HYDROGEN ISOTOPIC COMPOSITION OF WATER IN THE MARTIAN ATMOSPHERE AND RELEASED FROM ROCKNEST FINES.

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Introduction: The Mars Science Laboratory Curiosity rover sampled the aeolian bedform called Rocknest as its first solid samples to be analyzed by the analytical instruments CheMin and SAM. The instruments ingested aliquots from a sieved sample of <150 µm grains. As discussed in other reports at this conference [e.g., 1], CheMin discovered many crystalline phases, almost all of which are igneous minerals, plus some 10s of percent of x-ray amorphous material. The SAM instrument is focused on understanding volatiles and possible organics in the fines, performing evolved gas analysis (EGA) with the SAM quadrapole mass spectrometer (QMS), isotope measurements using both the QMS and the tunable laser spectrometer (TLS), which is sensitive to CO_2, water and methane, and organics with the gas chromatograph mass spectrometer (GCMS). As discussed in the abstract by Franz et al. [2] and others, EGA of Rocknest fines revealed the presence of significant amounts of H_2O as well as O-, C- and S-bearing materials. SAM has also tasted the martian atmosphere several times, analyzing the volatiles in both the TLS and QMS [e.g., 3,4]. This abstract will focus on presentation of initial hydrogen isotopic data from the TLS for Rocknest soils and the atmosphere, and their interpretation. Data for CO_2 isotopes and O isotopes in water are still being reduced, but should be available by at the conference.

Experimental Methods: The TLS portion of SAM is described by Webster et al. [3]. In the case of the Rocknest samples, we have the option of sending specific temperature cuts of gases evolved from the sample to the TLS and these are accumulated inside the Herriott Cell and analyzed in bulk. Hydrogen, carbon, and oxygen isotopes in water and CO_2 are analyzed in the evolved gases using the near-IR tunable diode laser at 2.78 µm [3].

The specific temperature cuts sent to the TLS for each of the four Rocknest sample runs are shown in Fig. 1. The goal of the different temperature cuts was to utilize the EGA data on what temperatures the gases were evolving to iteratively design experiments that would selectively focus on various peaks. For example, run 3 captured the bulk of the H_2O peak, and run 4 focused on the first CO_2 peak.

Atmosphere TLS Results: Hydrogen isotope composition of water in the martian atmosphere is reported by Webster et al. [3] to be in the range of +5000 to +7000 ‰. We expect to refine these values further with additional calibration. Noise-related precision on the measurements is good, on the order of ±100 ‰. So further refinements of the calibration should allow for values with uncertainties on this order, and will ultimately allow for observing variation in D/H with season and time of day.

Rocknest TLS Results: The spectra for the CO_2 measurements, and to a lesser degree the H_2O measurements, were somewhat complicated by the presence of additional species in the gas sent to the TLS, likely associated with other C- or S-bearing molecules released during the heating of Rocknest fines. Identification of these peaks is ongoing. These additional peaks, though generally small, add to the complexity in reducing the data from the Rocknest runs, so the results discussed here are considered preliminary.

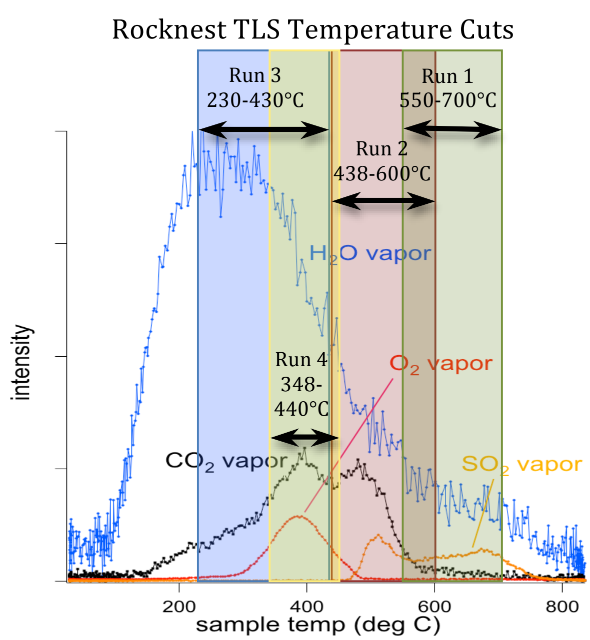

Figure 1. Temperature cuts sent to TLS in the SAM analyses of aliquots ~75 mm^3 of Rocknest fines. The ranges are superimposed on the EGA curves for major volatile species from the first Rocknest aliquot. The temperature cuts , especially for run 2, 3 and 4, were intended to separate as well as possible the two main CO2 peaks. Run 3 also captures the majority of the water peak.

The water released from Rocknest fines comprises a broad peak centered at just under 300°C. As reported in other abstracts [e.g., 5], the amount of water released is equivalent to an abundance in Rocknest soil of several weight percent, with uncertainty in the abundance related to uncertainty in the sample mass. However, given the relatively high temperature of release, pointing to bound water (rather than adsorbed water), and the lack of hydrous crystalline phases in the fines, as measured by CheMin [1], the water must be concentrated in the 10s of percent of the <150 µm fines that are x-ray amorphous. Therefore the water abundance in these x-ray amorphous materials must be 2-4 times the total amount measured by SAM, depending on the abundance of the amorphous material in the fines. This x-ray amorphous material appears to be extremely volatile rich.

The D/H ratio in all Rocknest samples are highly enriched in D over terrestrial values, with δD values ranging from ~+4000 to +6000 ‰. There appears to be some variation in the different temperature cuts, with the lower T cut having the highest D/H ratio and the highest T cut having the lowest. Of course only the lowest T cut (in run 3) sampled the main part of the water peak (Fig. 1), so this is likely the most relevant measurement. The average δD value of Rocknest water, weighted by the amount of water released, is about +5500 ‰.

Discussion: The range of preliminary δD values measured by SAM TLS of both the water in the martian atmosphere and the Rocknest fines overlap, with a current range of +4000 to +7000 ‰. The high D/H values reported here compare well to remote sensing analysis of D/H in the martian atmosphere [e.g., 6], as shown in Fig. 2, where telescopic measurements from Earth have previously suggested a reservoir enriched in D by about a factor of 5 over terrestrial values. The D-enriched values in a martian soil are also consistent with D-enriched water observed in both bulk [e.g., 7] and single grains [e.g., 8] in martian meteorites.

The close match between the atmospheric water results and the Rocknest evolved water suggests that the water-rich, likely carbonate-bearing phases in the x-ray amorphous material in the soil was either formed in direct contact with the atmosphere, or through interaction with volatiles directly derived from it.

Because the soil at Rocknest is consistent with the global soils analyzed elsewhere on Mars (see [9]), these data have implications for Mars' global water budget. This water represents a large apparently exchangeable reservoir in the near surface of Mars, and may be present nearly everywhere on the planet. The D-enriched nature of this reservoir also supports the idea that a significant amount of hydrogen has escaped Mars over time, and thus this reservoir is a remnant of what must have previously been more abundant water in the near-surface environment of Mars. Future measurements will help constrain diurnal and seasonal changes in these values, and their preservation within rocks at the Gale Crater site. Finally, C and O isotope measurements in the soils and rocks will constrain whether these volatile-bearing phases were also formed from volatiles in equilibrium with or derived from the atmosphere.

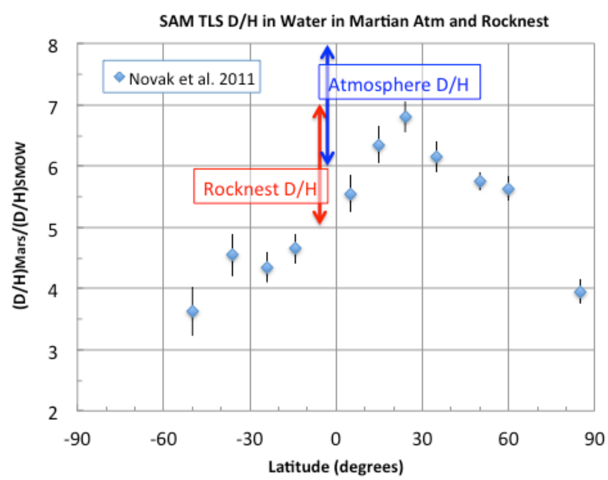

Figure 2. D/H measurements made by SAM TLS in the atmosphere and Rocknest fines. Values are shown as a ratio between the D/H measured and the terrestrial Standard Mean Ocean Water (SMOW). On this scale, a value of 5 (for example) corresponds to a δD value of +4000 ‰. The Curiosity measurements to date in the atmosphere and on the Rocknest fines are shown as ranges only. More refined data will be presented at the conference. The two MSL data ranges are shown near the latitude of Gale Crater (-4.5 °) but offset slightly for clarity. The data compare well with the most recent atmospheric D/H measurements, made telescopically, reported by Novak et al. [6]. Note the observed variation with latitude (and also with water abundance in the atmosphere), pointing to possible future variations with seasons which could be observed by Curiosity.

References: [1] Blake et al. (2013) LPSC XLIV. [2] Franz et al. (2013a) LPSC XLIV. [3] Webster et al. (2013a) LPSC XLIV. [4] Mahaffy et al. (2013) LPSC XLIV. [5] Archer et al. (2013) LPSC XLIV. [6] Novak et al. (2011) Planet. Space Sci. **59**, 163. [7] Leshin et al. (1996) GCA **60**, 2635. [8] Leshin (2000) GRL **27**, 2017. [9] Yen et al. (2013) LPSC XLIV.