ASSESSING INTERANNUAL VARIABILITY IN THE CHEMICAL AND ISOTOPIC COMPOSITION OF THE MARTIAN ATMOSPHERE. H. B. Franz[1], M. G. Trainer[1], S. K. Atreya[2], M. H. Wong[2], C. R. Webster[3], G. J. Flesch[3], P. R. Mahaffy[1], C. A. Malespin[1], and T. H. McConnochie[4]. [1]NASA Goddard Space Flight Center, Greenbelt, MD 20771, Heather.B.Franz@nasa.gov, [2]University of Michigan, Ann Arbor, MI 48109, [3]Jet Propulsion Laboratory, Pasadena, CA 91009, [4]University of Maryland, College Park, MD 20742..

Introduction: The Sample Analysis at Mars (SAM) instrument suite of the Mars Science Laboratory (MSL) "Curiosity" rover has been periodically sampling the martian atmosphere since landing at Gale crater in August 2012. These observations have produced an unprecedented dataset that allows assessment of interannual variability in chemical and isotopic composition across five Mars years (MY 31-35).

Volume mixing ratios for the five most abundant atmospheric gases (CO_2, N_2, Ar, O_2, and CO) during MY 31-34 indicated a faster timescale for transport than mixing, as evidenced by a lag of approximately 20-40° in solar longitude (L_s) between the pressure cycle driven by CO_2 condensation and sublimation from the polar regions and peak cyclical variations in CO_2, N_2, and Ar mixing ratios [1]. Significant seasonal and interannual variations were observed in the O_2 mixing ratio above those expected from known sources and sinks [1]. In addition, comparison between O_2 and CH_4 abundances showed that both gases experienced greater amplitudes in seasonal variations than N_2 and Ar, but the trends in O_2 and CH_4 were similar for only part of the year [1]. However, a gap in observations during the southern spring-summer seasons precluded assessment of the relationship between these gases throughout the martian year.

SAM's initial isotopic measurements revealed enrichment in heavy isotopes of all major atmospheric species [2-5], consistent with previous analyses suggesting that selective loss of light isotopes from the martian atmosphere has occurred due to escape processes [6-8]. Observations from MY 31-34 suggested a potential seasonal increase in heavy isotopes of CO_2 during the southern spring-summer seasons, but the measurement gap again has prevented its complete characterization.

We will report results of a recent campaign designed to fill gaps in SAM's atmospheric observations and implications for annual seasonal cycles.

Experimental Methods: To acquire the data described here, martian atmospheric gas was introduced directly into the manifold of SAM's gas processing system for sampling by the quadrupole mass spectrometer (QMS) and/or the tunable laser spectrometer (TLS). The QMS measures VMR and isotope ratios for major atmospheric species, while the TLS measures isotope ratios of CO_2, H_2O, as well as CH_4 abundance [3,9].

For QMS measurements, 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]. Reported VMR are computed from integrated fractional scan peak areas at each *m/z* ± 0.4, while CO_2 isotope ratios are computed from the ratio of count rates at integer *m/z* values, averaged over multiple scans [10-11].

The TLS measures isotope ratios of CO_2 through direct ingestion of atmospheric gas [3]. Abundance of atmospheric CH_4 can be determined both through direct ingestion and through an enrichment protocol [12].

For further details concerning data acquisition and reduction, please consult the cited references [1-3, 10-12].

Volume Mixing Ratios: The unexpected seasonal and interannual variability in O_2 VMR has become one of the most intriguing aspects of martian atmospheric science revealed by SAM. O_2 is expected to behave similarly to Ar and N_2 throughout the year due to its long photochemical equilibrium lifetime of ~10 years [13]. In contrast, SAM measurements acquired from MY 31-35 indicate an increase of ~30% during northern spring-summer, with interannual variations in amplitude, followed by a return to levels predicted by photochemical models [1]. This suggests operation of atmospheric or surface processes that provide a source of O_2 in northern spring-summer, coupled with an extremely fast destruction mechanism [1,14]. Equally intriguing are TLS observations indicating a seasonal trend in background CH_4 abundance, with an increase during northern spring-summer similar to that of O_2 [1,12].

SAM's recent atmospheric campaign has found a depletion in O_2 during southern spring-summer of MY 35, in contrast to results from previous years. Background CH_4 abundance at similar L_s (~240-360°) has also been found to vary interannually, with elevated levels in MY 32 and 35 compared to MY 33. The divergence of trends observed in O_2 and CH_4 abundances during southern spring-summer suggests complexity in the relationship between these gases and that no single process is likely responsible for the observed variability in both species (Fig. 1).

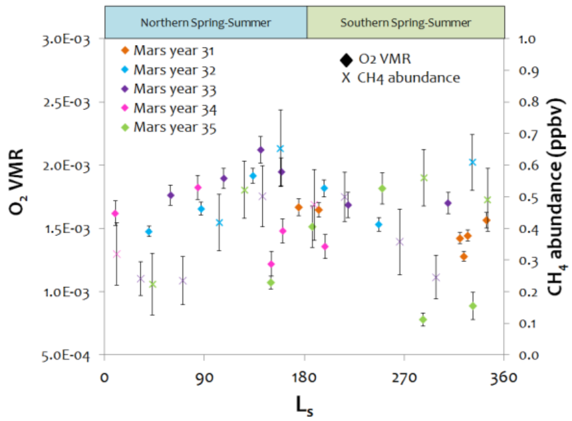

Fig. 1. O_2 and background CH_4 abundances measured over five Mars years

CO_2 Isotope Ratios: During Curiosity's first 100 sols, SAM analyzed Mars' atmosphere with the QMS three times. Initial analyses by the TLS yielded average $\delta^{13}C$ of 46 ± 4‰ and $\delta^{18}O$ of 48 ± 5‰ [2]. Similar values for $\delta^{13}C$ were obtained with the QMS, as reported in [3]. These 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 [2-8].

Repeated measurements of atmospheric CO_2 isotopes during MY 31-35 indicate a possible increase in heavy isotopes (^{13}C and ^{18}O) during southern spring-summer. Work is ongoing to identify and eliminate any instrument effects that could affect the amplitude of this increase. Because the isotopic fractionation during the seasonal CO_2 condensation-sublimation cycle at the poles is not expected to produce significant variations in CO_2 isotope ratios [15], we tentatively interpret the observed variability to indicate a seasonal communication between atmospheric and (sub)surface reservoirs as Mars is warmed during passage through perihelion.

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