# A FIRST LOOK AT CARBON AND OXYGEN STABLE ISOTOPE MEASUREMENTS OF MARTIAN ATMOSPHERIC CO₂ BY THE PHOENIX LANDER.

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*Introduction:* Precise stable isotope measurements of the $CO_2$ 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].

The isotopic composition of the martian atmosphere has been measured using a number of different methods (Table 1), however a precise value (<1%) has yet to be achieved. Given the elevated $\delta^{13}C$ values measured in carbonates in martian meteorites [2-4] it has been supposed that the martian atmosphere was enriched in $^{13}C$ [5]. This was supported by measurements of trapped $CO_2$ gas in EETA 79001[2] which showed elevated $\delta^{13}C$ values (Table 1). More recently, Earth-based spectroscopic measurements of the martian atmosphere have measured the martian $CO_2$ to be depleted in $^{13}C$ relative to $CO_2$ in the terrestrial atmosphere [6]. The spectroscopic measurements performed by Krasnopolsky et al. [6] were reported with ~2% uncertainties which are much smaller than the Viking measurements, but still remain very large in comparison to the magnitude of carbon and oxygen isotope fractionations under martian surface conditions.

The Thermal Evolved Gas Analyzer (TEGA) instrument on the Mars Phoenix Lander [7] included a magnetic sector mass spectrometer (EGA) [8] which had the goal of measuring the isotopic composition of martian atmospheric $CO_2$ to within 0.5%. The mass spectrometer is a miniature magnetic sector instrument intended to measure both the martian atmosphere as well as gases evolved from heating martian soils. Ions produced in the ion source are drawn out by a high voltage and focused by a magnetic field onto a set of collector slits. Four specific trajectories are selected to cover the mass ranges, 0.7 – 4, 7 – 35, 14 – 70, and 28 – 140 Da. Using four channels reduces the magnitude of the mass scan and provides simultaneous coverage of the mass ranges. Channel electron multiplier (CEM) detectors that operate in the pulse counting mode detect the ion beams.

*Analytical Methods:* The simple method used in nearly all isotope ratio mass spectrometry is to analyze an unknown gas against a known reference gas. In this case the atmospheric $CO_2$ is compared to $CO_2$ contained in a calibration gas that the instrument carried to Mars. Operational, instrumental, and scientific factors combined to create a situation where the best atmospheric analyses were separated by a large stretch of time from the calibration gas analyses. The best atmospheric analyses were obtained early in the mission on sols 9, 11, 12, and 16 while the best calibration gas data were obtained on sols 64, 66, 75, 76, and 77.

All of the analyses were performed using the "peak-hopping" feature of the flight software which allowed the instrument to hop in between individual masses of particular interest excluding the rest of the spectrum. This allowed for rapid scanning of the important mass peaks as each "peak-hopping" cycle was much shorter in duration than a full mass spectrum scan. This was useful for collecting larger amounts of counts on peaks of interest, increasing counting statistics.

A peak-hopping scan involves adjusting the ion accelerating voltage to hop from peak top to peak top. On a given peak, 5 or 7 measurements of counting rate are made while moving in very small steps over the top of the peak. These points are centered on the volt-

**Table 1.** Reported values for isotopic composition of martian atmospheric $CO_2$ including results from this study.

| Carbon | $^{13}C/^{12}C$ | uncertainty | $\delta^{13}C$ (VPDB) (‰) | uncertainty (‰) | Reference |
|---|---|---|---|---|---|
| SNC-Trapped Gas (EETA79001) | 0.0116 | 0.0001 | 36 | 10 | Carr et al. (1985) |
| Viking - Neutral MS | 0.0111 | 0.0007 | -10 | 58 | Nier and McElroy (1977) |
| Viking - GC MS | 0.0112 | 0.0006 | 0 | 50 | Owen et al. (1977) |
| Atm-Spectroscopy | 0.0104 | 0.0007 | -73 | 58 | Schrey et al. (1986) |
| Atm-Spectroscopy | 0.0106 | 0.0017 | -60 | 150 | Krasnopolsky et al. (1996) |
| Atm-Spectroscopy | 0.0112 | 0.0012 | 0 | 110 | Encrenaz et al. (2005) |
| Atm-Spectroscopy | 0.0110 | 0.0002 | -22 | 20 | Krasnopolsky et al. (2007) |
| **Phoenix MS** | **0.0110** | **0.0002** | **-18** | **17** | **This study** |
| Oxygen | $^{18}O/^{16}O$ | uncertainty | $\delta^{18}O$ (VSMOW) (‰) | uncertainty (‰) | Reference |
| Viking | 0.00204 | 0.00011 | 18 | 55 | Nier and McElroy (1977) |
| Viking-Atmosphere | 0.00201 | 0.00010 | 0 | 50 | Owen et al. (1977) |
| Atm-Spectroscopy - CO2 | 0.00193 | 0.00024 | -40 | 120 | Schrey et al. (1986) |
| Atm-Spectroscopy - CO2 | 0.00204 | 0.00004 | 18 | 18 | Krasnopolsky et al. (2007) |
| **Phoenix MS** | **0.00205** | **0.00003** | **20** | **17** | **This study** |

age value where the peak is expected to appear based on the sweep voltage to mass calibration conducted at the beginning of each day. Small variations in temperature caused shifts in the voltage to mass calibration that was corrected for by monitoring the magnet temperature. The peak-hopping scan was not always perfectly centered, but the span of 5 or 7 points across the peak was sufficient to ensure that the top of the peak was bracketed by at least two points.

Typically, a function describing the peak shape is fit to the 5 or 7 points to determine the count rate at the top of each peak-scan. The results reported in this abstract use a more simple routine which assumes that the highest point (of the 5 or 7 points) is at the top of the peak. This method is not ideal and introduces a small amount of error into the measurement, and we are continuing to work on refining our peak fitting routines to draw down the uncertainties of the measurement.

The peak rates were averaged over the analysis period for masses 44, 45 and 46 collected by channel 4. These averages were corrected for the deadtime in the system (measured at 100 ns). The background measured in the instrument prior to ingesting gas was subtracted, backgrounds were typically below 5% of the signal, but in some cases were as high as 30% when the instrument had been run multiple days in a row. A correction for $^{17}$O in mass 45 was also applied using the terrestrial value for standard mean ocean water (VSMOW) of 0.0003799.
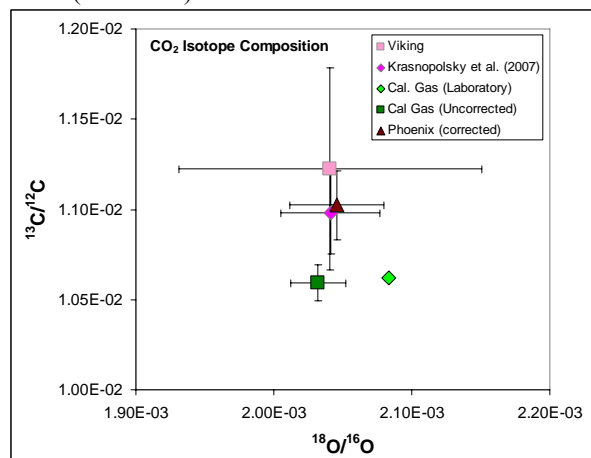


Figure 1. Carbon-Oxygen crossplot. The green points show how the TEGA analysis of calibration gas compares with a laboratory analysis. The difference between these points can be used to correct for any instrumental fractionation effects. The Phoenix value has been corrected for the instrumental fractionation and plots very near the value reported by Krasnopolsky (2007).

*Results:* The preliminary results are plotted in Figure 1 and listed in Table 1. The uncertainties at this preliminary stage remain very high, and we are confi-

dent that more work will bring them down significantly.

*Discussion:* The results reported here confirm that the carbon isotopic composition of martian atmospheric CO$_2$ is not enriched in $^{13}$C and are in agreement with Krasnopolsky et al. [6]. This result is different from measurements made on trapped gases in martian meteorites [2] and is contrary to the expectation that the isotopic composition of martian CO$_2$ would be enriched by atmospheric loss through time [9]. This result instead suggests that the supply of atmospheric CO$_2$ is being buffered by a source that has been protected from atmospheric loss throughout martian history.

Another interesting problem created by the results of this measurement lies in reconciling it to measurements of carbonate in martian meteorites, many of which are very enriched in $^{13}$C and have $\delta^{13}$C$_{VPDB}$ (VPDB: Vienna PeeDee Belemnite) values near +40‰ [2-4] with some as high as +65‰ [10]. This is a much larger range than observed on Earth and either indicates very large fluctuations in the isotope composition of atmospheric CO$_2$ on Mars in the past or very special formation environments for the martian carbonates.

*Conclusions:* Preliminary results from the TEGA instrument on the Phoenix Mars lander indicate that the carbon isotopic composition of martian atmospheric CO$_2$ is not significantly enriched in $^{13}$C. The oxygen isotopic composition is also slightly depleted from terrestrial atmospheric CO$_2$. The uncertainties on this measurement are large, and we expect that they will be reduced significantly as more work is done reducing the data returned from the spacecraft.

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