

MARS INTERIOR ACCRETED CHONDRITIC VOLATILES IN THE PRESENCE OF A GAS DISK. S. Mukhopadhyay¹ and S. Péron^{1,2}, ¹Department of Earth and Planetary Sciences, University of California Davis, One Shields Avenue, Davis CA 95616, USA (sujoy@ucdavis.edu), ²Institute of Geochemistry and Petrology, ETH Zürich, Clausiusstrasse 25, 8092 Zürich, Switzerland (sandrine.peron@erdw.ethz.ch).

Introduction: Volatile delivery was an important process that shaped the early environment of the terrestrial planets. Models for the acquisition of volatiles during terrestrial planet formation frequently start with gases being derived from the solar nebula [1,2]. Volatile escape and addition of chondritic volatiles, either during the main phase, or towards the end stages of planet formation, subsequently modify the volatile budgets and compositions. However, the sources, timing of accretion, and evolution of volatiles on terrestrial planets are still debated [2-8]. For example, gravitational capture of nebular volatiles by planets or planetary embryos has been argued against. Instead, delivery of chondritic volatiles by solid bodies during the main phases of terrestrial planet accretion and/or in a late veneer phase has been invoked. These bodies range from the inner solar system objects such as enstatite-like chondrites, to material from the outer solar system such as carbonaceous chondrites, or comets [4-8]. Here we utilize noble gas measurements in the Chassigny meteorite from Mars to obtain new insights into volatile accretion during the earliest stages of terrestrial planet formation.

Being inert, noble gases are invaluable tracers of the complex history of volatile accretion and the physical processes associated with accretion. For example, the relative proportion and isotopic compositions of the noble gases are linked to different sources such as solar nebula gases, solar wind irradiated material, and gases trapped in chondritic meteorites and comets.

Measurements of xenon isotopes in the Martian meteorite Chassigny, one of the only Martian meteorites that has unequivocal evidence for preserving mantle noble gases, suggest that the Martian mantle may contain solar xenon, and by inference solar krypton [9, 10]. While the isotopes of xenon in Mars' atmosphere is mass-fractionated towards heavy isotopes, the precursor xenon composition is consistent with a solar. A definite inference about the solar gases in Mars' atmosphere comes from in-situ and meteorite observations that the atmospheric krypton isotopic composition is solar [11,12]. Consequently, the entire growth of Mars could have occurred in the presence of the nebula with no clear indication of when, and if, chondritic gases might have been added. However, xenon isotopes may not be the best diagnostic tool to distinguish between solar and chondritic sources and the stable isotopes of krypton are better suited for this purpose due to significant isotopic

differences in the sources: solar krypton is enriched in light isotopes relative to Earth's atmosphere while chondritic krypton is enriched in the heavier isotopes. However, there are no krypton isotopic measurements from Chassigny with sufficient precision to distinguish between solar and chondritic sources.

Methods: We measured the noble gas (Ne, Ar, Kr, Xe) isotopic and elemental compositions of splits of Chassigny via laser step-heating. To overcome previous challenges, we used a new protocol for efficiently separating Kr from Ar and Xe, and using the latest generation of multi-collector noble gas mass spectrometer to measure all of the six krypton isotopes.

Results and discussions: The krypton isotopic data from Chassigny fall on a single line reflecting mixing of cosmogenic gases with trapped Martian mantle gases. With the exception of ^{86}Kr , all Kr isotopes are produced through spallation reaction, with the highest production rate associated with ^{83}Kr . Thus, when the $^{86}\text{Kr}/^{84}\text{Kr}$ ratio is regressed against $^{83}\text{Kr}/^{84}\text{Kr}$, the $^{86}\text{Kr}/^{84}\text{Kr}$ ratio corresponding to the $^{83}\text{Kr}/^{84}\text{Kr}$ value free of cosmogenic krypton identifies the trapped mantle component. The $^{86}\text{Kr}/^{84}\text{Kr}$ ratio of the Martian interior, corresponding to the cosmogenic free $^{83}\text{Kr}/^{84}\text{Kr}$ value, is very different from the solar composition but indistinguishable from Average Carbonaceous Chondrites (AVCC). The AVCC composition also provides a better match for the Martian mantle than Phase Q, which is a carbonaceous phase carrying the majority of heavy noble gases in chondrites, and sometimes the only trapped composition in achondrites [13]. However, we cannot rule out admixture of a small amount of solar gases with Q gases to explain the observed $^{86}\text{Kr}/^{84}\text{Kr}$ value. Overall, the $^{86}\text{Kr}/^{84}\text{Kr}$ ratio of the Martian interior suggests that dominantly chondritic gases, with AVCC providing the closest match, were incorporated into the Martian interior.

The similarity of the $^{86}\text{Kr}/^{84}\text{Kr}$ ratio in the Martian mantle with that of the chondritic krypton value cannot result from addition of fissiogenic krypton to solar or cometary krypton. The near-absence of fissiogenic xenon in the Martian mantle has been shown before, likely a result of the higher primordial gas abundances in the Martian mantle compared to Earth [10,14]. We estimate that at most 0.22% (upper limit) of the ^{86}Kr in the Martian mantle is produced from fission and it is more likely to be < 0.011% of the measured value. Hence, fission-produced krypton is negligible, and we

reaffirm that the krypton isotopic composition in Mars' mantle reflects incorporation of chondritic krypton.

The observation of chondritic krypton in the Martian interior is consistent with our xenon observations. Like krypton, the xenon isotopic data fall on a single mixing line, reflecting mixing of a trapped mantle component with cosmogenic xenon. The $^{136}\text{Xe}/^{130}\text{Xe}$ ratio of the Martian interior, free of cosmogenic contribution to ^{130}Xe , is distinct from the solar composition but close to the chondritic value. The evidence for chondritic gases is also supported by the observed elemental ratios, $^{36}\text{Ar}/^{132}\text{Xe}$ and $^{84}\text{Kr}/^{132}\text{Xe}$, which are close to carbonaceous chondrites and Phase Q values.

Implications for Mars' formation and early history: The incorporation of chondritic krypton and xenon into the Martian interior does not prevent other volatile species in the interior from being acquired from the solar nebula. For example, the nitrogen isotopic composition of Chassigny may reflect solar-derived nitrogen, although enstatite chondrites may be an equally valid source [10]. Objects that are larger than a lunar mass can gravitationally capture an atmosphere in the presence of a nebula, which might then be incorporated into the solid body [1]. However, even though the presence of a minor solar gas component cannot be ruled out, the lack of detectable solar krypton precludes incorporation of any significant amount of solar heavy (Kr-Xe) noble gases into the interior of proto-Mars, either via dissolution into magma oceans or through adsorption and burial beneath the surface during accretion [e.g., 1].

The chondritic krypton isotopic composition of the Martian mantle contrasts with a solar isotopic composition of krypton in the atmosphere. These distinct isotopic composition between the interior and atmosphere of Mars suggests chondritic krypton was incorporated into the interior prior to acquiring the atmospheric solar gas from the nebula. The solar gas in the atmosphere could have been acquired from the nebula after most of Mars accreted, reaffirming a rapid growth for Mars [15]. The accreted atmosphere, however, was not massive so that mantle ingassing of solar Kr-Xe noble gases was limited, or negligible. This view of incorporating chondritic volatiles in the interior of planets, or planetary embryos, followed by accretion of a solar atmosphere runs completely counter to models of planet formation where chondritic volatiles are delivered following the acquisition and fractionation of solar gases [e.g., 1].

The sharp contrast in composition between the interior and atmosphere requires that Mars' atmosphere could not be generated simply through outgassing of its interior, as sometimes assumed [2]. Moreover, since the atmosphere krypton isotopic composition is enriched in

the lighter krypton isotopes with respect to the Martian interior, interior outgassing followed by hydrodynamic loss is also ruled out as a potential pathway for generating the Martian atmosphere; hydrodynamic loss would leave the residual atmosphere enriched in the *heavier* isotopes of krypton.

Delivery of chondritic gases to Mars surface reservoirs following dissipation of the nebula was likely limited. Delivery of chondritic volatiles after the atmosphere was acquired would have polluted the nearly pure solar krypton composition with a chondritic signature. Note that while planetesimal impacts may add to the budget of non-volatile elements such as the Platinum Group Elements, they may not contribute significantly to the volatile budget, particularly if the parent bodies are volatile poor. Instead, planetesimal impacts can lead to net volatile loss by driving atmospheric loss from a planet or embryo without inducing an isotopic fractionation of the atmospheric gases [16].

Our study presents evidence that embryos in the inner solar system were incorporating chondritic volatiles into their interiors prior to nebular dissipation. During this early period of solar system history, volatiles were being incorporated into the interior of Mars in significant quantities such that Martian interior concentrations of the heavy noble gases were possibly up to two orders of magnitude higher than the concentrations in Earth's bulk mantle. The delivery of these chondritic volatiles to the inner solar system was occurring either from material similar to enstatite chondrites, or from outer solar system material through radial transport in the disk.

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