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MARS ATMOSPHERE

The imprint of atmospheric evolution in the D/H of Hesperian clay minerals on Mars

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The deuterium-to-hydrogen (D/H) ratio in strongly bound water or hydroxyl groups in ancient martian clays retains the imprint of the water of formation of these minerals. Curiosity's Sample Analysis at Mars (SAM) experiment measured thermally evolved water and hydrogen gas released between 550° and 950°C from samples of Hesperian-era Gale crater smectite to determine this isotope ratio. The D/H value is 3.0 (±0.2) times the ratio in standard mean ocean water. The D/H ratio in this ~3-billion-year-old mudstone, which is half that of the present martian atmosphere but substantially higher than that expected in very early Mars, indicates an extended history of hydrogen escape and desiccation of the planet.

We obtained a reference point for the evolution of the martian atmosphere and loss of near-surface water by comparing deuterium-to-hydrogen (D/H) ratios from the atmosphere with those in ancient clay minerals, such as those in the Yellowknife Bay lake bed on the floor of Gale crater (*1*). Each process of atmospheric loss to the surface or to space can leave an isotopic imprint, so models of the evolution of the atmosphere and ancient climates (*2*–*4*) can be constrained by isotopic measurements as well as by geological studies (*5*–*7*). The Sample Analysis at Mars (SAM) experiment (*8*) on the Curiosity rover of the Mars Science Laboratory (MSL) mission has refined the atmospheric measurements not only of D/H in water (*9*) but also of $\delta^{13}C$ in CO_2 (*9*, *10*), $\delta^{15}N$ in N_2 (*11*), and $^{36}Ar/^{38}Ar$ (*12*). These combined measurements consistently support the paradigm of continued atmospheric loss to space over the course of martian history, with this process dominating over loss to surface reservoirs.

The mechanism for enriching D in water over the past billions of years entails the photolysis of water by solar ultraviolet (UV) radiation and the more rapid escape to space of the lighter H, leaving D behind to be incorporated again in surface water. The present loss rate is estimated to be at least 10^{26} atoms s^{-1} (*13*). For the water that formed the clays of the Sheepbed member at Yellowknife Bay, we have now measured the D/H ratio from water and hydrogen that was released in stepped heating to 950°C and analyzed with SAM's tunable laser spectrometer (TLS) and quadrupole mass spectrometer (QMS). The clays sampled in the Hesperian-age (*14*–*16*) Yellowknife Bay formation were likely formed during diagenesis before lithification (*17*) more than 3 billion years ago. Thus, the D/H value provides a reference point for estimates of surface water loss over geologic time scales. The Hesperian period in martian history is not sampled by the present meteorite record.

The ancient record of D/H in water is preserved in the crystal structure of the clay minerals formed by aqueous transformation of basaltic materials because fractionation of D/H between water and clay minerals during formation is no greater than a few 10s per mil (*18*). In the absence of high levels of heating or recrystallization, the structural OH in the octahedral layers of clay minerals thus preserves the isotopic value of the liquid water of formation. Predictions of the global loss of water from Mars have used the D/H ratio measured in Mars meteorites (*19*–*22*), with the earliest martian value presumed to be near that of terrestrial oceans. Recent analysis of D/H in the primitive martian mantle melt Yamato 980459 supports this hypothesis, with its D/H of ≤1.28 × standard mean ocean water (SMOW) (*21*) close to terrestrial, although contributions of cometary water to both early Earth and Mars have been postulated (*23*). The terrestrial SMOW D/H value of 1.558×10^{-4} is half that of several Oort-class comets (*24*–*26*) but closer to the value found in the Kuiper Belt comet Hartley 2 (*27*) and in a range of carbonaceous chondrites (*28*). The Hesperian period in martian history explored with the MSL measurements is not sampled by the present meteorite record.

The age of the 150-km-diameter Gale crater is estimated, by modeling of crater densities, to be

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~3.6 billion years (*15*, *16*), whereas some regions on the crater floor are found to be younger at ~2.9 billion to 3.5 billion years old (*14*–*16*), having formed during the Hesperian period of martian history. Our analysis used samples from two drill holes designated John Klein and Cumberland from the Sheepbed member, the lowest stratigraphic unit in the Yellowknife Bay formation located ~500 m northeast of the Mars Curiosity rover landing site (*29*). These samples were analyzed by the full suite of instruments on the rover, including SAM and the Chemistry and Mineralogy (CheMin) instruments. These analyses revealed a mudstone containing a smectite clay mineral in addition to an amorphous component and basaltic minerals (*1*, *30*, *31*), with isochemical alteration that indicates authigenic smectite formation (*17*, *29*). The sandstones and mudstones of the Yellowknife Bay formation provide strong evidence for both flowing water in streams expressed in conglomerates and sandstones of the Gillespie member, and bodies of standing water as lakes that formed the Sheepbed member. The thickness of the Sheepbed member suggests that this body of water must have existed for at least hundreds to thousands of years (*1*). The existence of streams and stable lakes requires water production in the upper reaches of the Gale crater rim, which was a source for sediments that were transported to the Peace Vallis fan and its stratigraphic and facies equivalents. This is consistent with previous evidence for wetter Hesperian climates required by stream networks cut into bedrock (*32*) and deltas that built outward into bodies of standing water (*33*).

The D/H ratio in martian atmospheric water derived from spectroscopic observations was reported in 1988 as (6 ± 3) × SMOW (*34*), and some years later as (5.5 ± 2) × SMOW (*35*). Higher-resolution spectroscopy has allowed spatial variations to be mapped (*36*, *37*), and values of 6.5 × and 7 × SMOW have recently been reported (*37*, *38*). Early results from the SAM TLS gave a value of (6 ± 1) × SMOW for a single atmospheric sample (*9*). The variability in D/H in the meteorite record may point to somewhat isolated reservoirs with different D/H ratios (*19*, *20*), but the atmospheric D/H ratios are generally consistent with those reported in meteorites with younger rock formation ages, such as the 6.08 × SMOW value (*21*) in the geochemically enriched 183-million-year-old (*39*) Larkman Nunatak 06319 shergottite and the ~5.6 × SMOW value reported (*20*) from two fracture-free zones in apatite grains of the (~170-million-year-old) Shergotty meteorite.

A comparison of the evolved gas analysis (EGA) trace for H_2O from one of the Yellowknife Bay Cumberland drill hole samples (*30*) is shown in Fig. 1A with the same trace for a Rocknest aeolian deposit sample (*40*). The low-temperature water in the Cumberland sample, which peaks at ~200°C and extends to over 500°C, may have a number of sources, including water that is surface adsorbed, smectite interlayer, associated with amorphous materials, or structurally bound in compounds such as Fe-oxyhydroxides (*30*). The total water released from the Cumberland sample is ~2% by mass (*30*). The high-temperature water peak (600° to 800°C) evident in the Cumberland mudstone EGA trace is the signature of the structural hydroxyl hydrogen derived from the octahedral layer of a smectite component of this sample, which was definitively identified

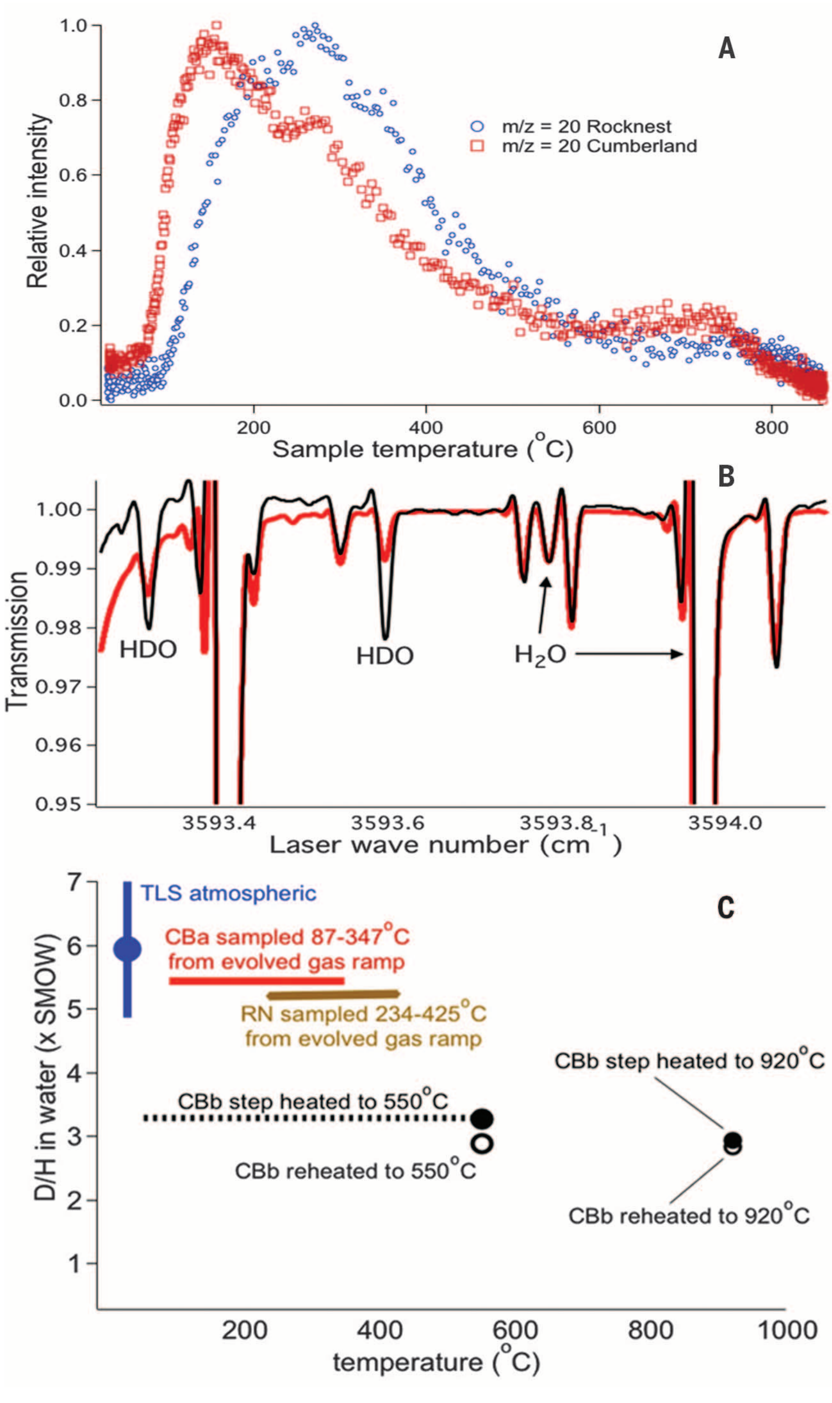

Fig. 1. Water released from martian samples. (**A**) Evolved water signature as monitored by the mass spectrometer at a mass-to-charge (*m/z*) ratio of 20 ($H_2{}^{18}O$) for both a Rocknest eolian deposit and the Cumberland mudstone. (**B**) TLS measurements showing the high-temperature water evolution from stepped heating in the black trace compared with the high-resolution transmission (HITRAN) spectrum in red normalized to the large $H_2{}^{16}O$ peak near 3594 cm^{-1}. (**C**) TLS measurements of D/H relative to terrestrial SMOW for water captured from a temperature ramp from Cumberland (CBa) and Rocknest (RN) samples, and water evolved at different temperatures in the step heating experiment from a second Cumberland sample (CBb). Rocknest D/H values in (*9*) and (*40*) are updated in (*41*).

by the CheMin x-ray diffraction analysis of the Cumberland mudstone (*31*).

Most of the solid samples analyzed with SAM used the EGA measurement protocol (*8*) that identified a suite of volatiles, including the most abundant gas, H_2O, as well as CO_2, O_2, SO_2, H_2S, HCl, NO, H_2, H_2S, and several chlorinated organic compounds. The gas stream was diverted to the TLS in selected temperature intervals to measure C, O, and H isotopes in CO_2 and H_2O and the abundances of these molecules (Fig. 1B). However, the D/H in the high-temperature water component cannot be accurately isolated with the EGA experiment by using a continuous temperature ramp because of the mixing of the tail of the low-temperature-evolved water with the smaller high-temperature peak. In order to better separate the low- and high-temperature components, a specialized experiment was designed and implemented (*41*) that used stepped heating. The D content of the water released in the four steps of this experiment compared with EGA runs is given in Fig. 1C and table S1. Three high-temperature water releases give nearly identical values of δD (table S1) as measured with the TLS. The mole-weighted average δD that includes a small volume of H_2, and a small H_2 blank correction, gives a high-temperature D/H of (3.0 ± 0.2) × SMOW.

As evidenced by meteorite studies and this result, escape of hydrogen from the upper atmosphere of Mars has left its imprint in the D/H ratio in near-surface water over the past 3 billion to 4 billion years. The loss of water on Mars can be modeled by using single or multiple near-surface reservoirs, with the amount of surface water often expressed as a water-equivalent global layer (GEL). In the single-reservoir model, the entire near-surface H_2O inventory is exposed to atmospheric loss through time. Using the notation of Kurokawa (*22*), the amount of water R_{t1} in a near-surface reservoir at a time $t1$ with a D/H ratio of I_{t1} can be related to the amount R_{t2} at a later time $t2$ with a D/H ratio of I_{t2} by the expression $\frac{R_{t1}}{R_{t2}} = \left(\frac{I_{t2}}{I_{t1}}\right)^{\frac{1}{1-f}}$, where f is the fractionation factor. Thus, knowledge of a present and past D/H ratio and an estimate of the present GEL allows the volume of past water to be established.

In the multiple-reservoir models (*42*) invoked to explain variability in meteorite studies, a surficial D/H reservoir continuously participates in atmospheric cycling and is exposed to atmospheric loss, whereas another reservoir consists of deeply buried ice that is not exposed to atmospheric loss processes. Vigorous escape during early stages of planetary evolution when both reservoirs would have been rapidly exchanging would have provided an initial enrichment of the δD of both reservoirs to a value of 2 × to 4 × SMOW (*20*, *42*, *43*). Early catastrophic atmospheric loss (*44*) and global cooling separate a majority of the water as ice in the upper crust, isolating it from atmospheric processes and atmospheric loss. Because the amount of H_2O available to readily exchange with the atmosphere is small, only small amounts of atmospheric loss would be needed to create large D/H enrichments. However, short periods of warm, wet conditions on Mars could cause mobilization and exchange with this subsurface reservoir, providing surface water with a lower D/H ratio such as observed with our D/H measurement in Yellowknife Bay sediments.

In the single-reservoir model, Yellowknife Bay D/H values are compared with data from selected martian meteorites assuming a continuous D/H evolutionary timeline (*22*). This approach allows constraints on the amount of near-surface Hesperian water. The Amazonian features a high D/H of ~6 × SMOW (*21*) based on the <200-million-year-old meteorites LAR 06319 and Shergotty; the Noachian has a mid-range D/H value of 2.2 to 4 × SMOW based on the 4.1 Ga ALH 84001 pyroxenite (obtained from analyses of carbonates and magmatic apatite); and the pre-Noachian 4.5-billion-year-old primordial martian water exhibits a D/H of ≤1.28 × SMOW, based on melt inclusions in the Yamato 980459 shergottite meteorite (*21*). Under the assumptions of a fractionation factor for H and D loss in the range of 0.016 (*22*) to the diffusion limit of 0.4, the amount of water lost to space since the time of formation of the Yellowknife Bay clay minerals would be approximately equal to 1 to 1.5 times the amount of water in current-surface and near-surface reservoirs. Current estimates of these reservoirs that include the observable polar cap water reservoir (20 to 30 m) and other sources of cryospheric ice not bound in minerals is at least 50 m (*45*). Thus, the GEL at the time of the Cumberland mudstone formation would be 100 to 150 m or more. The current very limited set of exospheric H observations (*46*) predict substantially less loss and are not consistent with this measurement. Earlier loss including nonthermal escape processes (*47*, *48*) would push the predicted surface-water volume before this time higher as indicated by this ~3 × SMOW D/H value and supported by geological studies (*7*, *49*).

The D/H ratio of Hesperian water is preserved within a Yellowknife Bay mudstone, whose clay minerals were formed in an active lacustrine environment (*1*) several hundred million years after the Gale cratering event. This ratio established with in situ measurements from instruments on the Curiosity rover provides a new data point to help constrain the volume of water lost through escape processes over the past 3 billion years.

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SUPPLEMENTARY MATERIALS

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Supplementary Material for

The Imprint of Atmospheric Evolution in the D/H of Hesperian Clay Minerals on Mars

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Figs. S1 to S4

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Materials and Methods

Experiment Design

The instruments of the Sample Analysis at Mars (SAM) suite (*8*) on the Mars Science Laboratory "Curiosity" rover utilized for the multi-step experiment described as the "combustion" experiment because a small volume of O_2 was added at one step in this process, are the quadrupole mass spectrometer (QMS) and the tunable laser spectrometer (TLS). Descriptions of both instruments are described in an earlier publication (*8*) and the details of data methods and processing described in the Supplemental Material to two recent Science publications (*9, 10*). The SAM sample manipulation system enabled a quartz cup to be hermetically sealed in an oven and heated to a preset temperature to release gases for analysis. Blank experiments consisted of heating an empty cup and monitoring the evolved gases. Triple portions of powdered sample sieved to a size of <150 microns were delivered to the quartz cup for this experiment using the rover arm's portioning hardware, following acquisition of the powdered sample with the rotary percussive drill. The estimate of the total sample mass delivered from experiments utilizing a testbed drill/sieve system and an analog mudstone was 135 $\pm$ 18 mg. Fig. S1 illustrates the elements of the SAM gas processing system.

The combustion experiment required 4 steps over 3 sols uploaded to the SAM instrument suite and executed on sequential sols (martian days). The experiment series was designed to convert reduced carbon to CO_2 for TLS measurements so oxygen from an internal SAM tank was introduced to the manifold and exposed to the sample in selected steps of this experiment. On the first sol the cup with its triple portion of fresh sample was heated to 550^{o}C held for 25 minutes at this temperature and the evolved water measured with the TLS. In this step no oxygen was introduced to the manifold because substantial oxygen was expected from the decomposition of the oxychloride compounds previously detected (*28*) in these samples. The manifolds and the TLS were then evacuated using the SAM turbomolecular pump. On sol 2 the sample was reheated to 550^{o}C in the presence of ~3.7 micromoles of oxygen. Evolved water was measured with the TLS and a full mass spectrum secured with the QMS. The manifold was then evacuated, the same volume of oxygen again reintroduced to the manifold and over the sample in the cup and the cup heated to ~920^{o}C with again measurements made by both the QMS and TLS. On the third sol the cup was reheated to 920^{o}C with oxygen again introduced over the sample.

Supplementary Text

TLS-SAM Data Processing:

The TLS data were processed according to the detailed description given in the supplemental material in *(48)*. The method involves determining volume mixing ratios for each spectral line and comparing with those calculated using the HITRAN 2012 database (*49*) for the same conditions of pressure, temperature, path length, spectral laser width, etc. The comparison is made between the integrated areas of the lines to generate mixing ratios of each isotopic component that are then compared to produce isotope ratios. We note that the TLS was calibrated pre-launch by recording spectra for a known water standard "Boulder water" whose isotopic ratios were determined by standard

Isotope Ratio Mass Spectrometry (IRMS). Calibration "multipliers" for the HITRAN 2012 comparison were very close to unity. Although the calibration water sample is somewhat depleted in deuterium (-110 ‰)[1], the large dynamic range of the TLS direct absorption method allows large enrichments to be reliably recorded and measured. In both pyrolysis and combustion evolved gas analysis, TLS cell pressures range from a few mbar up to ~14 mbar, and the line shapes are predominantly Gaussian (Doppler broadening) but with a Lorenzian contribution from pressure broadening by both the target gas itself (self-broadening) and the host gas (foreign broadening) that is helium. Because HITRAN 2012 reports foreign broadening coefficients only for nitrogen broadening, we conducted careful lab measurements to (i) verify the self-broadening coefficients of each water line; and (ii) to determine the helium and carbon dioxide broadening vs that of nitrogen. Our HITRAN 2012 calculations are therefore refined to partition the "foreign" broadening into components from both He and CO_2 to better represent the evolved gas environment in which helium and water vapor are the dominant gases. We note that because of the low pressures of our measurements, this refinement, while more accurate, produces little change to the derived isotope ratios except in the case of significant water vapor. Fig. S2 illustrates the comparison of the observed vs. HITRAN line shapes for the case of highest water abundance, namely the combustion Step 1. Figure S3 compares the observed TLS spectra for low-temperature Cumberland and combustion Step 3 with the HITRAN spectra generated with terrestrial isotope ratios.

Updates to TLS-SAM EGA D/H results:

We earlier reported TLS D/H values for water evolved during pyrolysis of fine-grained material from Rocknest, an Aeolian sand shadow, as published in Science by Webster et al. 2013 *(9)* and by Leshin et al. 2013 *(39)*. More recently, we have improved our data processing tools as described above to better include self- and foreign-broadening contributions. These improvements do not change the published values in *(9)* for the D/H of atmospheric water vapor or those of the various isotope ratios in atmospheric carbon dioxide *(9)*, but do lower values of D/H for the EGA pyrolysis results of Rocknest in which helium is the main foreign broadening gas and self-broadening by water is significant. In Table S1 below we provide new results that update and correct the earlier values given in *(9)* and *(39)*.

We note that during the pyrolysis EGA runs listed above the oven temperature is continually ramped during which a cut is given to TLS for analysis. We consider the low temperature results for Rocknest-3 and Cumberland-2 as representative of the D/H value of adsorbed/interstitial water. However, the high temperature D/H results are always higher than the true structural values since our measured values are a combination of both residual low temperature adsorbed/interstitial water and the higher temperature structural water components. The stepped heating combustion experiments avoid contamination by low temperature water release.

Evolved H_2 contributions to the D/H:

H_2 is the second most abundant hydrogen-containing molecule released from Cumberland samples in evolved gas experiments and the only released compound containing hydrogen (such as H_2S or chlorinated organic compounds) present in sufficient abundance to impact the high temperature D/H ratio. Fig. S4 illustrates behavior typical of evolved m/z 2 and m/z3 in separate EGA experiments with a continuous ramp. As previously reported (*28*) an average of 6.7 μmol/portion of H_2 were released from the four Cumberland samples leading to an expectation that 20.2 μmol would have been released from the triple portion delivered for this stepped heating experiment. However, since less than 1.5 μmol was detected by the QMS in steps 2-4 of the combustion experiment it is clear that the most of the evolved H_2 reacted with the terrestrial O_2 over the hot sample to produce additional water.

The *δD* of the EGA H_2 for six separate experiments (1954 $\pm$600 ‰) is the same within experimental error as the *δD* of the high temperature H_2O. In addition, an average of 1.4 μmoles of H_2 were released in three blank experiments from the SAM oven at high temperatures. Terrestrial D/H from oven wall outgassing serves to lower the measured dD and the required correction is included in the weighted average *δD* in Table S2. The dD in the evolved H_2 from the previous EGA experiments can be established from the QMS measured mass 3/2 ratio with small H_3^+ corrections established from measurements on the SAM testbed. Combining the mole weighted H_2O and H_2 dD measurements does not substantially change the dD secured from H_2O alone. Inclusion of the background terrestrial H_2 outgassed from the oven gives a dD that is higher than without this correction. The good agreement between water released during the second heating to 550°C and on heating to 920°C indicates that the low temperature water was completely eliminated before the high temperature measurements in the combustion experiment.

The mole weighted mean of the δD of H_2O is 1920 $\pm$51 ‰. The contribution of lesser amounts of H_2 that also is released at high temperatures must also be considered to establish the overall δD of hydrogen containing gases released at 550°C or above. The observation that the water released during the second heating to 550°C gives essentially the same δD value as 920°C water release and the residual water that is released on a second heating to 920°C (Table S1) gives us confidence that the low temperature adsorbed, smectite interlayer, and structural water from non-clay mineral phases was fully released in the first 550°C treatment and that the high temperature dehydroxylation of the structural smectite OH gives the D/H of this strongly bound component. After including the mole weighted average δD from both H_2O and the small volume of H_2 plus a small H_2 blank correction the overall high temperature δD is 2056 $\pm$ 60 ‰ or 3.06 x SMOW. Since the Step 2 water evolution with 2.9 x SMOW is not impacted by the higher temperature evolved hydrogen, a higher (double) weighting of this measurement leads to the reported 3.0 x SMOW value for the D/H of the water of formation of the sample.

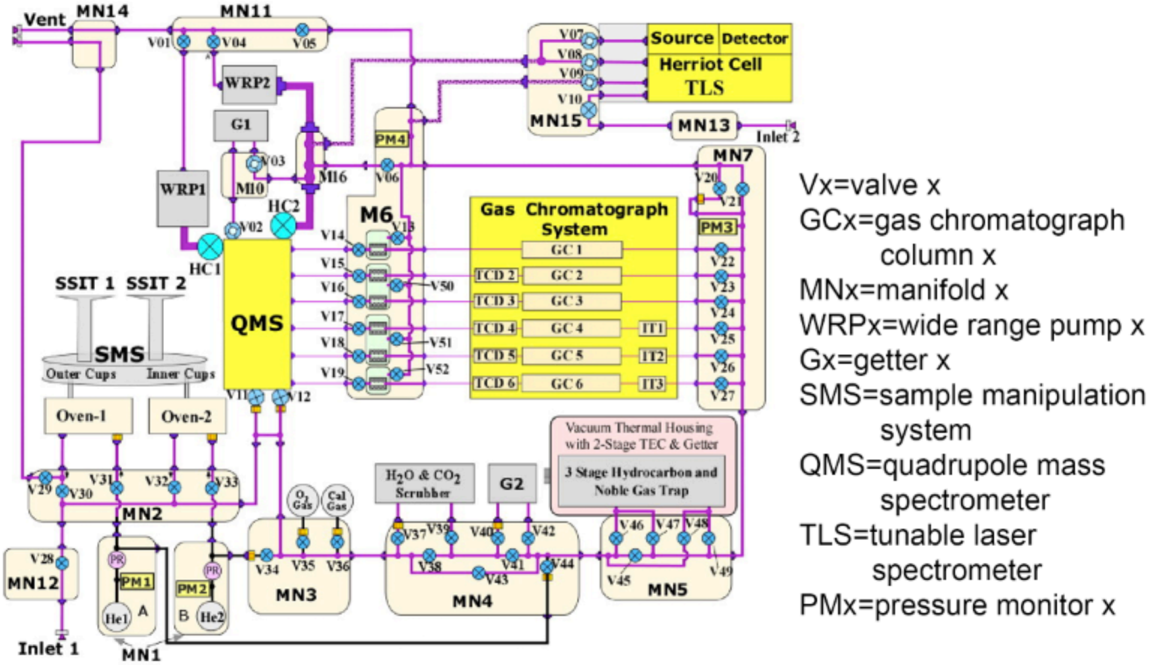

Fig. S1.

The SAM gas flow diagram. Instruments and subsystems utilized for the combustion experiment are illustrated.

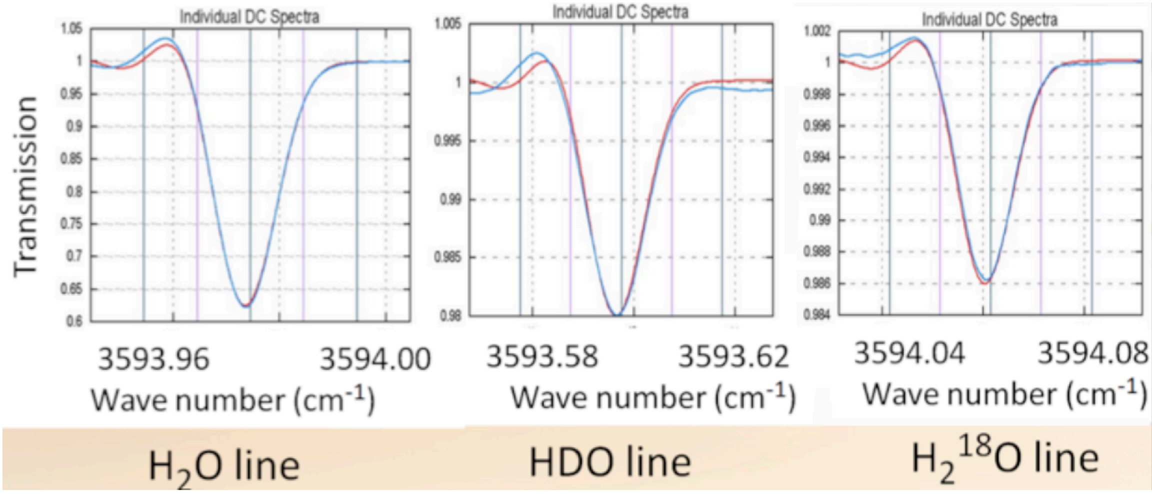

Fig. S2

TLS spectra fit to HITRAN. Comparison between spectral lines recorded by TLS during the first step of the combustion experiment, and those calculated from the HITRAN 2010 line list (48).

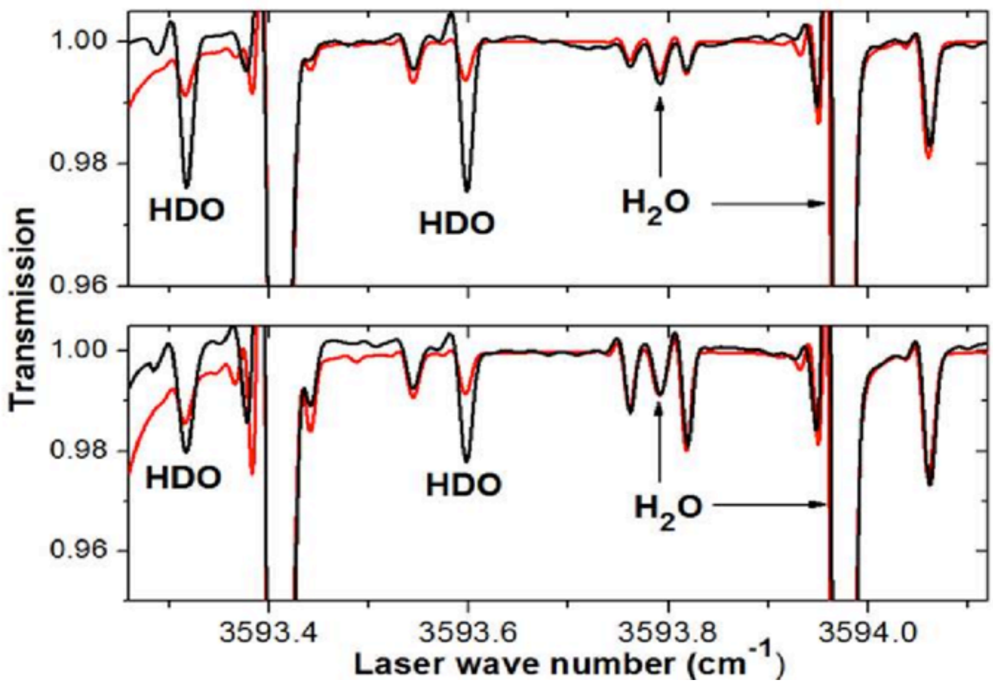

Fig. S3

TLS spectra comparison. (top) Water released during EGA analysis of the second Cumberland sample where a 87°C-347°C temperature cut was introduced into the TLS giving a δD of 4,434 ±25 ‰ is compared (bottom) with the TLS spectrum of the water released in step 3 of the combustion experiment (δD value of 1,941 ±45‰).

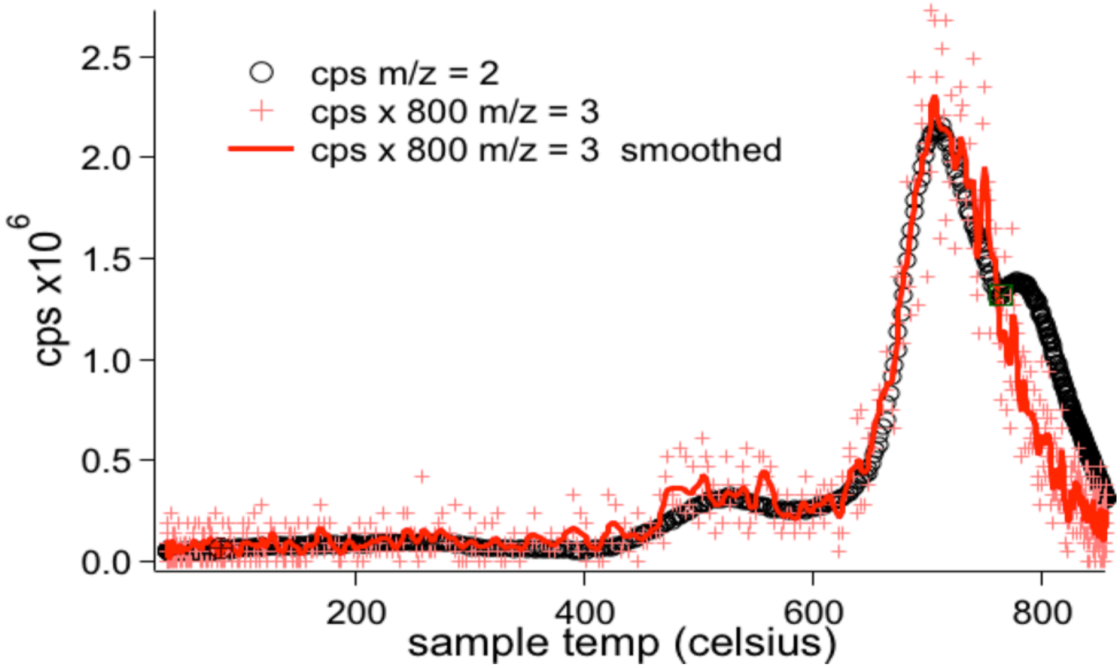

Fig. S4

Evolved H_2 (m/z 20) and HD (m/z 3) for one of the Cumberland EGA experiments. The solid trace gives the smoothed m/z 3 data since counting statistics produce scatter in this signal. The portion of the high temperature m/z 2 data that does not fall on the m/z 3 trace is presumed to be due to residual terrestrial H_2 from the SAM oven consistent with observation of evolved H_2 from the blank experiment.

Table S1. Updated TLS-SAM EGA results for water. For Rocknest 2, 3, and 4, these values correct those published earlier in *(9)* and *(39)*. The full set of Cumberland results is included here for completeness. 2SEM represents 2 times the standard error from the mean in the data, and ERR is the final error that combines the 2SEM with other systematic errors e.g. from spectral line parameters.					
SAM EGA run name	**Temperature cut (^oC)**	**Sol**	**delta-D water ±2SEM**	**delta-D water ±ERR**	**D/H water ±ERR**
Rocknest-3	234-425	101	4,231 ±33	4,231 ±52	5.231 ±0.052
Rocknest-4	350-443	117	3,568 ±49	3,568 ±63	4.568 ±0.063
Rocknest-2	440-601	96	3,633 ±38	3,633 ±55	4.633 ±0.055
Cumberland-2	87-347	286	4,434 ±25	4,434 ±47	5.434 ±0.047
Cumberland-3	445-755	290	3,180 ±72	3,180 ±82	4.180 ±0.082
Cumberland-5	445-755	368	2,745 ±56	2,745 ±69	3.745 ±0.069
Cumberland-6	445-755	382	3,912 ±25	3,912 ±47	4.912 ±0.047
Cumberland-7	157-495	415	3,859 ±35	3,859 ±53	4.859 ±0.053
Combustion Step 1	550	556	2,277 ±36	2,277 ±54	3.277 ±0.054
Combustion Step 2	550	557	1,891 ±35	1,891 ±53	2.891 ±0.053
Combustion Step 3	920	557	1,941 ±20	1,941 ±45	2.941 ±0.045
Combustion Step 4	920	558	1,831 ±84	1,831 ±93	2.831 ±0.093

Table S2. Water and hydrogen release. Quantities of water and hydrogen released in the combustion, EGA, and blank experiments and mole-averaged D/H values.	
Combustion experiment: quantity of water released in steps 1-4.	Step 1: 60.1 μmoles Step 2: 4.9 μmoles Step 3: 14.6 μmoles Step 4: 1.8 μmoles
Average quantity of hydrogen released per triple portion equivalent sample volume in 7 EGA Cumberland experiments and average δD	20.2 μmoles 1954 $\pm$ 600 ‰ (2.95 x SMOW)
Quantity of hydrogen released in a blank cup experiment.	1.47 μmoles
Mole weighted δD of H_2O from steps 2-4 from TLS measurement	1920 $\pm$ 51 ‰ (2.92 x SMOW)
Mole weighted δD that includes H_2O from steps 2-4 evolved H_2, and corrections for blank cup experiment H_2 (assumed to be terrestrial D/H and converted into H_2O). The blank correction increases the H_2O δD from the sample above that derived from H_2O alone.	2056 $\pm$ 60 ‰ (3.06 x SMOW)
Increased mole weighting of Step 2 D/H (550^{o}C) where evolved H_2 does not come into play and estimates of additional systematic errors gives reported value.	2024 + 59 ‰ (3.0 $\pm$ 0.2) x SMOW
[1] δD (‰) =1000 (R/R_{SMOW} -1), where R=D/H in sample, and R_{SMOW}=D/H in Standard Mean Ocean Water (1.558×10^{-4}).	

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