internal field (<10^{-4} the strength of the terrestrial field) precludes the existence of an Earth-like magnetosphere capable of deflecting the solar wind around the bulk of the atmosphere. Remnant magnetism studies by *Cisowski* [1986] on the SNC meteorites suggest an intrinsic field of ~10^{-3} times the terrestrial field upon crystallization (for Shergotty). *McSween* [1994] attributed the remnant magnetism in Shergotty to impact-induced shock due, in part, to the inplausibility of an active magnetic dynamo at the currently accepted crystallization age of 180 Ma [*Jones*, 1986]. As some controversy exists regarding the age of crystallization for the shergottites (see review by *McSween*, [1994]), the possible implications of a Martian paleomagnetic field until even more recent history cannot be ignored. In this paper we explore the impact of a paleomagnetic field on the sputtering loss rate, the resulting argon isotopic fractionation, and the implications for Martian volatile evolution.

The Magnetic Field of Mars and Sputtering Loss

A planetary magnetic field can "protect" against sputtering losses in several ways. First, if the field deflects the solar wind around the bulk of the atmosphere, it limits the ion production rate in the upper atmosphere by eliminating solar-wind-induced ionization processes. Second, and perhaps more important, the field shields any ions produced in the upper atmosphere (e.g., by photoionization) from the solar wind magnetic field. Thus losses of atmospheric ions and atoms by direct sweeping or collisional sputtering, respectively, are minimized. As suggested in Figure 1, the degree of magnetic field protection afforded to the atmosphere depends on the height of the dayside magnetopause boundary produced by the planetary field's pressure.

Models of the thermal evolution of the Martian core predict the development of a substantial magnetic field at

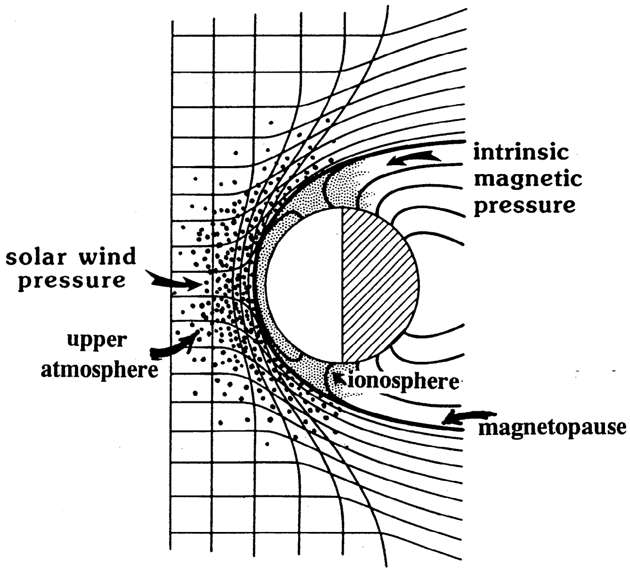

Figure 1. Illustration of a Martian magnetosphere at some stage during its evolution. The numbers of atmospheric atoms present outside of the magnetopause boundary available for ionization and pick up by the solar wind (represented by the larger black dots), and hence sputtering, decrease as the magnetopause moves outward with a stronger intrinsic field.

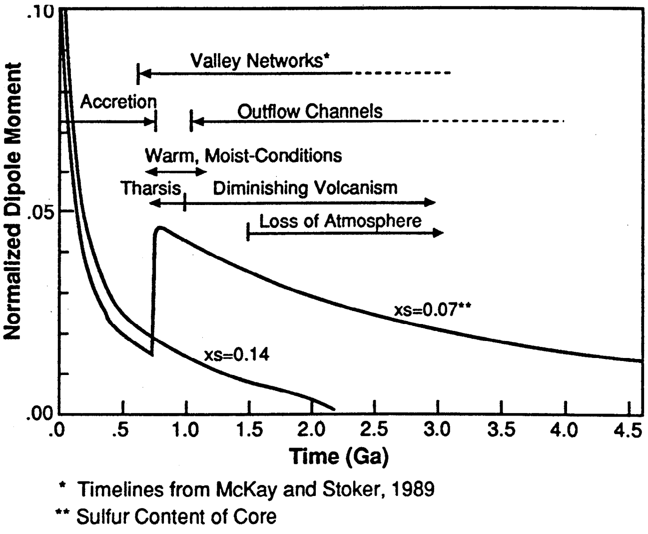

Figure 2. Models for the evolution of a Martian magnetic field as proposed by *Schubert and Spohn* [1990]. The parameter xs refers to the sulfur content of the core assumed in the model. The greater sulfur content model (without the secondary increase in field strength due to the onset of solid core formation) appears more consistent with the inferred limit on the present-day Martian magnetic field. Historical periods of interest on Mars from the perspective of atmospheric evolution are also shown [*McKay and Stoker*, 1989].

some point in geologic history [*Schubert and Spohn*, 1990]. In their modeling effort, Schubert and Spohn assumed two different models of core formation, mainly dependent upon the concentration of sulfur, which determines the physical state of the inner core (Figure 2, which shows the model strength of the Martian magnetic field as compared to the terrestrial field). In the lesser [S] model, a solid inner core develops at approximately 1.3 Gyr, which adds heat and renews the vigor of molten core convection and the strength of the magnetic field even until present day. Based on the position of the Martian bow shock and the inferred strength of the magnetic field at the present, and the estimates of [S] in the Martian core, this does not seem to be a likely scenario [*Treiman et al.*, 1987; *Schubert and Spohn*, 1990; *Luhmann et al.*, 1992b]. For the liquid core model (greater [S] model), postaccretionary heat drives vigorous thermal convection within the core and sustains a planetary magnetic field. As the core cools throughout time, the magnetic field diminishes until shutting off between 2.0 and 2.5 Gyr.

The ability of this postaccretionary model magnetic field to shield the early Martian atmosphere from solar-wind-related scavenging processes can be assessed by adopting the *Newkirk* [1980] solar wind velocity model used by *Luhmann et al.* [1992a]. The magnetopause boundary, the effective barrier to the solar wind, is located where the incident solar wind dynamic pressure is balanced by the pressure created by the planet's magnetic field (see Figure 1). The location of the magnetopause boundary with time can be calculated (for example, with the *Newkirk* [1980] velocity model and the *Schubert and Spohn* [1990] magnetic field model as inputs) using a formula from *Kivelson and Russell* [1995] which accounts for compression of the planetary field by the solar wind (Figure 3). As the sputtering rate is related to the production rate of oxygen ions that can be "picked-up" by the solar wind [*Luhmann and Kozyra*, 1991; *Luhmann et al.*, 1992a], recalculating the production rate above the magnetopause gives the effect of a magnetic field on atmospheric sputtering. Using the upper atmospheric models of *Zhang et al.* [1993] at 1, 2, and 4.5 Gyr, and the corresponding solar EUV fluxes of 1, 3, and 6 times the present value from the *Zahnle and Walker* [1982] model of early solar output, we can calculate the rate of oxygen ion production above the appropriate magnetopause altitudes. The results, Figure 4, show substantial reduction in the oxygen ion production rate, hence the sputtering loss rate (as compared to the unshielded case shown in Figure 5), for all three EUV histories. Note that even a small magnetosphere can significantly decrease the ion production rate by approximately 2 orders of magnitude (Figure 4).

Sputtering Model Description

Under the assumption that a planetary magnetic field could have been important at some point in Martian history, we investigate the effects of limiting sputtering on previous results for the evolution of argon and neon. Calculations were performed using the evolutionary model from Paper 1, which in each time step (which varies from 260,000 years to 30 Myr depending on model resolution), integrates the atmospheric abundances of ^{36}Ar, ^{38}Ar, and ^{40}Ar, based upon (1) the argon abundance at the beginning of the time step, (2) the amount of argon added to the atmosphere by outgassing of intrusive and extrusive volcanic material, and (3) the amount of argon lost from the exobase by sputtering. Owing to the uncertainty in the timing of a magnetic field capable of displacing the solar wind, we assume that a magnetic field starts early (as consistent with

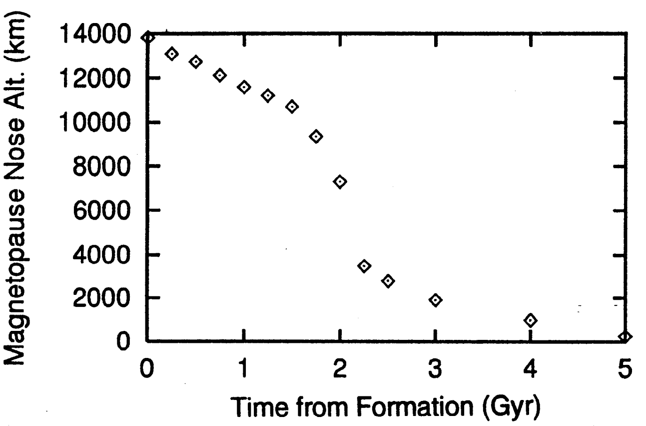

Figure 3. Mars magnetopause nose altitude above the subsolar point based on a formula from *Kivelson and Russell* [1995]. Magnetopauses produced by dipole magnetic fields are well represented by a conic section with an eccentricity of 0.4 and a semilatus rectum (terminator radius, in this case) at ~1.5 "nose" radii. This position (the magnetopause boundary) is determined by the balance between the dynamic pressure of the solar wind and the opposing pressure of the magnetic field derived from the greater xs model of Figure 2 (see text for discussion).

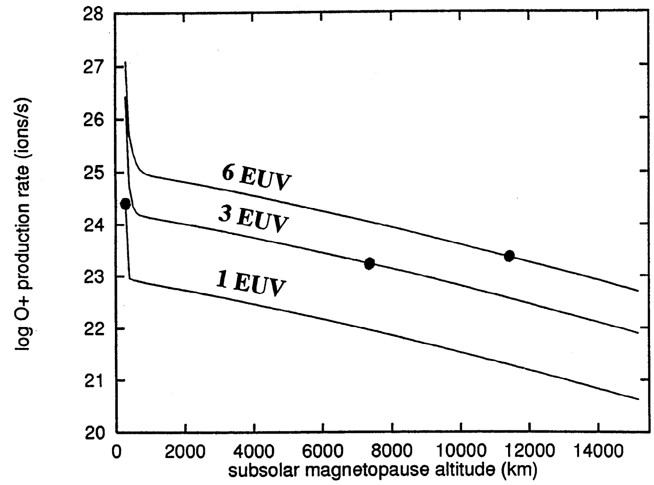

Figure 4. Oxygen ion production rates above the magnetopause as a function of the magnetopause altitude (from Figure 3) and the solar EUV flux (as discussed by *Luhmann et al.,* [1992a]). Sputtering loss rates for atmospheric species are directly related to the production of pickup ions above the magnetopause [*Luhmann et al.*, 1992a]. The case without a magnetic field is represented by the left-hand end points. The dots indicate the rates assuming the magnetopause locations, as determined by the model of *Schubert and Spohn* [1990], at the same time as the given EUV flux [from *Zahnle and Walker*, 1982]. Comparison of the dot positions with the corresponding left-hand end point shows the substantial reduction in sputtering loss due to the presence of Martian magnetic field.

the thermal model of *Schubert and Spohn*, [1990]) and shuts off at a time ($t_{sputter}$) that can be varied. As an upper limit on magnetic field effects, we assume that while the magnetic field is active, the solar wind is deflected and sputtering loss reduces to zero. Once the magnetic field dissipates (at $t_{sputter}$), sputtering from the atmosphere occurs at some rate referenced to that calculated by *Luhmann et al.* [1992a]. This

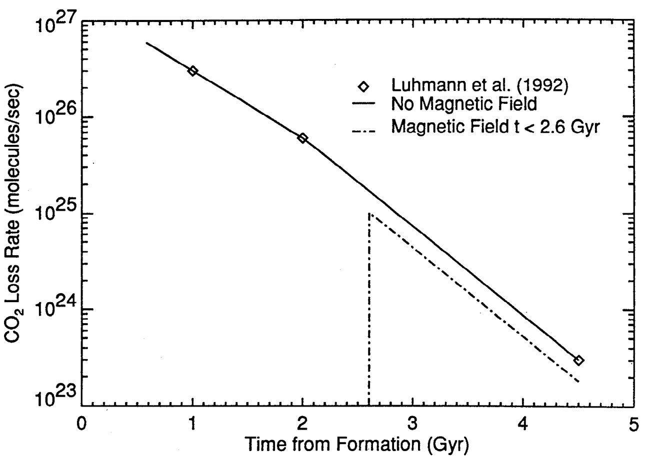

Figure 5. Sputtering loss rate of CO_2 (molecules/s) versus time as determined by *Luhmann et al.* [1992a]. Dotted line represents a sputtering model limited by a paleomagnetic field until 2.6 Gyr into Martian history (offset by a factor of 0.6 for clarity). Details of model are provided in text or in *Hutchins and Jakosky* [1996].

is demonstrated in Figure 5 comparing the sputtering model used in Paper 1 against a sputtering model limited by the effect of a magnetic field which shuts off at 2.6 Gyr into Martian history.

Note that sputtering may not be completely suppressed under the influence of a magnetic field. The calculations of magnetic field effects on sputtering presented in the previous section indicate, for example, that sputtering during the earliest epochs of Martian history may have been reduced only to present-day levels (Figure 4). Additionally, dissipation of the magnetic field is likely to be more gradual than modeled here as a result of slow cooling in the Martian core (Figure 2). However, assuming that the presence of a magnetic field completely eliminates sputtering loss provides an upper bound on the model abundance of argon in the Martian atmosphere and the fractionation in $^{36}Ar/^{38}Ar$ (while a model without a magnetic field, Paper 1, provides the lower bound).

Results

Comparing the evolution of model $^{36}Ar/^{38}Ar$ results at 4.5 Gyr against measurements from trapped gas component within the EETA 79001 member of the SNC meteorites [*Pepin*, 1991] illustrates the effect of a magnetic field (with respect to time) and the range of allowable sputtering rates. The results of this investigation are presented in Figure 6, which tracks the model $^{36}Ar/^{38}Ar$ (at 4.5 Gyr) versus $t_{sputter}$ for sf values of 0.1, 0.5, 1.0, 2.0, and 6.0 times the loss rate calculated by *Luhmann et al.* [1992a] and a bulk potassium concentration of 350 ppm. (Note that we consider the $^{36}Ar/^{38}Ar$ measurement from the trapped gas component as representative of the present-day Martian atmosphere. Based on the EETA 79001 cosmic ray exposure age of ~ 0.5 Ma (see review by *McSween*, [1994]), the trapped gas was implanted only recently and should not differ significantly from the present Martian atmosphere.) If sputtering turns

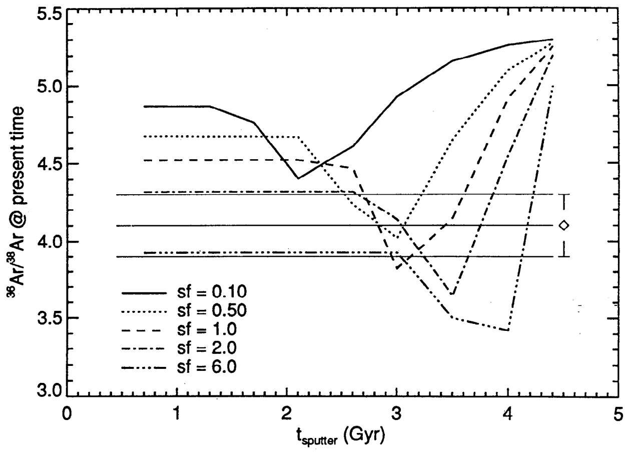

Figure 6. Model predicted $^{36}Ar/^{38}Ar$ ratio at present-day versus $t_{sputter}$, which represents the time when the magnetic field dissipates and sputtering loss from the atmosphere begins. Five different model sputtering rates are used, which are related to *Luhmann et al.* [1992a] via the multiplicative factor (sf). Symbol and lines represent the Martian atmospheric $^{36}Ar/^{38}Ar$ as measured from the trapped gas component in EETA 79001 [*Pepin*, 1991]. This provides a primary constraint on evolution models of argon which include a magnetic field.

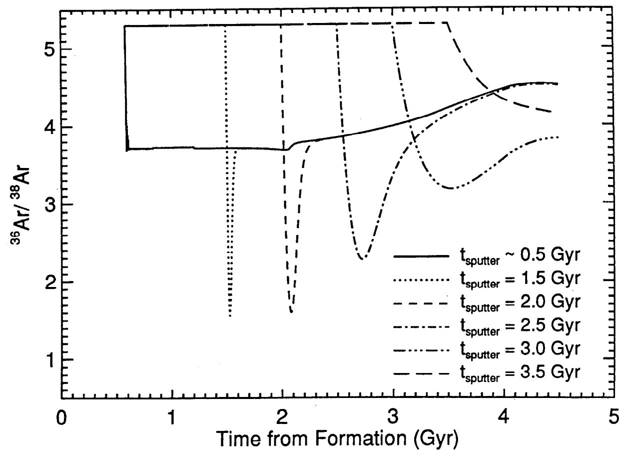

Figure 7. Evolution of $^{36}Ar/^{38}Ar$ in the Martian atmosphere through time for sf = 1.0 and different values of $t_{sputter}$. At $t_{sputter}$, the onset of sputtering loss from the atmosphere is accompanied by a substantial isotopic fractionation. At lower values of $t_{sputter}$, continued outgassing from the interior and sputtering loss quickly returns the $^{36}Ar/^{38}Ar$ evolutionary history to a balance similar to a model without a magnetic field.

on prior to about 2.5 Gyr ($t_{sputter}$), the degree of argon isotopic fractionation does not change, thus the range of sputtering rates remains between 2 and 6 times the *Luhmann et al.* rate as found in Paper 1. The introduction of atmospheric sputtering loss between ~ 2.0 Gyr and 3.5 Gyr causes the resultant present-day $^{36}Ar/^{38}Ar$ ratio first to decrease with $t_{sputter}$ due to the relative importance of fractionation by sputtering loss versus dilution by outgassing. At greater values of $t_{sputter}$, the model present-day $^{36}Ar/^{38}Ar$ ratio increases as dilution from outgassing dominates isotopic evolution of the atmosphere. In other words, the model present-day $^{36}Ar/^{38}Ar$ value is dependent on (1) the rate of sputtering, which varies with time, after the magnetic field dissipates (Figure 5) and (2) the amount of time remaining (between $t_{sputter}$ and 4.5 Gyr) for outgassing to further dilute the isotopic signature of the atmosphere. Figure 7 provides further insight into the effects on the model present-day $^{36}Ar/^{38}Ar$ value by showing how the time-history of $^{36}Ar/^{38}Ar$ evolution changes with respect to $t_{sputter}$ (in this example for sf = 1.0). Pivoting between dominant atmospheric effects (Figure 6) occurs at earlier $t_{sputter}$ values for lower sputtering rates due to the dependence of the sputtering rate on the atmospheric concentration [*Jakosky et al.,* 1994]. Furthermore, since higher loss rates are capable of efficiently removing any atmospheric argon available at $t_{sputter}$, the magnetic field would have to limit sputtering until later in Martian history to produce a notable change in the atmospheric isotopic signature. As mentioned before, the existence of an intrinsic magnetic field until the present time is not supported by the limited available data [*Schubert and Spohn*, 1990; *Luhmann et al.*, 1992b], nor by the results shown in Figure 8.

Figure 8 tracks the fraction of outgassed ^{36}Ar lost by sputtering with respect to $t_{sputter}$. Holding off the solar wind and atmospheric sputtering until late into geologic history, after $t_{sputter}$ ~ 3.8 Gyr, precludes a reasonable explanation of the anomalous fractionation in Martian atmospheric $^{36}Ar/^{38}Ar$ which requires that at least 50% of outgassed ^{36}Ar has been lost from the atmosphere [*Jakosky et al.,* 1994]. However, this inferred upper limit of $t_{sputter}$ could be as early as ~ 2.3 Gyr or as late as ~ 4.2 Gyr, depending on the choice of atmospheric sputtering rate.

Assuming that the strength of the magnetic field was sufficient to limit atmospheric sputtering loss, the degree of fractionation in nonradiogenic argon (Figures 6 and 8) indicates that the sputtering rate plausibly ranges from (1) sf equal to between 2 and 6 for $t_{sputter} \leq 2.5$ Gyr, (2) sf equal to between 0.3 and 6 for $2.5 < t_{sputter} \leq 3.0$ Gyr, (3) sf equal to between 0.5 and ~ 2.0 for $3.0 < t_{ssputter} \leq 3.25$ Gyr, (4) sf equal to between 0.6 and 1.5 for $3.25 < t_{ssputter} \leq 3.6$. Later than 3.6 Gyr, much higher sputtering rates are required to fractionate the atmospheric argon.

Implications for Martian Atmospheric Evolution

The results of including a paleomagnetic field continue to support atmospheric loss by sputtering (Figure 8) and suggest that any intrinsic magnetic field dissipated sometime prior to about 3.8 Gyr. This is consistent with the results of *Schubert and Spohn* [1990] and any remnant magnetization inferred from the SNC meteorites [*Cisowski*, 1986; *McSween*, 1994]. Changing the sputtering rates with respect to $t_{ssputter}$ directly impacts the degree of loss from the atmosphere and the requirement for outgassing in addition to volcanism (i.e., the volcanic factors). However, it should be noted that the variation of $t_{ssputter}$ will not affect the evolution of atmospheric neon (vf_{20}) from that predicted in Paper 1, since its residence time in the atmosphere is only 100 Myr at the *Luhmann et al.* [1992a] sputtering rate. At the lowest sputtering rate considered (sf = 0.10), the atmospheric residence time would increase to 1.0 Gyr. However, from Figure 8, the onset of sputtering at sf = 0.10 is precluded after 2.3 Gyr and the remaining time would be too long to affect the evolution of neon. Therefore any changes in vf_{20} reflect changes in the sputtering rates, rather than $t_{ssputter}$. Based on the four cases of sputtering rates presented in Table 1, the range of volcanic release factor for argon (vf_{36}) has been expanded to conceivably range from 4

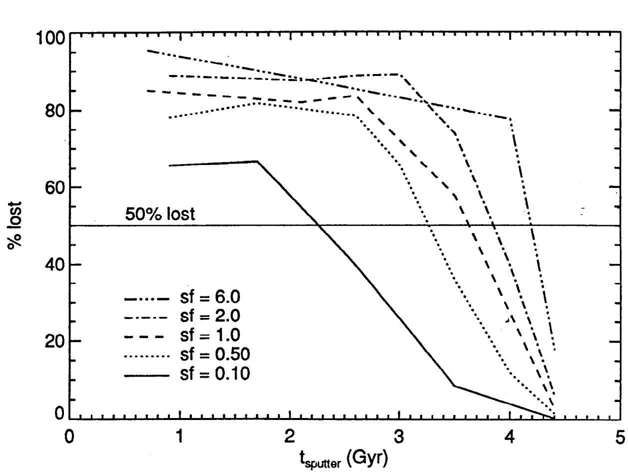

Figure 8. Percent of outgassed argon lost by sputtering over 4.0 Gyr versus $t_{sputter}$. As calculated by *Jakosky et al.* [1994], the measured $^{36}Ar/^{38}Ar$ fractionation in the Martian atmosphere requires that greater than 50% of the argon be lost. Thus this provides an additional constraint on evolution models which include a magnetic field.

Table 1. Effect of a Paleomagnetic Field on Atmospheric Sputtering Loss of Argon, Neon, and CO_2

Case	$t_{sputter}$, Gyr	Sputtering Factor sf	vf_{36}	vf_{20}	vf_{20}/vf_{36}	CO_2 Lost, mbar
1	≤2.5	2.0-6.0	10 - 100	100-1800	10-18	250-750
2	2.5 to 3.0	0.3-6.0	4-100	40-1800	10-18	30-750
3	3.0 to 3.25	0.5-2.0	4-70	60-750	11-15	50-250
4	3.25 to 3.6	0.6-1.5	4-25	85-655	21-26	60-150

Here, $t_{sputter}$ is the time from formation at which the magnetic field no longer supresses sputtering loss; sf is a multiplicative factor of the sputtering rate calculated by *Luhmann et al.* [1992a]; volcanic release factors (vf) represent the contribution of argon and neon by additional sources (relative to outgassing by intrusive and extrusive volcanism); CO_2 lost from the atmosphere by sputtering based on calculations by *Luhmann et al.* [1992a].

to 100 and from 40 to 1800 for neon. Thus, upon outgassing, any additional source(s) must preferentially release neon by a factor between 10 to 26 (vf_{20}/vf_{36}). The particular values of these variables are not resolvable, as they depend on the choice of sputtering rate, $t_{sputter}$, extent of early catastrophic degassing, and the Martian bulk potassium concentration (Paper 1).

If, for example, the thermal model of *Schubert and Spohn* [1990] accurately predicts the magnetic field history, then sputtering would begin to modify the atmosphere after ~ 2.0 - 2.5 Gyr. In this case, the sputtering rates would range from 2-6 times the *Luhmann et al.* [1992a] rate and require input from an additional source(s) contributing 10-100 times more argon and 100-1800 times more neon (same as found in the original results of Paper 1). Alternatively, if we consider that a substantial magnetic field extended until ~1.3 Ga, then our results would predict a sputtering rate of between 0.5 and 2.0 times the *Luhmann et al.* [1992a] rate in order to create the observed argon isotopic fractionation. Although the sputtering rates are much lower and $t_{ssputter}$ is much higher, the model still predicts source(s), in addition to volcanic outgassing, that release 4 - 70 times more argon and 60 - 750 times more neon, resulting in an outgassed Ne/Ar ratio of 11-15. However, this late magnetic field model would predict loss of only ~50 to 250 mbar of CO_2, indicating that some additional process, such as carbonate formation, has participated in the global budget of CO_2 (Paper 1). Unfortunately, our model results do not support a magnetic field until ~180 Ma, which has also been proposed as the crystallization age of the shergottites [*Jones*, 1986; *McSween*, 1994]. However, it may be possible that the magnetization of the shergottites was set by impact shock (as discussed) or by remanent magnetic fields created in the surrounding crust at some prior, indeterminate time [*Luhmann et al.*, 1992b].

Our results may not be directly indicative of the actual Martian atmospheric evolution under the influence of a magnetic field. The model presented here, like in Paper 1, assumed a constant atmospheric CO_2 pressure of 6 mbar. If the pressure was allowed to vary, either due to a lack of sputtering loss or other evolutionary factors [*Jakosky et al.*, 1994; *Pepin*, 1994], the initial argon isotopic fractionation, which occurs when sputtering begins, would be changed due to a different mixing ratio in the bulk atmosphere [*Jakosky et al.*, 1994]. At early $t_{ssputter}$, the effect will probably not be that great, as sputtering and outgassing quickly adjust to their original evolutionary path [*Jakosky et al.*, 1994; Paper 1]. At later $t_{ssputter}$, higher atmospheric pressures of CO_2 may force higher sputtering rates in order to match the observed atmospheric $^{36}Ar/^{38}Ar$.

As discussed in Paper 1, applying the atmospheric $^{36}Ar/^{38}Ar$ ratio as a constraint on the sputtering rate is dependent upon the choice of outgassing histories. For our previous results, we related outgassing to the history of volcanic activity determined by *Greeley and Schneid* [1991]. We also considered an outgassing similar to that used by *Pepin* [1994], which has outgassing declining to zero in late Martian history (see discussion in Paper 1). Considering the effect of a magnetic field on this alternative outgassing history, we find a similar behavior to that presented in Figures 6 and 7. However, we find that if the magnetic field extends beyond about 1.5 - 1.7 Gyr, that a sputtering rate < 0.1 (e.g., sf = 0.04 for $t_{ssputter}$ = 2.0 Gyr) is required to match the $^{36}Ar/^{38}Ar$ ratio, which probably is not consistent with the order of magnitude uncertainty found in the sputtering rate or with the removal of significant quantities of atmospheric CO_2. Nonetheless, the result of this lower sputtering rate model still requires source(s) of volatiles capable of supplying additional argon and neon.

Bogard [1997] has reanalyzed the $^{36}Ar/^{36}Ar$ measurements from the trapped gas components in the Martian meteorites EETA 79001 and Zagami that were used as reasonable proxy representatives of the actual Martian atmosphere. Based on his evaluation, Bogard concluded that the previously accepted value of 4.1 ± 0.2 was higher owing to the interpretation of the contribution of the mantle component to the trapped gas measurement. When this component is removed, a measurement of $^{36}Ar/^{38}Ar$ between 3.0 and 3.6 is more representative of the trapped gas component (with an extreme upper limit of 3.9) and the Martian atmosphere [*Bogard*, 1997]. Thus the Martian atmosphere is even more anomalous as compared to other solar system bodies and loss to space has been even more extensive than determined in Paper 1. In order to fit the range of $^{36}Ar/^{38}Ar$ measurements determined by *Bogard* [1997], the sputtering rates (without a magnetic field) must have been greater than 6 times the *Luhmann et al.* [1992a] rate. The presence of a substantial magnetic field does not change the constraint on the sputtering rate until after $t_{sputter}$ ~ 3.0 Gyr (Figure 6).

Conclusions

The impact of a Martian paleomagnetic field on the sputtering loss rates of atmospheric argon and neon have been discussed. Even under the influence of a magnetic field limiting sputtering loss up until 3.6 Gyr in Martian history, the results presented here support the conclusion that (1) sputtering has played a significant role in the modification of the Martian atmosphere, and (2) sources in addition to outgassing from intrusive and extrusive volcanic material are required to reproduce the present Martian atmospheric abundance of argon and neon. The volcanic factors calculated here represent constraints on additional volatile source(s) which must provide 4 -100 times more argon (vf_{36}) and 40 - 1800 times more neon (vf_{20}), depending on model input parameters. In addition, the other source(s) must preferentially outgas neon to the atmosphere relative to argon by a factor of between 10 - 26 (vf_{20}/vf_{36}), also dependent on model input parameters. Implications of these additional sources of volatiles are discussed separately (K.S. Hutchins and B.M. Jakosky, Sources of Martian volatiles, submitted to *Journal of Geophysical Research*, 1996)

However, much uncertainty remains in our understanding of Martian atmospheric evolution, climate change, and the role of a planetary magnetic field. The Mars Global Surveyor mission (MGS; see *Albee* [1996] for details) will obtain a magnetic survey of the planet from an altitude of ~120 km altitude during the aerobraking phase and ~400 km for the remainder of the mission. However, interpretation of these data may be complicated by the presence of the ionosphere and the solar wind interaction. Planet-B, the Japanese space physics and aeronomy mission scheduled for launch in 1998, will make magnetic field measurements from ~150 km altitude, but its low-inclination, elliptical orbit will limit the coverage of any potential remnant global field patterns. In either of these cases, the only possibility for chronological information would derive from association of the measured remanent fields with dated geologic domains. Only distributed landed science with both magnetics and dating capabilities, or analysis of returned samples can yield verified paleomagnetic data through time.

Further constraint on atmospheric evolution models would be substantially advanced by additional measurements of the stable isotopic composition of the Martian atmosphere, measurements of initial volatile content of the magma through magma inclusions or xenoliths, and dating of geologic units to calibrate crater-derived ages and models of volcanism through time. To some degree, these goals may be served by the Mars Volatile and Climate Surveyor (MVACS) lander, which may be able to make measurements of $\delta^{13}C$, D/H, and $\delta^{18}O$ from the atmosphere and gas sequestered in the soil layer. However, a sample return mission could provide a sample of atmosphere and surface rocks/soils to allow for highly precise determination of the composition of the Martian atmosphere, age dating of the Martian surface, and further calibrate our understanding of the Martian interior/crust as determined from the SNC meteorites.

Acknowledgments. We would like to thank T. Swindle and A. Treiman for helpful suggestions that improved the quality of this manuscript. B.M.J. would like to thank A. Treiman for acting as editor for this manuscript. This research was supported in part by NASA through grant NAGW-3995 from the Planetary Atmospheres Program.

References

Albee, A., Mission to Mars to collect a storehouse of scientific data, *Eos Trans. AGU, 77*, (45), 441-442, 1996.

Bogard, D.D., A reappraisal of the Martian $^{36}Ar/^{38}Ar$ ratio, *J. Geophys. Res., 102*, 1653-1661, 1997.

Carr, M.H., Mars: A water rich planet?, *Icarus, 56*, 476-495, 1986.

Cisowski, S.M., Magnetic studies on Shergotty and other SNC meteorites, *Geochim. Cosmochim. Acta, 50*, 1043, 1986.

Craddock, R.A., and T.A. Maxwell, Geomorphic evolution of the Martian highlands through ancient fluvial processes, *J. Geophys. Res., 98*, 3453-3468, 1993.

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

Hutchins, K.S., and B.M. Jakosky, Evolution of Martian atmospheric argon: Implications for sources of volatiles, *J. Geophys. Res., 101*, 14933-14949, 1996.

Jakosky, B.M., R.O. Pepin, R.E. Johnson, and J.L. Fox, Mars atmospheric loss and isotopic fractionation by solar-wind-induced sputtering and photochemical escape, *Icarus, 111*, 271-288, 1994.

Johnson, R.E., and M.A. McGrath, Stability of the Io plasma torus/atmosphere interaction, *Geophys. Res. Lett., 20*, 1735-1738, 1993.

Jones, J.H., A discussion of isotopic systematics and mineral zoning in the Shergottites: Evidence for a 180 m.y. igneous crystallization age, *Geochim. Cosmochim. Acta, 50*, 969-977, 1986.

Kasting, J.F., CO_2 condensation and the climate of early Mars, *Icarus, 94*, 1-13, 1991.

Kivelson, M.G., and C.T. Russell, *Introduction to Space Physics*, Cambridge Univ. Press, New York, 1995.

Lucchitta, B.K., A.S. McEwen, G.D. Clow, P.E. Geissler, R.B. Singer, R.A. Schultz, and S.W. Squyres, The canyon system on Mars, in *Mars,* edited by H.H. Kieffer, B.M. Jakosky, C.W. Snyder, and M.S. Matthews, pp. 453-492, Univ. of Ariz. Press, Tucson, 1992.

Luhmann, J.G., and J.U. Kozyra, Dayside pickup oxygen ion precipitation at Venus and Mars: Spatial distributions, energy deposition, and consequences, *J. Geophys. Res., 96*, 5457-5467, 1991.

Luhmann, J.G., R. E. Johnson, and M.H.G. Zhang, Evolutionary impact of sputtering of the Martian atmosphere by O^+ pickup ions, *Geophys. Res. Lett., 19* (21), 2151-2154, 1992a.

Luhmann, J.G., C.T. Russell, L.H. Brace, and O.L. Vaisberg, The intrinsic magnetic field and solar wind interactions of Mars, in *Mars,* edited by H.H. Kieffer, B.M. Jakosky, C.W. Snyder, and M.S. Matthews, pp. 1090-1134, Univ. of Ariz. Press, Tucson, 1992.

McKay, C.P., and C.R. Stoker, The early environment and its evolution on Mars: Implications for life, *Rev. Geophys., 27*, 189-214, 1989.

McSween, H.Y., What we have learned about Mars from SNC meteorites, *Meteoritics, 29*, 757-779, 1994.

Newkirk, G., Jr., Solar variability on the time scales of 10^5 years to $10^{9.6}$ years, in *The Ancient Sun*, edited by R.O. Pepin, J.A. Eddy, and R.B. Merrill), *Geochim. Cosmochim. Acta Suppl., 13*, p. 293, 1980.

Pepin, R.O., On the origin and early evolution of terrestrial planet atmospheres and meteoritic volatiles, *Icarus, 92*, 2-79, 1991.

Pepin, R.O., Evolution of the Martian atmosphere, *Icarus, 111*, 289-304, 1994.

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

Schubert, G., and T. Spohn, Thermal history of Mars and the sulfur content of its core, *J. Geophys. Res., 95*, 14,095-14,104, 1990.

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

Treiman, A.H., J.H. Jones, and M.J. Drake, Core formation in the shergottite parent body and comparison with the Earth, *Proc. Lunar Planet. Sci. Conf. 17th*, Part 2, *J. Geophys. Res., 92*, suppl., E627-E632, 1987.

Zahnle, K., and J.C.G. Walker, The evolution of solar ultraviolet luminosity, *Rev. Geophys., 20*, 280, 1982.

Zhang, M.H.G., J.G. Luhmann, S.W. Bougher, and A.F. Nagy, The ancient oxygen exopshere of Mars: Implications for atmospheric evolution, *J. Geophys. Res., 98*, 10,915-10,923, 1993.

K.S. Hutchins and B.M. Jakosky, LASP, Campus Box 392, University of Colorado, Boulder, CO 80309-0392. (e-mail: hutchins@argyre.colorado.edu)

J.G. Luhmann, Space Sciences Laboratory, Grizzley Peak Boulevard, University of California, Berkeley, Berkeley, CA 94720.

(Received June 5, 1996; revised November 25, 1996; accepted December 10, 1996.)