PRELIMINARY INTERPRETATIONS OF ATMOSPHERIC STABLE ISOTOPES AND ARGON FROM MARS SCIENCE LABORATORY (SAM).

J.H. Jones[1], P.B. Niles[1], C.R. Webster[2], P.R. Mahaffy[3], G.J. Flesch[2], L.E. Christensen[2], L.A. Leshin[4], H. Franz[3], M. Wong[5], S.K. Atreya[5], P.G. Conrad[3], H. Manning[6], R. Navarro-Gonzalez[7], T. Owen[8], B. Pepin[9], J.C. Stern[3], M. Trainer[3], S.P. Schwenzer[10] and the MSL Science Team, [1]NASA/JSC, Houston, TX 77058 (john.h.jones@nasa.gov), [2]Jet Propulsion Laboratory, Caltech, 4800 Oak Grove Dr., Pasadena, CA 91109, [3]NASA Goddard Space Flight Center (GSFC), Greenbelt, MD 20771, [4]Rensselaer Polytechnic Institute, Troy, NY 12180, [5]Univ. of Michigan, MI 48105, [6]Concordia College, Moorhead, MN, [7]Universidad Nacional Autónoma de México, Mexico City, Mexico, [8]Univ. of Hawaii, Honolulu, HI 96822, [9]Univ. of Minnesota, Minneapolis, MN, [10]The Open University, Milton Keynes, UK.

Introduction: The first analysis of the martian atmosphere was performed by the Viking missions [1, 2]. The elevated $^{129}Xe/^{132}Xe$ ratio measured by Viking allowed [3] to note the similarity of the Xe extracted from quenched shock melts in the EETA 79001 Antarctic shergottite with the Viking measurements. This was the first solid evidence that meteorites had been delivered from Mars to the Earth [3, 4]. The timing of this discovery was serendipitous. Only two years before, a lunar meteorite had been found in Antarctica. Thus, there was now solid evidence that impacts on other planets could deliver material to the Earth.

In addition to the large ^{129}Xe anomaly, Viking also noted that the $^{40}Ar/^{36}Ar$ of the martian atmosphere was ~3000 and that $\delta^{15}N$ was about +600‰ [1, 2]. Earth-based spectroscopic measurements subsequently indicated that the D/H ratio of the martian atmosphere (δD) was ~+4000‰ [5]. The combination of isotopically heavy N and H led to speculation that the isotopic composition of these elements had been modified by atmospheric escape processes [6]. The chemical and isotopic composition of the martian atmosphere was further refined by laboratory measurements of martian meteorites. One example of this is the $^{40}Ar/^{36}Ar$ of the martian atmosphere, where more refined analyses of EET 79001 shock glasses yielded a $^{40}Ar/^{36}Ar$ ratio of ~1900, as opposed to the Viking measurement of ~3000 [7, 8]. Another example is that of $^{36}Ar/^{38}Ar = <4$ in these glasses, which is significantly lower than the chondritic ratio of ~5.4. This also seems to support the idea of preferential atmospheric loss of lighter Ar isotopes over geologic time [7-9].

However, other measurements of CO_2 isotopes have not been consistent with this atmospheric loss story. Viking measured $\delta^{13}C$ and $\delta^{18}O$ values of 0± 50‰. Earth-based spectroscopy has in fact suggested depleted values for $\delta^{13}C$ of -22± 20‰ [10]. Finally, the recent Phoenix lander measured a $\delta^{13}C$ for CO_2 in the martian atmosphere of -2‰ [11]. This is in contrast to measurements of trapped gas in martian meteorite EETA 79001 which yielded a $\delta^{13}C$ of +36 ± 10‰ [12].

Thus, a combination of robotic, laboratory, and telescopic measurements have set the stage for the SAM/MSL analysis of the martian atmosphere. The SAM analyses are performed in two very different ways within a single instrument package: (i) Tunable Laser (TLS) measurements of $^{18}O/^{16}O$ and $^{13}C/^{12}C$ in atmospheric CO_2; and (ii) Quadrupole mass spectroscopy (QMS) of $^{13}C/^{12}C$, and $^{40}Ar/^{36}Ar$. TLS has also measured δD both in the Martian atmosphere and as evolved from a heated soil sample from Rocknest [13], with results currently under refinement.

Preliminary Results: TLS results yield an isotopic composition of atmospheric CO_2 to be: +48±6‰ in $\delta^{18}O$ and +45±4‰ for $\delta^{13}C$ [14]. QMS results for $\delta^{13}C$ are also in agreement with an average of +40.4±15.5‰ [15]. These measurements agree well with previous $\delta^{18}O$ results and are similar to previous martian meteorite measurements of $\delta^{13}C$.

By QMS the $^{40}Ar/^{36}Ar$ ratio of the atmosphere is ~1900, in good agreement with martian meteorite studies [7, 8]. Refinement of this measurement is also underway, but it is clear that the martian atmospheric Ar has been highly influenced by degassing of radiogenic ^{40}Ar from the crust.

δD measurements by TLS on water in the atmosphere yielded values of +5000 to +7000‰ [14], in good agreement with both telescopic measurements and with a new ion probe analysis of D/H in an olivine-hosted melt inclusion in the shergottite LAR 06319 [9]. In addition $\delta^{18}O$ of atmospheric water was measured at +50 ±10‰ by the TLS [14].

Implications: Taken at face value, our measured enrichments in the heavy isotopes of O, C, and H supports the paradigm of atmospheric loss processes at Mars. Estimates of thermal and non-thermal escape processes during Mars' initial history suggest that early loss was catastrophic, suggesting that very little atmosphere survived earliest accretion and outgassing [9, 16]. Minerals in ALH 84001 whose crystallization and alteration ages have been dated to be near 4 Ga contain our best record of these events and contain enriched C and H isotopes. Measurements of ALH 84001 minerals show $\delta^{13}C$ ~+40‰, and δD values ~+3000‰ [17-19]. In this view, the $\delta^{13}C$ and δD of the martian atmosphere has not changed much over about 4 Ga. This would also be consistent with the measurement of a large enrichment of $\delta^{18}O$ in atmospheric water vapor which could suggest that water on Mars is not in equi-

librium with the crust and has also been enriched in heavy isotopes through atmospheric loss.

An alternate interpretation of the data suggests that buffering of surface volatiles by crustal reservoirs could play an important role in the evolution of the atmosphere as well as its isotopic composition. Crustal reservoirs may represent a much larger volume of volatiles whose isotopic composition was largely established very early. Thus, exchanges between atmosphere and crustal reservoirs could provide a viable means for preserving the fingerprint of ancient processes observed in both the ALH 84001 meteorite and in the modern atmosphere.

The $\delta^{18}O$ of martian CO_2 is very heavy with respect to silicates in martian meteorites but is remarkably similar to terrestrial CO_2. Thus, this ^{18}O enrichment could be a signature either of low temperature equilibration between water and CO_2 [11] or enrichment through atmospheric loss. The oxygen isotopic composition of CO_2 in the martian atmosphere and in carbonates from martian meteorites indicate that some sort of buffering has indeed taken place. Jakosky and Jones [20] argued, based on the Viking measurement of $\delta^{18}O$ ~ 0‰, that oxygen could be buffered by hydrothermal interaction between the crust and atmosphere. The discovery of extensive clay mineral formation in the ancient crust of Mars [21] is evidence for substantial ancient exchange of oxygen isotopes between water and the silicate crust. This buffering between crust and water is not indicated by our water vapor $\delta^{18}O$ data. However, this might be explained by atmospheric exchange between CO_2 and H_2O with the high $\delta^{18}O$ values being transferred from the more abundant ^{18}O-rich CO_2 to the less abundant water vapor.

While the current reservoir of CO_2 on Mars is small, ~12 mbar [22], substantial CO_2 may be stored as carbonate in crustal materials and may be as large as 1-3 bars [23]. The size and isotopic composition of this reservoir remains a large unknown. Some younger martian meteorites have at least trace levels of carbonates with low $\delta^{13}C$ that have been a interpreted to be martian [24-26], suggesting that modern carbonate formation is ongoing [11]. It is expected that volcanic degassing and carbonate precipitation should act to decrease the carbon isotopic composition of atmospheric CO_2, but exchange with an ancient, high-$\delta^{13}C$ crustal reservoir may provide a means for explaining why $\delta^{13}C$ has remained heavy through time.

In contrast, the low $^{36}Ar/^{38}Ar$ from martian meteorite gas probably requires loss over geologic time. If the escape modeling is correct, minor gases like N, Ne, and Ar were totally removed following atmospheric collapse near 4 Ga and then replaced by later outgassing of the martian interior. It is expected that de-

gassed $^{36}Ar/^{38}Ar$ was initially chondritic/solar and then that ratio became sub-chondritic as ^{36}Ar was preferentially lost [6]. The enriched ^{15}N signature of the atmosphere is also attributed to this process.

Summary: Given the broad agreement between C, H, and O isotopic ratios in the modern atmosphere and the ALH 84001 meteorite, it is possible that these reservoirs were established after early atmospheric loss prior to 4 Ga. The preservation of these signals over this long period of history can be explained in several slightly different ways: 1) C, O, and H have remained static in the atmosphere and have not exchanged with the surface over the past 4 Ga; 2) C, O, and H in the atmosphere have potentially varied widely over history but have been continually buffered by larger reservoirs in the crust which have remained unchanged over the past 4 Ga. This second possiblility allows for potentially large variations in atmospheric pressure to occur as CO_2 is recycled back into the atmosphere from crustal reservoirs or degassed from the mantle.

Future Work: A planned SAM experiment that concentrates minor atmospheric constitutents may allow the measurement of the isotopic compositions of N_2, ^{38}Ar, Kr and Xe. Measurement of those isotopes that are most easily influenced by spallation and n-capture would allow determination of the influence of impact vaporization processes on the martian atmosphere. In particular, the abundances of ^{80}Kr, ^{82}Kr, ^{124}Xe, and ^{126}Xe should be especially sensitive to cosmogenic production in the martian crust.

References: 1. McElroy M.B., et al. (1976) *Science*, *194*, 1295-1298. 2. Nier A.O., et al. (1976) *Science*, *194*, 68-70. 3. Bogard D.D. and Johnson P. (1983) *Science*, *221*, 651-654. 4. Pepin R.O. (1985) *Nature*, *317*, 473-475. 5. Krasnopolsky V.A., et al. (1998) *Science*, *280*, 1576-1580. 6. McElroy M.B., et al. (1976) *Science*, *194*, 70-72. 7. Garrison D.H. and Bogard D.D. (1998) *Meteoritics & Planetary Science*, *33*, 721-736. 8. Garrison D. and Bogard D. (2000) *Meteoritics and Planetary Science Supplement*, *35*, 58. 9. Pepin R.O. (1994) *Icarus*, *111*, 289-304. 10. Krasnopolsky V.A., et al. (2007) *Icarus*, *192*, 396-403. 11. Niles P.B., et al. (2010) *Science*, *329*, 1334-1337. 12. Carr R.H., et al. (1985) *Nature*, *314*, 248-250. 13. Leshin L., et al. (2013) *LPSC*. 14. Webster C.R. et al. (2013) *LPSC*. 15. Franz H., et al. (2013) *LPSC*. 16. Lammer H., et al. (2012) *Space Science Reviews*, 1-42. 17. Leshin L.A., et al. (1996) *Geochimica et Cosmochimica Acta*, *60*, 2635-2650. 18. Greenwood J.P., et al. (2008) *Geophysical Research Letters*, *35*, 05203. 19. Romanek C.S., et al. (1994) *Nature*, *372*, 655-657. 20. Jakosky B.M. and Jones J.H. (1994) *Nature*, *370*, 328-329. 21. Bibring J.P., et al. (2006) *Science*, *312*, 400-404. 22. Phillips R.J., et al. (2011) *Science*. 23. Bandfield J.L., et al. (2003) *Science*, *301*, 1084-1087. 24. Clayton R.N. and Mayeda T.K. (1988) *Geochimica et Cosmochimica Acta*, *52*, 925-927. 25. Jull A.J.T., et al. (1997) *Journal of Geophysical Research-Planets*, *102*, 1663-1669. 26. Wright I.P., et al. (1992) *Geochimica Et Cosmochimica Acta*, *56*, 817-826.