

REVISED $^{40}\text{Ar}/^{14}\text{N}$ FOR THE MARTIAN ATMOSPHERE BASED ON SAM CALIBRATION GAS CELL RESULTS. H. B. Franz¹, M. G. Trainer¹, C. A. Malespin^{1,2}, P. R. Mahaffy¹, S. K. Atreya³, M. Benna^{1,4}, P. G. Conrad¹, J. L. Eigenbrode¹, C. Freissinet^{1,4}, H. L. K. Manning⁵, B. D. Prats⁶, E. Raaen¹, and M. H. Wong³. ¹NASA Goddard Space Flight Center, Greenbelt, MD 20771, Heather.B.Franz@nasa.gov, ²Universities Space Research Association, Houston, TX 77058, ³University of Michigan, Ann Arbor, MI 48109, ⁴University of Maryland, Baltimore, MD 21228, ⁵Concordia College, Moorhead, MN 56562, ⁶SGT, Inc., Greenbelt, MD 20770

Introduction: To facilitate measurements of the chemical and isotopic composition of the martian atmosphere, the Sample Analysis at Mars (SAM) instrument suite on the Mars Science Laboratory (MSL) “Curiosity” rover carries a calibration gas cell to provide a mechanism for linking observations acquired on Mars with “ground truth” data acquired before launch [1-2]. The first two experiments (“CG1” and “CG2”) utilizing the calibration cell were performed in July and December 2015 on MSL sols 1042 and 1204. Here we describe results of volume mixing ratios (VMR) determined by the SAM quadrupole mass spectrometer (QMS) for these experiments and discuss implications for the $^{40}\text{Ar}/^{14}\text{N}$ of the martian atmosphere as measured by SAM.

Pre-flight Calibration: Calibration constants necessary for SAM quantitative analyses on Mars were generated from data acquired prior to launch. To enable atmospheric measurements, a gas mixture comprising CO_2 , N_2 , Ar and O_2 in proportions of ~25% each was prepared at NASA Goddard Space Flight Center (GSFC). This “EQ mix” tank and a commercially prepared “Mars mix” tank with contents approximating the martian atmospheric composition as determined by Viking [3] were used to establish empirical calibration constants required to calculate volume mixing ratios (VMR) of the top five atmospheric gases: CO_2 , N_2 , Ar, O_2 , and CO [2,4]. These gas mixes were also used for calibration of CO_2 isotopic analyses. Ground truth for CO_2 isotopes was provided through independent measurements with commercial mass spectrometers at NASA GSFC [2]. A noble gas mix containing ~10% each Ne, Ar, Kr and Xe in balance of He was used to determine mass fractionation corrections for Kr and Xe isotope ratios [5].

Calibration Gas Cell: The SAM calibration cell contains approximately equimolar proportions of CO_2 , N_2 , Ar, and Xe enriched in the ^{129}Xe isotope, with trace amounts of four fluorinated hydrocarbons (F-HCs) to ensure detection of organic compounds by the GC (Table 1). The calibration cell was exercised several times during pre-flight testing, allowing derivation of corrections for isobaric interferences at masses corresponding to Xe isotopes due to the F-HCs [6].

Experimental Methods: At the start of each cal-

ibration cell experiment, the gas manifold and transfer lines were heated and evacuated, and background measurements were obtained. Calibration gas was then introduced into the manifold through a 0.02-second “squirt,” producing an initial pressure of ~6 mb. A portion of the manifold was evacuated by the SAM turbopump, followed by a volume expansion that reduced the calibration gas pressure in the manifold to ~3 mb before beginning QMS measurements. Successive volume expansions allowed QMS analyses at multiple pressures. Calibration gas was leaked from the manifold into the ion source of the QMS through a capillary tube. The QMS scanned continually through a pre-selected set of m/z values relevant to the compounds present in the calibration cell [2,4].

Table 1. Calibration gas cell contents [1]

Compound*	Molecular weight	100 °C MR
CO_2	44	24.32%
N_2	28	24.10%
Ar	40	24.04%
Xe_T	131	8.48%
^{129}Xe	129	15.51%
PFTBA	671	3.00%
1-FN	146.161	0.54%
DFBP	190.189	0.016%
PFBP	334.112	0.0078%

* Xe_T = Xenon of near-terrestrial isotopic composition;

PFTBA = perfluorotributylamine;

1-FN = 1-Fluoronaphthalene;

DFBP = 2,2'-Difluoro-1,1'-biphenyl;

PFBP = Perfluorobiphenyl.

Data Reduction: QMS data acquired during the calibration cell experiments were processed by first applying corrections to account for detector dead time, pressure and background effects, as discussed at length in [2,4]. For initial data reduction, a nominal background model assuming constant relative proportions of background gas and calibration gas was applied. VMR and isotope ratios were then computed from integrated fractional scan peak areas at each $m/z \pm 0.4$, averaged over multiple scans. VMR were determined from marker fragments at m/z 22, 14, 40 and 132 for CO_2 , N_2 , Ar, and Xe, respectively. CO_2 iso-

tope ratios were calculated from m/z 22, 45 and 46, while Xe isotope ratios were calculated from m/z 124, 126, 128-132, 134 and 136 after correction for interferences by F-HCs.

Volume mixing ratios obtained during initial reduction of data from both CG1 and CG2 suggested introduction of additional atmospheric gas to the manifold during volume expansions, which complicated efforts to model the instrument background, particularly at the lowest calibration gas pressures. This behavior was evident in VMR calculations showing the presence of excess CO_2 as well as in CO_2 isotope ratios. Values of $\delta^{13}\text{C}$ computed from QMS data matched the known composition of the calibration gas at the highest pressure in each experiment, but drifted to heavier compositions at lower pressures, consistent with addition of isotopically enriched atmospheric CO_2 [7-8] during the volume expansions.

To eliminate contributions from excess background gas not properly removed during initial data reduction, revised background proportions were computed by targeting the signal at marker m/z for CO_2 , N_2 and Ar to the corresponding pressure-normalized signal obtained during ground calibration. The background signal for Xe was determined as that required to achieve the expected Xe VMR for the calibration cell after subtraction of F-HCs. The resulting VMR for CO_2 , N_2 , and Ar were then evaluated. Comparison to the known calibration cell composition indicated that adjustments were needed to the calibration constants for computing CO_2 and N_2 . The most significant change involved an adjustment to the N_2 constant to address gradual elimination of a contaminant in the QMS ion source region that affected measurements of both CO and N_2 VMR, with marker fragments at m/z 12 and 14, respectively [2,4]. Both CO_2 and N_2 constants were also adjusted slightly to correct for a minor air leak suspected to have occurred during analysis of the EQ mix tank during ground calibration [6].

Results: The impact of the modified calibration constants on measurements of martian atmospheric composition was assessed by application to data from SAM experiments performed during Curiosity's first Mars year of operations. As expected, the largest change in VMR was seen for N_2 , with revised weighted average of ~ 2.6 vol%, compared to earlier reports of ~ 2.0 wt% for SAM's first two atmospheric measurements [1,4]. Earlier results also indicated a difference between the ratio of atmospheric $^{40}\text{Ar}/^{14}\text{N}$ as determined by SAM (~ 0.5) [1,5] and Viking ($\sim 0.3 - 0.35$) [3,9]. Although initial investigation into this difference considered the possibility that the same ion source contaminant that had been determined to affect

the CO calibration constant may have also affected the N_2 constant [2,4], data from the calibration cell experiments were needed to verify this hypothesis [6]. The revised SAM average value of ~ 0.38 for the first Mars year is in closer agreement with that determined by Viking.

It is also of interest to compare results for SAM $\delta^{15}\text{N}$ vs. $^{40}\text{Ar}/^{14}\text{N}$ with those obtained by Viking as well as those observed in atmospheric gas released through thermal processing of meteorite shock melt gases, as shown in Fig. 1. The figure shows a linear trend in composition of gas trapped in glasses from the Zagami [10], EET 79001 [11-12], and Tissint [13] meteorites. The coincidence of this trend with results obtained by Viking and SAM suggests that it represents a mixing line between indigenous crustal gas and martian atmospheric gas [12]. While a temporal trend toward enrichment in martian atmospheric ^{15}N is well-modeled by escape processes [13], no known mechanism can produce variability in atmospheric $^{40}\text{Ar}/^{14}\text{N}$, particularly at the time interval of Viking and SAM measurements. Future SAM experiments designed to measure $\delta^{15}\text{N}$ in NO released from nitrates in solid samples may help constrain the evolution of $\delta^{15}\text{N}$ and the $^{40}\text{Ar}/^{14}\text{N}$ ratio over time.

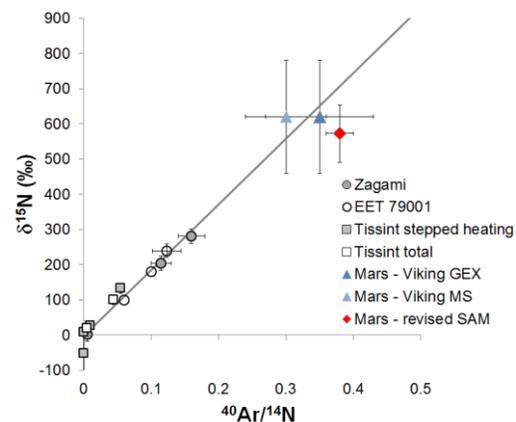


Fig 1. $\delta^{15}\text{N}$ vs. $^{40}\text{Ar}/^{14}\text{N}$ data for meteorites, Viking and SAM [6]

References: [1] Mahaffy et al. (2012) *SSR* 170. [2] Franz et al. (2014) *PSS* 96. [3] Owen et al. (1977) *JGR* 82. [4] Franz et al. (2015) *PSS* 109-110. [5] Conrad et al. (2016) *EPSL* 454. [6] Franz et al, *PSS*, in review. [7] Webster et al. (2013) *Science* 341. [8] Mahaffy et al. (2013) *Science* 341. [9] Oyama and Berdahl (1977) *JGR* 82. [10] Marti et al. (1995) *Science* 267. [11] Becker and Pepin (1984) *EPSL* 69 [12] Wiens et al. (1986) *EPSL* 77 [13] Wong et al. (2013) *GRL* 40.