



Abundance and Isotopic Composition of Gases in the Martian Atmosphere from the Curiosity Rover

Paul R. Mahaffy *et al.*
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Table 2. Water isotope ratios ‰ ± 2 SEM. *, not measured.

Measurement	δD	$\delta^{18}O$
SAM-TLS atmosphere	4950 ± 1,080	*
SAM-TLS evolved water: Rocknest fines 230° to 430°C (23)	5880 ± 60	84 ± 10
Meteoritic crustal reservoirs (26)	~5000	*
Earth telescopes (24)	1700–8900	*
ALH 84001 (17)	3000	*
Shergotty USNM 321-1 (17)	4600	*

$\delta^{18}O$ values (32). These values are similar to the composition of the modern martian atmosphere, suggesting that the $\delta^{13}C$, δD , and $\delta^{18}O$ of the martian atmosphere were enriched early and have not changed much over ~4 billion years. Our higher values of δD and $\delta^{18}O$ measured in the atmosphere suggest that escape processes may have also continued since 4.0 Ga, in accordance with a two-stage evolutionary process (17) described above.

We observe large enrichments of $\delta^{18}O$ in atmospheric water vapor and CO_2 . The $\delta^{18}O$ values of the water vapor are much larger than the $\delta^{18}O$ observed in carbonates and sulfates in martian meteorites and suggest that the oxygen in water vapor in the martian atmosphere is not in equilibrium with the crust (33, 34) and could have been enriched in heavy isotopes through atmospheric loss. Another possibility is that the elevated oxygen isotope values in the more abundant martian CO_2 are being transferred to the water vapor through photochemical reactions in the atmosphere. However, $\delta^{18}O$ values of CO_2 in Earth's atmosphere are similarly elevated because of low-temperature equilibration between CO_2 and H_2O , and this process could also be operative on Mars (12).

In addition to atmospheric loss, other processes such as volcanic degassing and weathering might act to change the isotopic composition of the atmosphere through time. Estimates for the magnitude of these two contributions over the ~4-billion-year history of Mars vary widely (30, 34, 35), yet could have a strong impact on the isotopic composition of the atmosphere and challenge the status quo model described above.

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Supplementary Materials

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Materials and Methods
Supplementary Text
Figs. S1 to S3
Tables S1 to S4
Reference (37)
MSL Science Team Authors and Affiliations
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Abundance and Isotopic Composition of Gases in the Martian Atmosphere from the Curiosity Rover

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Volume mixing and isotope ratios secured with repeated atmospheric measurements taken with the Sample Analysis at Mars instrument suite on the Curiosity rover are: carbon dioxide (CO_2), 0.960(±0.007); argon-40 (^{40}Ar), 0.0193(±0.0001); nitrogen (N_2), 0.0189(±0.0003); oxygen, 1.45(±0.09) × 10⁻³; carbon monoxide, < 1.0 × 10⁻³; and $^{40}Ar/^{36}Ar$, 1.9(±0.3) × 10³. The $^{40}Ar/N_2$ ratio is 1.7 times greater and the $^{40}Ar/^{36}Ar$ ratio 1.6 times lower than values reported by the Viking Lander mass spectrometer in 1976, whereas other values are generally consistent with Viking and remote sensing observations. The $^{40}Ar/^{36}Ar$ ratio is consistent with martian meteoritic values, which provides additional strong support for a martian origin of these rocks. The isotopic signature $\delta^{13}C$ from CO_2 of ~45 per mil is independently measured with two instruments. This heavy isotope enrichment in carbon supports the hypothesis of substantial atmospheric loss.

The science and exploration goal of the Mars Science Laboratory (MSL) (1) is to advance our understanding of the potential of the present or past martian environments to support life. An understanding of how the present environment in Gale crater differs from the environment at the time of its forma-

tion requires comprehensive chemical characterization. The first set of experiments of the Sample Analysis at Mars (SAM) investigation (2) (Fig. 1) of the Curiosity rover included measurements of the chemical and isotopic composition of the atmosphere with sequences that employed two of SAM's three instruments. When

combined with composition and isotope data from atmospheric gases trapped in martian meteorites, measurements of the rate of atmospheric escape from orbiting spacecraft, and studies of atmosphere-surface exchange, SAM atmosphere measurements are intended to constrain models of atmospheric loss and climate evolution over geological time.

We report here on results from samples of the martian atmosphere analyzed by SAM's quadrupole mass spectrometer (QMS) and tunable laser spectrometer (TLS) during the first 105 sols (1 sol is a martian day) of the landed mission. These experiments were among the first carried out by SAM (Fig. 1) after several health checks of the instrument. The experiments took place over a period of several weeks from Mars solar longitude (3) of 163.7 to 211.2 (31 August to 21 November 2012) in Gale crater south of the equator (4.5°S, 137°E). All measurements were taken at night (table S1), and weighted means (table S2) are reported.

The mixing ratios of CO₂, N₂, Ar, O₂, CO, Ne, Kr, and Xe at the martian surface were determined by the mass spectrometers on the 1976 Viking Landers (4) more than 3 decades ago. Mass spectrometers on the Viking aeroshells also detected CO₂, N₂, Ar, CO, O₂, O, and NO (5) over an altitude range from 200 to 120 km, approaching or reaching the homopause or the altitude below which the atmosphere is well mixed. Spectroscopic measurements of CO have also been obtained from the Mars Reconnaissance Orbiter [e.g., (6)], the Mars Express Spacecraft (7, 8), and a number of ground-based observations [e.g., (9)], revealing long-term variations correlated with solar activity (9). Recent Herschel submillimeter observations (10) have provided an additional measurement of the mixing ratios for CO (10) of $9.8(\pm 1.5) \times 10^{-4}$ and for O₂ (11) of $1.40(\pm 0.12) \times 10^{-3}$. The CO mixing ratio is found to vary by more than a factor of 4 (from $\sim 3 \times 10^{-4}$ to 1.2×10^{-3}) seasonally at polar latitudes, with smaller changes in the equatorial region (6). The relative change in CO reflects enrichment and depletion of noncondensable volatiles during the condensation and sublimation of CO₂, the principal component of the martian atmosphere.

Argon (⁴⁰Ar) has also been monitored globally from orbit by the gamma-ray spectrometer (GRS) on the Mars Odyssey spacecraft and from the martian surface by the alpha particle x-ray spectrometers (APXS) on the Mars Exploration

rovers at latitudes of -2° and -15°. The GRS-derived Ar mixing ratio exhibits a large seasonal change by as much as a factor of 6 over the southern pole in winter (12) as the atmospheric CO₂ undergoes an annual cycle of condensation and sublimation, producing a 25% change in the surface pressure. Although the GRS data exhibit no seasonal change in Ar in the equatorial region (12), APXS finds that Ar nearly tracks the seasonal changes in surface pressure with a 2- to 3-month phase lag (13).

The mixing ratio of nitrogen can best be determined by in situ measurements because meteorite measurements do not give definitive answers for this atmospheric gas. Variations in isotopic composition of nitrogen in impact glasses of the martian shergottite meteorites EET79001 (14, 15), Zagami (16), and Tissint [e.g., (16, 17)] suggest that, in these samples, atmospheric nitrogen is mixed with an interior component with a lower ¹⁵N/¹⁴N ratio.

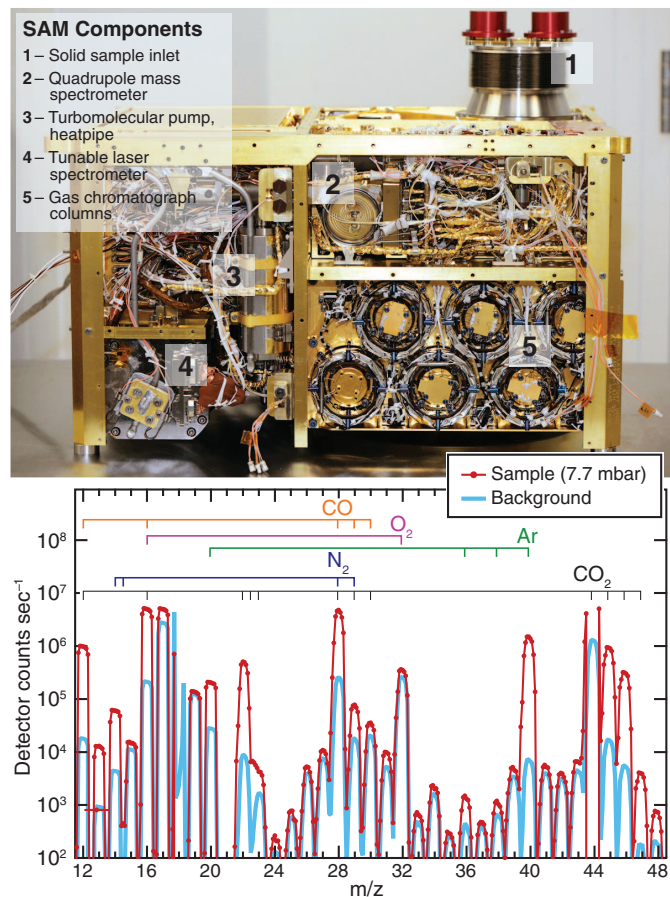
The atmospheric CO₂ isotope $\delta^{13}\text{C}_{\text{VPDB}}$ (VPDB, Vienna Pee Dee belemnite) (18) has been reported as -2.5 ± 4.3 per mil (‰) from the Thermal and Evolved Gas Analyzer (TEGA) mass spectrometer on the Phoenix lander (19) and as -22 ± 20 ‰ from Fourier transform Earth-based spectroscopy (20). The higher-uncertainty measurements of the Viking lander found CO₂ isotopes to be within 50% of terrestrial isotopes (4). The aeroshell measurements had similarly

large error bars with reported carbon isotopic composition equivalent to $\delta^{13}\text{C}_{\text{VPDB}}$ of $23 \pm 50\%$ (5).

Detailed characterization of the SNC (Shergotty, Nakhla, and Chassigny) meteorites (14, 16, 21–24) has revealed a combination of volatile abundances and isotope systematics (14, 15, 21, 25–27) for noble gases, N₂, and CO₂ that is possible only with origin on Mars or a very Mars-like parent body (28). Although the Viking abundance and isotope measurements provided evidence supporting the hypothesis that the SNCs are from Mars, the meteorites contain volatiles from other sources [for example, magmatic or possible cometary delivery (29)], in addition to trapped atmospheric gases that cause some variations among the meteorite values and differences between meteorite and Viking measurements. In addition to the uncertainties introduced by multiple sources of volatiles in the SNC meteorites, the solubility of the volatiles and their partitioning in glass and in the constituent mineral phases affects both the abundance value and the isotopic signature, including those of the noble gases (30, 31). The SAM data are therefore key to constraining the atmospheric component of data obtainable from meteorites with in situ observations.

Many previous composition measurements analyzed only a single or a small number of species. The SAM instrument suite, with the use of

Fig. 1. The SAM suite located in the interior of the Curiosity rover uses three instruments to test either atmospheric gas or solid samples. (Top) An image of SAM with the side panels removed. **(Bottom)** Mass spectrum of the martian atmosphere from sol 45, with mass peaks labeled for the main atmospheric species. Isotopes of argon appear above the background level (blue traces) at mass/charge ratio (*m/z*) 36, 38, and 40 (green ticks at top of plot). Primary ions from isotopologues of CO₂, containing ¹³C, ¹⁷C, and/or ¹⁸O, appear at *m/z* 45, 46, and 47 (black ticks at top of plot).



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Table 1. Volume mixing ratio measurements from Curiosity during the first 105 sols of the landed mission.

Gas	Volume mixing ratio (QMS)
CO ₂	0.960(±0.007)
Ar	0.0193(±0.0003)
N ₂	0.0189(±0.0003)
O ₂	1.45(±0.09) × 10 ⁻³
CO	<1.0 × 10 ⁻³

both the TLS and QMS, is able to make multiple, high-precision composition measurements over the course of the mission. In addition, SAM's QMS and TLS provide fully independent analyses of carbon isotopes. Repeat runs reported here were carried out at nearly the same time in the early evening on Mars to validate results. Each measurement set of the type implemented to date (32) represents a comprehensive analysis of the main constituents of the martian atmosphere.

SAM confirms the identity of the four most abundant gases in the martian atmosphere, with CO₂ being by far the major constituent. The SAM results for O₂ (Tables 1 and 2) are consistent with the recent Herschel (11) observations. SAM secures an upper limit for the CO mixing ratio (Tables 1 and 2) that is consistent with the Herschel data and the mean of all remote sensing spectroscopic measurements (~9 × 10⁻⁴). Differences in CO mixing ratios are expected and are related to the abovementioned seasonal effects, as dynamics and mixing rather than chemistry are expected to dominate the behavior of CO in the homosphere due to the 3-year photochemical lifetime of CO. In addition to seasonal effects, localized, heterogeneous surface effects may also affect SAM measurements of CO because of possible adsorption of CO onto the surface during cold martian nights—when SAM data were collected—and reevaporation during warmer daytime. The Herschel observations, on the other hand, are weighted to higher in the atmosphere. Unlike CO, seasonal variation in O₂ has not yet been observed.

The most notable differences between the SAM measurements and previous data are in the relative abundances of Ar and N₂ and in the isotopic compositions of Ar and CO₂. The Ar/N₂ ratio and the N isotopes provide important constraints to models for assessing the relative contributions of internal and atmospheric sources to gas inclusions in shock-produced glassy martian meteorites. The isotope data are important for constraining models of atmospheric evolution. Whereas Viking found nitrogen and argon to be the second and third most abundant atmospheric gases at 2.7 and 1.6% by volume, respectively, SAM determines nearly equal volume mixing ratios for these constituents. Ar is found to be 21% greater, whereas N₂ is 30% lower than the Viking values. The resulting Ar/N₂ ratio of 1.02

Table 2. Isotopic composition measurements from Curiosity during the first 105 sols of the landed mission. N/A, not applicable.

Isotopes	Isotopic composition (QMS)	Isotopic composition (TLS)
⁴⁰ Ar/ ³⁶ Ar	1.9(±0.3) × 10 ³	N/A
δ ¹³ C _{VDPB}	45(±12) ‰*	46(±4) ‰†
δ ¹⁸ O _{VDPB}	N/A	48(±5) ‰

*δ¹³C_{VDPB} is derived from *m/z* 12 and 13. †δ¹³C_{VDPB}, as derived from *m/z* 45 and 46, is described in the supplementary materials.

measured by SAM is ~1.7 times greater than the value reported from Viking measurement (4). Both Ar and N₂ are noncondensable and practically inert gases on Mars, so their relative abundances are not expected to change considerably with time. We suspect that the difference from Viking results is due to different instrumental characteristics rather than some unknown atmospheric process, although seasonal variation in N₂ is yet to be tracked. The use on Mars of a turbomolecular pumping system (33), as well as repeated SAM analyses are expected to produce a more accurate determination of the ratio of these gases than the previous Viking in situ measurements whose mass spectrometers employed small ion pumps.

The SAM QMS offers independent validation of the δ¹³C_{VDPB} value in CO₂ measured by the TLS (34). The average of three SAM QMS atmosphere measurements gives δ¹³C_{VDPB} value of 45 ± 12 ‰, which is fully consistent with the independently measured TLS value of 46 ± 4 ‰ (34). This observed ~5% enrichment in the heavier carbon isotope in the martian atmosphere compares well with previous measurements of ¹³C-enriched carbon of atmospheric origin in martian meteorite EETA79001 (22, 35). The data support the hypothesis that significant carbon has been lost from the martian atmosphere over time by sputtering (36).

The ⁴⁰Ar/³⁶Ar ratio of 1900 ± 300 measured by SAM is within error of the trapped atmosphere measured (15) to be 2050 ± 170 in quenched shock-produced melts in martian meteorite EETA79001 (27, 37, 38) but is considerably smaller than the value of 3000 ± 500 reported by Viking (4). Laboratory studies of shock implantation into silicate liquid have demonstrated that this process is a nearly quantitative recorder of atmospheric composition (39, 40), and the implanted gases in meteorite shock-produced melts compared with the Viking in situ measurements of the atmosphere have been used as the best evidence to tie these meteorites to Mars (14, 15, 21, 41). However, noble gases released from shock-produced glasses in EETA79001 contained at least three components (27): (i) martian air, (ii) terrestrial contamination, and (iii) a martian interior component with low ⁴⁰Ar/³⁶Ar.

Even with the somewhat lower value measured by SAM, the ⁴⁰Ar/³⁶Ar of the martian atmosphere is highly elevated relative to the terrestrial ratio of 296. The enrichment in the

radiogenic ⁴⁰Ar over nonradiogenic ³⁶Ar has been interpreted as evidence for significant loss of the primordial martian atmosphere early in the planet's history, followed by partial degassing of Ar. Subsequent loss to space is expected to lead to enrichment of the ⁴⁰Ar over ³⁶Ar (42, 43) by the same processes that have reduced the ³⁶Ar/³⁸Ar ratio in the martian atmosphere. The latter ratio as inferred from EETA79001 glasses (15, 38) was found to be ~4, much different from the terrestrial, chondritic, solar, and jovian (44) values which range in order from 5.3 to ~5.5. It is notable that the ⁴⁰Ar/³⁶Ar ratio has not changed appreciably since the ejection of EETA79001 from the planet ~700,000 years ago. This provides a constraint on the extent of very recent inputs of gas to the atmosphere from volcanic or cometary sources. The carbon dioxide isotope data support the hypothesis that a significant amount of carbon has escaped from the martian atmosphere over time, resulting in preferential loss of the lighter isotope of carbon and the observed enrichment in ¹³C (45). This implies that atmospheric escape has dominated over exchange with unfractionated surface reservoirs that exist in the crust or mantle.

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Supplementary Materials

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Materials and Methods

Tables S1 and S2

References (46, 47)

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This PDF file includes:

Materials and Methods
Tables S1 and S2
Full Reference List
MSL Science Team Author List

Supplementary Materials:

Materials and Methods

The Sample Analysis at Mars (SAM) suite on the Mars Science Laboratory “Curiosity” rover consists of three instruments supported by a gas separation and processing subsystem and a solid sample manipulation system. Results presented here were obtained with the quadrupole mass spectrometer (QMS) and the tunable laser spectrometer (TLS). The third SAM instrument, a 6-column gas chromatograph (GC) system, was not used in these atmospheric experiments. Separate miniaturized turbomolecular pumps (compression ratio $\sim 5 \times 10^8$) evacuate the QMS and the TLS and gas manifold prior to martian atmosphere ingestion through heated inlets.

Although the first two atmospheric experiments on Mars utilized both the TLS and the QMS, the two instruments were operated separately in the seven subsequent experiments (2 QMS-only and 5 TLS-only) to allow longer integration times for each instrument. The atmospheric samples were acquired between 6:06 pm and 4:41 am local mean solar time. Temperature and pressure conditions recorded during each ingestion by the Rover Environmental Monitoring Station, or REMS (46), are reported in Table S1.

The atmospheric samples were ingested into a pre-evacuated manifold. For QMS measurements, the gas manifold was preconditioned to 50°C during evacuation, prior to introduction of Mars atmosphere. Background measurements were taken with the QMS open to the evacuated manifold. A valve to the sample inlet tube was subsequently opened for ~ 30 seconds to introduce atmospheric gas to a portion of the manifold. A small fraction of this gas was leaked into the QMS in a dynamic sampling mode as it was pumped by one of the turbomolecular pumps.

The QMS employs hyperbolic rods, redundant 70-eV electron beam energy ion sources, and redundant pulse counting Channeltron detectors. Mass resolution enables half unit m/z values to be clearly separated from the unit mass values in the high frequency portion (1.5-19.5 Da) of the spectrum. QMS data were acquired in both a fractional scan mode with 0.1-Da step size and a unit scan mode with 1.0-Da step size. Results reported in this contribution were obtained through processing of data acquired in fractional scan mode, which entails integration of peak areas at a given $m/z \pm 0.4$. Volume mixing ratios were derived from application of empirical calibration constants describing relative instrument response to the five most abundant atmospheric species, CO₂, Ar, N₂, O₂, and CO.

Data from the two QMS-only experiments, from which average composition was computed, are provided in Table S2. The first of these experiments, TID 25012, utilized a single atmospheric analysis segment, while the second experiment, TID 25027, included two analysis segments. The table gives values of volume mixing ratios as well as carbon and argon isotope ratios determined from the individual experiments. Carbon isotope ratios ($\delta^{13}\text{C}$) were computed in two ways: directly from the ratio of m/z 13 to m/z 12 and from the signal at m/z 45 and 46, after accounting for contributions from oxygen at these m/z values. For the latter method, the oxygen isotopic composition ($\delta^{18}\text{O}$) determined by the TLS was applied, assuming $\Delta^{17}\text{O}$ of 0.32 (47). Argon ratios were computed with both a constant background and a trending background to explore how the difference in these methods affects calculations with the low-abundance m/z 36. Uncertainties include contributions from statistical noise, detector corrections, background subtraction, and accuracy of the calibration constants as determined during pre-launch testing. Uncertainties in the oxygen isotopic composition contributed to the reported uncertainties for

$\delta^{13}\text{C}$ obtained from m/z 45 and 46. Variations in composition retrieved by repeated analyses of a commercially-produced calibration gas tank, prepared with specifications to match the martian atmospheric composition as reported by Viking, represent the dominant source of uncertainty in volume mixing ratio calculations. This is especially true for the constituents present at lowest abundance, O_2 and CO . The instrument background is dominated by atmospheric gases that backstream through the turbomolecular pump and by residual instrument water. The apparent drop in background signal at m/z 18 in Fig. 1 and the lack of atmospheric signal there, reflects saturation of the QMS detector by the high H_2O background.

For the TLS isotope measurements, gas introduced to the manifold at 7 mbar was expanded into the TLS in a series of steps to reach a pressure of ~ 0.74 mbar in the Herriott cell to avoid saturation on the strongest infrared absorption lines. The TLS utilizes spherical mirrors set 20 cm apart. For CO_2 measurements 43 passes in the TLS Herriott cell are utilized with a NIR tunable diode laser at $2.78 \mu\text{m}$ to measure both carbon and oxygen isotopes. Typical experiments include collection of 2-minute averaged spectra over a total duration of ~ 30 minutes, during which the laser scans once per second. Individual spectral lines that have been normalized to the laser power and zero light pulse are integrated over the line shape and quantified via calibration results.

Supplementary Tables

Table S1

SAM atmospheric ingestion events and REMS environmental conditions. Where REMS measurements are not available at the exact times of atmospheric ingestions, interpolated values are reported based on measurements nearby in time.

ID	Sol	Valve	Ingest start LMST	Ingest Duration (hh:mm:ss)	Target	REMS Ground Temp (C)		REMS Air Temp (C)		REMS P (mbar)	
25008	18	28	21:13	01:18:29	QMS, TLS	-	-	-	-	-	-
	19	10	22:56	00:02:22	TLS	-	-	-	-	-	-
25009	27	10	23:03	00:00:45	TLS	-72	± 5	-62	± 3	7.58	± 0.05
	28	28	01:34	00:29:10	QMS	-79	± 5	-69	± 3	7.66	± 0.07
	28	28	02:29	00:01:01	TLS	-81	± 5	-70	± 3	7.69	± 0.05
	28	28	02:31	00:01:01	TLS	-81	± 5	-70	± 3	7.69	± 0.05
	28	28	02:33	00:01:01	TLS	-81	± 5	-70	± 3	7.69	± 0.05
	28	28	02:35	00:01:01	TLS	-81	± 5	-70	± 3	7.69	± 0.05
	28	10	04:36	00:04:26	TLS (not used)	-83	± 5	-74	± 3	7.70	± 0.06
25012	45	28	22:43	00:00:31	QMS	-72	± 5	-59	± 3	7.71	± 0.07
25014	52	10	20:37	00:01:07	TLS	-62	± 7	-52	± 5	7.59	± 0.07
	52	28	21:51	00:00:31	TLS	-64	± 5	-52	± 3	7.70	± 0.05
	52	28	21:53	00:00:32	TLS	-64	± 5	-51	± 3	7.70	± 0.05
	53	10	00:20	00:20:03	TLS (not used)	-74	± 5	-62	± 3	7.79	± 0.06
25026	73	28	20:44	00:00:31	TLS	-64	± 5	-50	± 3	7.86	± 0.05
	73	28	20:46	00:00:32	TLS	-64	± 5	-49	± 3	7.86	± 0.05

	73	10	23:18	00:20:02	TLS (not used)	-76	± 7	-62	± 6	8.04	± 0.06
25027	77	28	21:08	00:00:31	QMS	-66	± 5	-54	± 3	7.93	± 0.05
	77	28	22:42	00:00:31	QMS	-73	± 5	-56	± 3	8.06	± 0.05
25028	79	28	20:25	00:00:31	TLS	-60	± 5	-50	± 3	7.89	± 0.05
	79	28	20:26	00:00:32	TLS	-60	± 5	-48	± 3	7.89	± 0.05
	79	10	23:00	00:20:02	TLS (not used)	-74	± 5	-62	± 4	8.09	± 0.06
25029	81	28	18:06	00:00:31	TLS	-44	± 4	-38	± 3	7.71	± 0.05
	81	28	18:08	00:00:31	TLS	-44	± 4	-36	± 3	7.72	± 0.05
	81	10	21:18	00:20:02	TLS (not used)	-68	± 6	-55	± 6	8.03	± 0.08

Table S2

Chemical and isotopic composition of the martian atmosphere as measured by the SAM QMS.

	TID 25012 (Sol 45)	TID 25027: Segment 1 (Sol 77)	TID 25027: Segment 2 (Sol 77)	Weighted mean*
Volume mixing ratio:				
CO ₂	0.959 ± 0.015	0.960 ± 0.016	0.960 ± 0.017	0.960 ± 0.009
Ar	0.0196 ± 0.0002	0.0192 ± 0.0002	0.0192 ± 0.0002	0.0193 ± 0.0001
N ₂	0.0193 ± 0.0006	0.0188 ± 0.0006	0.0186 ± 0.0006	0.0189 ± 0.0003
O ₂	1.40(±0.15)×10⁻³	1.45(±0.15)×10⁻³	1.52(±0.15)×10⁻³	1.45(±0.09)×10⁻³
CO ^{**}	8.81(±4.58)×10⁻⁴	7.94(±4.14)×10⁻⁴	5.81(±3.05)×10⁻⁴	7.06(±2.16)×10⁻⁴
δ ¹³ C from m/z 12 & 13	58.3 ± 5.3	35.3 ± 2.9	52.4 ± 3.7	44.5 ± 2.1
δ ¹³ C from m/z 45 & 46 [†]	40.3 ± 2.5	40.2 ± 3.3	40.4 ± 3.2	40.3 ± 1.6
⁴⁰ Ar/ ³⁶ Ar:				
Constant background;	1904 ± 42	1972 ± 45	1771 ± 49	1889 ± 26
Trending background	1726 ± 22	1904 ± 21	1705 ± 38	1803 ± 14

*Uncertainties on the weighted mean are given in the table. Uncertainties cited in the text are the greater of the root-sum-squared of the uncertainties of individual measurements or the standard deviation of individual measurements included in the mean.

**The calibration constant for calculation of CO abundances has been modified from that derived during pre-launch calibration due to an apparent small reduction in instrument background at m/z 12. After subtracting the $m/z = 12$ contribution from CO_2 based on the measured CO_2^{++} signal at m/z 22, the residual is attributed to CO. The calibration constant was adjusted by assuming that the shift in measured signal at m/z 12 since pre-flight testing is due solely to a reduction in instrument background and not from a difference in relative abundances of CO_2 and CO on Mars compared to our calibration gas tank. Since application of the pre-flight calibration constant to Mars data predicts zero CO abundance, values obtained with the modified calibration constant are reported only as an upper limit in Table 1. The on-board calibration cell, which has not yet been used on Mars, contains CO_2 but no CO and is designed to secure the relative contribution from CO_2 at m/z 22 and 12.

†For calculation of $\delta^{13}\text{C}$ from m/z 45 & 46, the oxygen isotopic composition was assumed as the $\delta^{18}\text{O}$ measured by the TLS for atmospheric CO_2 , with $\Delta^{17}\text{O} = 0.32$.

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