

**CONSTRAINTS, QUESTIONS, AND FUTURE DIRECTIONS ON VOLATILES IN THE MARTIAN INTERIOR: A SUMMARY OF THE WORKSHOP.** J. Filiberto<sup>1</sup>, D. Baratoux<sup>2</sup>, D. Beaty<sup>3</sup>, D. Breuer<sup>4</sup>, B.J. Farcy<sup>1</sup>, M. Grott<sup>4</sup>, J.H. Jones<sup>5</sup>, W.S. Kiefer<sup>6</sup>, P. Mane<sup>7</sup>, F.M. McCubbin<sup>8</sup>, and S.P. Schwenzer<sup>9</sup>, <sup>1</sup>Dept of Geology, Southern Illinois University, Carbondale, IL 62901, USA, [Filiberto@siu.edu](mailto:Filiberto@siu.edu), <sup>2</sup>Geosciences Environnement Toulouse, University of Toulouse & Institut de Recherche pour le Développement, 31 400, France, <sup>3</sup>Mars Program Office, JPL/Caltech, Pasadena, CA 91109, USA, <sup>4</sup>Institute of Planetary Research, German Aerospace Center (DLR), Berlin, Germany, <sup>5</sup>XI, NASA/JSC Houston, TX 77058, USA, <sup>6</sup> Lunar and Planetary Institute, Houston TX 77058, USA, <sup>7</sup>School of Earth and Space Exploration, Arizona State University, Tempe, AZ 85287, USA <sup>8</sup>Institute of Meteoritics, University of New Mexico, MSC03-2050, Albuquerque, NM 87131, USA <sup>9</sup>The Open University, Walton Hall, Milton Keynes MK7 6AA, UK.

**Introduction:** The Workshop on Volatiles in the Martian Interior was held Nov. 3 – 4, 2014 at the Lunar and Planetary Institute in Houston, TX (<http://www.hou.usra.edu/meetings/volatiles2014/>) and gathered scientists from diverse disciplines to discuss the state of knowledge of volatiles in the interior of Mars. The goals were to discuss the latest developments in the field, synthesize our current knowledge, and develop primary scientific questions that still need to be addressed. The workshop included discussions from studies of meteorites, remote sensing, laboratory experimental investigations, in situ surface investigations, astrobiological implications, and geophysical and geochemical modeling. The workshop started with an overview of volatile reservoirs, including the current and ancient atmosphere. It was then organized into sessions by volatile components: chlorine, water, sulfur, and carbon, with highlights on bulk content and reservoirs, effects on mantle melting and basalt genesis, degassing to the crust and atmosphere, and potential for habitability. The martian meteorites' bulk and mineral chemistries were the main tools used to constrain the volatile contents of the interior. This abstract will summarize the key findings of the workshop and the primary open questions.

**Current State of Knowledge: Noble Gases.** From a noble gas perspective, Chassigny appears to be our best example of the interior. It has solar-like Xe-isotopes, but a second (<sup>136</sup>Xe-enriched) reservoir has also been found in Chassigny that is likely a sign of very minor crustal contamination/assimilation [1]. Similarly, Ar isotopes are distinctive in the Martian interior, but a second reservoir could exist. The interior component has been found in mineral separates of all SNC meteorite types and in ALH84001. Interestingly, during crustal processes, elementally-fractionated atmospheric noble gas signatures were incorporated into the nakhlite Martian meteorites, complicating the noble gas signature [1].

**Halogens, Water, Carbon and Sulfur.** The concentrations of halogens in the interior are largely constrained from bulk compositions of the martian

meteorites: The Cl content in the shergottite source region is  $25 \pm 8$  ppm and similar to the terrestrial enriched mantle, while the F content of the martian shergottite source region is  $21 \pm 15$  ppm and similar to the terrestrial bulk mantle [2, 3]. The S content of the martian interior is higher than in the bulk terrestrial mantle, and martian magmas are not sulfide saturated [4, 5]. In contrast, the water content of the martian mantle is much less well constrained, and water seems to be heterogeneously distributed within the martian interior [6]. Shergottites contain tens to hundreds of ppm water, which suggests a mantle drier than the terrestrial MORB source [7]. Hydrous phases within the martian meteorites are consistent with a terrestrial depleted MORB-like source region while being enriched in chlorine [6, 8, 9]. The C content of the martian interior is currently not well constrained with estimates over more than 3 orders of magnitude [10]. However, dissolved C will reduce the martian mantle solidus and potentially drive volcanism [10]. Given the C-concentrations, degassing of a martian magma ocean may have released CH<sub>4</sub> to the atmosphere [11]. However, the exact carbon species present in the martian mantle is highly dependent on the ambient oxygen fugacity [10, 12]. And the measured oxygen fugacities of martian meteorites vary from about IW to QFM [13]. This complicates the interpretation of the effect of carbon on basalt genesis. Further, the reduced C, in the form of graphitic carbon and organic compounds, in the meteorites is consistent with an abiotic origin [14].

**Isotopes and Crustal Contamination.** Complicating our understanding of volatiles in the martian interior is the potential for significant amounts volatiles being stored in the crust [15-17]. Isotopic measurements of the meteorites and atmosphere (D/H, Cl isotopes, S isotopes, and noble gases) suggest heavier(?) crustal or atmospheric isotopic compositions than the mantle reservoir [1, 18-21]. Meteorite isotopic studies imply contamination of some martian magmas with this heavier fractionated source, which is assumed to be the crust; however the contamination is not consistent or

correlated across all isotopic systems which strongly suggests multiple sources and processes. For example, there could be more than just one source in the crust and fractionation processes could act upon them, and there could be more than one reservoir in the interior, e.g., through incomplete homogenization or radioactive processes adding specific isotopes. Interestingly, some enriched shergottites have non-chondritic, positive values of  $\Delta^{33}\text{S}$  [19]. Presently, the only known martian source of such deviations is through UV photo-chemical reactions in the martian atmosphere. This implies that an atmospheric component has been incorporated into some enriched shergottites. The converse is not observed: no depleted shergottites have significant  $\Delta^{33}\text{S}$  anomalies [19].

**Implications.** Volatile elements are known to affect conditions for mantle melting, the composition of partial melts, as well as the rheology of the mantle [10, 22, 23]. In addition, volatile elements have a large influence on the viscosity of mantle rocks, thus exerting significant control on mantle dynamics and the thermo-chemical evolution of the planet [23-25]. However, it is required to know the exact volatile content of the source region in order to constrain how water, halogens, sulfur, or carbon affected mantle melting, crust formation, and mantle and crustal evolution [23-27]. In particular, have volatiles aided in generating a diversity of martian magmas, now that new studies suggest possible occurrences of evolved rocks in the martian crust [24, 26]? Volatile outgassing can also influence atmospheric pressure, and potentially elevate surface temperatures [25, 28].

The diversity of geochemical reservoirs identified to date challenges geodynamical models of martian evolution [25]. While reservoir formation by magma-ocean crystallization and subsequent overturn [29] appears to be possible, the associated large density gradients tend to prevent reservoir interaction with the surface [30]. On the other hand, reservoirs can also be formed by partial melting of the mantle [31], but it remains to be investigated if the isotopic signatures of the SNCs are compatible with this model.

**Primary Open Questions:** Discussion at the workshop focused on the differences between martian meteorites and the chemistry and mineralogy of the surface, and between Mars and Earth. These comparisons lead to multiple, focused, scientific questions. Some of these questions include: what is the composition of volatiles in martian meteorite source regions and bulk Mars, what is the distribution of volatiles in the martian mantle, how did early degassing of the mantle deplete the volatile content of the mantle and contributed to a greenhouse atmosphere, how has secondary basalt genesis further

depleted the volatile content of the interior, how has interaction with crustal and atmospheric fluids overprinted the volatile element and isotopic composition of the martian meteorites, and what does the isotopic composition of martian volatiles imply about the sources and delivery mechanisms of volatiles to Mars?

The community at the workshop concluded that in order to constrain bulk volatile and isotopic composition, and importantly the heterogeneity of the martian interior, it is vital to increase the diversity of the sample collection, ideally including sample return. Detailed experimental campaigns are required to understand how volatiles affect mantle melting, magma genesis, and crustal evolution. The results of these experiments should be taken into consideration for the interpretation of global surface mineralogical or chemical trends in terms of planetary cooling and/or mantle chemical evolution and heterogeneity. Finally, geophysical models will have to include these experimental results along with the constraints from martian the samples.

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