

**ATMOSPHERIC HISTORY AND SURFACE REDOX PROCESSES INFERRED FROM MSL AND MAVEN ISOTOPE RATIOS.** P. R. Mahaffy<sup>1</sup>, H. B. Franz<sup>1</sup>, C. R. Webster<sup>2</sup>, C. Malespin<sup>1</sup>, S. K. Atreya<sup>3</sup>, S. P. Schwenzer<sup>4</sup>, J. C. Stern<sup>1</sup>, A. A. Pavlov<sup>1</sup>, P. E. Martin<sup>5</sup>, K. A. Farley<sup>5</sup>, R. Navarro-Gonzalez<sup>6</sup>, M. Benna<sup>1</sup>, and M. Slipski<sup>6</sup>, <sup>1</sup>Goddard Space Flight Center, Greenbelt, MD 20771 paul.r.mahaffy@nasa.gov, <sup>2</sup>Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA 91109, <sup>3</sup>University of Michigan, Ann Arbor, MI 48109, <sup>4</sup>Open University, Milton Keynes MK6 3AQ, UK, <sup>5</sup>California Institute of Technology, Pasadena, CA 91125. <sup>6</sup>Universidad Nacional Autonoma de Mexico, Mexico City 04510, Mexico, <sup>6</sup>University of Colorado, Boulder, CO 80309.

**Introduction:** Atmospheric loss and atmosphere/surface exchange processes put their emphatic stamp over billions of years on martian isotope ratios in light elements and noble gases. Several of these ratios together with their seasonal variation can be measured in the well mixed atmosphere at the surface or in the diffusively separated upper atmosphere. Likewise, isotope ratios of these elements present on early Mars and their transformation by secondary processes, for example redox processes in a wet environment can be preserved in ancient rocks. Mass spectrometers on the Mars Science Laboratory (MSL) and Mars Atmosphere and Volatile Evolution (MAVEN) missions and the Tunable Laser Spectrometer (TLS) on the MSL mission have greatly improved our knowledge from what was known from the Viking GCMS and from the study of martian meteorites.

Here we will provide an overview of these measurements, to date, and their implications for atmospheric evolution and aqueous surface processes. The quadrupole mass spectrometer (QMS) on MSL and the Neutral Gas and Ion Mass Spectrometer (NGIMS) on MAVEN are similar in design and performance. Both the MSL and MAVEN missions are ongoing so the final chapters for this science may still be written.

**D/H in Water:** Deuterium to hydrogen measurements provide the basis for models of loss of water from Mars over time. Recent observations from the Trace Gas Orbiter [1] have secured vertical profiles of D/H in water from the boundary layer up to 80 km complementing previous telescopic observations [2] and surface atmospheric measurements from SAM [3]. These measurements secured average values of 5-7 x Vienna standard mean ocean water (SMOW) values but with substantial vertical, spatial, and seasonal variations. D/H measured in Hesperian era Gale crater smectite clays [4] gave much lower values of ~3 x VSMOW thus further constraining water loss prior to the time of Gale crater aqueous activity.

**Argon isotopes:** <sup>36</sup>Ar released in SAM ovens from drilled rocks can provide one of several chronometers for cosmic radiation surface exposure duration [5], <sup>40</sup>Ar the K/Ar formation age of that rock[5,6], while the ratio of <sup>40</sup>Ar to the primordial <sup>36</sup>Ar and <sup>38</sup>Ar [7]

provides information on surface volatile release into the atmosphere. However, it is the <sup>36</sup>Ar/<sup>38</sup>Ar ratio that is of greatest relevance for understanding the rate of escape to space by pickup-ion sputtering mechanisms. A precise measurement of this ratio was done from the surface of Mars with SAM, giving <sup>36</sup>Ar/<sup>38</sup>Ar=4.2±0.1 [8]. MAVEN NGIMS measurements used the surface ratio of N<sub>2</sub>/<sup>40</sup>Ar from the QMS and these ratios in the upper atmosphere from NGIMS to derive both the homopause and exobase altitudes for each of many orbits [9]. Considering the fractionation of <sup>36</sup>Ar/<sup>38</sup>Ar between these two altitudes and using the above SAM <sup>36</sup>Ar/<sup>38</sup>Ar ratio for the lower atmosphere, allows an estimate of the loss to space of 66% of the argon by sputtering. The argon loss rate can be used as constraint on the determination of the loss of CO<sub>2</sub> atmosphere, which is estimated to be at least 0.5-1 bar or more over 4 billion years [9].

**$\delta^{13}\text{C}$ ,  $\delta^{18}\text{O}$  and  $\delta^{17}\text{O}$  in CO<sub>2</sub>, and  $\delta^{18}\text{O}$  in H<sub>2</sub>O:** Mechanisms such as dissociative recombination account for losses to space in addition to the argon derived pickup-ion sputtering. Early in the MSL mission these were determined by both the TLS and the QMS on MSL. Atmospheric values of  $\delta^{13}\text{C}$  in CO<sub>2</sub>,  $\delta^{18}\text{O}$  and  $\delta^{17}\text{O}$  in CO<sub>2</sub>, were substantially fractionated at 46±4, 48±5 and 24±5 per mil (‰) respectively [3] as was  $\delta^{18}\text{O}$  in H<sub>2</sub>O at 84±10 ‰. While some carbonates have been identified from orbital spectroscopic and SAM ground-based observations no massive carbonate deposits have been identified, to date. It seems likely that atmospheric loss to space over time is the dominant factor leading to the present enrichment of the heavy C and O isotopes in the bulk atmosphere.

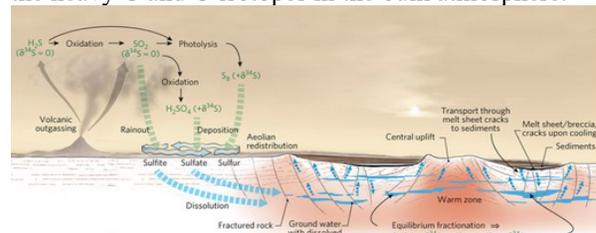


Figure 1. Proposed mechanisms including reduction-oxidation cycles and atmospheric processing for the wide variation in sulfur isotopes sampled from Gale crater sediments (Figure from [10]).

**Sulfur isotopes:** Large variations in  $\delta^{34}\text{S}$  were measured [10] in ten sediment samples delivered to the SAM instrument as the rover traversed 13 km and up 100 meter in elevation in Gale crater moving toward and up the central mound. The wider range of fractionation compared to the variation seen in Mars meteorites [11] suggested that there was a component of atmospherically processed sulfur in these samples and that additional variation was driven by repeated reduction-oxidation processing in an impact driven hydrothermal system as illustrated in Figure 1.

**Chlorine Isotopes:** Decomposition of perchlorates produces both oxygen and hydrochloric acid. This EGA signal has been found in most but not all of the solid samples analyzed by SAM. Similar to the behavior of the sulfur isotopes, seven samples analyzed by the SAM QMS showed wide variability in  $\delta^{37}\text{Cl}$  [12] with values ranging from  $-1\pm 25\%$  to  $-51\pm 5\%$ . Mechanisms suggested for the large variation in these ratios included atmospheric transformation of volcanically produced oxychlorine compounds or alternately variable degrees of reduction of perchlorate to chloride.

**Nitrogen Isotopes:** The  $\delta^{15}\text{N}$  measured by SAM [13] is higher than the fractionation observed in C and O but lower than that in H. Use of a flight calibration cell on SAM [14] enabled a correction to a previously reported  $\text{N}_2/\text{Ar}$  ratio that brought these results into agreement with linear trends in the  $^{40}\text{Ar}/^{14}\text{N}$  vs.  $\delta^{15}\text{N}$  observed in data from gas trapped in Zagami, EETA79001, and Tissint Mars meteorites (Figure 2). Work to identify the  $\delta^{15}\text{N}$  of NO produced from decomposition of nitrates is ongoing. Like measurements of D/H this data could provide another ancient reference point for the effect of atmospheric loss on isotopic compositions.

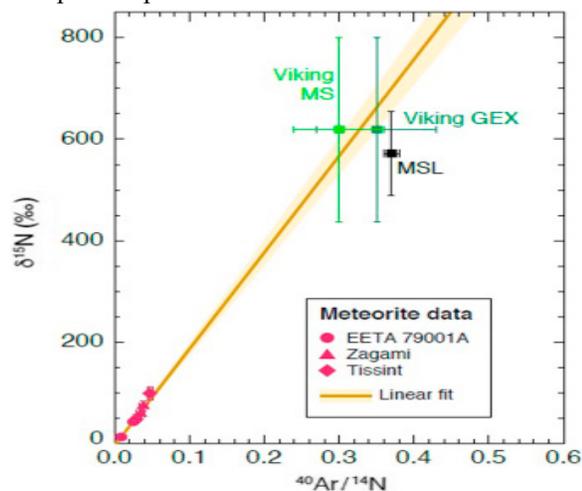


Figure 2. SAM and Viking nitrogen isotope data compared with mixing lines from gases trapped in martian meteorites (Figure from [14]).

**Heavy Noble Gases:** The low mixing ratios of krypton and xenon in the atmosphere makes their detection challenging. An enrichment protocol was developed and implemented for SAM that utilized multiple stages of carbon dioxide scrubbing combined with static mass spectrometry to enhance the signals from these atmospheric gases in the mass spectrometer. The in situ measurements remove ambiguity in meteorite measurements caused by mixing of trapped atmospheric gas and mantle Kr and Xe.  $^{80}\text{Kr}$  and  $^{82}\text{Kr}$  appear to have contributions from neutron capture on Br and enhancements of  $^{124}\text{Xe}$  and  $^{126}\text{Xe}$  suggest a contribution of spallation and neutron capture products degassed to the atmosphere to increase these isotopic abundances [15]. The data from one of these runs and the contrast with data from EETA79001 and Zagami meteorites is shown in Figure 3.

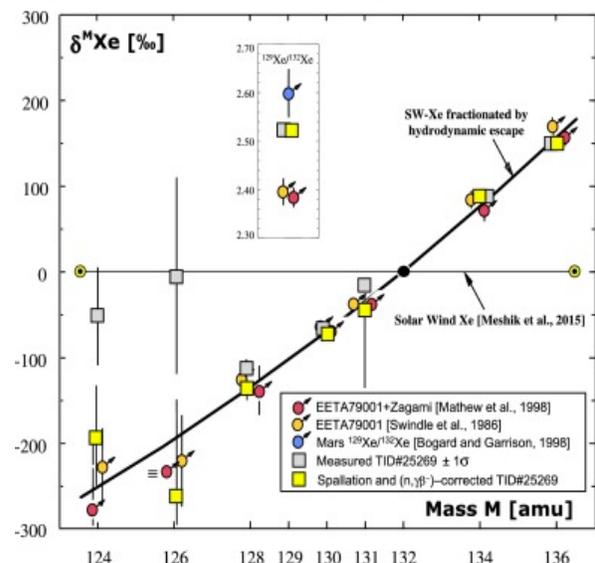


Figure 3. Xenon isotope measurements from one of the SAM noble gas atmospheric runs is shown and compared with meteorite data (Figure from [15]).

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