OUTGASSING OF VOLATILES ON MARS: VOLCANISM THROUGH TIME OR EARLY CATASTROPHIC RELEASE?

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Introduction: Formation of the Martian atmosphere by outgassing may include release of volatiles during accretion and core formation, an early magma-ocean stage, volcanism associated with early crust formation, and/or volcanism through time. We examine the connection between volatiles in the mantle as determined from the Martian meteorites and in the atmosphere as reconstructed from present-day abundances/isotopes and inferred loss to surface/subsurface sinks and to space. Our goal is to constrain the total volatile inventory and the role played by outgassing from the mantle by volcanism through time.

Our approach initially will be to see if outgassing from the mantle associated with volcanism through time can reproduce the surface and atmospheric gas abundances.

Atmospheric Constraints: In order to compare the mantle's ability to provide volatiles to the atmospheric volatiles, we use reconstructed atmospheric abundances that include volatiles that have been lost from the atmosphere through time. The gases we will focus on are H_2O, ^{36}Ar, and ^{40}Ar.

Reconstructed H_2O abundances. Significant amounts of water have been lost to space or to the crust. Estimates of the global water inventory have been made using forward modelling [1, 2] and quantification of these sinks [3]. Table 1 shows the estimates obtained by Jakosky and Hallis [3] by looking at the abundances of water lost to each sink. Their global integrated estimate of initial water inventory (across all sinks) is between 380-1970 m H_2O (expressed as a global equivalent layer, GEL). This represents the current best estimate of the initial water inventory for Mars.

Water Sink	Amount (m H_2O GEL)
Present-day exchangeable water	20-30
Lost to space	110-570
Water incorporated into minerals	130-260
Potential buried ice from an early ocean	110
Identifiable water sinks	***380-970***
Inferred crustal water	315-1000
Total amount of water	***685-1970***

Table 1. Abundances of H_2O lost to non-atmospheric sinks through time, from [3].

Reconstructed ^{36}Ar abundance. The original abundances of ^{36}Ar and ^{38}Ar were estimated from the enrichment in the ratio of ^{38}Ar/^{36}Ar due to loss to space resulting primarily from sputtering. Detailed modeling of loss was based on the current abundances, the isotope ratio, and the structure of the upper atmosphere. It indicates that ~2/3 of the ^{36}Ar has been lost to space through time [4, 5]. Thus, the current atmospheric abundance of 1.5×10^{14}g is augmented to provide a reconstructed initial value of 4.5×10^{14}g. This estimate does not include any Ar lost during an early phase of catastrophic loss, but that presumably would have removed all of the Ar and not affected the isotope ratio.

Reconstructed ^{40}Ar abundance. ^{40}Ar is produced by decay of ^{40}K, so estimating its original abundance requires knowing the planet's K abundance and assuming an outgassing history relative to the timing of loss to space by sputtering. An added complication is ^{40}K concentrated in the crust during crust formation and the release of ^{40}Ar by weathering. The reconstructed ^{40}Ar abundance was estimated using the same model as for ^{36}Ar [4]. They estimated that 18-36 % of the ^{40}Ar has been lost to space, yielding a reconstructed abundance of $3.4\text{-}4.4 \times 10^{17}$g. This amount does not depend strongly on behavior during Mars' earliest history, as very little ^{40}Ar would have been created and outgassed early due to the long half life for decay of ^{40}K.

Mantle constraints: We use mantle volatile abundances inferred from measurements of the Martian meteorites.

Mantle H_2O abundance. Filiberto et al. [6] and McCubbin et al. [7] compiled a list of the mantle water abundances inferred from Martian meteorites. These estimates come from the Shergottites, which are volcanic basalts, based on the measured ratio of H_2O/Ce, and from Chassigny, thought to represent a direct sample of the mantle. Derived mantle abundances range between about 15-250 ppm. For the mantle mass of ~4.6×10^{26}g, this yields a range of H_2O masses between 6.9×10^{21} - 1.15×10^{23}g, and corresponds to a global layer of water between ~50-800 m deep if it were all to outgas to the surface. It is not clear whether the range of estimated abundances represents variability within a non-uniform mantle, assumptions in the various analyses that might not be correct or exact, or a combination of the two.

Mantle ^{36}Ar abundance. ^{36}Ar abundances measured in Chassigny were reported by Mathew and Marti [8] as $0.9\text{-}2.2 \times 10^{-9}$ cm^3 STP/g. Multiplying by the mass of the mantle and converting to g yields $6.6\text{-}16.2 \times 10^{14}$g of ^{36}Ar in the present-day mantle. This number assumes no loss of Ar in the sample between the time it was part of the mantle and its analysis in the laboratory on Earth; this assumption may not be correct.

^{40}Ar mass. Because it has a production function and because some ^{40}Ar is released from the crust and not just from the mantle, comparing mantle abundances with the atmosphere is not as useful. Instead, we calculate the total amount of ^{40}Ar produced on Mars through time and compare this with the atmospheric reconstructed abundance. We use the K abundance estimated for the bulk silicate Mars [9], and standard values for the ^{40}K fraction, the branching ratio, and the decay half life. For a K abundance of 309 ppm, this yields an estimated production of ^{40}Ar since planetary formation of 1.44 x 10^{19}g.

Can Volcanism Through Time Produce The Atmospheric Gas Abundances? We use the estimates of volcanic eruption volumes from Greeley and Schneid [10]. We assume a representative 10 % partial melting of mantle material to produce volcanic magma, and diffusion of volatiles into the melt from nearby material. For the total volume of volcanism (intrusive plus extrusive), this means that ~5% of the mantle will have degassed since the Noachian.

H_2O. Degassing 5 % of the mantle would release between 2.4-40 m GEL H_2O. This is less than 10 % of the reconstructed global inventory derived from the known sinks for H_2O, and possibly much less. Identifying additional sinks that hold water that had been at the surface (e.g., more hydrated minerals) would lower this fraction further.

^{36}Ar. Volcanism would have contributed 0.33-0.81 x 10^{14} g ^{36}Ar, compared to a reconstructed inventory of 4.5 x 10^{14}g, or less than 20% of the atmospheric abundance.

^{40}Ar. The reconstructed atmospheric abundance of 3.4-4.4 x 10^{17}g represents only 2.4-3.1 % of the total ^{40}Ar produced over time (see also [11]). This compares with an estimated 58 % outgassing to the atmosphere on Earth.

Discussion/Conclusions. Clearly, outgassing associated with volcanism through time was not able to produce the observed atmospheric gases. Even pushing all of the uncertainties to their extreme values would not resolve the problem. The low reconstructed ^{40}Ar abundance, in particular, places strong constraints on the ability of the mantle and crust to have outgassed through time. Its production function means that outgassing of ^{40}Ar is strongly decoupled from the earliest history of Mars, but instead reflects the efficacy of subsequent outgassing through time – the low ^{40}Ar outgassing fraction underscores the inefficiency of mantle degassing.

Rather, (i) volcanism through time would have produced only incremental increases to the Mars global volatile abundances, and (ii) it is likely that the majority of outgassing occurred prior to the late Noachian, either during a magma-ocean stage or associated with early crust formation.

Outgassing during early crust formation is a likely source of volatiles. Crust production during the first 300-500 m.y. would have produced ~10x the amount of crust as was produced by volcanism through time [12, 13], and could have resulted in degassing of as much as half of the mantle [14]. These amounts of gas would be much more consistent with the reconstructed abundances.

Outgassing also could have occurred during a magma-ocean stage that might have accompanied planetary accretion and core formation [15, 16]. Volatiles released during either of these two early phases might have been stripped away to space very quickly by hydrodynamic outflow of H or H_2, by the more-active Sun and solar wind, or by impact erosion of the atmosphere [e.g., 17]. The uncertainties in where the volatiles resided and in the efficacy of the early loss processes preclude a stronger statement on early loss.

Mars appears to have had a thick atmosphere at the time of onset of the geological record in the Noachian. Subsequent evolution would have been dominated by incremental outgassing and additions by impact and by a steady draw-down of the atmosphere via loss to the various sinks [3, 18]. We recognize that there is an apparent inconsistency created by the potential rapid and thorough loss prior to about 4 b.y.a. [19, 17] combined with the difficulty of producing the observed abundance of gas at the surface and in the atmosphere via outgassing subsequent to that time.

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