THE ISOTOPIC COMPOSITION OF MARTIAN ATMOSPHERIC CO2: MEASUREMENTS WITH THE SAMPLE ANALYSIS AT MARS (SAM) QUADRUPOLE MASS SPECTROMETER. H. B. Franz1,2, P. R. Mahaffy1, M. H. Wong3, J. C. Stern1, S. K. Atreya1, P. G. Conrad1, G. J. Flesch2, L. A. Leshin3, H. L. K. Manning3, C. P. McKay7, T. C. Owen4, M. G. Trainer4, C. R. Webster4, and the MSL Science Team. 1NASA Goddard Space Flight Center, Code 699, Greenbelt, MD 20771, 2Heather.B.Franz@nasa.gov, 3University of Maryland Baltimore County, Baltimore, MD 21228, 4University of Michigan, Ann Arbor, MI 48109, 5Jet Propulsion Laboratory, Pasadena, CA 91009, 6Renssalaer Polytechnic Institute, Troy, NY 12180, 7Concordia College, Moorhead, MN 56562, 8NASA Ames Research Center, Moffett Field, CA 94035, 9University of Hawaii, Honolulu, HI 96822.

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 δ13C 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 detector 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, δ13C is 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]. The analyses reported here were performed with an oxygen isotopic composition determined from TLS measurements [1], while δ17O was assumed to 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. Pre-flight calibration, involving QMS analysis of CO2 for which δ13C and δ18O were determined independently at high-precision with a ThermoFinnigan MAT-253 mass spectrometer, indicated no significant instrument bias for measurements at m/z 45 and 46 that would require additional correction [12].

Carbon Isotope Ratios: During Curiosity’s first 100 sols, SAM analyzed Mars’ atmosphere with the QMS three times. Initial analyses by the TLS yielded average δ13C of 46 ± 4‰ and δ18O of 48 ± 5‰ [1]. Similar values for δ13C were obtained with the QMS, as reported in [2]. To evaluate possible changes in δ13C over time, we have applied the average δ13C from m/z 45 and 46 for all SAM direct atmospheric experiments performed to date. Our results are consistent with enrichments in heavy isotopes of other elements in the martian atmos-
phere, including hydrogen, nitrogen, argon, and other noble gases, and support models invoking large-scale atmospheric loss processes on Mars [1-7]. The analysis described here reveals no seasonal trends in $\delta^{13}C$ within the QMS measurement precision, given the assumption of constant $\delta^{18}O$. Additional work to coordinate QMS and TLS observations and to evaluate the potential effects of changing $\delta^{18}O$ on QMS $\delta^{13}C$ calculations is ongoing.