

RECONCILING THE DIFFERENCES BETWEEN THE MEASUREMENTS OF CO₂ ISOTOPES BY THE PHOENIX AND MSL LANDERS. P. B. Niles¹, P. R. Mahaffy², S. Atreya³, A. A. Pavlov², M. Trainer², C. R. Webster⁴, M. Wong³, and the MSL Science Team. ¹Astromaterials Research and Exploration Science, NASA Johnson Space Center, Houston, TX 77058; (paul.b.niles@nasa.gov); ²NASA Goddard Space Flight Center, Greenbelt, MD; ³University of Michigan, Ann Arbor, MI; ⁴Jet Propulsion Laboratory, Pasadena, CA.

Introduction: Precise stable isotope measurements of the CO₂ in the martian atmosphere have the potential to provide important constraints for our understanding of the history of volatiles, the carbon cycle, current atmospheric processes, and the degree of water/rock interaction on Mars [1]. There have been several different measurements by landers and Earth based systems performed in recent years that have not been in agreement (Table 1).

In particular, measurements of the isotopic composition of martian atmospheric CO₂ by the Thermal and Evolved Gas Analyzer (TEGA) instrument on the Mars Phoenix Lander [2] and the Sample Analysis at Mars (SAM) instrument on the Mars Science Laboratory (MSL) [3] are in stark disagreement (Table 1). Since both of these instruments feature a mass spectrometer capable of measuring the isotopic composition of martian atmospheric CO₂, it is possible to make an apples to apples comparison to try to determine the causes of the disagreement. This work attempts to use measurements of mass 45 and mass 46 of martian atmospheric CO₂ by the SAM [4] and TEGA [5] instruments to search for agreement as a first step towards reaching a consensus measurement that might be supported by data from both instruments.

Analytical Methods: The data reduction methods were designed to obtain the best apples to apples comparison possible and therefore are different from previously published results (Table 1). For both data sets, measurements of mass 45 and 46 of Mars atmospheric CO₂ were calibrated to similar measurements of CO₂ in a calibration gas that was either analyzed on Earth or on the surface of Mars. The SAM data were compared to measurement of an equimolar calibration gas measured prior to launch containing equal parts CO₂, Ar, O₂ and N₂. The TEGA data were calibrated using measurements of a calibration gas measured on the surface of Mars which was a mixture of N₂ and CO₂.

Masses 45 and 46 correspond to CO₂ that is dominated by substitutions of ¹³C and ¹⁸O for masses 45 and 46 respectively. In Figure 1, the 45/46 ratios plot as

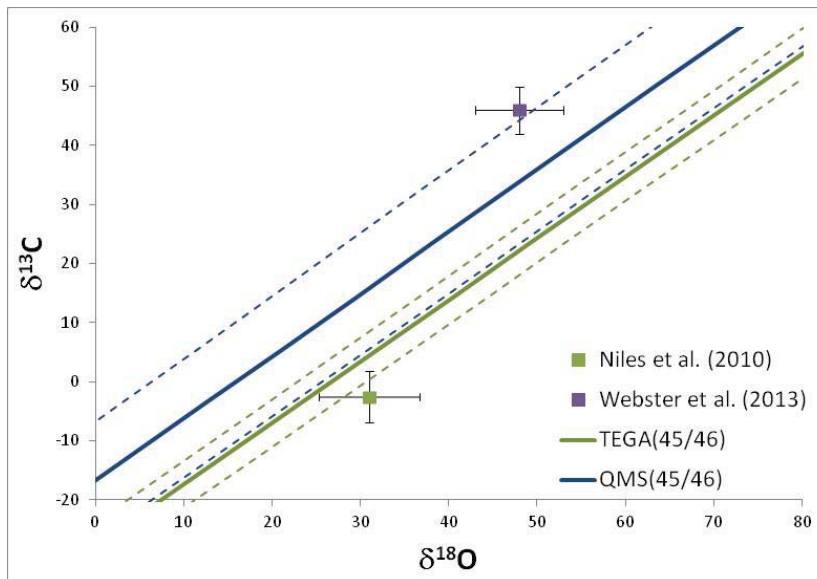


Figure 1. The solid green (TEGA) and blue (MSL QMS) diagonal lines show results from the 45/46 ratio analysis performed in this study. A 45/46 ratio plots as a diagonal line on a carbon-oxygen crossplot. The dotted lines indicate the range of uncertainties. The data points are from published studies cited in the legend.

diagonal lines and their range of uncertainties are displayed as dotted lines. This ratio can constrain the composition of the martian atmosphere, but does not provide an absolute measurement of $\delta^{13}\text{C}$ or $\delta^{18}\text{O}$ by itself. However, $\delta^{13}\text{C}$ can be calculated given a $\delta^{18}\text{O}$ value or vice versa.

Both the SAM and TEGA data used in this analysis are from the same sols as reported in Mahaffy et al. [4] and Niles et al. [5]. SAM quadrupole mass spectrometer (QMS) data were corrected for deadtime as described previously [4], while the TEGA data deadtime corrections for masses 45 and 46 were not significant due to low count rates. The data were also background corrected using a background level measured during each run. Uncertainties are calculated as 2-sigma standard error.

Results: The results are plotted in Figure 1 and listed in Table 1. The mass 45/46 ratios measured in this study by the TEGA instrument and SAM instrument agree within the calculated uncertainties after calibration (Table 1).

These results are different from previously reported values from Niles et al. [5] and Mahaffy et al.

[4] (Table 1). These differences are due to several factors. One important factor is the absolute carbon isotope ratio used in the calculations. This study and previous SAM results used a value of 0.0112372 which originally defined PDB [6]. The Niles et al. study used a value of 0.111797 which was based on more recent measurements of NBS-19 [7]. These values are about 5‰ different and partly explain why the Phoenix data do not plot on the 45/46 line in figure 1.

The correction factors derived from the calibration gas measurements to correct both the SAM data and TEGA data are also different in this study compared to previous studies [4, 5]. In particular, data from the sol 67 measurement of calibration gas by TEGA was left out of the data set because it showed anomalous ratios and count rates compared to the other 6 sols. Also measurement of an equimolar gas mix by the SAM QMS was used to calibrate the SAM 45/46 ratio measurement of the martian atmosphere using the same method used for the TEGA data in an attempt to make an apples to apples comparison which is slightly different than the method used by [4].

Discussion: The agreement within uncertainty between the two different measurements of 45/46 ratio in this study suggests that there may be a common basis from which to interpret the data returned by both instruments to achieve a result for the isotopic composition of martian CO₂. However, this potential agreement is not present when comparing the 45/46 results for TEGA and previous work by Mahaffy et al. [4] using techniques derived by the SAM team. Thus, there remains disagreement between the TEGA and SAM results that suggests that more work is needed to better understand all of the factors that contribute to the final result.

Based on the limited agreement in 45/46 ratios seen in this work, it is clear that the measurement of mass 44 by the TEGA instrument is the likely cause of the large disagreement in the $\delta^{13}\text{C}$ measurements, and this is probably due to the large deadtime correction needed for this data [5]. Even small uncertainties in

this deadtime correction may result in large changes to the isotopic measurements and it probable that the deadtime correction used in Niles et al. [5] was not the appropriate value; work to better constrain this value is ongoing. Decreasing the deadtime correction will cause the isotopic composition to move upward along the green diagonal line in Figure 1, suggesting that a TEGA measurement using a different deadtime correction will likely be higher in both $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$.

Another feature of the results of this study is that the TEGA measurement of the 45/46 ratio in the atmospheric CO₂ is not consistent with the isotopic value measured by the SAM TLS [3] (Figure 1), although the TLS value does agree with measurements from Mahaffy et al. [4] and is within the uncertainty envelope of the QMS 45/46 ratio reported in this study (Figure 1). This could suggest that the TEGA measurement has problems other than the deadtime. The SAM QMS results from this study have larger uncertainties, mostly due to calibration data that lacked the typical instrumental precision. An analysis of calibration gas on the surface of Mars by SAM could help bring this uncertainty downwards and further clarify this potential disagreement.

Conclusions: Results from this preliminary study suggest a potential basis for agreement between the TEGA and SAM datasets which may reconcile the apparent differences between the TEGA and SAM/TLS results. However, further work is needed to understand the differences between this work and previous studies.

References:

- [1] Jakosky B.M. and Phillips R.J. (2001) *Nature*, 412, 237-244. [2] Smith P.H., et al. (2008) *Journal of Geophysical Research-Planets*, 113. [3] Webster C.R., et al. (2013) *Science*, 341, 260-263. [4] Mahaffy P.R., et al. (2013) *Science*, 341, 263-266. [5] Niles P.B., et al. (2010) *Science*, 329, 1334-1337. [6] Craig H. (1957) *Geochimica Et Cosmochimica Acta*, 12, 133-149. [7] Chang T.L. and Wen-Jun L. (1990) *Chinese Science Bulletin*, 35.

Table 1. Reported isotopic compositions of the martian atmosphere from previous studies. Where $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values are listed, 45/46 ratios were calculated based on an absolute $^{13}\text{C}/^{12}\text{C}$ ratio of 0.0112372 and $^{18}\text{O}/^{16}\text{O}$ ratio of 0.0020052 for VPDB and VSMOW respectively. The ^{17}O correction used a ratio of 0.00038902. (*) The SAM QMS value reported by Mahaffy et al. [4] utilized a 45/46 measurement and the $\delta^{18}\text{O}$ reported by the TLS to calculate $\delta^{13}\text{C}$.

MEASUREMENT	45/46	UNCERTAINTY	$\delta^{13}\text{C}$ (VPDB) (‰)	+/- (‰)	$\delta^{18}\text{O}$ (VSMOW) (‰)	+/- (‰)	REFERENCE
SPECTROSCOPY	2.882	0.108	-22	20	18	18	KRASNOPOLSKY ET AL. (2007)
TEGA MS	2.899	0.028	-2.5	4.3	31.0	5.7	NILES ET AL. (2010)
SAM TLS	2.982	0.026	46	4	48	5	WEBSTER ET AL. (2013)
SAM QMS	2.967	0.005	40.6	1.6	48*	-	MAHAFFY ET AL. (2013)
THIS STUDY - SAM QMS	2.949	0.028	-	-	-	-	THIS STUDY
THIS STUDY - TEGA MS	2.918	0.011	-	-	-	-	THIS STUDY