**Seasonal variation of atmospheric mixing ratios on Mars measured by the MSL SAM instrument** M. G. Trainer[1], H. B. Franz[1,9], P. R. Mahaffy[1], M. H. Wong[2,3], S. K. Atreya[2], C. P. McKay[4], P. G. Conrad[1], C. A. Malespin[1,10], A. E. Brunner[1,11], R. O. Pepin[5], R. H. Becker[5], T. C. Owen[6], H. L. K. Manning[7], R. Navarro-González[8], Robert M. Haberle[4], and the MSL Science Team. [1]NASA Goddard Space Flight Center, Greenbelt, MD 20771 (melissa.trainer@nasa.gov), [2]University of Michigan, Ann Arbor, MI 48109, [3]University of California, Berkeley, CA 94720, [4]NASA Ames Research Center, Moffett Field, CA 94035, [5]University of Minnesota, Minneapolis, MN 55455, [6]University of Hawaii, Honolulu, HI 96822, [7]Concordia College, Moorhead, MN 56562, [8]Universidad Nacional Autónoma de México, México, D.F. 04510, Mexico, [9]University of Maryland Baltimore County, Baltimore, MD 21228, [10]Universities Space Research Association, Houston, TX 77058, [11]CRESST, University of Maryland, College Park, MD 20740.

**Introduction:** The Sample Analysis at Mars (SAM) instrument on Curiosity measures the chemical and isotopic composition of atmospheric volatiles in the vicinity of the rover through a dedicated atmospheric inlet [1]. The SAM quadrupole mass spectrometer (QMS) is able to conduct a survey of the atmosphere to identify and quantify atmospheric species and isotope ratios; alternatively enrichment measurements are utilized to remove major and reactive species ($CO_2$, $O_2$, $H_2O$, etc.) to allow for high precision measurements of trace species such as noble gases. When combined with composition and isotope data from gases trapped in martian meteorites, other lander and orbital missions, and meteorological measurements conducted by the Mars Science Laboratory (MSL) rover environmental monitoring station (REMS) [2], the SAM atmosphere measurements inform our understanding of current atmospheric cycling and climate evolution over recent and geological time.

Here we discuss the SAM QMS measurements of the major atmospheric species over the course of the mission through southern summer. An additional measurement during southern fall will be presented to represent a nearly full seasonal cycle on Mars. We will focus primarily on the ratio of $CO_2$/Ar, which shows a distinct trend with season as a result of $CO_2$ transported to and from the poles, coinciding with changes in local atmospheric pressure. This is the first comprehensive measurement of composition bridging several seasons that can link the pressure variation to changes in specific atmospheric mixing ratios.

**SAM Atmospheric Measurement Details:** The direct atmospheric experiments took place over a period of almost two years from Mars Years (MY) and solar longitude ($L_s$) of MY31, $L_s$ 163 - MY32, $L_s$ 40 (31 August 2012 to 24 October 2013, Fig. 1) in Gale crater south of the equator (4.5°S, 137°E). Most measurements were taken at night, with two runs that sampled daytime air to search for diurnal variations.

During a typical atmospheric experiment, a sample is ingested into a pre-evacuated manifold, preconditioned to 50 °C. Background QMS measurements are taken of the evacuated instrument and manifold prior to introduction of the atmospheric sample. A valve to the sample inlet tube is then opened briefly (~30 seconds) to introduce atmospheric gas to a portion of the manifold. A small fraction of this gas is leaked into the QMS in a dynamic sampling mode (i.e., as the instrument is pumped by one of the turbomolecular pumps).

Enrichment experiments have been run in dynamic and semi-static modes [1]. In either case the atmospheric sample in the SAM manifold is exposed to chemical scrubbers to remove $H_2O$, $CO_2$ and other chemically active gases. The process of ingestion of an atmospheric sample, followed by scrubbing, is repeated multiple times, gradually enriching the sample in noble/inert gases.

Volume mixing ratios were derived from application of empirical calibration constants describing relative instrument response to the five most abundant atmospheric species, $CO_2$, Ar, $N_2$, $O_2$, and CO [3].

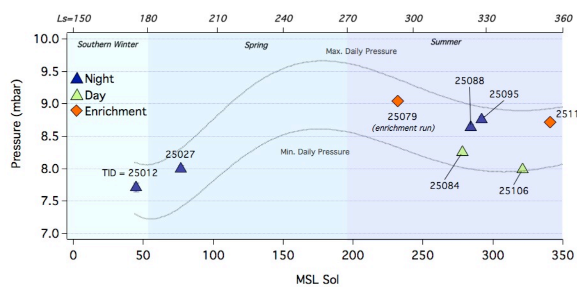


**Figure 1.** SAM Atmospheric QMS experiments are plotted with the atmospheric pressure measurement taken by REMS at or near time of ingestion (left axis) as a function of MSL mission sol (bottom axis) and solar longitude (top axis). The experiments are identified by their test identification number ("TID") and type (nighttime, daytime, and enrichment run). The background is shaded by southern season, and the REMS daily pressure maximum and minimum values are given by the dotted lines. Seasonal trends are tracked through the direct atmospheric runs, with attention paid to possible diurnal variations. Enrichment runs, performed at night, provide sensitive atmospheric noble gas measurements and insight on long-term temporal trends, but do not inform seasonal mixing ratio data as the major components of the atmosphere were scrubbed.

**Results:** *Initial Mixing Ratio Measurements.* The composition of the Mars atmosphere was measured following landing in Gale Crater during the first 105 sols, during the transition from southern winter into spring ($L_s$ 163 and 211, respectively) [4]. The mixing ratios of the major species are listed in Table 1.

**Table 1.** Mixing ratios of major species from first 105 sols of the landed mission [4].

| Gas | Volume mixing ratio |
|---|---|
| $CO_2$ | 0.960 (± 0.007) |
| Ar | 0.0193 (± 0.0003) |
| $N_2$ | 0.0189 (± 0.0003) |
| $O_2$ | $1.45 (\pm 0.09) \times 10^{-3}$ |
| CO | $<1.0 \times 10^{-3}$ |

Continued atmospheric sampling has allowed for tracking of changes in mixing ratios with season and atmospheric pressure, including the CO mixing ratio. These will be reported through $L_s$ 449, which represents the beginning of fall in Gale crater.

The QMS also determines the isotopic composition of $CO_2$ as a complement to measurements by SAM's tunable laser spectrometer [1], but these results will be discussed elsewhere [5].

*Variation in $CO_2$ mixing ratio.* The SAM QMS mixing ratio measurements have observed a variation in the $CO_2/^{40}Ar$ ratio, tracking with the atmospheric pressure cycle (Fig. 2). This trend is almost certainly a result of changes in the atmospheric $CO_2$ abundance due to the annual cycle of condensation and sublimation at the polar caps of this principal component of the martian atmosphere.

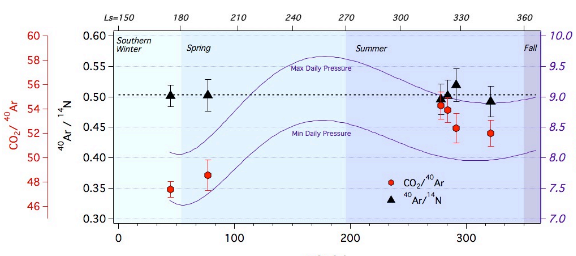


**Figure 2.** The atmospheric $CO_2/^{40}Ar$ ratio (left red axis) as a function of MSL mission sol (bottom) and solar longitude (top). These data overlay the daily pressure measurements (purple lines, right axis) and southern seasons (shading). Seasonal trends in this ratio appear to track pressure changes. In contrast, the ratio of Ar to $N_2$, two inert, non-condensable species, does not change seasonally.

The MSL observations of seasonal $CO_2/^{40}Ar$ trend can be compared to previous measurements of $^{40}Ar$ as monitored globally from orbit [6] and in situ in southern low-latitudes [7]. In the case of both the Odyssey gamma-ray spectrometer (GRS) and the Mars Exploration Rovers (MER) alpha particle x-ray spectrometers (APXS), the variation in Ar mixing ratio is detected as a proportion of the total pressure and the change in $CO_2$ is inferred. Furthermore, the APXS measurements indicate that there is a 2- to 3-month lag in the $Ar/CO_2$ as compared to total pressure (Fig. 3). The ODY/GRS and MER/APXS data on $^{40}Ar$ seasonal change and phase lag in the equatorial region are controversial [8], however – the latter show seasonal change, while the former don't but have relatively large uncertainty.

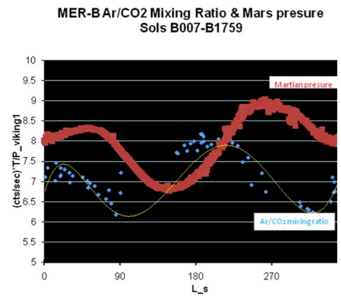


**Figure 3.** The $Ar/CO_2$ as measured by the MER APXS and surface pressure as measured by Viking, from Economou et al. (2010) [7].

The SAM measurements allow for the confirmation that it is the $CO_2$ abundance driving the seasonal change. We will explore this with our dataset to the extent possible given the sampling frequency.

*$^{40}Ar/^{14}N$.* The $^{40}Ar/^{14}N$ ratio is also shown in Fig. 2, and does not display seasonal trends to date. The reported ratio of ~0.5 is significantly greater than that measured by the Viking Landers (VL), which were reported as Ar/N = 0.3 from the VL2 mass spectrometer [9] and Ar/N = 0.34 from the gas chromatograph experiments [10]. The SAM calibration and data analysis procedures used to derive this ratio from the mass spectra have thus far been shown to be robust [3]. We will discuss possible explanations for the discrepancy between the SAM and MSL values, as well as the implications for deviations from the meteorite mixing line when the MSL $^{15}N/^{14}N$ measurements are taken into account, as reported by Wong et al. [11].

Isotopic composition of Ar ($^{40}Ar/^{36}Ar = 1900 \pm 300$ and $^{36}Ar/^{38}Ar = 4.2 \pm 0.1$) have been reported previously and will be discussed in the context of understanding the evolution of Ar/N over time [1,12]. In addition to the primordial Ar isotopes, atmospheric enrichment experiments have allowed for the measurement of the heavy noble gas Kr, and the Ar/Kr ratios also shed light on this issue [13].

**References:** [1] Mahaffy P. R. et al. (2012) *Space Sci. Res., 170,* 401-478. [2] Gómez-Elvira J. et al. (2012) *Space Sci. Res., 170,* 583-640. [3] Franz H. B. et al. (2013) *Planet. & Space Sci.,* in review. [4] Mahaffy P. R. et al. (2013) *Science, 341,* 263. [5] Franz, H. B. et al. (2014) *LPSC 2014 abs.*; Webster C. R. et al., (2014) *LPSC 2014 abs*.; Niles P. B. et al., (2014) *LPSC 2014 abs.* [6] Sprague A. L. et al. (2004) *Science, 306,* 1364-1367. [7] Economou R. T. et al. (2010) *45th LPSC*, #2179. [8] Atreya S. K. et al. (2013) *LPI Contributions 1719*, 2130. [9] Owen T. et al. (1977) *JGR 82*, 4635-4639. [10] Oyama V. I. and Berdahl B. J. (1977) *JGR 82*, 4669-4676. [11] Wong M. H. et al. (2013) *GRL,* DOI: 10.1002/2013GL057840. [12] Atreya S. K. et al. (2013) *GRL, 40,* 5605-5609. [13] Conrad, P. G. et al. (2014) *LPSC 2014 abs.*