FORMATION AND EVOLUTION OF MARS BASED ON DIFFERENCES IN ITS INTERIOR AND ATMOSPHERIC VOLATILES. S. Mukhopadhyay[1] and S. C. Péron[2], [1]Department of Earth and Planetary Sciences, University of California Davis, One Shields Avenue, Davis CA 95616, USA (sujoy@ucdavis.edu), [2]Institute of Geochemistry and Petrology, ETH Zürich, Clausiusstrasse 25, 8092 Zürich, Switzerland (Sandrine.peron@erdw.ethz.cn).

Introduction: Planetary habitability is tied to the history of volatile accretion, volatile loss, and the evolution of surficial environments. Models for the evolution of volatile species during terrestrial planet formation often start with gases derived from the solar nebula [1-3]. These nebular volatiles are subsequently lost by fractionation during gravitational escape, or significantly modified and overprinted by addition of chondritic volatiles. The addition of chondritic volatiles may occur either during the main phase, or towards the end stages of planet formation. The sources and timing of volatile accretion by terrestrial planets, however, remains a subject of intense debate [4-8].

As a planetary embryo which formed rapidly in a few million years [9], Mars provides a unique observational window into inner Solar System volatile delivery during the earliest planet formation stages. Such observations will be crucial for testing models of volatile accretion. Furthermore, constraints on Martian interior volatile compositions, and volatile degassing rates, provides insights into the formation and evolution of the Martian atmosphere. The inert noble gases are invaluable tracers of the history of volatile accretion and degassing. For example, the relative proportion of primordial noble gas isotopes can be linked to different sources such as solar nebula gases, as well as gases trapped in chondritic meteorites and comets. The radiogenic and fissiogenic noble gases on the other hand provide timescales and rates of volatile accretion and magmatic degassing.

Previously, the noble gas composition of the Martian interior has been determined primarily from the dunitic meteorite Chassigny. Based on xenon isotopic analyses of Chassigny, noble gases in the Martian mantle were inferred to be solar [10, 11]. However, recent krypton isotopic measurements, which can clearly distinguish between solar and chondritic sources due to their significant isotopic differences, documents the occurrence of chondritic krypton in Chassigny [12]. This inference of chondritic krypton in the Martian interior contrasts with solar krypton in the atmosphere [13,14]. The strong compositional contrast between the interior and atmosphere indicates that the Martian atmosphere could not be generated primarily through outgassing of its interior. However, given the evidence for volatile heterogeneity in the Martian interior [15], noble gases in Chassigny may not represent the composition of the entire Martian mantle. Here we present noble gases from the ferroan chassignite NWA 8694 [16]. NWA 8694 has been proposed to represent a link between chassignites and nakhlites [16].

Methods: We measured the abundances and isotopic compositions of Ne, Ar, Kr, and Xe in two separate splits of NWA 8694 via laser step-heating. Gases were separated from each other using cryogenic techniques and let into the latest generation of multi-collector noble gas mass spectrometer. We measured all six krypton isotopes and all nine xenon isotopes.

Results and discussions: The noble gas elemental ratios (^{36}Ar/^{132}Xe and ^{84}Kr/^{132}Xe) in NWA 8694 are similar to those observed in Chassigny. Likewise, the trapped ^{40}Ar/^{36}Ar ratio in NWA 8694 corrected for cosmogenic argon is around 400, similar to the value inferred from Chassigny [12]. These low values point to the relatively undegassed nature and the high concentration of primordial noble gas concentrations in the Martian interior. For example, assuming an abundance of 360 ppm for bulk silicate Mars [17], and a closed system evolution of 4.0 Ga, a ^{40}Ar/^{36}Ar ratio of ~400 indicates ^{36}Ar abundances of ~2×10^{-12} mol/g. An open system evolution would indicate even higher ^{36}Ar abundances. Compared to Earth's interior ^{36}Ar abundances [6], the Martian interior abundance is a factor of 30 to 90 higher, demonstrating the significant enrichment in the primordial noble gases.

The noble gases in NWA 8694 appears to show a trend towards a Martian atmospheric component. High ^{129}Xe/^{132}Xe ratios in lower temperature steps indicates the presence of the Martian atmospheric component while the ^{129}Xe/^{132}Xe ratios in higher temperature steps are compatible with a chondritic component.

The best evidence for a chondritic component however, comes from krypton isotopes. Except for ^{86}Kr, all of the Kr isotopes are produced through spallation reactions, with ^{83}Kr having the highest production rate. When regressed against ^{83}Kr/^{84}Kr, the ^{86}Kr/^{84}Kr ratio corresponding to the ^{83}Kr/^{84}Kr value free of cosmogenic Kr identifies the trapped component. NWA 8694 shows two trapped Kr components – one that is compatible with solar and the 2nd that is chondritic. We interpret the solar component to reflect Martian atmosphere because it is known to have a solar krypton isotopic composition [13,14]. The Martian atmospheric component was likely incorporated in NWA 8694 through assimilation/

interaction of crustal fluids. The chondritic component is interpreted to reflect the interior component and is associated with chondritic like ^{36}Ar/^{132}Xe and ^{84}Kr/^{132}Xe ratios. For the interior component, the Kr isotopic measurements cannot currently distinguish between Average Carbonaceous Chondrites (AVCC) composition and Phase Q composition, which is a carbonaceous phase carrying the majority of heavy noble gases in chondrites and sometimes the only trapped composition in achondrites [18].

Implications for Mars' early history: The observations of chondritic Kr in the Martian interior based on analyses of NWA 8694 strengthens the conclusions of chondritic gases in the Martian interior from the meteorite Chassigny [12]. The chondritic origin for Kr in the Martian mantle is in contrast with a solar origin for Kr in the atmosphere [13,14]. This contrast in composition suggests chondritic Kr was acquired prior to acquisition of the solar Kr. Given the rapid timescale of Mars' formation [9,19], our observations indicate incorporation of chondritic volatiles into the interiors of terrestrial planets during the earliest stages of planet formation and in the presence of the nebula.

The stark compositional contrast between interior and atmospheric Kr indicates that the Martian atmosphere could not be generated primarily through outgassing of its interior as often modeled [20,21]. Moreover, as chondritic Kr is enriched in the heavier isotopes compared to solar Kr, outgassing followed by hydrodynamic loss, is also ruled out as a potential pathway for the origin of the Martian atmosphere. This is because a mass fractionating atmospheric loss process would leave the atmosphere enriched in the *heavier* isotopes of Kr.

If the solar Kr in the atmosphere was acquired from the nebula, then solar Kr must have been trapped in the regolith or polar ice cap to prevent mass fractionating loss via hydrodynamic escape, a process that is expected to be an efficient mechanism on Mars following dissipation of the nebula [20,22]. This scenario requires Mars surface to be cold, below the freezing point of water, following dissipation of the nebula. Later planetesimal impacts, or episodic periods of warmth may have released the solar Kr into the atmosphere. Alternatively, solar Kr may have been acquired through later delivery of comets. However, there are no direct observations of solar Kr in comets and in the one instance Kr isotopes were measured in a comet, in 67P/C-G, a deficit in ^{86}Kr relative to solar was observed [23]. In all scenarios however, the solar Kr in the Martian atmosphere indicates very limited delivery of volatile rich chondritic material following closure of the Martian interior as otherwise the near-pure solar Kr composition would have been polluted with a chondritic signature. Thus, hypotheses about an early massive H_2O/H_2-CO_2 atmosphere acquired either from impact degassing of chondritic planetesimals, or from interior outgassing, is difficult to reconcile with atmospheric Kr. We note that while volatile-poor planetesimal impacts may add to the budget of platinum group elements, they are likely to lead to net volatile loss and drive atmospheric loss from a planet or embryo without inducing an isotopic fractionation [24].

Our study of the Martian chassignites provide observational evidence that embryos in the inner solar system were incorporating chondritic volatiles into their interiors possibly as early as the first Myr of solar system formation, and prior to nebula dissipation. Volatiles during this early period of solar system history were being incorporated into the interior of Mars in significant quantities. The delivery of these chondritic volatiles to the inner solar system was occurring either from material similar to enstatite chondrites (7), or from outer solar system material through radial transport in the disk. The nearly two orders of magnitude higher noble gas concentrations in the Martian interior relative to Earth's bulk mantle as documented by the Chassignite source suggests very modest levels of magmatic degassing over Martian history.

Acknowledgments: We thank the French National Museum of Natural History (MNHN, Paris, France) for providing the NWA 8694 sample for this study.

References: [1] Pepin R. O. (1991) *Icarus 92*, 2-79, 1991. [2] Pepin R. O. (1994) *Icarus 111*, 289-304. [3] Pepin R. O. and Porcelli D. (2002) *RIMG 47*, 191–246. [4] Broadly M. W. et al. (2020) *PNAS 117*, 13997-14004. [5] Alexander C.M.O.D et al. (1996) *Science 337, 721-723.* [6] Marty B. (2012) *EPSL 313-314*, 56-66. [7] Piani L. et al. (2020) *Science 369*, 1110-1113. [8] Grewal D. S. et al (2021) *Nat. Astronomy 5*, 356-364. [9] Dauphas N. and Pourmand A. (2011) *Nature 473*, 489. [10] Ott U. (1988) *GCA 52*, 1937-1948. [11] Mathew K. J. and Marti K. (2001) *JGR 106*, 1401-1422. [12] Peron and Mukhopadhyay (2022) *Science 377*, 320-324. [13] Swindle T. D. (2002) *RIMG 47*, 171-190. [14] Conrad P. G. et al. (2016) *EPSL 454*, 1-9. [15] Barnes J. J. et al. (2020) *Nat. Geosci. 13*, 260-264. [16] Hewins R. H., et al. (2020) *GCA 282*, 201-226, [17] Yoshizaki and McDonough (2020) *GCA 273*, 137-162. [18]. Busemann H. et al. (2000) MAPS 35, 949-973. [19] Tang H and Dauphas N. (2014) *EPSL 390*, 264-274. [20]. Lammer H. et al. (2018) *Astron Astrophys Rev 26*, 2. [21] Pahlevan K. et al. (2022) *EPSL 595*, 117772. [22] Erkaev et al (2014) *Planet. Space Sci. 98*, 106-119. [23]. Rubin M., et al. (2018) *Sci. Adv. 4*, eaar6297. [24] Schlichting H. and Mukhopadhyay S. (2018) *Space Sci. Rev 214*, 34.