

THE ISOTOPIC COMPOSITION OF MARTIAN ATMOSPHERIC CO₂: MEASUREMENTS WITH THE SAMPLE ANALYSIS AT MARS (SAM) QUADRUPOLE MASS SPECTROMETER. H. B. Franz^{1,2}, P. R. Mahaffy¹, S. K. Atreya³, R. Navarro-González⁴, J. C. Stern¹, M. G. Trainer¹, M. H. Wong³, and the MSL Science Team. ¹NASA Goddard Space Flight Center, Code 699, Greenbelt, MD 20771, Heather.B.Franz@nasa.gov, ²University of Maryland Baltimore County, Baltimore, MD 21228, ³University of Michigan, Ann Arbor, MI 48109, ⁴Universidad Nacional Autónoma de México, México, D.F. 04510, Mexico.

Introduction: Since the Mars Science Laboratory (MSL) “Curiosity” rover landed at Gale Crater in August 2012, the Sample Analysis at Mars (SAM) instrument suite has periodically sampled the martian atmosphere to determine its chemical and isotopic composition. Initial results have revealed enrichment in heavy isotopes of all major atmospheric species [1-4], consistent with previous analyses suggesting that selective loss of light isotopes from the martian atmosphere has occurred due to escape processes [5-7].

Isotope ratios are measured by SAM with the quadrupole mass spectrometer (QMS) and the tunable laser spectrometer (TLS) [8-9]. The TLS is designed to perform *in situ* measurements of the abundances and isotope ratios of carbon, oxygen, and hydrogen in CH₄, CO₂, and H₂O at unprecedented precision. Isotope ratios of other compounds must be determined with the QMS, which can scan continuously over *m/z* values of 1.5 to 535.5. Carbon isotope ratios may also be determined from QMS atmospheric data to complement the high-precision measurements performed with the TLS. Here we discuss results for measurements of $\delta^{13}\text{C}$ from martian atmospheric CO₂ using the SAM QMS.

Experimental Methods: The data described here were obtained via SAM’s direct atmospheric experiment mode, in which martian atmospheric gas is introduced directly into the manifold of SAM’s gas processing system for sampling by the QMS and/or the TLS. The procedure is described in detail in [10]. Briefly, prior to measuring martian atmospheric gas, the gas manifold and transfer lines are heated and evacuated, and background measurements are obtained. Martian atmospheric gas is then introduced directly into the manifold and leaked into the ion source of the QMS through a capillary tube. The QMS scans continually across *m/z* values from 1.5 to 149.9 for a specified duration and mass step size.

The QMS employs different three scanning modes through control of the quadrupole rod voltages, as described in [10]. Isotope ratios for atmospheric experiments are computed either from integrated fractional scan peak areas at each *m/z* ± 0.4 or from the ratio of count rates at integer *m/z* values, averaged over multiple scans.

Data Reduction: Data corrections are applied before computation of isotope ratios to account for detec-

tor dead time and background effects, as discussed at length in [10]. The carbon isotopic composition of CO₂ may be computed directly from the ratio of signals at *m/z* 12 and 13, although the presence of hydrocarbons at those *m/z* may cause interferences with CO₂ measurements. Interferences at *m/z* 12 and 13 have been more problematic in atmospheric experiments performed since SAM began analyzing solid samples, which introduced products of derivatization reagent *N*-methyl-*N*-(*tert*-butyldimethylsilyl)-trifluoro-acetamide (MTBSTFA) into the gas manifold [11]. Because the major molecular ion of CO₂ at *m/z* 44 saturates the detector under nominal direct atmospheric experiment conditions, $\delta^{13}\text{C}$ has to date been nominally computed from SAM QMS data from the signal at *m/z* 45 and 46, applying corrections based on an assumed oxygen isotopic composition [12]. This has been done because the signal at *m/z* 22, representing CO₂⁺⁺ ions, displays pressure-related instrument effects at pressures encountered during SAM atmospheric experiments.

For the analyses reported here, extensive calibration work was performed to derive a correction for the pressure-related effects at *m/z* 22, so that it can be used to derive $\delta^{18}\text{O}$ from CO₂. This effort involved experiments performed on the SAM breadboard instrument at NASA Goddard Space Flight Center [12]. All analyses of CO₂ isotopic composition on Mars include an assumed $\Delta^{17}\text{O}$ of 0.32‰, the average value for martian silicates [13]. Uncertainties for individual experiments include propagation of statistical errors through the normalization process, while the uncertainties given for the weighted mean values include additional sources of systematic error. Additional calibration for instrument effects, including changes observed in flight compared to pre-flight calibration, was also incorporated into isotope ratio calculations [14].

Carbon Isotope Ratios: During Curiosity’s first full martian year, SAM analyzed Mars’ atmosphere with the QMS nine times. Initial analyses by the TLS yielded average $\delta^{13}\text{C}$ of $46 \pm 4\%$ and $\delta^{18}\text{O}$ of $48 \pm 5\%$ [1]. Similar values for $\delta^{13}\text{C}$ were obtained with the QMS, as reported in [2]. To evaluate possible changes in $\delta^{13}\text{C}$ over time, we have computed $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ from for all SAM QMS direct atmospheric experiments performed to date.

Our results are consistent with enrichments in

heavy isotopes of other elements in the martian atmosphere, including hydrogen, nitrogen, argon, and other noble gases, and support models invoking large-scale atmospheric loss processes on Mars [1-7]. Results of our analyses reveal variations in both $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ that suggest a seasonal trend in the isotopic composition of atmospheric CO_2 . We will examine this finding particularly in the context of isotopic fractionation expected during CO_2 condensation and sublimation cycles [15] and discuss implications for the martian atmosphere.

References: [1] Webster et al. (2013) *Science* 341. [2] Mahaffy et al. (2013) *Science* 341. [3] Atreya et al. (2013) *Geophys. Res. Lett.* 40. [4] Wong et al. (2013) *Geophys. Res. Lett.*, in press. [5] Biemann et al. (1976) *Science* 194. [6] Nier et al. (1976) *Science* 194. [7] Owen et al. (1977) *J. Geophys. Res.* 82. [8] Mahaffy (2008) *Space Sci. Rev.* 135. [9] Mahaffy et al. (2012) *Space Sci. Rev.* 170. [10] Franz et al., *Planet. Space Sci.*, in review. [11] Glavin et al. (2013) *J. Geophys. Res.* 118. [12] Franz et al., *Planet. Space Sci.*, submitted. [13] Franchi et al. (1999) *Met. Planet. Sci.* 34. [14] Franz et al., in prep. [15] Eiler et al. (2000) *Geochim. Cosmochim. Acta* 64.