**IS MARS ENRICHED IN ALKALI ELEMENTS?: CONSTRAINTS FROM ARGON 40 OUTGASING**

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**Introduction**

A variety of thermal evolution models have been developed for Mars [e.g., 1-3]. Observational constraints used to test these models commonly include the crustal thickness, near-surface heat flow (or equivalently, the elastic lithosphere thickness), the mantle water content, and the time history of the magnetic dynamo.

Argon 40 is a radioactive decay product of potassium 40. Because ⁴⁰Ar is volcanically outgassed from the interior of Mars to the atmosphere, it can be used as an additional test of Mars thermal evolution models. ⁴⁰Ar in the martian atmosphere has been well measured by the SAM mass spectrometer on the Curiosity rover. Argon constitutes 2.08% of the atmosphere, and ⁴⁰Ar is 99.9% of the total Ar [4, 5]. Measurements of the ³⁶Ar/³⁸Ar isotope ratio indicate that early Mars lost substantial amounts of argon to space [6, 7]. We account for this loss in the modeling described here.

**Methods**

We have developed a box model for the evolution of ⁴⁰Ar in the mantle, crust, and atmosphere of Mars (Figure 1). Our box model closely resembles those of previous studies of both Earth [8, 9] and Mars [6, 10]. ⁴⁰K can decay to ⁴⁰Ar in the mantle, and the ⁴⁰Ar can subsequently be carried by volcanism toward the surface. Because argon is a highly incompatible element [11, 12], it is assumed to be outgassed directly from the magma to the atmosphere rather than being stored in the crust. In addition, ⁴⁰K can be carried magmatically from the mantle to the crust, where it may subsequently undergo radioactive decay to produce ⁴⁰Ar in the crust.

Figure 1: Box model for the evolution of Ar and K between the mantle, atmosphere and crust of Mars.

Whether crustal ⁴⁰Ar can be subsequently released to the atmosphere, for example by high temperature metamorphism or by hydrothermal alteration of the crust, is an important, unresolved question for Mars. Existing models of argon outgassing on Mars require 30-90% of the crustal ⁴⁰Ar to be subsequently outgassed to the atmosphere in order to explain the observed atmospheric Ar [6, 10]. However, it is not clear that such a high proportion of crustally produced ⁴⁰Ar can actually be released to the atmosphere. A key motivation for the present study is to search for thermal evolution and volcanic outgassing models that explain the observed atmospheric ⁴⁰Ar while requiring little or no release of crustal ⁴⁰Ar to the atmosphere.

A key aspect of the outgassing model is the volcanic flux from the mantle to the crust and atmosphere. Our model uses the volcanic flux from the parameterized thermal evolution model of Sandu and Kiefer [3]. Magma production occurs by adiabatic decompression melting, and the rate of melt production as a function of time depends on the rate at which material flows through the melting zone. The convective velocity is determined from a Rayleigh number parameterization for stagnant lid convection. Water and the radioactive elements K, Th, and U are all highly incompatible and are transported magmatically from the mantle to the crust. Differences in the Na abundance and Mg## for Mars relative to Earth tend to lower the solidus of the martian mantle [13]. The effect of water on reducing the mantle solidus is parameterized based on [14]. Cooling and loss of water from the mantle causes a strong decline in the magma production rate over time, consistent with the geologic record of Mars.

The volcanic history of Mars depends on a number of different physical and chemical control parameters, including the initial temperature, the initial water content, and the abundance of radioactive elements. Our model allows us to control each of these control parameters individually in order to assess how they influence the ⁴⁰Ar outgassing history. In contrast, prior studies of ⁴⁰Ar outgassing on Mars [6, 10] assumed a volcanic history that had a fixed shape as a function of time and could only be varied by changing the total amplitude of the volcanic production. This is an important difference between the present study and earlier work, which allows us to identify possible successful outgassing models that could not be assessed in earlier studies.
Results

The results of the $^{40}$Ar outgassing model depend on the initial temperature, the initial mantle water content, and the initial concentration of $^{40}$K. Because K and Na are both alkali elements, we assume that the initial K/Na ratio is fixed using the ratio from Taylor’s recent bulk composition model for Mars [15]. Thus, models with higher mantle K abundances also start with higher mantle Na abundances and modify the initial solidus based on [13]. Our sweep through the plausible parameter space is on-going. We focus here on a new class of possible models that explain the observed atmospheric $^{40}$Ar on Mars, but we caution that additional successful model classes may emerge in our on-going work.

One successful approach to explaining the atmospheric $^{40}$Ar involves increasing the assumed initial $^{40}$K in the mantle. Figure 2 compares argon outgassing as a function of time for two different models. The black line has 310 ppm K, Na$_2$O=0.53% (the canonical martian values of [15, 16]), and $T_0=1900$ K. The red line has 600 ppm K, Na$_2$O=1.03%, and $T_0=1715$ K. $T_0$ is changed to maintain the same total crust production, and Na is changed to maintain constant K/Na. Both models have 300 ppm initial water, and all other parameters are identical for the two models. The red line model closely approaches the observed value of $^{40}$Ar, producing 4.4 times as much atmospheric $^{40}$Ar as the black line model with only twice as much K. The total crustal production in the two models, expressed as mean crustal thickness, is nearly identical for the two models (Figure 3). A key difference is that the higher K model produces more volcanism at later times in martian history due to the combination of a cooler start and more radioactive heating. $^{40}$K has a half-life of 1.25 Ga, so the delayed volcanic production in the high K model occurs after more $^{40}$Ar has been produced in the mantle, resulting in a strongly non-linear relationship between initial $^{40}$K and the final outgassing of $^{40}$Ar. This can explain the observed atmospheric $^{40}$Ar without needing to invoke loss of $^{40}$Ar from the crust.

Figure 3: Mean crustal thickness versus time for models with initial K of 310 ppm (black line) and 600 ppm (red line).

The bulk silicate Earth is believed to have 260 ppm K [17] and the most widely accepted Mars bulk composition models have 305-310 ppm K [15, 16]. The results presented here therefore suggest that Mars may be an alkali-enriched planet, although our results remain far below the 920-1040 ppm K found in some Mars bulk composition models [18-20].