



Supplementary Materials for

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

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Published 19 July 2013, *Science* **341**, 263 (2013)

DOI: 10.1126/science.1237966

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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
δ¹³C from m/z 12 & 13	58.3 ± 5.3	35.3 ± 2.9	52.4 ± 3.7	44.5 ± 2.1
δ¹³C from m/z 45 & 46[†]	40.3 ± 2.5	40.2 ± 3.3	40.4 ± 3.2	40.3 ± 1.6
⁴⁰Ar/³⁶Ar:				
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 CO₂ based on the measured CO₂⁺⁺ 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 CO₂ 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 CO₂ but no CO and is designed to secure the relative contribution from CO₂ 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 CO₂, with $\Delta^{17}\text{O} = 0.32$.

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