HYDROGEN, OXYGEN and CARBON ISOTOPIC RATIOS IN THE MARTIAN ATMOSPHERE. G. L. Villanueva[1,2], M. J. Mumma[1], and R. E. Novak[3], [1]NASA-Goddard Space Flight Center (geronimo.villanueva@nasa.gov), [2]Catholic University of America, [3]Iona College.

Introduction: Isotopic ratios provide unique insights into the evolution and history of Mars' atmosphere. The atmosphere acts as a buffer between the main reservoirs of H, C and O (e.g., regolith, polar caps, rocks) and the exosphere, consequently, atmospheric isotopic ratios and their variability can be used to investigate mechanisms affecting exchange between these environments.

Our latest measurement of atmospheric D/H on Mars (1) reveals a value much higher than the one on Earth (VSMOW, Vienna Standard Mean Ocean Water, 1.56×10^{-4}), probably indicative of a significant loss of water owing to the preferential escape of the lighter fraction over geologic times. How much water was lost and when this loss mainly occurred are (once again) topics of intense debate.

The two main elements used to infer the loss of water over time (D/H ratios in present atmospheric water, and in ancient water from Martian meteorites) are based on highly disputed results. Previous studies of Martian meteorites have shown highly variable D/H and lower values (~2 VSMOW) than current Mars atmospheric values (2). However, Greenwood et al. (3) reported a D/H of 4 VSMOW for the ancient ALH84001 meteorite (4.5—3.9 Ga) and 5.6 VSMOW for the young shergottites (0.17 Ga), and suggested that the earlier measurements may have been biased by significant terrestrial contamination. Greenwood et al. ultimately concluded that Mars lost the majority of its water by 3.9 Ga. However, little is known about the current reservoirs of water on Mars and their D/H content. The fact that we observe strong geographic and seasonal changes of D/H on Mars (4) suggests the presence of multiple water reservoirs of varying sizes, that gain and lose water to the atmosphere as functions of time (5).

The $^{13}C/^{12}C$ and $^{18}O/^{16}O$ isotopic ratios are much closer to terrestrial values. The latest results by Krasnopolsky et al. (6) indicate $^{13}C/^{12}C = 0.978 \pm 0.020$ PDB and $^{18}O/^{16}O = 1.018 \pm 0.018$. Both results are practically consistent with terrestrial standards at the one sigma level. Spatial or temporal variations of these numbers have not yet been investigated, although they are expected to be much less variable than is D/H.

These measurements point to the urgent need for new measurements, resolved in space and time. In this report, we present new global maps of D/H and $^{13}C/^{12}C$ and $^{18}O/^{16}O$ obtained using high-resolution infrared spectroscopy.

Observations: We use high-resolution spectroscopy at infrared wavelengths with ground-based telescopes to sample several isotopic bands of CO_2 and H_2O. Considering Mars' CO_2-enriched atmosphere, no Doppler-shift is needed to measure CO_2 with ground-based telescopes in the L-band, but a Doppler shift >12 km s^{-1} is necessary when sampling weaker Martian H_2O lines through Earth's water-rich atmosphere. The optically thin lines that we target are very narrow, and very high spectral resolving power (RP or $\lambda/\delta\lambda \sim$ 1,000,000) is required to measure their intrinsic line shapes. However, lower RP (~30,000) is sufficient to separate the lines of Mars from their terrestrial counterparts at a Doppler shift >12 km s^{-1}, and so to measure their equivalent widths. So long as the line shape is not resolved, the measured contrast ratio (line depth relative to continuum intensity) improves with increasing resolving power, leading to improved differentiation among telluric, solar and Martian spectral features. We use high-resolution spectrometers (RP > 40,000) at high altitude observatories, to minimize the effects of telluric extinction.

The observations were taken between 2008 and 2012 using NIRSPEC at Keck II (Mauna Kea, HI), CRIRES at VLT (Paranal, Chile) and CSHELL at NASA-IRTF (Maunea Kea, HI), and the data span a broad range of seasons, Doppler shifts and spatial coverage.

Mapping: We map the isotopic abundances on Mars by orienting the spectrometer slit North-South (or East-West) on the planet and by taking spectra at 9 slit-positions across the Mars' disk. We typically extract 40 spectra along the slit, leading to 360 points for each isotope. This mapping technique provides a full sample of the visible Martian disk, revealing seasonal (North-South) and diurnal (East-West) variations. An example of a D/H study along the East-West direction is presented in Figure 1. Further results for D/H and $^{13}C/^{12}C$ and $^{18}O/^{16}O$ will be presented at the meeting.

References: [1] Villanueva, G.L. et al. (2012) JQSRT, 113, 202–220. [2] Leshin, L.A. et al. (1996), Geochim. Cosmochim. Ac, 60, 2635. [3] Greenwood, J.P. et al. (2008) Geophys. Res. Lett, 35, 1–5. [4] Villanueva, G.L. et al. (2008) Mars Atmosphere: Modeling and Observations, Williamsburg. [5] Fisher, D. et al. (2008) JGR, 113, E00A15. [6] Krasnopolsky, V.A. et al. (2007). Icarus, 192, 396–403.

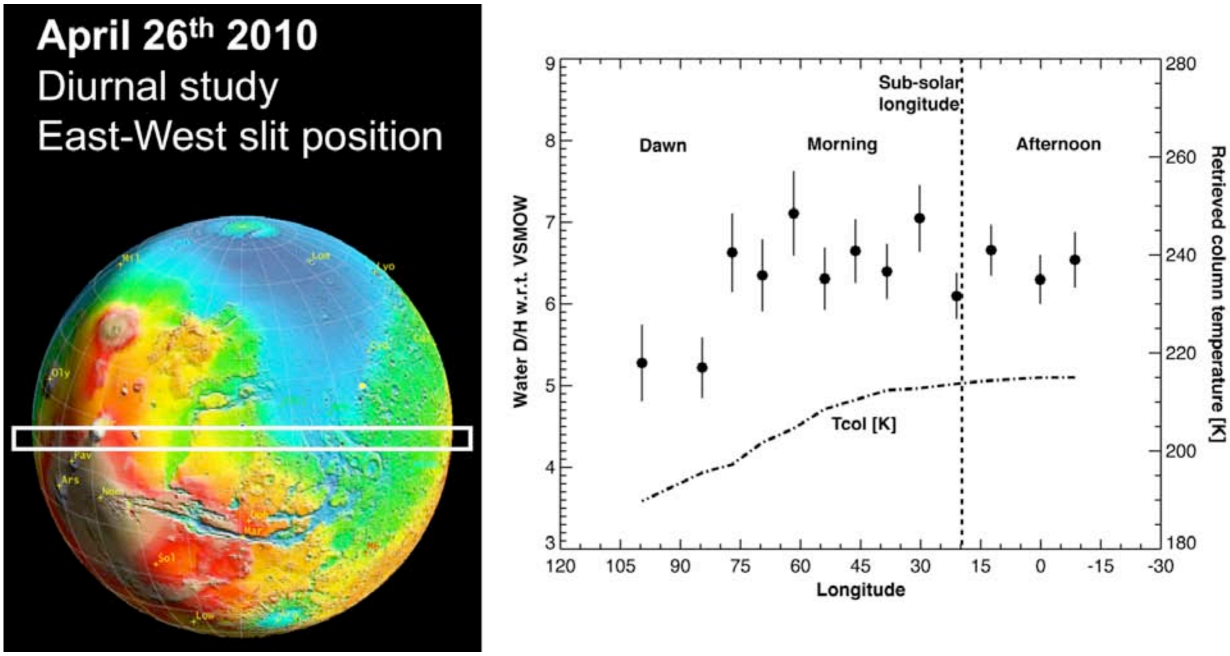

Figure 1: Measurements of D/H in Mars' water, obtained with NIRSPEC at Keck II on April 26th 2010. H_2O and HDO profiles were measured simultaneously using a single instrument setting. The slit was oriented East-West in this example, revealing higher D/H (~7 VSMOW) in the morning and afternoon (T>205 K), and lower D/H (~5 VSMOW) at dawn. Such diurnal variations could be associated with the formation of water ice clouds. Extraction of spatially-resolved isotopic measurements together with local atmospheric conditions (e.g., temperature, as shown) would permit to correctly identify and remove meteorological effects.