

THE DEUTERIUM TO HYDROGEN RATIO IN THE WATER THAT FORMED THE YELLOWKNIFE BAY MUDSTONES IN GALE CRATER. P.R. Mahaffy¹, A. Brunner^{1,2}, C.R. Webster³, S.K. Atreya⁴, A. McAdam¹, J. Stern¹, L.A. Leshin⁵, R. Navarro-Gonzalez⁶, J. Jones⁷, S. Kashyap¹ and the MSL Science Team. ¹NASA Goddard Space Flight Center, Greenbelt, MD 20771 (Paul.R.Mahaffy@nasa.gov), ²CRESST, U. Maryland, College Park, MD 20740, ³Jet Propulsion Laboratory, Pasadena, CA 91109, ⁴U. Michigan, Ann Arbor, MI 48109, ⁵Rensselaer Polytechnic Institute, Troy, NY 12180, ⁶Universidad Nacional Autónoma de México, México, D.F. 04510, Mexico, NASA Johnson Space Flight Center, Houston, TX 77058

Introduction: A suite of isotope ratios of light elements in the present martian atmosphere ($^{13}\text{C}/^{12}\text{C}$, $^{15}\text{N}/^{14}\text{N}$, $^{18}\text{O}/^{16}\text{O}$, $^{38}\text{Ar}/^{36}\text{Ar}$, and D/H) are all substantially enriched in the heavy element suggesting atmospheric loss to space over the past billions of years with preferential loss of the lighter isotope from each pair. *In situ* measurements from MSL's Sample Analysis at Mars (SAM) instrument [e.g. 1,2,3] have considerably refined previous measurements from the Viking mass spectrometers [e.g. 4], from remote spectroscopic observations [e.g. 5,6], and from martian meteorite studies [e.g. 7,8].

The persistence of habitable environments such as the ancient Yellowknife Bay lake recently revealed by measurements from the Curiosity rover [9] depends on the surface temperatures and the duration of an atmosphere thicker than that at present. Current and planned measurements from orbit with the Mars Express and MAVEN missions respectively intend to study the processes of atmospheric escape including solar wind interaction, sputtering, thermal escape, and dissociative recombination, and determine or refine the current rate of atmospheric loss caused by these and other mechanisms. The goal of these programs is to understand the physical processes sufficiently well so that robust extrapolations over the past billions of years can be made to predict the atmospheric and surface conditions on early Mars.

However, the study of the history of martian atmospheric evolution will be greatly facilitated if we are able to also directly measure the isotopic composition of volatiles captured in rocks that are representative of the ancient atmosphere. To date, D/H is one of the most promising candidates for this study since water is the most abundant volatile thermally released from the Yellowknife Bay phyllosilicates discovered by the SAM and CheMin experiments of MSL and its D/H is measured by both the Tunable Laser Spectrometer (TLS) and the Quadrupole Mass Spectrometer (QMS) of the SAM suite.

Methods: One mode of operation of SAM is to continuously sample gases with the QMS as they are evolved from 1 or more ~50 milligram portions of powdered sample delivered to a quartz cup and heated in a helium stream from a selected starting temperature to ~900 °C. At any point in this evolved gas analysis (EGA) heating sequence the stream of gas may be directed for a period of time to the TLS which has been previously evacuated by a turbomolecular pump where

the gas is stored for later analysis of abundances and C, O, and H isotopes of CO_2 and H_2O . Since the TLS obtains a batch sample another run is required to select an alternate temperature range for isotopic analysis. The QMS, on the other hand, samples continuously over the entire EGA sequence. Isotope ratios for D/H in water are secured with the TLS by scanning with a near infrared (NIR) laser over the wave number range of 3594.4 cm^{-1} to 3593.2 cm^{-1} , where multiple HD^{16}O and H_2^{16}O absorption lines are present. The QMS analysis utilizes primarily the m/z 19 and 20 signals where primary contributions come from HD^{16}O^+ and $\text{H}_2^{18}\text{O}^+$ respectively. The TLS $^{18}\text{O}/^{16}\text{O}$ is used to predict the intensity of the QMS m/z 18 peak from $\text{H}_2^{16}\text{O}^+$ which is often saturated. Corrections for contributions from other isotopologues such as $\text{H}_2^{17}\text{O}^+$, HD^{16}O^+ , H^{18}O^+ , and $^{40}\text{Ar}^{++}$ are also necessary as are careful corrections for background effects because water is a significant instrument background gas. Most of the hydrogen released during the EGA sequence is contained in H_2O with a smaller fraction in H_2 . The hydrogen in other reduced species such as H_2S has a negligible contribution to the variation in D/H ratio.

Results: Fig. 1 illustrates the QMS and TLS data from one of the runs used to independently derive isotope ratios for D/H in evolved water. Fig. 2 gives TLS results for both the John Klein and Cumberland drill holes. The temperature range selected for the TLS cut

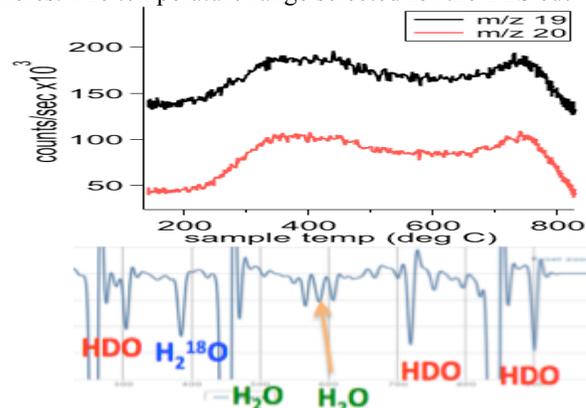


Figure 1. (top) QMS EGA traces of m/z 19 and 20 used to derive D/H ratios. The high temperature peak in the water is primarily dehydroxylation of the clay while the low temperature peak comes from adsorbed and interstitial water. (bottom) TLS spectra from the same run showing the multiple HDO and H_2O lines that can be utilized to derive the D/H ratio.

is illustrated by the horizontal bars. For the points where sampling started above 445 °C the average δD is 4992‰ with a standard deviation of 659‰. The bottom pane of Fig. 2 gives the H₂O and H₂ averaged δD from the QMS in the 450-800 °C temperature range for the six of the seven CB samples (in the 5th run the m/z 2, 19, and 20 were not sampled during the EGA part of the run). The evolved water dominates the δD value although on average the evolved hydrogen δD value is lower than that in the evolved water.

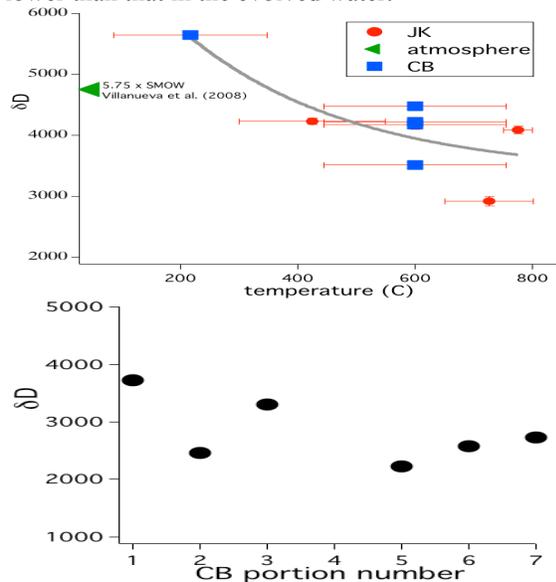


Figure 2. (top) TLS data from John Klein (JK) and Cumberland (CB) drill holes where different temperature cuts illustrated by the horizontal bars were sent to the TLS. (bottom) the 450-800 °C average QMS derived δD values that combine both the water and the hydrogen H and D.

Differences between TLS and QMS and scatter in the data: The error bars within an individual TLS run are considerably less than the scatter shown between different runs. A similar trend has been noted in the EGA of other gases such as CO₂, O₂, HCl, SO₂, H₂S, and H₂ suggesting that the portions delivered to SAM from each drill hole are not homogeneous. With mixing of the low temperature higher δD water into the cut sampled by the TLS it is possible that the trend-line shown in Fig. 2 (top) reflects an upper limit to the D/H value of high temperature water. The QMS samples gas directly evolved from the pyrolysis oven while the gas sampled by the TLS has a greater opportunity in the long transfer lines [10] to the TLS to be mixed with the lower temperature water.

It is possible that future SAM sequences [11] that remove the low temperature water more effectively in a two step desorption sequence may provide a more accurate TLS δD measurement of the high temperature water that is formed on dehydroxylation of the OH groups in the phyllosilicate lattice.

Discussion: The low temperature adsorbed and interstitial water in the Yellowknife Bay samples can more readily exchange with the atmosphere and its δD may represent that of the present atmosphere (4950±1080 ‰ [8]) with some additional fractionation. In this way, the JK and CB samples are consistent with Rocknest results, in which the low T water had the highest δD values [12].

The high temperature water in JK and CB, on the other hand, very likely comes from the dehydroxylation of the smectite clays, and thus should better represent the isotopic composition of the water that transformed the basaltic material washed down from the crater rim into the Sheepbed mudstone sampled by Curiosity's drill. Recent K-Ar results from combined SAM and CheMin data [13] have established the formation age of the Yellowknife source rocks as 4.21 ± 0.35 Gyr thus providing a constraint on the time of the formation of these smectite clays. With consideration of the QMS results and of the likely mixing of some of the low temperature component of the evolved water into the water sampled by the TLS, the data support the hypothesis that the δD of the water that formed the clay minerals was somewhat below 3000 ‰. If the δD value of the original inventory of martian water was similar to that of the Earth's ocean as suggested by recent studies of the Yamato 980459 shergottite [14] then early processes such as hydrodynamic escape [e.g. 15,16] driven by intense EUV and giant impacts must have substantially fractionated hydrogen prior to the formation of the Yellowknife mudstones. Additional fractionation is required to attain the values recorded in the current atmosphere and the low temperature water evolved from materials analyzed by SAM.

References: [1] Atreya, S.K. et al., GRL 40, 5605-5609 (2013). [2] Wong, M. et al., GRL DOI: 10.1002/2013GL057840 [3] Webster et al., Science 341, 3 (2013). [4] Nier, A.O., McElroy, M.B., Science (1976) 194, 1298-1300. [5] VKrasnopolsky, V.A. et al., Icarus (2007) 192, 396-403. [6] Novak, R.E. et al, PSS (2011) 59, 163-168. [7] Weins, R.C., et al., Earth Planet. Sci. Lett. (1986) 77, 149-158. [8] Bogard, D.D. and Garrison, D.H., GCA 62: 1829-1835, 1998 [9] Grotzinger et al., Science 1242777 (2013). [10] Mahaffy, P. et al. (2012) *Space Sci. Res.*, 170, 401-478. [11] Stern et al., LPSC XLV [12] Leshin, L. et al., Science 341, 1238937 (2013). [13] Farley, K. et al., Science 1247166 (2013). [14] Usui, T. EPSL 357-358, 119-129 (2012). [15] Pepin, R. O., Icarus 92, 2-79 (1991). [16] Lammer, H. et al., SSR 174, 113-154 (2013).

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